APPENDIX D

STANDARD OPERATING PROCEDURES

D-1. ANALYTICAL METHOD AND SOP CROSSWALK

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APPENDIX D-1

ANALYTICAL METHOD AND SOP CROSSWALK

APPENDIX D-1. ANALYTICAL METHOD AND SOP CROSSWALK
WEST LAKE LANDFILL OU-3
REMEDIAL INVESTIGATION/FEASIBILITY STUDY QUALITY ASSURANCE PROJECT PLAN

Location	Appendix Number	Method Number	Medium	Description	SOP/Document Number	SOP Name
Pace-I	D-2a	EPA Method 200.2	Water	Acid Digestion of Aqueous Samples for ICP and ICP-MS Analysis	ENV-SOP-IND1-0035	Acid Digestion of Aqueous Samples for ICP and ICP-MS Analysis
	D-2b	EPA Method 353.2, Rev 2.0	Water	Nitrate/Nitrite Nitrogen	ENV-SOP-IND1-0045	Nitrate/Nitrite
	D-2c	NA	NA	Outline the procedures involved with the receipt, login, storage, and disposal of samples.	ENV-SOP-IND1-0001 Rev.01	Sample Management
	D-2d	NA	NA	Establish a uniform system in the event that samples must be transferred to another laboratory for analysis.	ENV-SOP-IND1-0005 Rev.00	Subcontracting Samples
	D-2e	NA	NA	Outline the procedures involved with bottle preparation and shipment.	ENV- SOP-IND1-0008 Rev.00	Bottle Preparation
	D-2f	EPA Method 410.4, Rev 2.0	Water	Provide a laboratory specific procedure for determining Chemical Oxygen Demand (COD).	ENV-SOP-IND1-0019 Rev.01	The Determination of Chemical Oxygen Demand (COD)
	D-2g	EPA Method 350.1, Rev 2.0 & Standard Method 4500-NH_3 G (1997/2011)	Water & Solid	Provide a laboratory specific procedure for determining Ammonia Nitrogen.	ENV-SOP-IND1-0046 Rev.01	The Determination of Ammonia Nitrogen
	D-2h	Standard Method 4500-S^2-D (2000)	Water	Provide a laboratory specific procedure for determining sulfide.	ENV-SOP-IND1-0062 Rev.01	The Determination of Sulfide Colorimetric; Methylene Blue Method
	D-2i	Standard Methods 2540 B, C, D, E and F (1997/2011)	Water	Provide a laboratory specific procedure for determining Total Solids (TS).	ENV-SOP-IND1-0065 Rev.01	The Measurement of Solids in Wastewater and Water
	D-2j	Standard Method 5310C (2011)	Water	Provide a laboratory specific procedure for determining Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC).	ENV-SOP-IND1-0095 Rev.00	The Determination of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC)
	D-2k	EPA SW-846 Method 6010B	Water & Solid	Provide a laboratory specific procedure for determining the concentration of metals.	ENV-SOP-IND1-0025 Rev.01	The Determination of Metals by Inductively Coupled Plasma (ICP)
	D-2l	Standard Method 2340 B (2011)	Water	Provide a laboratory specific procedure for determining total hardness.	ENV-SOP-IND1-0038 Rev.01	The Determination of Total Hardness
	D-2m	EPA SW-846 Methods 7470A & 7471A	Water & Solid	Provide a laboratory specific procedure for determining total mercury concentration.	ENV-SOP-IND1-0044 Rev.01	The Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy
	D-2n	EPA SW-846 Method 6020	Water & Solid	Provide a laboratory specific procedure for determining the concentration of metals.	ENV-SOP-IND1-0106 Rev.01	The Determination of Metals by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)
	D-2o	EPA SW-846 Methods 8260C, 5030A, 5030B & 5035A	Water & Solid	Determine the concentration of Volatile Organic Compounds (VOCs)	ENV-SOP-IND1-0034 Rev.01	The Determination of Volatile Organics by GC/MS
	D-2p	EPA SW-846 Method 8082A	Water	Determine the concentration of polychlorinated biphenyls (PCBs)	ENV-SOP-IND1-0049 Rev.00	The Determination of Polychlorinated Biphenyls (PCBs)
	D-2q	EPA SW-846 METHOD 3510C	Water	Provide a laboratory specific procedure for extracting non-volatile and semi-volatile organic compounds.	ENV-SOP-IND1-0050 Rev.01	Separatory Funnel Extraction
	D-2r	EPA SW-846 METHOD 8270C	Water	Provide a laboratory specific procedure for determining the concentration of semi-volatile organic compounds.	ENV-SOP-IND1-0057 Rev.00	The Determination of Semi-Volatile Compounds by GC/MS
	D-2s	EPA Method 300.0, Rev. 2.1 & EPA SW-846 Method 9056A	Water & Solid	Provide a laboratory specific procedure for determining the concentration of anions.	ENV-SOP-IND1-0096 Rev.01	The Determination of Anions by Ion Chromatography
	D-2t	NA	NA	Documents the systems, processes and procedures that this location uses to manage generated wastes.	ENV-SOP-IND1-0004 Rev.00	Waste Handling and Management
	D-2u	NA	NA	Detail the procedures for training all employees in waste management.	ENV-SOP-IND1-0007 Rev.00	Waste Management Training Requirements
	D-2v	EPA 9045C	Water	Soil and Waste pH	ENV-SOP-IND1-0058, REV 02	Determination of pH in soil and waste
	D-2w	EPA 7196A	Water	Hexavalent Chromium	ENV-SOP-IND1-0056	Determination of hexavalent chromium
	D-2x	EPA 8011	Water	EDB and DBCP in Aqueous Samples	ENV-SOP-IND1-0093	EDB and DBCP in Aqueous Samples
	D-2y	EPA 8081B	Water	The Determination of Organochlorine Pesticides by Gas Chromatography	ENV-SOP-IND1-0099	Organochlorine Pesticides
	D-2z	SM 2320B	Water/Soil	Alkalinity	ENV-SOP-IND1-0006	Alkalinity
	D-2aa	EPA Method 365.1	Water	Phosphorus (used to calculate Phosphate)	ENV-SOP-IND1-0100, Rev 00	Total Phosphorus (365.1)
Pace-P	D-3a	ASTM Method D-3972-90 & HASL 300 Method U-02	Water & Solid	Determination of micro-quantities of Americium, Curium, Thorium, Plutonium (including Pu-241), Neptunium and Uranium	ENV-SOP-GBUR-0068	Analysis of Samples for Alpha Emitting Actinides and Pu-241
	D-3b	EPA 903.1, SM7500-Ra C	Water	Documents the analytical procedure to be used for analysis for Ra-226.	ENV-SOP-GBUR-0067	Analysis of Water Samples for Ra-226 Content - 903.1
	D-3c	EPA 904.0 & 9320/SM7500-RaD (Ra-228)	Water	Documents the analytical procedure to be used for analysis for Ra-228.	ENV-SOP-GBUR-0064	Analysis of Water Samples for Ra-228 Content - 904.0
	D-3d	NA	NA	Outline the procedures involved with the receipt, login, storage, and disposal of samples.	ENV-SOP-GBUR-0001	Sample Management
	D-3e	EPA Method 901.1	Water & Solid	Documents the analytical process of preparing and analyzing a variety of matrices for gamma emitters using the HPGe gamma spectrometry detector.	ENV-SOP-GBUR-0088	Gamma Spectroscopy Analysis - Prep - 901.1
	D-3f	NA	NA	Describes the general operation and maintenance of the gamma spectroscopy instrumentation.	ENV-SOP-GBUR-0078	Gamma Spec Instrument Operations - 901.1
Pace-E	D-4a	NA	NA	Outline the procedures for sample receipt and storage.	ENV-SOP-PITTS-0027, Rev 00	Sample Receiving
	D-4b	NA	NA	Outline the procedures for sample waste handling.	ENV-SOP-PITTS-0023, Rev 00	Sample Disposal
	D-4c	AM20GAX	Water	Describes the standard operating procedures for the analyses of methane and carbon dioxide.	ENV-SOP-PITTS-0018	AM20GAx

APPENDIX D-1. ANALYTICAL METHOD AND SOP CROSSWALK
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REMEDIAL INVESTIGATION/FEASIBILITY STUDY QUALITY ASSURANCE PROJECT PLAN

Location	Appendix Number	Method Number	Medium	Description	SOP/Document Number	SOP Name
Pace-K	D-5a	NA	NA	Outline the procedures for sample receipt and storage.	ENV-SOP-LENE-0021, Rev 01	Sample Management
	D-5b	NA	NA	Outline the procedures for sample waste handling.	ENV-SOP-LENE-0127, Rev 00	Sample Disposal
	D-5c	3510C	Water	Extraction method for volatiles and non-volatiles	ENV-SOP-LENE-0039, Rev 02	Separatory Funnel Extraction
	D-5d	8015B/C	Water	Gasoline Range Organics	ENV-SOP-LENE-0111	GRO by 8015B/C
	D-5e	8270C	Water	Diesel Range Organics/Oil Range Organics	ENV-SOP-LENE-0031	TPH-DRO/ORO by 8270C
	D-5f	9081	Soil	Cation Exchange Capacity	ENV-SOP-LENE-0103	Cation Exchange Capacity
Pace-G	D-6a	NA	NA	Sample Management	ENV-SOP-GBAY-006, Rev 01	Sample Management
	D-6b	ASTM D 2974-87	Soil	Percent Moisture	ENV-SOP-GBAY-0004, Rev 00	Measurement of Percent Moisture in Soils and Solids
	D-6c	Walkley Black Procedure	Soil	Total Organic Carbon	ENV-SOP-GBAY-0032, Rev 00	Determination of Total Organic Carbon Using the Walkley-Black Procedure
MCLInc	D-7a	NA	NA	Operators Aids	MCL-7756	Sample Receiving
	D-7b	NA	NA	Waste Handling	MCL7718	Sample Disposal
	D-7c	Modified Sequential Extraction Procedure for Characterizing Source Materials from the West Lake Landfill (Project Specific)	Soil	Sequential Extraction Procedure	MCL-7775	Sequential Extraction Procedure
	D-7d	MCLInc-7708	Soil	Operation Guidance: Electron Microscopy	MCL-7708	Electron Microscopy
	D-7e	Operation Guide X-Ray Diffraction	Soil	X-ray Diffraction Operation Guide	MCL-7712	Operation Guide X-Ray Diffraction
	D-7f	Inductively Coupled Plasma-Atomic Emission Spectrometry Metals Analysis	Soil	Metal Analyses by USEPA 6010B	MCL-7751	Inductively Coupled Plasma-Atomic Emission Spectrometry Metals Analysis
	D-7g	Inductively Coupled Plasma-Mass Spectrometry Element/Metals Inducing Tc99 Sample Preparation and Analysis	Soil	Metal Analyses by USEPA 6020A-C	MCL-7768	Inductively Coupled Plasma-Mass Spectrometry Element/Metals Inducing Tc99 Sample Preparation and Analysis
	D-7h	Determination of Uranium by a Modified Davies-Gray Titration	Soil	Determination of Uranium	MCL-7737	Determination of Uranium by a Modified Davies-Gray Titration
	D-7i	EPA Method 3050B	Soil	Acid Digestion for Metals by EPA Method 3050B	MCL-7746	Acid Digestion for Metals Based on EPA Method 3050B
	D-7j	pH by Method 9045D	Soil	Determination of pH Value	MCL-7801	Determination of pH Value
	D-7k	SM 3500-Fe B, Modified	Soil	Determination of Ferric and Ferrous Iron	MCL-7799	Ferric Iron Analysis by Visible Light Spectroscopy (Colorimetric)
ALS-S	D-8a	NA	Air	Sample Management	SMO-SMPL_REC	Sample Receiving, Acceptance, and Login
	D-8b	NA	Air	Canister Certification	SMO-CAN_CERT	Cleaning and Certification of Summa Canisters and Other Specially Prepared Containers
	D-8c	USEPA TO-15	Air	Measurement of Volatile Organic Compounds in Air	VOA-TO-15, Rev 26	Determination of Volatile Organic Compounds in Air Samples Collected in Specially Prepared Canisters and Gas Collection Bags by Gas Chromatography/Mass Spectrometry (GC/MS)
	D-8d	USEPA TO-3 for Methane	Air	Analysis of C1-C6+ using Gas Chromatography with Flame Ionization Detection in Accordance with a Modification of EPA Compendium Method TO-3	VOA-TO3C1C6, Rev 14	This gas chromatographic method is used in the analysis of methane, ethane, ethene, acetylene, propane, propene, n-butane, n-pentane, n-hexane and hydrocarbon ranges from C2 to greater than C6 by a modification of EPA Compendium Method TO-3 and modified ASTM D1945-03.
ALS-W	NA	NA	Air	Sample Receipt[1]	TBD	TBD
	D-9a	NA	Air	Radon analyses in Indoor Air Samples[2]	NA	Indoor Radon and Radon Decay Product Measurement Device Protocols

Note:
1 - This SOP was not included due to security requirements of the laboratory. The SOP will be available, if requested.
2 - The laboratory will follow the methodology in the Method with the exception of the electret stability check.
The electret stability check will follow the Rad-Elec E-Perm System user manual's limits (ST 6V/month over 1 month and LT 4V/month over 3 months) rather than the EPA-recommended limits in the Method since the Rad-Elec document is directly from the manufacturer.

Abbreviations:

ALS-S: ALS in Simi Valley, California
ALS-W: ALS in Winnipeg, Canada
ASTM: American Society of Testing and Materials
COD: Chemical Oxygen Demand
DBCP: 1,2-Dibromo-3-chloropropane
DOC: Dissolved Organic Carbon
DRO: Diesel Range Organics
EDB: ethylene dibromide
EPA/USEPA: United States Environmental Protection Agency
GC: Gas Chromatography
GRO: Gasoline Range Organics
HPGe: High Purity Germanium
ICP: Inductively Coupled Plasma
MCLInc: Materials and Chemistry Laboratory, Inc.
MS: Mass Spectrometry
NA: Not Applicable
Pace-E: Pace Analytical located in Pittsburgh, Pennsylvania
Pace-G: Pace Analytical located in Green Bay, Wisconsin
Pace-I: Pace Analytical located in Indianapolis, Indiana
Pace-K: Pace Analytical located in Lenexa, Kansas
Pace-P: Pace Analytical located in Pittsburgh, Pennsylvania
PCBs: Polychlorinated biphenyls
SM: Standard Method
SOP: Standard Operating Procedure
SW-846: Hazardous Waste Test Methods
TBD: To be determined
TOC: Total Organic Carbon
TPH: Total Petroleum Hydrocarbons
TS: Total Solids
VOCs: Volatile Organic Compounds

APPENDIX D-2

PACE INDIANAPOLIS SOPS

Document Information

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Department(s): Metals

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ENV-SOP-IND1-0035

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	18 Nov 2018, 08:11:27 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Sayer (004775)	General Manager	19 Nov 2018, 07:54:31 AM	Approved
Felicia Walker (005354)	Manager - Lab Services	20 Nov 2018, 11:20:02 AM	Approved

1. Purpose

1.1. The purpose of this SOP is to provide a laboratory specific procedure for acid digestion of aqueous samples for metals analysis while meeting the requirements specified in EPA methods 3005A and 3010A for analysis by ICP and in EPA Method 200.2 for analysis by ICP-MS.

2. Summary of Method

2.1. A portion of sample is digested with strong acid and heat in a block digester and then brought to volume with reagent water.

3. Scope and Application

3.1. This procedure is used to determine total metals and dissolved metals.

3.2. Volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of metals digestion equipment. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Not applicable to this SOP.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection	Preservation	Storage	Hold time
Aqueous - Total	250mL in plastic container	- HNO_3 to pH <2 - Samples received at pH>2 must be preserved to pH<2 with HNO_3 and be allowed to equilibrate for 24 hours before being prepared for analysis. Acidification date and time are recorded in the Sample Preservation Logbook.	Ambient or Cool to ≤6°C	Must be analyzed within 6 months of the collection date.
Aqueous - Dissolved	250mL in plastic container	- Filter; HNO_3 to pH<2 - For all dissolved elements by methods 200.7 or 200.8, samples must be filtered within 15 minutes of collection and before adding HNO_3, or data must be qualified that filtration occurred beyond 15 minutes of collection. Samples filtered in the lab are preserved to pH<2 with HNO_3 and allowed to equilibrate for 24 hours before being prepared for analysis. Filtration and acidification date and time are recorded in the metals digestion prep log.	Ambient or Cool to ≤6°C	Must be analyzed within 6 months of the collection date.
Aqueous – Drinking Water	1L plastic container for Pb/Cu Rule compliance.	-Samples must be acidified to pH<2 with HNO_3 as soon as possible but not more than 14 days after sample collection. -Samples must stand in the original container used for collection for at least 28 hours after acidification.	Ambient or Cool to ≤6°C	Must be analyzed within 6 months of the collection date.

Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Description / Comments
Hot Block Digester	Environmental Express or equivalent, adjustable and capable of maintaining a temperature of 92°C to 98°C.
Centrifuge	Fisher Centrific centrifuge Model 225 or equivalent
Vacuum pump	For lab filtration for dissolved elements.

9.2. General Supplies

Item	Description
Volumetric Flasks	Class A , various capacities
Volumetric Pipettors	Eppendorf or equivalent, various sizes
Digestion Tubes	Environmental Express or equivalent, volumetrically certified and contaminant free
Thermometer	Ever Safe or equivalent, calibrated, used for monitoring Hot Block temperature
Plunger Filters	Environmental Express or equivalent
Graduated Cylinders	Class A, various capacities
pH strips	Fisher or equivalent, full range
Filtration system	FlipMate or equivalent 0.45 um fiber filter disc caps and cups for lab filtration for dissolved elements.

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II
Nitric acid	Concentrated, trace metal analyzed or equivalent
Hydrochloric acid	Concentrated, trace metal analyzed or equivalent

10.2. Analytical Standards

10.2.1. Definitions

Table 10.1 Standard Definitions

Standard	Description	Comments
Spiking Standard	This solution contains the target analytes and is generally prepared using a standard source secondary to the standards used for calibration.	Same solution can be used for the LCS and MS/MSD

10.2.2. Storage Conditions

Table 10.2 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
ICP Stock Spiking Standards	Inorganic Ventures; catalog #s PA-STD-1B; PA-STD-2B; PA-STD-3B, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
ICP Working Spiking Standard	Refer to Section 10.2.3.1.	Expires 6 months from date of preparation.	Same as stock standard
ICP-MS Stock Spiking Standard #1	Inorganic Ventures; catalog #HERT-CAL-2A or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
ICP-MS Stock Spiking Standard #2	Inorganic Ventures; catalog #HERT-CAL-2B or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions

10.2.3. Preparation Procedures

Table 10.3 – ICP Stock Spiking Standard Details

Analyte	Concentration (mg/L)
Inorganic Ventures PA-STD-1B	
Arsenic	200
Barium	200
Beryllium	200
Cadmium	200
Chromium	200
Cobalt	200
Copper	200
Lead	200
Lithium	200
Manganese	200
Nickel	200
Phosphorus	200
Selenium	200
Strontium	200
Thallium	200
Vanadium	200
Zinc	200
Inorganic Ventures PA-STD-2B	
Antimony	200
Boron	200
Molybdenum	200
Silicon	1000
Inorganic Ventures PA-STD-2B continued	
Silver	100
Tin	200
Titanium	200
Inorganic Ventures PA-STD-3B	
Aluminum	2000
Calcium	2000
Iron	2000
Magnesium	2000
Potassium	2000
Sodium	2000

Table 10.4 – ICP-MS Stock Spiking Standard Details

Analyte	Concentration (mg/L)
Inorganic Ventures HERT-CAL-2A	
Antimony	2
Molybdenum	2
Tin	2
Titanium	2
Inorganic Ventures HERT-CAL-2B	
Aluminum	20
Arsenic	2
Barium	2
Beryllium	2
Boron	2
Cadmium	2
Chromium	2
Cobalt	2
Copper	2
Lead	2
Manganese	2
Nickel	2
Selenium	2
Silver	2
Strontium	2
Thallium	2
Thorium	2
Uranium	2
Vanadium	2
Zinc	2

10.2.3.1. Working Spiking Standard Preparation

Dilute 25mL of each stock spiking standard (solutions 1B, 2B and 3B) to 100mL with reagent water for a final nominal concentration of 50mg/L.

11. Calibration

11.1. Not applicable to this SOP.

12. Procedures

12.1. If lower reporting limits are required, digestate concentration may be performed provided that final acid concentration and final spike concentration remain consistent with unconcentrated digestates. Refer to Section 12.4.

12.2. Lab Filtration for Dissolved Elements

12.2.1. Prepare the filtration apparatus by attaching a filter disc cap to a sample cup for each sample to be filtered.

12.2.2. To filter, attach the filtration apparatus to the vacuum pump and turn the pump on. Turn the vacuum pump off when filtration is complete and an adequate volume of filtrate has been collected.

12.2.3. Prepare a Method Blank by filtering reagent water through the filter disc cap and into a labeled sample cup. Filter enough volume to support all analyses requested.

12.2.4. Prepare an LCS by filtering an LCS prepared as described in Section 12.3.3 or 12.4.3 through the filter disc cap and into a labeled sample cup. Filter enough volume to support all analyses requested.

12.2.5. Filter samples by pouring the sample from the original sample container into the filter disc cap and collecting approximately 100mL of the sample filtrate in a labeled sample cup.

12.2.6. Preserve all filtrates to pH<2 with concentrated nitric acid. Hold preserved samples for a minimum of 24 hours before digestion and/or analysis.

12.2.7. Record all filtration information including sample cup lot number, filter disc cap lot number, and date and time of preservation in the metals digestion log.

12.3. Aqueous Sample Digestion for ICP

12.3.1. Transfer 50mL of well-mixed sample into a labeled digestion tube.

12.3.2. Prepare a Method Blank by transferring 50mL of reagent water to a digestion tube.

12.3.3. Prepare an LCS by adding 1mL of the ICP Working Spiking Standard (50mg/L nominal) to 50mL of reagent water for a nominal spike concentration of 1mg/L.

12.3.4. Prepare a Matrix Spike by adding 1mL of the ICP Working Spiking Standard (50mg/L nominal) to 50mL of sample for a nominal spike concentration of 1mg/L.

12.3.5. Add 2.5mL concentrated nitric acid to each digestion tube. Place the tubes into the block digester which has been preheated to achieve a temperature of 95°C (+/- 3°C) in the digestion tubes.

12.3.6. If digestate is generating brown fumes, add another 2.5mL concentrated nitric acid and reflux gently. Continue heating and adding acid as necessary, until the digestion is complete, generally indicated when the digestate is light in color and brown fumes are no longer generated.

12.3.7. Evaporate without boiling to approximately 10mL. Do not allow samples to go dry.

12.3.8. Cool the samples then add 2mL concentrated hydrochloric acid, return the samples to the hot block and heat for 15 minutes to dissolve any precipitate then allow samples to cool.

12.3.9. Dilute the digestates to 50mL in the digestion tube with reagent water. If necessary, filter the digestates to remove particulates by using a plunger filter. If any sample digestates in a batch are filtered, the Method Blank and LCS must also be filtered. Alternatively, reduce the effect of particulates by placing the samples into a centrifuge for approximately 5 minutes at 3500 rpm.

12.4. Aqueous Sample Digestion for ICP-MS

12.4.1. Transfer 50mL of well-mixed sample into a labeled digestion tube.

12.4.2. Prepare a Method Blank by transferring 50mL of reagent water to a digestion tube.

12.4.3. Prepare an LCS by adding 1mL of the ICP-MS Stock Spiking Standard #1 (2mg/L) and 1mL of the ICP-MS Stock Spiking Standard #2 (2mg/L nominal) to 50mL of reagent water for a nominal spike concentration of 0.04mg/L.

12.4.4. Prepare a Matrix Spike by adding 1mL of the ICP-MS Stock Spiking Standard #1 (2mg/L) and 1mL of the ICP-MS Stock Spiking Standard #2 (2mg/L nominal) to 50mL of sample for a nominal spike concentration of 0.04mg/L.

12.4.5. Add 0.5mL concentrated nitric acid and 0.25mL concentrated hydrochloric acid to each digestion tube. Place the tubes into the block digester which has been preheated to achieve a temperature of

95°C (+/- 3°C) in the digestion tubes.

12.4.6. If digestate is generating brown fumes, add another 0.5mL concentrated nitric acid and reflux gently. Continue heating and adding acid as necessary, until the digestion is complete, generally indicated when the digestate is light in color and brown fumes are no longer generated.

12.4.7. Evaporate without boiling to approximately 10mL. Do not allow samples to go dry.

12.4.8. Remove the samples from the hot block and allow them to cool.

12.4.9. Dilute the digestates to 50mL in the digestion tube with reagent water. If necessary, reduce the effect of particulates by placing the samples into a centrifuge for approximately 5 minutes at 3500 rpm.

12.5. Aqueous Sample Digestion with Concentration for ICP

12.5.1. Transfer 50mL of well-mixed sample into a labeled digestion tube.

12.5.2. Prepare a Method Blank by transferring 50mL of reagent water to a digestion tube.

12.5.3. Prepare an LCS by adding 0.2mL of the ICP Working Spiking Standard (50mg/L nominal) to 50mL of reagent water for a nominal spike concentration of 1mg/L.

12.5.4. Prepare a Matrix Spike by adding 0.2mL of the ICP Working Spiking Standard (50mg/L nominal) to 50mL of sample for a nominal spike concentration of 1mg/L.

12.5.5. Add 0.5mL concentrated nitric acid to each digestion tube. Place the tubes into the block digester and set the temperature to achieve 95°C (+/- 3°C) in the digestion tubes.

12.5.6. If digestate is generating brown fumes, add another 0.5mL concentrated nitric acid and reflux gently. Continue heating and adding acid as necessary, until the digestion is complete, generally indicated when the digestate is light in color and brown fumes are no longer generated.

12.5.7. Evaporate without boiling to approximately 10mL. Do not allow samples to go dry.

12.5.8. Cool the samples then add 0.4mL concentrated hydrochloric acid, return the samples to the hot block and heat for 15 minutes to dissolve any precipitate then allow samples to cool.

12.5.9. Dilute the digestates to 10mL in the digestion tube with reagent water. If necessary, filter the digestates to remove particulates using a plunger filter. If any sample digestates in a batch are filtered, the Method Blank and LCS must also be filtered. Alternatively, reduce the effect of particulates by placing the samples into a centrifuge for approximately 5 minutes at 3500 rpm.

12.6. Record all preparation information including standard numbers, reagent numbers, digestion tube lot numbers, filter lot numbers, Hot Block number, thermometer ID and correction factor, and digestion temperature in the metals digestion log and deliver the digestates to the ICP analyst.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples, per matrix.	Refer to the SOP for the determinative method.	Refer to the SOP for the determinative method
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples, per matrix.	Refer to the SOP for the determinative method.	Refer to the SOP for the determinative method.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analyte	One MS/MSD set per preparation batch of up to 20 samples, per matrix.	Refer to the SOP for the determinative method.	Refer to the SOP for the determinative method.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Action for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Samples are digested for the ICP analysis of Antimony, Boron, Lithium, Silicon, Silver, Strontium, Tin and Titanium in addition to the analytes listed in the method.

19.2. Samples are digested for the ICP-MS analysis of Titanium in addition to the analytes listed in the method.

19.3. Volumes of acid used for ICP digestion vary from those in the methods.

19.4. Method modified for use with Hot Block digesters and digestion tubes are never capped while heating.

19.5. A digestion temperature range of 95°C +/-3°C is observed.

19.6. Samples are verified to be pH<2 prior to digestions but this verification may not take place "immediately" prior to digestion.

20. Instrument/Equipment Maintenance

20.1. Refer to maintenance log and/or instrument manufacturer's instructions.

21. Troubleshooting

21.1. Refer to maintenance log and/or instrument manufacturer's instructions.

22. Safety

22.1. Standards and Reagents: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible. The stock metals standards are toxic and should be handled with extreme care. Also handle concentrated acids with care, making sure to wear appropriate personal protective equipment.

22.2. Samples: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves**,** lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All distillations should be conducted under a fume hood.

22.3. Equipment: Portions of the preparation and analytical equipment operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Preventions

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", EPA SW-846, latest revision, Methods 3005A and 3010A.

25.2. U.S. EPA, EMSL Method 200.2, Revision 2.8, 1994.

25.3. Pace Analytical Quality Manual; latest revision.

25.4. TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-IN-M-030-rev.11	1. Cover Page: changed phone number, changed method reference to 3010A and 200.2, add ICP-MS reference updated effective date format and changed SOP naming format from inorganics to metals. 2. Table of Contents: added new Section 14, Method Modifications. 3. Section 1.1: changed method reference to 3010A and 200.2 and added ICP-MS reference. 4. Table 7.1: added preservation for lab-filtered samples. 5. Table 8.1: updated required temperature range of Hot Block. 6. Section 9: added ICP-MS spiking standards. 7. Section 11: revised to include batch QC preparation, added guidance for non-standard final volumes, revised acid-addition to reflect current process, and separated process for ICP and ICP-MS digestion. Added specific procedure for digestate concentration to achieve lower limits. 8. Table 12.1: updated Method Blank corrective action. 9. Section 13: removed MDL requirement. 10. Section 14: new Method Modifications section added. 11. Section 16.1: changed method reference to 3010A and added 200.2 reference.	17Sep2015
S-IN-M-030-rev.12	1. Converted to 27 section format. 2. Table 7.1: added requirement to filter within 15 minutes of collection for methods 200.7 and 200.8 and revised storage temperature format. 3. Section 9.1: added centrifuge. 4. Section 12.2: changed final evaporation volume from 5mL to 10mL and added centrifuge as option to filter. 5. Section 12.3: changed final evaporation volume from 5mL to 10mL and changed filtration to centrifugation. 6. Section 12.4: changed final evaporation volume from 5mL to 10mL and added centrifuge as option to filter. 7. Table 13.1: referred to SOP for determinative method for acceptance criteria. 8. Section 25.4: added years 2003 and 2009 to TNI reference.	08Oct2017
S-IN-M-030-rev.13	1. Cover page: added reference to method 3005A. 2. Section 1.1: added reference to method 3005A. 3. Table 7.1: added requirement that all West Virginia samples for dissolved elements must be filtered within 15 minutes of collection. 4. Section 9.1: added vacuum pump. 5. Section 9.2: added filtration apparatus. 6. Section 12.2: added section to describe lab filtration procedure for dissolved elements. 7. Table 13.1: referred to determinative method for corrective actions. 8. Section 25.1 added reference to method 3005A.	24Oct2017
ENV-SOP-IND1-0035-rev.01	1. Removed cover, table of contents and headers for use in Master Control. 2. Table 7.1: added preservation and handling for drinking water samples to comply with the Pb/Cu rule. 3. Section 19.6: added a modification to indicate that sample pH is not always checked "immediately" prior to digestion. 4. Section 27: updated Document Number to Master Control number.	11Nov2018

Document Information

Document Number: ENV-SOP-IND1-0100 **Revision:** 00

Document Title: Total Phosphorus (365.1)

Department(s): Wet Chemistry

Previous Document Number: S-IN-I-174-rev.01

Date Information

Effective Date: 23 Oct 2017

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Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

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STANDARD OPERATING PROCEDURE

THE DETERMINATION OF TOTAL PHOSPHORUS
REFERENCE METHOD: EPA METHOD 365.1, REVISION 2.0

SOP NUMBER:	S-IN-I-174-rev.01
EFFECTIVE DATE:	October 23, 2017
SUPERSEDES:	S-IN-I-174-rev.00

APPROVAL

General Manager	October 13, 2017 Date
Quality Manager	October 13, 2017 Date
Department Manager	October 13, 2017 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____

S-IN-I-174-rev.01

Table of Contents

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining total phosphorus in aqueous samples while meeting the requirements specified in EPA Method 365.1, Revision 2.0.

2. Summary of Method

2.1. Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This is reduced to an intensely blue-colored complex by adding ascorbic acid. The color is measured with an automated spectrometer and is proportional to the phosphorus concentration.

3. Scope and Application

3.1. Reporting limits, control limits, volumes used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.2. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of phosphorus analysis equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable for the measurement of Total Phosphorus in groundwater, drinking, surface, and saline waters.

5. Limits of Detection and Quantitation

5.1. The reporting limit is 0.05mg/L. Refer to LIMS for method detection limits.

6. Interferences

6.1. Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate. Concentrations as low as 0.1 mg As/L interfere with the Phosphorous determination.

6.2. Hexavalent chromium and nitrite interfere to give results about 3% low at concentrations of 1 mg/L and 10% to 15% low at 10 mg/L.

6.3. High iron and calcium concentration can cause precipitation of and therefore loss of phosphorus.

6.4. Sample color that absorbs in the photometric range used for analysis may also interfere.

6.5. Many commercially available detergents contain phosphorus and should never be used to clean glassware used for this analysis. Glassware must be rinsed with 1:1 HCl and reagent water prior to use for this method. Preferably dedicated glassware would be used for this method.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous samples for Total Phosphorus	125mL in plastic or glass container	H_2SO_4 to pH <2	Cool to ≤6°C	Analysis must be completed within 28 days of collection

Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation/Equipment

Equipment	Model / ID	Description / Comments
Automated Spectrophotometer	SmartChem 200 Discrete Analyzer, or equivalent	Equipped with an autosampler and data system. Capable of measuring at 880nm or 650nm with a light path of 1cm or greater
Analytical Balance	OHaus AV412 or equivalent	Capable of weighing to the nearest 0.01g
Block Digester or Hot Plate	Fisher or equivalent	For sample digestion

9.2. General Supplies

Item	Description
Volumetric flasks	Class A, various sizes
Graduated cylinders	Class A, various sizes
Mechanical pipettors	Various sizes
Digestion Tubes	Glass 100mL capacity or equivalent
Erlenmeyer Flasks	125mL capacity
Boiling Chips	Chemware Ultra Pure PTFE chips or equivalent
Filters	Environmental Express syringe filters or equivalent
Sample tubes	Environmental Express 50mL screw top plastic tubes with lids or equivalent
Autosampler cups	Fisher 02-544-4 or equivalent, 4mL capacity

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
Sulfuric acid	Concentrated, reagent grade or equivalent
Sulfuric acid solution (11N)	Aqua Solutions #ERL192, or equivalent.
Ammonium peroxydisulfate	Fisher #A682, or equivalent
Sulfuric acid solution (5N)	Aqua Solutions #9109-4LC, or equivalent
Antimony potassium tartrate	Fisher #A867, or equivalent
Antimony potassium tartrate solution	Dissolve 0.3g of antimony potassium tartrate in reagent water in a 100mL volumetric flask. Dilute to volume with reagent water and mix well. Store in a dark glass bottle and refrigerate when not in use. This solution expires 6 months from date of preparation.
Ammonium Molybdate	Fisher #A674, or equivalent
Ammonium Molybdate solution	Dissolve 4g of ammonium molybdate in reagent water in a 100mL volumetric flask. Dilute to volume with reagent water and mix well. Store in a plastic bottle and refrigerate when not in use. This solution expires 6 months from date of preparation.
Sodium Dodecyl Sulfate (SDS)	Acros Organics #23042, or equivalent
Sodium Dodecyl Sulfate Solution, 15%	Dissolve 15g of Sodium Dodecyl Sulfate in 85mL of reagent water. This solution may require gentle stirring and heat to fully dissolve. This solution expires 6 months from date of preparation.
Ascorbic acid	Fisher #A62, or equivalent
Ascorbic acid solution (Reagent 3)	Dissolve 0.88g of ascorbic acid in reagent water in a 50mL volumetric flask. Add 0.5mL 15% SDS solution and dilute to volume with reagent water. Mix gently to minimize foaming. This solution must be prepared fresh daily. Do not refrigerate.
Color Reagent (Reagent 2)	Mix together in order, 17.8mL of 5N sulfuric acid, 15mL of ammonium molybdate solution, 5mL of antimony potassium tartrate solution, 10mL of 15% sodium dodecyl sulfate solution and 52.2mL of reagent water. Mix solution after addition of each ingredient. Store the solution at room temperature and prepare fresh weekly. When this Color Reagent is prepared as described, acid digested samples can be analyzed without pH adjustment of digestate.
Cuvette Cleaning Solution Concentrate	Westco part number 3AS-RN00-20 or equivalent. Dilute 50mL of this concentrated solution to 1L with reagent water and invert five times to mix, for use as the Cuvette Wash Solution. Store at room temperature.
Probe Rinse Solution Concentrate	Westco part number 3AS-RN00-21 or equivalent. Dilute 0.5mL of this concentrated solution to 1L with reagent water and invert five times to mix, for use as the Probe Rinse Solution. Store at room temperature.
Diluent (Reagent 1)	Reagent water which has been digested per the procedure in Section 11.1.

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification standards, second source verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	ICAL
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This solution contains all target analytes and should be prepared from a different source than the calibration standards.	This solution is used for the LCS and MS.

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Phosphorous Calibration Standard	Ricca catalog # 5839-4; 326mg/L or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate Phosphorous Calibration Standard	Refer to Section 10.2.3.1	Solution good for 6 months from date of preparation	Same as stock standard
Working Phosphorous Calibration Standard	Refer to Section 10.2.3.2 and 10.2.3.3	Must be prepared fresh each day of use	Not applicable
Stock Phosphorous ICV Standard	HACH catalog #2321142; 1000ppm or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate Phosphorous ICV Standard	Refer to Section 10.2.3.4	Solution good for 6 months from date of preparation	Same as stock standard
Working Phosphorous ICV Standard	Refer to Section 10.2.3.5	Must be prepared fresh each day of use	Not applicable

10.2.3. Standard Preparation Procedures

Refer to the standard preparation logbook or database for additional instructions regarding preparation of standards.

10.2.3.1. Intermediate Phosphorous Calibration Standard Preparation

Dilute 15.33mL of the Stock Phosphorous Calibration Standard (326mg/L) to 100mL with reagent water for a final concentration of 50mg/L.

10.2.3.2. Working Phosphorous Manual Calibration Standard Preparation

Working calibration standards are prepared using the Intermediate Phosphorous Calibration Standard (50mg/L) and must be prepared fresh daily in diluent. Examples of possible calibration standards are as follows:

Standard ID	Amt. of Intermediate Calibration Std. Used	Final Volume	Final Concentration
Calibration Blank	0mL	50mL	0mg/L
Cal. Std. 1	0.05mL	50mL	0.05mg/L
Cal. Std. 2	0.1mL	50mL	0.10mg/L
Cal. Std. 3	0.25mL	50mL	0.25mg/L
Cal. Std. 4 (CCV)	0.50mL	50mL	0.50mg/L
Cal. Std. 5	0.75mL	50mL	0.75mg/L
Cal. Std. 6	1.0mL	50mL	1.0mg/L

10.2.3.3. Working Phosphorus Auto-dilution Calibration Standard Preparation

Dilute 0.2mL of the Intermediate Phosphorus Calibration Standard (50mg/L) to 10mL in diluent for a final concentration of 1.0mg/L. This standard must be prepared fresh daily and will be auto-diluted by the SmartChem autosampler to prepare the other calibration curve standards as detailed below:

Standard ID	Percentage of 1.0mg/L Calibration Std. Used	Final Concentration
Calibration Blank	0%	0mg/L
Cal. Std. 1	5%	0.05mg/L
Cal. Std. 2	10%	0.10mg/L
Cal. Std. 3	25%	0.25mg/L
Cal. Std. 4 (CCV)	50%	0.50mg/L
Cal. Std. 5	75%	0.75mg/L
Cal. Std. 6	100%	1.0mg/L

10.2.3.4. Intermediate Phosphorous ICV Standard Preparation

Dilute 5mL of the Stock Phosphorous ICV Standard (1000mg/L) to 100mL with reagent water for a final concentration of 50mg/L. This standard is also used for the LCS and MS/MSD spiking solution.

10.2.3.5. Working Phosphorous ICV Standard Preparation

Dilute 0.1mL of the Intermediate Phosphorous ICV Standard (50mg/L) to 10mL with diluent for a final concentration of 0.5mg/L.

11. Calibration

11.1. Initial Calibration: The instrument is calibrated each day that phosphorus analysis is performed. A minimum of 5 calibration standards and a calibration blank is required. The lowest calibration standard must be at or below the reporting limit. The instrument automatically dilutes a prepared standard to create the individual calibration points. Calibration points are analyzed in order of increasing concentration. Refer to the Quality Manual for more information regarding calibration curves.

11.2. Linear Calibration: The instrumentation software constructs a standard curve by plotting optical density versus concentration of each calibration standard. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be ≥ 0.995.

11.3. Initial Calibration Corrective Action: If the curve does not meet the acceptance criteria, then a new calibration curve must be analyzed. If the second curve attempt does not meet the acceptance criteria, the analyst must consult the department manager and instrument maintenance and/or preparation of new standards must be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.4. Initial Calibration Verification (ICV): In addition to meeting the linearity requirement, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known value of the standard. This step is referred to as Initial Calibration Verification. The ICV is analyzed immediately following an initial calibration curve. Acceptable recovery range for the ICV is 90-110%.

11.5. ICV Corrective Action: If the ICV is not acceptable, another ICV may be analyzed. If the second ICV fails, then a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICV must be reanalyzed. Exception: If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.6. Initial Calibration Blank (ICB): The ICB consists of reagent water. An ICB must be analyzed after each ICV. If the ICB result is above the reporting limit, sample analysis cannot proceed. Samples associated with a failed ICB must be reanalyzed. Exception: If the ICB is >RL, associated samples determined to be <RL are reportable.

11.7. Continuing Calibration Verification (CCV): A CCV must be analyzed after every 10 samples and at the end of the analytical sequence to verify the system is still calibrated. The CCV should be from the same material as the curve standards. The acceptable recovery range for the CCV is 90-110%.

11.8. CCV Corrective Action: If a CCV fails the acceptance criteria, another CCV may be analyzed. If the second CCV fails, then a new initial calibration curve must be analyzed. Samples must be bracketed by acceptable CCVs in order to be reportable. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable.

11.9. Continuing Calibration Blank (CCB): A CCB consists of reagent water. A CCB must be analyzed after each ICV or CCV. If the CCB result is above the reporting limit, another CCB may be analyzed. If the second CCB fails, then a new calibration curve must be analyzed. Samples associated with a failed CCB must be reanalyzed. **Exception**: If the CCB is >RL, associated samples determined to be <RL are reportable.

12. Procedures

12.1. Digestion of Aqueous Samples for Total Phosphorus

12.1.1. Place 50mL of well mixed aqueous sample into a labeled 125mL flask or block digester tube. A smaller volume may be used if sample is high in solids content or historically above the linear range of the curve.

12.1.2. Prepare a Method Blank by placing 50mL of reagent water into a labeled 125mL flask or block digester tube.

12.1.3. Prepare an LCS by placing 50mL of reagent water and 0.5mL of the Working Phosphorus ICV Standard (50mg/L) into a labeled 125mL flask or block digester tube for a spike concentration of 0.5mg/L.

12.1.4. Prepare a Matrix Spike by placing 50mL of sample and 0.5mL of the Working Phosphorus ICV Standard (50mg/L) into a labeled 125mL flask or block digester tube for a spike concentration of 0.5mg/L

12.1.5. Add 1mL of 11N sulfuric acid solution, 0.4g of ammonium peroxydisulfate and 3 or 4 boiling chips to each 125mL flask or block digester tube.

12.1.6. Boil gently on a pre-heated hot plate or in a block digester for approximately 90 minutes or until a final volume of about 10mL is reached. Do not allow sample to boil dry.

12.1.7. Allow samples to cool. Quantitatively transfer each sample to a 50mL sample tube and dilute to 50mL with reagent water.

12.1.8. If sample digestate is not clear, it may be filtered. Method Blank and LCS must also be filtered if any samples in the batch are filtered.

12.2. Digestion of Aqueous Samples for Acid Hydrolyzable Phosphorus

12.2.1. Place 50mL of well mixed aqueous sample into a labeled 125mL flask or block digester tube. A smaller volume may be used if sample is high in solids content or historically above the linear range of the curve.

12.2.2. Add 1mL of 11N sulfuric acid solution and 3 or 4 boiling chips to each 125mL flask or block digester tube.

12.2.3. Boil gently on a pre-heated hot plate or in a block digester for approximately 90 minutes or until a final volume of about 10mL is reached. Do not allow sample to boil dry.

12.2.4. Allow samples to cool. Quantitatively transfer each sample to a 50mL sample tube and dilute to 50mL with reagent water.

12.2.5. If sample digestate is not clear, it may be filtered.

12.3. Phosphorus Determination

12.3.1. Configure the instrument per manufacturer's instructions.

12.3.2. Fill disposable sample cups with samples and load them into the autosampler in the desired order. Fill clean reagent bottles with the appropriate reagents for this method as noted in Section 9.1.

12.3.3. Select the appropriate method in the software with the following parameters. The method as described here is equivalent to the EPA Method 365.1:

Type	End Point
Direction	Up
Decimals	3
Model	Linear
Filter 1	880 or 660 nm
Sample Blanking	No after Reagent 1
Calibration Code	OP1W

Method Code: WP1W **Range: 0.01 to 1.0 mg/L P**	**Volume uL**	**Delay Time sec.**	**Read Time sec.**	**Rinse uL**	**Code**
Sample Volume	290				
Reagent 1: Digested Blank Diluent	9	36	0	0	DIL1
Reagent 2: Color Reagent	65	0	0	0	MOL1
Reagent 3: Ascorbic Acid	28	0	342	0	ASC1

12.3.4. A typical run sequence may be as follows:

ICAL Standards
CCV
CCB
ICV
ICB
CCV
CCB
Method blank
LCS
Client samples
CCV
CCB
Client samples
CCV
CCB

12.3.5. Any sample with a concentration that exceeds the linear range of the calibration curve must be diluted and reanalyzed or qualified as an estimated concentration.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples.	Target analyte must be less than the reporting limit.	Reanalyze method blank. If target compound is still >RL in method blank and associated samples, re-prepare and reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples.	90-110% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, re-prepare and reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analyte	One MS/MSD set per batch plus an additional MS if >10 samples in the batch.	90-110% Recovery ≤20% RPD	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

$$\text{Aqueous Sample (mg/L as P)} = \frac{(X)(V_f)(D)}{(V_i)}$$

Where: X = Phosphorus concentration, mg/L
V_f = Final sample volume, L
D = Dilution factor
V_i = Initial sample volume, L

14.2. Phosphate = Total Phosphorus x 3.064

14.3. Phosphonate Phosphorus = Total Phosphorus – Acid Hydrolyzable Phosphorus

14.4. Total Hydrolyzable Phosphorus = Acid Hydrolyzable Phos. – Ortho Phosphate

14.5. Total Organic Phosphorus = Total Phosphorus – (Acid Hydrolyzable Phos. + Orthophosphate)

(Orthophosphate determined separately)

14.6. LCS equation:

$$R = (C/S) * 100$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.7. MS/MSD equation:

$$R = \frac{(Cs - C)}{S} * 100$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.8. RPD equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. An MDL study and/or LOD/LOQ verification must be conducted every 6 months for each matrix per instrument.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

14.1 Method modified for use with a block digester or hot plate for the digestion step.

14.2 Method adapted for use with the SmartChem 200 per SmartChem Method 410-3651.

14.3 Method Blank is evaluated to the reporting limit, not the MDL as indicated in Method 365.1.

14.4 Sample pH adjustment prior to analysis is not performed because it is not required per the SmartChem Method.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. EPA EMSL Method 365.1, Revision 2.0, August 1993.

25.2. SmartChem 200 Method 410-3651, Rev. A-03-1206

25.3. Standard Methods for the Examination of Waste and Wastewater; method 4500-P B, E, Phosphorus, 1999 with editorial revisions 2011.

25.4. Pace Analytical Quality Manual; latest revision.

25.5. TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-174-rev.00	1. Converted to Pace SOP format. 2. Section 11: added procedure for Acid Hydrolyzable Phosphorus and added calculation for multiple species of P.	23Sep2015
S-IN-I-174-rev.01	1. Converted to 27 section format. 2. Table 7.1: revised storage temperature format. 3. Section 9.1: revised balance specifications. 4. Section 9.2: updated digestion tubes specifications. 5. Table 10.3: updated Stock ICV. 6. Section 12.1.6: updated digestion time. 7. Section 12.2.3: updated digestion time. 8. Section 12.3.3: updated table for no sample blanking. 9. Section 12.3.4: updated example sequence. 10. Table 13.1: updated corrective action for MB and LCS. 11. Section 14.4: revised modification for clarity. 12. Section 25.5: added years 2003 and 2009 to TNI reference.	11Oct2017

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QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	18 Nov 2018, 08:04:37 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Sayer (004775)	General Manager	19 Nov 2018, 07:54:44 AM	Approved
Anne Troyer (008754)	Manager - Lab Services	19 Nov 2018, 02:58:52 PM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining Nitrate/Nitrite Nitrogen in aqueous samples while meeting the requirements specified in EPA method 353.2 rev. 2.0.

2. Summary of Method

2.1. This method is based upon an aqueous sample being passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined, nitrate/nitrite values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.

3. Scope and Application

3.1. The applicable range for this method is 0.1-5mg/L of nitrate/nitrite. The reporting limit for water samples is 0.1mg/L and for soil samples is 5mg/Kg. Refer to the LIMS for method detection limits.

3.2. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of nitrate-nitrite analysis equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable to the measurement of nitrate/nitrite in ground water, drinking, surface and saline waters, domestic and industrial wastes, and aqueous extracts of solid samples.

5. Limits of Detection and Quantitation

5.1. Refer to LIMS for method detection limits. Reporting limits are shown below:

Analyte	Aqueous mg/L	Solid mg/kg
Nitrogen, Nitrate	0.1	5
Nitrogen, NO2 plus NO3	0.1	5
Nitrogen, Nitrite	0.1	5

6. Interferences

6.1. Suspended matter in the reduction column will restrict sample flow. Samples may be pre-filtered.

6.2. Low results may be obtained from samples containing high concentrations of metals, such as iron or copper. EDTA can be added to eliminate this interference.

6.3. Residual chlorine can produce a negative interference by limiting reduction efficiency. Before analysis, samples should be checked and if required, dechlorinated with sodium thiosulfate. NOT DOING THIS.

6.4. Samples that contain large amounts of oil and grease can interfere with the cadmium in the procedure. This can be eliminated by pre-extracting the sample using an organic solvent. Oily samples are generally rejected for analysis.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	250mL in plastic container	For combined nitrate/nitrite analysis, H_2SO_4 to pH<2 For nitrate or nitrite individually, unpreserved.	Cool to ≤6°C	For preserved samples, analysis must be completed within 28 days of collection date. For unpreserved samples, analysis must be completed within 48 hours of collection.
Solid	50-100g in a glass jar	None required	Cool to ≤6°C	Sample preparation must be completed within 14 days of collection. Analysis must be completed within 48 hours of sample preparation.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Vendor	Description / Comments
Autoanalyzer	Lachat Quikchem 8000, 8500 or equivalent	Equipped with autosampler, flow cell spectrophotometer for use at 520nm and data reduction system.

9.2. General Supplies

Item	Description
Graduated cylinders	Various sizes, Class A
Automatic-pipettors	Eppendorf or equivalent, various sizes
Volumetric flasks	Class A, various sizes
Beakers	125mL glass, 50mL disposable or equivalent
Filter paper	Whatman 4 or equivalent
Syringe filter	Environmental Express 0.45um or equivalent
Stir plate and stir bars	For preparation of solid samples
Balance	Accurate to 0.1g or equivalent
Chlorine Test Strips	HF Scientific Micro Check or equivalent
Sand	Or equivalent to be used as a simulated soil matrix.

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
Sodium Thiosulfate	Reagent grade crystals
Sulfuric acid	Concentrated, Fisher catalog #A510-P212, or equivalent.
Sodium Hydroxide	Reagent grade pellets or equivalent.
10N Sodium Hydroxide solution	Reagent grade, Fisher catalog #S5410-4 or equivalent
Hydrochloric acid	Concentrated, JT Baker catalog #9530-33 or equivalent
Ammonium Hydroxide	Spectrum Chemical catalog #AM180 or equivalent
Ammonium Chloride	Reagent grade crystals or equivalent.
Disodium EDTA	Fisher catalog # O2793-500 or equivalent
Ammonium Chloride Buffer (pH 8.5) **for QuickChem 8000**	CAUTION: prepare this under a hood! To a 1L flask, add 500mL reagent water, 105mL conc. hydrochloric acid, 95mL ammonium hydroxide, and 1g disodium EDTA. Dissolve and dilute to mark with reagent water. Invert to mix. After cooling, adjust the pH to 8.5 using HCl or 10N sodium hydroxide solution. Solution expires 6 months from date of preparation.
Ammonium Chloride Buffer (pH 8.5) **for QuickChem 8500**	CAUTION: prepare this under a hood! To a 1L flask, add 500mL reagent water, 85g ammonium chloride, 1g disodium EDTA, and 9.2g sodium hydroxide. Dissolve and dilute to mark with reagent water. Invert to mix. After cooling, adjust the pH to 8.5 using HCl or 10N sodium hydroxide solution. Solution expires 6 months from date of preparation.
Phosphoric acid	85% solution, Fisher/ catalog # A242-4 or equivalent
Sulfanilamide	Fisher catalog #O4525 or equivalent
N-(1-naphthyl)-ethylenediamine dihydrochloride	Acros catalog # 42399-250 or equivalent
Sulfanilamide color reagent	In a 1L flask, add approx. 600mL of reagent water, add 100mL of phosphoric acid, 40g of sulfanilamide, and 1g of N-(1-naphthyl)-ethylenediamine dihydrochloride. Stir for 30 minute to dissolve and then dilute to the mark with reagent water. Invert to mix and then store in a dark bottle. This solution is stable for one month from preparation.

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification standards, second source verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions and vendors

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This standard is used for spiking MS/MSD sets.	Same solution can be used for the LCS and MS/MSD

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Nitrate calibration standard	Ricca; catalog # R5307900-120A; 1000mg/L or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Stock Nitrite calibration standard	Ricca; catalog # R5444900-120C; 1000mg/L or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate #1 Nitrate/Nitrite calibration standards	Refer to Section 10.2.3.1	Must be prepared fresh monthly	Same as stock standard.
Intermediate #2 Nitrate/Nitrite calibration standards	Refer to Section 10.2.3.2	Must be prepared fresh daily	Same as stock standard.
Working Nitrate/Nitrite calibration standards	Refer to Section 10.2.3.3	Must be prepared fresh daily.	Must be prepared fresh daily.
Stock Nitrate ICV standard	SPEX; catalog # AS-NO3N9-2Y; 1000mg/L or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Stock Nitrite ICV standard	SPEX; catalog # AS-NO2N9-2Y; 1000mg/L or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate Nitrate/Nitrite ICV Standard	Refer to Section 10.2.3.4	Must be prepared fresh monthly	Same as stock standard.
Working Nitrate/Nitrite ICV standard	Refer to Section 10.2.3.5	Must be prepared fresh daily.	Must be prepared fresh daily.
Working Nitrate Check Standard	Refer to Section 10.2.3.6	Must be prepared fresh daily	Must be prepared fresh daily.
Working Nitrite Check Standard	Refer to Section 10.2.3.7	Must be prepared fresh daily	Must be prepared fresh daily.

10.2.3. Standard Preparation Procedures

Refer to the standard preparation logbook or database for additional instructions regarding preparation of standards for Nitrate/Nitrite analysis. Instructions for preparation of fresh daily standards are detailed below.

10.2.3.1. Intermediate #1 Nitrate/Nitrite Calibration Standard Preparation

Dilute 10mL of each of the Stock Nitrate calibration standard (1000mg/L) and Stock Nitrite calibration standard (1000mg/L) to 100mL with reagent water for a final concentration of 100mg/L for each Nitrate and Nitrite or 200mg/L Nitrate+Nitrite.

10.2.3.2. Intermediate #2 Nitrate/Nitrite Calibration Standard Preparation

Dilute 5mL of the Intermediate #1 Nitrate/Nitrite Calibration Standard (200mg/L Nitrate+Nitrite) to 100mL with reagent water for a final concentration of 10mg/L Nitrate+Nitrite.

10.2.3.3. Working Nitrate/Nitrite Calibration Standard Preparation

Working calibration standards for the **QuickChem 8000** must be prepared fresh daily in reagent water using either the Intermediate #1 Nitrate/Nitrite Calibration Standard (100mg/L each NO3,NO2) or the CAL7 Nitrate/Nitrite Calibration Standard (2.5mg/L each NO3, NO2). Examples of possible calibration standards are as follows but may vary:

Standard	Standard Volume	Intermediate Standard used	Final Volume	Final Conc. each NO3, NO2	Final Conc. NO3+NO2
CAL0	0 mL	N/A	50mL	0 mg/L	0 mg/L
CAL1	0.2 mL	CAL7	50mL	0.01 mg/L	0.02 mg/L
CAL2	0.4 mL	CAL7	50mL	0.02 mg/L	0.04 mg/L
CAL3	2.0 mL	CAL7	50mL	0.1 mg/L	0.2 mg/L
CAL4	0.2 mL	Intermediate #1	50mL	0.4 mg/L	0.8 mg/L
CAL5 (CCV)	1.0 mL	Intermediate #1	100mL	1 mg/L	2 mg/L
CAL6	1.0 mL	Intermediate #1	50mL	2 mg/L	4 mg/L
CAL7	2.5 mL	Intermediate #1	100mL	2.5 mg/L	5 mg/L

Working calibration standards for the **QuickChem 8500** must be prepared fresh daily and are auto-diluted by the instrument using the Intermediate #2 Nitrate/Nitrite Calibration Standard (10mg/L Nitrate+Nitrite). Examples of possible calibration standards are as follows but may vary:

Standard	Auto-Dilution Factor	Final Conc. NO3+NO2
CAL0	N/A	0 mg/L
CAL1	500	0.02 mg/L
CAL2	250	0.04 mg/L
CAL3	50	0.2 mg/L
CAL4	12.5	0.8 mg/L
CAL5 (CCV)	5	2 mg/L
CAL6	2.5	4 mg/L
CAL7	2	5 mg/L

10.2.3.4. Intermediate Nitrate/Nitrite ICV Standard Preparation

Dilute 10mL of each of the Stock Nitrate ICV standard (1000mg/L) and Stock Nitrite ICV standard (1000mg/L) to 100mL with reagent water to give a final concentration of 100mg/L for each Nitrate and Nitrite or 200mg/L Nitrate+Nitrite.

10.2.3.5. Working Nitrate/Nitrite ICV Standard Preparation

Dilute 1mL of the Intermediate Nitrate/Nitrite ICV standard (100mg/L) to 100mL with reagent water to give a standard concentration of 2mg/L Nitrate+Nitrite. This standard must be prepared fresh daily.

10.2.3.6. Working Nitrate Check Standard Preparation

Dilute 0.1mL of the Stock Nitrate calibration standard (1000mg/L) to 50mL with reagent water to give a standard concentration of 2mg/L. This standard must be prepared fresh daily.

10.2.3.7. Working Nitrite Check Standard Preparation

Dilute 0.1mL of the Stock Nitrite calibration standard (1000mg/L) to 50mL with reagent water to give a standard concentration of 2mg/L. This standard must be prepared fresh daily.

11. Calibration and Standardization

11.1. Initial Calibration: A minimum of five initial calibration standards are analyzed in decreasing order of concentration. The lowest calibration standard must be at or below the reporting limit. A new initial calibration curve is run on each working day. Refer to the Quality Manual for more information regarding calibration curves.

11.2. Linear Calibration: Using the Lachat software, prepare a standard curve by plotting area versus concentration. The analyst may employ a regression equation that does not pass through the origin. Weighting factors of $1/x$ or $1/x^2$ may be used to gain accuracy at lower concentrations. The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

where: y = instrument response (peak area)
a = slope of the line (the coefficient of x)
x = concentration of the calibration standard
b = y-intercept of the line

The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient or r must be ≥ 0.995.

11.3. Non-linear Calibration: In situations where a linear model does not meet the acceptance criteria, a non-linear calibration model may be employed provided that a minimum of six initial calibration standards have been analyzed. Weighting factors of $1/x$ or $1/x^2$ may be used to gain accuracy at lower concentrations. The non-linear or quadratic model produces the following equation:

$$y = ax^2 + bx + c$$

The coefficient of the determination (COD) or r^2 can be used at a measure of the "goodness of fit." In order to be used for quantitative purposes, the COD or r^2 must be ≥ 0.99.

11.4. Initial Calibration Corrective Action: If the initial calibration does not meet the acceptance criteria, then a new calibration curve must be analyzed. If the second curve attempt does not meet the acceptance criteria, the analyst must consult the department manager and instrument maintenance and/or preparation of new standards must be considered.

11.5. Initial Calibration Verification (ICV): In addition to meeting the linearity requirement, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy of the calibration, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known value of the standard. This step is referred to as Initial Calibration Verification. The ICV is analyzed immediately after an initial calibration curve. The acceptable range for the ICV is +/-10% Difference, which is equivalent to 90-110% Recovery.

$$\% \text{ Difference} = \frac{(\text{Calculated concentration} - \text{Theoretical concentration})}{\text{Theoretical concentration}} \times 100$$

$$\% \text{ Recovery} = \frac{\text{Calculated concentration}}{\text{Theoretical concentration}} \times 100$$

11.6. ICV Corrective Action: If the ICV is not acceptable, another ICV may be analyzed. If the second ICV fails, then a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICV must be reanalyzed. **Exception:** If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.7. Initial Calibration Blank (ICB): The ICB consists of reagent water. A ICB must be analyzed after each ICV. If any ICB result is above the reporting limit, sample analysis must be stopped. Samples associated with a failed ICB must be reanalyzed. Exception: If the ICB is >RL, associated samples determined to be <RL are reportable.

11.8. Nitrite Check Standard: A 2mg/L nitrite (NO2) check standard must be analyzed after each initial calibration curve.

11.9. Nitrate Check Standard: A 2mg/L nitrate (NO3) check standard must be analyzed after each initial calibration curve. This standard is used to verify the efficiency of the cadmium reduction column. Calculate the ratio of the nitrate and nitrite check standards observed concentrations as follows to determine the percent efficiency of the cadmium column:

$$\frac{\text{NO3 Check Standard conc.}}{\text{NO2 Check Standard conc.}} \times 100$$

The calculated cadmium column efficiency must be $\geq$90%.

11.10. Nitrate/Nitrite Check Standard Corrective Action: If the calculated percent efficiency of the cadmium column fails the acceptance criteria, another set of nitrate/nitrite check standards may be analyzed. If the percent efficiency of the cadmium column fails again, then a new cadmium reduction column must be installed and a new initial calibration curve must be analyzed.

11.11. Continuing Calibration Verification (CCV): A CCV must be analyzed after every 10 samples and at the end of the analytical batch to verify the system is still calibrated. The CCV should be from the same material as the curve standards. The acceptable range for these standards is +/-10% Difference, which is equivalent to 90-110% Recovery. NOTE: certain clients or programs may require that CCVs at two concentrations, low and high, be analyzed when a non-linear or quadratic calibration model is used.

11.12. CCV Corrective Action: If a CCV fails the acceptance criteria, another CCV may be analyzed. If the second CCV fails, then a new initial calibration curve must be analyzed. Samples must be bracketed by acceptable CCVs in order to be reportable. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable.

11.13. Continuing Calibration Blank (CCB): The CCB consists of reagent water. A CCB must be analyzed after each ICV/CCV. If any CCB result is above the reporting limit, sample analysis must be stopped. Samples associated with a failed CCB must be reanalyzed. **Exception**: If the CCB is >RL, associated samples determined to be <RL are reportable.

12. Procedures

12.1. Aqueous Sample Preparation

12.1.1. Filter any samples that contain suspended solids using a 0.45um syringe filter. Alternatively, samples can be centrifuged.

12.1.2. Check each sample for residual chlorine using a chlorine test strip. Remove any residual chlorine detected using sodium thiosulfate.

12.1.3. **QuickChem 8000:** for preserved samples, adjust sample pH to 5-9 with HCl or NaOH prior to analysis. NOTE: No pH adjustment of preserved samples is required for QuickChem 8500.

12.1.4. Prepare a Method Blank by adding 10mL reagent water to an autosampler tube for analysis. Method Blank should be filtered if associated samples in the batch required filtration.

12.1.5. Prepare an LCS by diluting 0.1mL of the Intermediate Nitrate/Nitrite ICV Standard (100mg/L) to 10mL with reagent water for a final concentration of 1mg/L each NO3or NO2 or 2mg/L NO3+NO2. LCS should be filtered if associated samples in the batch required filtration.

12.1.6. Prepare a Matrix Spike by diluting 0.1mL of the Intermediate Nitrate/Nitrite ICV Standard (100mg/L) to 10mL with sample for a final concentration of 1mg/L each NO3or NO2 or 2mg/L NO3+NO2. MS should be filtered if associated parent sample required filtration.

12.2. Solid Sample Preparation

12.2.1. Weigh 10g of well-mixed sample into a beaker and add 100mL reagent water. Stir for 30 minutes and then allow it to settle before gravity filtering. If necessary, filtrate may be further filtered through a 0.45um syringe filter before analysis.

12.2.2. Prepare a Method Blank by weighing 10g of sand into a beaker and adding 100mL reagent water. Stir for 30 minutes and then allow it to settle before gravity filtering. If necessary, filtrate may be further filtered through a 0.45um syringe filter before analysis.

12.2.3. Prepare an LCS by diluting 0.1mL of the Intermediate Nitrate/Nitrite ICV Standard (100mg/L) to 10mL with the filtrate from Section 12.2.2 for a final concentration of 10mg/kg each each NO3or NO2 or 20mg/kg NO3+NO2.

12.2.4. Prepare a Matrix Spike by diluting 0.1mL of the Intermediate Nitrate/Nitrite ICV Standard (100mg/L) to 10mL with the sample filtrate from Section 12.2.1 for a final concentration of 10mg/kg each each NO3or NO2 or 20mg/kg NO3+NO2.

12.3. Configure the instrument according to manufacturer's instructions. Allow the colorimeter and recorder to warm up. Run a baseline with all reagents, using reagent water to flush the tubing. Whenever new tubing is used, allow ample time to flush residual compounds from the tubing.

12.4. Establish initial calibration as described in Sections 11.1 through 11.11.

12.5. Once initial calibration is established, analyze 10mL portions of each sample, Method Blank, LCS and MS/MSD. An example sequence may be as follows:

Initial calibration standards
ICV
ICB
NO2 Check Standard

NO3 Check Standard
Method blank
LCS
Client samples
CCV
CCB
Client samples
CCV
CCB

12.6. Sample concentrations exceeding the linear range must be diluted and reanalyzed or the result must be qualified as estimated.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples.	Target analyte must be less than reporting limits	Reanalyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples.	90-110% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, re-prepare and reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analyte	One MS/MSD set per batch plus an additional MS if >10 samples in the batch.	90-110% Recovery ≤20% RPD	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

$$\text{Aqueous Sample (mg/L)} = (X_s)(D) \qquad \text{Solid Sample (mg/kg)} = \frac{(X_s)(V_f)(D)}{(W_s)}$$

Where: X_s = Nitrate/Nitrite concentration, mg/L
V_f = Final sample volume in milliliters
D = Dilution factor
W_s = Weight of solid sample extracted in grams

$$\text{Moisture corrected concentration} = \frac{\text{(Final concentration as received)}}{\text{(100 - \%Moisture)}} \times 100$$

14.2. LCS equation:

$$\mathbf{R = (C/S) * 100}$$

Where R = percent recovery
C = observed LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation:

$$\mathbf{R = \frac{(Cs - C)}{S} * 100}$$

Where R = percent recovery
Cs = observed spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD equation:

$$\mathbf{RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100}$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Section 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. MDLs must be determined per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. This procedure has been adapted for the analysis of solid samples.

19.2. Cadmium reduction column is purchased and not prepared in the lab.

19.3. Stock Nitrate and Nitrite standards are purchased as certified solutions and not prepared from dry chemicals.

19.4. Initial calibration acceptance based on correlation coefficient (r) or coefficient of the determination (COD or r^2) rather than the difference between the measured value of the calibration solutions and the true value concentration.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP. All wastes are accumulated, managed and disposed of in accordance with all federal and state laws and regulations.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. USEPA, Methods 353.2, Revision 2, "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, August 1993.

25.2. Lachat QuickChem Methods 10-107-04-1-A, July 2008, 10-107-04-1-C, August 2000 and 10-107-05-1-A, November 2007.

25.3. Pace Analytical Quality Manual; latest revision.

25.4. NELAC/TNI Standards; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not Applicable

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-042-rev.13	1. Table of Contents: added new Section 14, Method Modifications 2. Section 3: added references to solid samples and MDLs. 3. Table 7.1: added information for the collection of solid samples 4. Table 8.2: added supplies for the preparation of solid samples 5. Table 9.1: updated reagent details 6. Section 9.2.3: clarified final concentration of standards is for each NO3 and NO2. 7. Section 9.2.3.2: identified the standard used as the CCV 8. Sections 11.2-11.5: detailed the preparation of solid samples, MB, LCS and MS. 9. Section 11.9: 10. Section 11.10: added calculation of solid samples final concentration 11. Table 12.1: revised corrective action for Method Blank. 12. Section 13.1: revised MDL frequency to every 6 months and as necessary. 13. New Section 14, Method Modifications added. 14. Section 15.1: updated SOP reference.	09May2013

S-IN-I-042-rev.14	1. Cover page: revised format for effective date and document control. 2. Section 5.1: added table for water and soil RLs. 3. Table 7.1: revised storage temperature. 4. Section 9.1: added QuickChem 8500. 5. Section 9.2: added sand and chlorine test strips. 6. Section 10.1: added sodium thiosulfate, sulfuric acid, buffer and diluents for QuickChem 8500. Added expiration period for buffer. 7. Table 10.3: added Int. #2 standard and working NO3 check standard. 8. Section 10.2.3: added Int. #2 standard, separated working calibration standards for QuickChem 8000 and 8500, added ICV for QuickChem 8500 and added working NO3 check standard. 9. Section 11.2: specified that a minimum of 5 calibration standards is required. 10.Section 11.3: specified that weighting may be used for linear calibrations. 11.Section 11.4: added non-linear calibration specifications. 12.Section 11.8: added ICB 13.Section 11.9: revised NO2 check standard requirements 14.Section 11.10: added NO3 check standard and column efficiency equation. 15.Section 11.11: added NO3/NO2 check standard corrective action. 16.Section 11.12: added a note regarding CCVs associated with non-linear calibration. 17.Section 12: separated aqueous and solid sample handling procedures. 18.Section 12.1: added chlorine check and pH adjustment of aqueous samples. 19.Table 13.1: clarified MS frequency 20.Section 14.1: clarified aqueous sample calculation. 21.Section 19: added method modification for ICAL evaluation/acceptance. 22.Section 25: added reference to Lachat methods.	07Oct2016
ENV-SOP-IND1-0045-rev.01	1. Removed cover, table of contents and headers for use in Master Control. 2. Section 6.4: added language that oily samples are usually rejected for analysis. 3. Section 10.2.3.2: corrected standard ID used from Int #2 to Int #1. 4. Sections 12.2.1 and 12.2.2: corrected dilution procedure to match practice. 5. Table 13.1: updated LCS corrective action to include one rerun attempt. 6. Section 18.1: updated MDL procedure reference. 7. Section 25.4: updated reference to include 2003 and 2009. 8. Section 27: updated Document Number with Master Control number.	11Nov2018

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QM Approval

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Management Approval

Name/Signature	Title	Date	Meaning/Reason
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1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to outline the procedures involved with the receipt, login, storage, and disposal of samples received by Pace Analytical Services, LLC.

2. Summary of Method

2.1. Samples are delivered to the laboratory via several delivery mechanisms. Samples received are checked for adherence to the Sample Acceptance Policy (see Attachment I) with any discrepancies noted. Discrepancies are communicated to the client if necessary for their acknowledgement and decision making.

2.2. The Laboratory Information Management System (LIMS) assigns all samples with a unique sample number and manages the analyses assigned to each sample.

2.3. Samples are labeled with the appropriate information and staged in refrigerated sample storage coolers if temperature preservation is required or possibly stored on open shelves for samples not requiring sub-ambient temperature preservation. Samples will remain under these conditions until prepared and/or analyzed. Samples received under United States Department of Agriculture (USDA) protocols need to be stored separately (please refer to the lab's Regulated Soils SOP, if applicable).

2.4. Samples and associated sub-samples (digestates, extracts, etc.), are maintained for a minimum of 45 days from receipt of samples unless otherwise requested by the client or other regulatory agency.

2.5. Samples are disposed of in accordance with local laboratory regulatory requirements, waste handling procedures, and any USDA regulated soil requirements.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP apply to all personnel involved in the receipt, login, storage, and disposal of samples.

3.2. The Sample Acceptance Policy (Attachment I) contains the guidelines for acceptable sample conditions. Any deviation from these guidelines requires detailed documentation within the report, usually as a footnote, or on the chain-of-custody (COC), or Sample Condition Upon Receipt (SCUR) form and may require client contact.

3.3. **Parameters**: Not applicable to this SOP.

4. Applicable Matrices

4.1. Refer to Table 8.1 in this SOP for the applicable matrices.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Samples may be prone to cross contamination from others within the same delivery group or from other client projects. The sample receiving personnel must make every effort to minimize cross- contamination.

6.2. Preservation checks are one of the most likely situations where cross-contamination may occur. Materials used in the process must be specific to each sample and may not used for multiple samples or multiple containers of the same sample.

6.3. Samples are stored under specific conditions and in specific locations, typically per the requirements of the analytical method. However, consideration must be given to samples that are uniquely different from others. Samples that are anticipated to be severely contaminated must be segregated from others in anticipation that the high levels of contaminants may cross-contaminate others in close proximity. USDA samples must also be distinctly segregated for storage.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Acceptable sample preservation, containers, and hold times can be referenced in the Bottle and Preservation Table, available within the Pace Quality Assurance Manual, or as a separate document. Samples are stored separately from all standards and reagents and any known highly contaminated samples.

7.2. **NOTE**: To avoid contamination, no food or drink products can be located near the areas where samples are unpacked, labeled, or staged.

7.3. Sample Storage – See Section 12.3 for general storage guidelines.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual.

8.2. **Chain-of-Custody (COC):** a form used to record the field identification of samples collected, analyses requested, date and time of collection, sample preservation used, and traceability of samples from time of collection until delivery to the laboratory. This is a legal document. See example Attachment II.

8.3. **Laboratory Information Management System (LIMS):** a computer system used to manage the flow and traceability of environmental samples and associated data within the laboratory.

8.4. **Matrix:** the bulk characteristics of a sample. See Table 8.1 below.

8.5. **Safety Data Sheet (SDS):** contains information on chemicals used in the laboratory.

8.6. **Sample Custody:** a sample is considered to be in someone's custody if:

8.6.1. It is in one's physical possession;

8.6.2. It is in someone's view, after being in someone's physical possession;

8.6.3. It is kept in a secured area, restricted to authorized personnel only.

8.7. **Sample Condition Upon Receipt (SCUR) form:** a form used to record the condition of samples received in the laboratory.

8.8. **Sample Receipt Form (SRF):** form generated by LIMS system after a project is logged in. Contains sample and project information.

8.9. **UN Number -** identification numbers preceded by the letters UN are associated with proper shipping names considered appropriate for international and domestic transportation. These shipping names along with the identification numbers are located in the Federal Register (49CFR172.101).

Table 8.1

NELAC/TNI defined matrix	Corresponding EPIC Pro matrices
Air and Emissions: Whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbant tube, impinger solution, filter, or other device.	Air (AR)
Aqueous: any aqueous sample excluded from the definition of Drinking Water or Saline/Estuarine. Includes surface water, ground water effluents, and TCLP or other extracts.	Water (WT)
Biological tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.	Tissue (TS) or Tissue Dry (TD)
Chemical Waste: a product or by-product of an industrial process that results in a matrix not previously defined.	Oil (OL) or Other (OT)
Drinking Water: any aqueous sample that has been designated a potable or potentially potable water source.	Drinking Water (DW)
Non-aqueous liquid: any organic liquid with < 15% settleable solids.	Other (OT)
Saline/Estuarine: any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake.	Water (WT)- not assigned as a separate matrix.
Solids: includes soils, sediments, sludges and other matrices with > 15% settleable solids.	Solid (SL)
(No corresponding matrix to wipes; wipes would be included in with solids)	Wipe (WP) or Swab (SW)

9. Equipment and Supplies (Including Computer Hardware and Software)

Table 9.1

Equipment/Supplies	Description
Sample Labels	
Thermometers	Infrared, digital, NIST traceable
Sample storage cooling units	Capable of holding required storage temperatures
COC forms	Chain of Custody forms
SCUR forms	
pH paper	Wide range, 0-14
Label Printer	
LIMS computer system	EPIC Pro
Disposable pipettes	
Sample containers	
Residual chlorine strips	Capable of measuring 0.5mg/L of chlorine
Temperature blank	

10. Reagents and Standards

10.1. All reagents used in this procedure must be labeled with:

10.1.1. Laboratory reagent identification number;

10.1.2. Unless otherwise noted, the name and concentration of the reagent;

10.1.3. Date the reagent was received, opened and, as needed, prepared;

10.1.4. Person preparing reagent;

10.1.5. Expiration date.

10.2. **Reagents: Table 10.1**

Reagent	Formula	Concentration
Sulfuric Acid	H_2SO_4	1:1
Nitric Acid	HNO_3	1:1
Hydrochloric Acid	HCl	1:1
Sodium Hydroxide	NaOH	50% or Pellets
Sodium Thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	
Zinc Acetate Solution (for sulfide)		
Methanol	CH_3OH	Purge and Trap Grade
Hexane	C_6H_{14}	Pesticide Grade
Ascorbic Acid (for cyanide)		
Sodium Bisulfate	$NaHSO_4$	

10.3. For acids, bases and other reagents obtained from other laboratory departments, this information is located in the appropriate hardcopy or electronic standards/reagent preparation log. In the event that these reagents are managed within the Sample Receiving group, the department must maintain its own reagent preparation log.

10.4. Alternatively, pre-preserved sample containers can be used. In this case, documentation must be maintained for bottleware and preservation traceability.

11. Calibration and Standardization

11.1. Thermometers, IR-Guns, and other equipment used for measuring temperatures must be calibrated according to SOP S-IN-Q-157 **Support Equipment**, or its equivalent revision or replacement.

12. Procedure

12.1. **Sample Receipt**

12.1.1. The laboratory receives client samples via three major methods: mail/commercial delivery service, Pace Analytical courier/field services and hand delivery.

12.1.2. **Courier COC Procedures**: Pace labs use courier services that pick up client samples on either a regular schedule or on an as-needed basis as communicated by Project Managers (PMs) or by the client.

12.1.2.1. When the client is present during courier pick-up, the client signs the COC relinquishing custody to the courier. The courier signs the COC as accepting the samples and provides the client with a copy of the COC. When the courier returns to the lab with the client samples, the courier signs the COC as relinquishing the samples to the lab.

12.1.2.2. If the client is not present during courier pick-up, the courier signs the COC as accepting the samples and leaves a copy of the COC for the client. If a client also has a sample log, the courier must sign and date the log when the samples are picked up. When the courier returns to the lab with the client samples, the courier signs the COC as relinquishing the samples to the lab. The date/time of delivery to the lab by the courier is the official date/time received by the lab (analogous to the official date/time of receipt by an outside commercial carrier or courier).

12.1.2.3. To ensure the sample security, the Pace courier vehicle is locked at each client pick-up location. IMPORTANT: Pace Analytical courier/field services personnel must open the sample coolers and verify there is adequate ice in the coolers before transporting or shipping to the laboratory. An exception to this policy would be for coolers already custody-sealed by the client. These coolers are not to be opened except by the receiving lab personnel.

12.1.3. **Lab COC Procedures**: If the client drops off the samples, the COC is signed by laboratory receiving personnel and a copy of the signed COC is given to the client at that time. If samples are received via commercial carrier or mail delivery, the COC is signed when the cooler or package is opened and processed for login. The delivery date and time is considered the date/time received.

12.1.3.1. **Samples Dropped Off:** Sample receiving personnel must review the COC for any evidence of rush turnaround requests, analyses with short hold times, or samples with very little hold time remaining. Projects that fall under these conditions must be given immediate attention. The PM responsible for that client must be alerted in the event that they have not already alerted the laboratory to the project as it may be possible that the client did not pre-schedule the project. Once the samples are received and logged into the LIMS, the sample technician and project manager will coordinate the notification and delivery of samples to the laboratory.

12.1.3.2. Internal Chain-of-Custody: If a client or program requires internal chain-of-custody (ICOC) procedures, the PM must determine, prior to log-in, which projects require ICOC processing and must clearly communicate the requirement to the laboratory. Refer to SOP S-IN-C-055 **Internal Chain-of-Custody** for detailed information.

12.1.4. **Sample Acceptance Policy -** Copies of the Sample Acceptance Policy must be provided, in the form of a letter, fax, or e-mail to each client or sampler, as necessary. Samples are considered acceptable if they meet the criteria listed in the Sample Acceptance Policy (see Attachment I)

12.1.4.1. Some labs may have agreements with clients regarding exceptions to the client contact requirements for sample acceptance policy deviations. If a lab has such agreements, two conditions must be met: 1) the agreement must be a formal document showing client approval; 2) the lab must qualify the final report as appropriate to their applicable regulatory bodies.

12.1.4.2. For Wisconsin Drinking Water samples: Samples that do not meet the criteria in the Sample Acceptance Policy will be rejected by sample custody. Sample custody will notify the PM and the client will be notified before proceeding with login. If the client wishes to proceed with analysis, the project manager will retain documentation of the request to proceed.

12.1.5. **Measuring cooler temperature – temperature blank:** Open the cooler and verify the temperature of the samples by taking the temperature of the temperature blank. If there is no temperature blank in the cooler, proceed to Section 12.1.6. The temperature of the temperature blank must be determined using a NIST-traceable stick thermometer. Remove the temperature blank bottle from the cooler and sit it on the benchtop. Remove the lid of the temperature blank and place the stick thermometer into the bottle. If the observed temperature of the temperature blank is outside of the acceptable range of 0°C to 6°C, proceed to Section 12.1.6.

12.1.6. **Contingency - measuring the temperature of cooler melt water:** If there is no temperature blank in the cooler or if the observed temperature of the temperature blank is outside of the acceptable

range of 0°C to 6°C, measure the temperature of visible cooler melt water**.** The temperature must be determined using a NIST-traceable stick thermometer. Place the stick thermometer into the cooler melt water. If the observed temperature of the visible cooler melt water is outside of the acceptable range of 0°C to 6°C, proceed to Section 12.1.7.

12.1.7. **Contingency - measuring temperature of a centrally located sample container:** If there is no temperature blank in the cooler, if there is no visible cooler melt water, or if the observed temperature of the temperature blank and/or cooler melt water is outside of the acceptable range of 0°C to 6°C, measure the temperature of a representative sample container. A representative sample container will be centrally located within the cooler. The temperature must be determined using a NIST-traceable IR gun. Remove the representative sample container from the cooler. While holding the container by the lid, take the container temperature using an IR gun pointed at an opaque surface such as the bottle label. If the observed temperature of the representative sample container is outside of the acceptable range of 0°C to 6°C, proceed to Section 12.1.8.

12.1.8. **Contingency – all measured temperatures are outside of the acceptable range:** If the observed temperature of the temperature blank, cooler melt water, and representative sample container are all outside of the acceptable range of 0°C to 6°C, immediately consult with the Sample Receiving Manager, the Project Manager, or the Customer Service Manager to initiate client notification and the need for additional documentation that may include photos of the cooler conditions upon receipt.

12.1.9. **Measuring the temperature of West Virginia samples:** measure the temperature of each sample container using an IR gun as described in Section 12.1.7 and document any container that is outside of the acceptable range of 0°C to 6°C.

12.1.10. Record the uncorrected (observed) and corrected cooler temperatures on the COC (example in Attachment II) and/or SCUR form (example in Attachment III. In addition, record the type of "ice" used for packing the cooler (e.g., wet ice, "blue ice", gel packs, etc.).

12.1.11. If samples within a project are spread over multiple coolers and one or more of the coolers are outside of the temperature criteria, then the contents of the cooler must be itemized and the samples and sample containers affected by the out-of-control temperature must be documented on the SCUR form for communication to the client. This itemization must be retained in the project file for future reference.

12.1.12. Make a copy of the COC. Give the original COC to login personnel to begin live login while the cooler is being unpacked.

12.1.13. Carefully unpack the cooler and organize the samples, grouped by client sample ID, according to the order on the COC. Review COC against samples to make sure the bottles received match the analysis requested. All anomalies must be recorded on the SCUR form and/or the Sample Container Count form (example in Attachment IV).

> 12.1.13.1. If a cooler is received at the end of the day and will not be checked in until the next day, the temperature of the cooler must be determined and documented. The COC must be evaluated for any requested short hold analyses before the cooler is placed into the walk-in overnight. If there are short hold analyses requested, the supervisor of the affected department must be notified.

12.1.14. For USDA samples, the cooler and all contents must be decontaminated with a 10% bleach solution (refer to Regulated Soil SOP for procedure). For non-USDA samples, discard any ice or water that remains in the cooler and the packing material used to secure the samples. Water or ice should be discarded down a drain that connects to the local sewer. Packing materials should be placed in the garbage. If a sample container was broken, the contents remaining in the cooler MUST be discarded in a manner consistent with the hazardous waste handling standard operating procedure. Refer to SOP S-IN-C-007 **Regulated Soil Handling** for detailed instructions.

12.1.15. **pH Verification Instructions:**

12.1.15.1. The pH of the sample must be verified on all preserved sample bottles requiring pH preservation (see exceptions in Section 12.1.11.3).

12.1.15.2. Open each preserved bottle (except as noted below). Use a new disposable pipette, a stirring rod or another inert utensil to withdraw a small portion of the sample. Dispense the aliquot onto an unused pH strip and check the pH.

12.1.15.3. **NOTE:** Do not check the pH of samples for coliform, volatiles, Wisconsin Diesel Range Organics (WI-DRO), oil and grease, hexane extractable materials (HEM), or any bottle with a septum lid. These analyses will be checked by the analyst at the bench and must not be opened by sample management personnel.

Table 12.1 – General pH Preservation Requirements by Preservative

Sample Preservatives	Sample pH Requirement
Hydrochloric Acid (HCl)	must be less than 2
Nitric Acid (HNO_3)	must be less than 2
Sulfuric Acid (H_2SO_4)	must be less than 2
Sodium Hydroxide (NaOH)	must be greater than 12
Zinc Acetate and Sodium Hydroxide (NaOH)	must be greater than 9

12.1.15.4. If the pH for a sample container that is supposed to be preserved is not within the required range, indicate the anomaly on the SCUR form or on the COC and mark the container with a red dot. If a sample does not require preservation, write N/A in the applicable section of the SCUR form.

12.1.15.5. Any pH adjustments will be made by the analytical departments.

12.1.16. **Total Residual Chlorine Verification Instructions -** Total residual chlorine must be verified at the time of receipt for certain analyses (see Table 12.2). Do not check the sample bottles for those analyses listed in 12.1.11.3.

12.1.16.1. Open the appropriate sample container. Utilizing a new disposable pipette, stirring bar or other inert utensil; withdraw a small portion of the sample. Dispense the aliquot on an unused residual chlorine test strip.

12.1.16.2. If any chlorine is detected, regardless of amount, note the information on the COC, SCUR or analytical bench sheet.

12.1.16.3. Samples that are positive for residual chlorine are immediately taken to the appropriate department for dechlorination.

Table 12.2 – Analyses requiring Residual Chlorine Verification

Analyses
Cyanides SM4500 CN, EPA 335.4, 9012, 9014
EPA 608
EPA 625

12.1.17. Note any discrepancies pertaining to samples as defined by the sample acceptance policy detailed above on the COC, SCUR, or Sample Container Count form, as applicable. Any discrepancies involving temperature, preservation, hold time, collection dates and times, sample volume, sample containers, and unclear analysis, must be reported to project management as soon as possible.

12.1.18. For short hold samples, the laboratory is notified and the samples are staged per Table 12.3.

Table 12.3 – Analyses with Short Holding Times

24-48 Hr. Short Hold Analyses

Waters

Method/Analytes	ACODE(S) & Department	Holding Time
Biochemical Oxygen Demand (BOD, CBOD, SM5210B)	5210BW, 5210BWC / **Wet Chem**	48 Hour
Color (SM2120B)	2120B W / **Wet Chem**	48 Hour
Hexavalent Chromium (Cr+6, CrVI, Cr6+,7196, SM3500-Cr B)	7196 W, 3500CrDW / **Wet Chem Unpreserved**	24 Hour
Nitrate/Nitrite (NO3, NO2, 353.2, 300.0, 9056)	3000 S, 3000 W, 9056 S, 9056 W / **GC** 3532 W / **Wet Chem**	48 Hour
Ortho-Phosphate (O-Phos, PO4, SM4500-P E)	4500PE WO / **Wet Chem**	48 Hour
Settleable Matter/Solids (SM2540F)	2540F W / **Wet Chem**	48 Hour
Sulfide Unpreserved (SM4500-S2 D)	4500S2D W / **Wet Chem**	24 Hour
Surfactant (MBAS, SM5540C)	5540C W / **Wet Chem**	48 Hour
Turbidity (Turb, 180.1)	1801 W / **Wet Chem**	48 Hour

Solids

Method/Analytes	ACODE(S) & Department	Holding Time
BP Volatile Soils	8260 S	Subsample within 48 hours
Volatile (8260 Terracore 5035A)	8260E5035A, 8260TCUST / **RCVG Freezer** or **VOA Freezer**	Frozen within 48 Hours of sampling

12.2. **Sample Login**

12.2.1. All samples received by the laboratory must be logged into the LIMS. Rush projects and/or projects with short holds are prioritized into four categories during the triage process. The four categories are Critical A (HT or TAT ≤ 24 hrs.), Critical B (HT or TAT ≤48 hrs.), Critical C (HT or TAT ≤4 days), and Non-Critical (HT or TAT ≥5 days). Critical A projects should be processed first, followed by Critical B, Critical C, then Non-Critical.

12.2.1.1. Samples must be logged into the LIMS so the samples can be uniquely identified (lab sample identification numbers). These lab sample ID numbers are used to track the prep and analysis activities of the samples, as well as identify the sub-samples, digestates, extracts, and other sample byproducts. This laboratory code maintains an unequivocal link with the unique client field sample ID code assigned to each sample.

12.2.1.2. Using the COC and LIMS profile, login the container types, number of containers, matrix, and requested tests. Once saved, LIMS will give the project a workorder number and each sample will be given a sequential sample number. Any special instructions to the lab should be communicated as a comment at the time of login, such as Regulated Soils, OH VAP, WC, etc. Once logged in, a Sample Receipt Form (SRF) will be generated by LIMS.

12.2.1.3. For foreign or domestic regulated soils, the project must be commented in LIMS at the time of login and a LabTrack must be created in the Hazardous Disposal queue to alert the lab to the special handling and disposal requirements of regulated soils.

12.2.2. Cross-check the SRF with the COC and then generate labels for each sample container.

12.2.3. Cross-check the information on the sample container and the sample label and attach the sample label to the appropriate sample container. Inform the Project Coordinator or Project Manager if there are any discrepancies between the sample containers and the sample labels.

12.2.4. If any samples require analyses performed outside of the laboratory, prepare the samples for subcontracting according to the procedures listed in the SOP describing the subcontracting of analytical services, S-IN-C-003 **Subcontracting Samples**, or equivalent revision or replacement.

12.2.5. SRF Review: The Project Manager, Project Coordinator, or designated Client Services personnel must review and verify the following information by comparing the COC to the SRF. Some of this information may not be provided by the client and those fields should be left blank:

12.2.5.1. Report Recipient(s);

12.2.5.2. Invoice Recipient;

12.2.5.3. PO#;

12.2.5.4. Project Name;

12.2.5.5. Project Number;

12.2.5.6. Requested Due Date;

12.2.5.7. Sample ID;

12.2.5.8. Matrix;

12.2.5.9. Collection Date & Time;

12.2.5.10. Received Date & Time;

12.2.5.11. Analysis: Double check compound lists;

12.2.5.12. Comments for special instructions to the lab (Regulated Soils, OH VAP, WV, etc.);

12.2.5.13. Price;

12.2.5.14. Region Codes;

12.2.5.15. Work Region % Split (for Pace internal subcontracted work).

12.3. **Sample Storage**

12.3.1. Once unpacked, samples will be logged into the LIMS in a timely manner and returned to appropriate storage conditions as soon as possible. Labs must make every effort to keep samples under the required thermal conditions during the login process. For the exceptional case where samples are not logged in the day they were received, they must be stored under appropriate temperature-controlled conditions until login takes place. In all cases, the sample temperatures must be taken as soon after receipt as possible and the samples stored to maintain the required storage conditions while awaiting login or labeling.

12.3.1.1. For ESI BP-XA projects, samples must be kept in the cooler while being processed. If not kept in the cooler, the temperature must be checked and documented every 20 minutes during processing.

12.3.2. Once logged into the LIMS and labeled, samples are placed in the appropriate storage areas. Specific temperature requirements are outlined in the analytical methods, but general guidelines are outlined below:

12.3.2.1. Short hold samples are delivered directly to the laboratory.

12.3.2.2. Summa canisters and Tedlar bags are stored on designated shelving at ambient temperature.

12.3.2.3. Volatiles- Aqueous samples are stored by receiving date or by project number in segregated volatiles cooler. Associated trip blanks are stored with the samples.

12.3.2.4. Volatiles- Soil and other solid samples received preserved in methanol are stored by receiving date or by project number in a segregated volatile cooler or freezer. Associated trip blanks are stored with the samples.

12.3.2.5. Volatiles- Soil and other solid samples received preserved with a stir bar, or deionized water and a stir bar, are stored by receiving date or by project number in a segregated volatiles freezer. Associated trip blanks are stored with samples when compatible with storage conditions.

12.3.2.6. Volatiles- Soil and other solid samples received in 4oz containers or similar bottleware are stored by receiving date or by project number in a segregated volatile cooler. If required by client or program, these samples may be sub-sampled and preserved upon receipt. In order to preserve these samples when required, it is necessary to collect a 5g aliquot of the sample and transfer it to a 40mL vial. One of the following preservation options must be utilized:

12.3.2.6.1. Add 5mL of deionized water and a stir bar to the 5g aliquot and preserve by storing in a freezer until analysis, or;

12.3.2.6.2. Within 48 hours of collection in the field, the 5g aliquot must be immediately extracted with 5mL of methanol and stored in a segregated volatiles cooler until analysis, or;

12.3.2.6.3. Within 48 hours of collection in the field, the 5g aliquot can be preserved with 10mL of deionized water and a stir bar, stored in a segregated volatile cooler and analyzed within 48 hours of collection.

12.3.2.7. Volatiles- Soil and other solid samples received in Encore samplers must be managed within 48 hours of collection by freezing the Encore or extruding it.

12.3.2.7.1. If extruding the sample into a 40mL vial containing a stir bar or a stir bar and 10mL of deionized water, then the sample is stored in the segregated volatile freezer until analysis.

12.3.2.7.2. If extruding the sample into methanol, then the sample is extracted within 48 hours of collection and the sample is stored in a segregated volatile cooler until analysis.

12.3.2.7.3. NOTE: if samples are not received within 48 hours of collection or are not received with enough time to process the samples correctly within 48 hours of collection, this must be noted in a way that will be visible on the final report (e.g., footnote in LIMS).

12.3.2.8. General Chemistry/Semi-volatiles- Waters and other liquid samples are staged by receiving date or by project number on the shelves in the appropriate sample storage cooler.

12.3.2.9. General Chemistry/Semi-volatiles- Soils and other solid samples are staged by receiving date or by project number on the shelves in the appropriate sample storage cooler.

12.3.2.10. Metals Solids and Liquids: These samples are staged by receiving date or by project number on designated shelving in the laboratory or appropriate designated area. These samples may be stored at ambient temperature unless Mercury or Hexavalent Chromium analysis is needed. If Mercury or Hexavalent Chromium analysis will be performed, the samples are staged by receiving date or by project number in the appropriate sample storage cooler. Samples requiring low level mercury analysis by Method 1631 are taken to the clean room for ambient storage and preservation, as needed.

12.4. **Sample Retention and Disposal**

12.4.1. If samples must be returned to customers, the lab must take special care to ensure that the samples are not damaged during any handling, testing, storing, or transporting processes.

12.4.2. Samples may need to be retained longer than the normal sample retention time (45 days from sample receipt). Reasons for this extended sample retention include: customer, program, or contract requirements so that samples can be retained in a secure location for the customers that is designated as a long-term storage area. In these cases, the samples are noted in LabTrack, labeled, and segregated by extended hold.

12.4.3. Disposal of unconsumed samples: Refer to the laboratory SOPs regarding waste handling and disposal: **Waste Management and Handling S-IN-W-002**, and **Regulated Soil Handling S-IN-C-007**, or current revisions or replacements.

13. Quality Control

13.1. For any sample received at the laboratory that does not meet the sample acceptance, hold time or preservation criteria, the client must be contacted by project management and advised of the situation.

13.1.1. If the client instructs the laboratory to proceed with the analysis, all appropriate personnel/departments must be informed and the client approval must be documented on the SCUR or COC. Data will be appropriately qualified.

13.1.2. The client may also instruct the laboratory to preserve the samples at the laboratory prior to proceeding with analysis. This must be documented on the COC or the SCUR, and must be noted in the final laboratory report.

13.2. All supporting documentation related to sample custody must be retained by the laboratory. This includes: memorandums, fax transmissions, the original COC, all paperwork received with the COC, the completed SCUR form and copies of email transmissions. Please contact the laboratory QM/SQM for documentation retention time frames required.

13.3. Documenting discrepancies during receipt of samples:

13.3.1. The following are examples of client discrepancies that need to be documented on the appropriate paperwork (e.g., SCUR form):

13.3.1.1. Lost samples/insufficient sample volume;

13.3.1.2. Broken or missing bottles;

13.3.1.3. Missing COC;

13.3.1.4. Mislabeled bottles;

13.3.1.5. Preservation error;

13.3.1.6. Missing sample related details (date, time, sample type).

13.3.2. Pace sample management discrepancies will be documented on the SCUR form, COC or within the project files. Discrepancies attributable to errors and omissions on the part of the laboratory will be addressed and resolved through the formal corrective action process.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. Hazards and Precautions - Use extreme caution in handling samples and wastes as they may be hazardous. Each reagent and chemical used in this method should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats, safety glasses, and ventilation hoods. SDS are on file and available to all personnel.

22.2. All personnel involved in sample management are responsible for complying with OSHA and DOT regulations. These regulations pertain to the safe handling and/or shipping of the chemicals specified in this procedure. Refer to the Sample Control Supervisor for any questions or concerns related to the safe handling and shipment of hazardous materials.

22.3. Other laboratory safety requirements are contained in the Chemical Hygiene Plan/Safety Manual. Immediate questions can also be addressed with the local Safety Officer.

23. Waste Management

23.1. Not applicable to this SOP.

24. Pollution Prevention

24.1. Not applicable to this SOP.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. The NELAC Institute (TNI) Standard- 2003 and 2009.

25.3. SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA, current revision.

25.4. American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1995, Standard Methods for the Examination of Water and Wastewater, A.E. Greenberg, L.W. Clesceri, A.D. Eaton and M.A.H. Franson, eds., 19th ed., American Public Health Association, Washington D.C.

25.5. U.S. Environmental Protection Agency, 1983, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

25.6. U.S. Environmental Protection Agency, 1988, Methods for Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.

25.7. Code of Federal Regulations- most recent version.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: Sample Acceptance Policy

26.2. Attachment II – Example Chain of Custody

26.3. Attachment III – Example Sample Condition Upon Receipt form

26.4. Attachment IV - Example Sample Container Count Form

27. Revisions

Document Number	Reason for Change	Date
S-IN-C-001-rev.07	1. Cover page: changed phone number, added SOP Template number and updated document control format. 2. Section 4.3: added that highly contaminated samples are double bagged. 3. Section 5.1: changed MSDS to SDS 4. Section 6: added Table 6.1 and updated the definition of matrix and MSDS to SDS. 5. Table 9.1: added ascorbic acid, sodium bisulfate and monochloroacetic acid. 6. Section 11.1.2: added more detail regarding courier procedures. 7. Section 11.5.7: added detail regarding required sample temperature upon receipt. 8. Section 11.1.5.8: added WI drinking water acceptance requirements. 9. Section 11.1.6: changed IR temp reading from an average of multiple bottles to a single reading of a representative sample. Added West Virginia sample temp requirements. 10. Section 11.3.1: added that chlorine checks should not be performed for containers upon which chemical preservation should not be checked as in Section 11.2.1. 11. Table 11.2: added 625, 608 and Cyanide. 12. Table 11.3: added bacteria, odor, color, MBAS and settleable solids. 13. Section 11.8: added section for sample retention and disposal. 14. Section 13.1: added that applicable personnel must read and understand this SOP. 15. Updated attachments.	13Oct2015
S-IN-C-001-rev.08	1. Adapted from SOT-ALL-C-001-rev.06. 2. Table 9.1: added requirements for residual chlorine test strips. 3. Table 10.1: added hexane 4. Section 12.1.3: added general statement regarding internal COC. 5. Section 12.1.7: added temperature measurement for West Virginia samples. 6. Section 12.1.11: added procedure for coolers received late in the day. 7. Section 12.1.13: removed TOC as a parameter not pH-checked at receipt. Added procedure to mark the lid of sample determined to be under-preserved and added statement that pH adjustments are made by the analytical departments. 8. Section 12.1.14: added details for handling samples determined to contain residual chlorine. 9. Table 12.2: added methods 9012 and 9014. 10. Section 12.2: added detail for current login procedures. 11. Section 12.3: added detail for current sample storage procedures. 12. Section 12.4: added use of LabTrack for tracking extended hold of samples. 13. Section 25.2: added years 2003 and 2009 to TNI reference. 14. Attachment I: removed TOC as parameter not pH-checked at time of receipt. 15. Attachment III: added example of SCUR.	30Oct2017
S-IN-C-001-rev.09	1. Cover page: added signature line for Sample Receiving Manager. 2. Section 12.1.3: revised language to match our process for signing the COC. 3. Section 12.1.5: added detail to procedure for measuring temperature blank. 4. Sections 12.1.6 – 12.1.8: added contingencies for measuring cooler temperature. 5. Section 12.1.9: added detail for measuring West Virginia sample temperatures. 6. Table 12.3: updated to current information. 7. Section 26.4: added Attachment VI for Sample Container Count 8. Attachments: updated all to current version.	6Aug2018

Attachment I – Sample Acceptance Policy

In accordance with regulatory guidelines, Pace Analytical facilities comply with the following sample acceptance policy for all samples received.

If the samples do not meet the sample receipt acceptance criteria outlined below, the Pace facility is required to document all non-compliances, contact the client, and either reject the samples or fully document any decisions to proceed with analyses of samples that do not meet these criteria. Any results reported from samples not meeting these criteria are appropriately communicated to the client.

Sample Acceptance Policy requirements**:**

1. Sample containers must have unique client identification designations, and dates and times of collection, that are clearly marked with indelible ink on durable, water-resistant labels. The client identifications must match those on the chain-of-custody (COC);
2. There must be clear documentation on the COC, or related documents such as the Sample Condition Upon Receipt (SCUR) form, that lists the unique sample identification, sampling site location (including state; some regulations may require city, county, etc.), date and time of sample collection, and name and signature of the sample collector;
3. There must be clear documentation on the COC, or related documents, that lists the requested analyses, the preservatives used, sample matrix, and any special remarks concerning the samples (i.e., data deliverables, samples are for evidentiary purposes, field filtration, etc.);
4. Samples must be in appropriate sample containers. If the sample containers show signs of damage (i.e., broken or leaking) or if the samples show signs of contamination, the samples will not be processed without prior client approval;
5. Samples must be correctly preserved upon receipt, unless the method requested allows for laboratory preservation. If the samples are received with inadequate preservation, and the samples cannot be preserved by the lab appropriately, the samples will not be processed without prior client approval;
6. Samples must be received within required holding time. Any samples with hold times that are exceeded will not be processed without prior client approval;
7. Samples must be received with sufficient sample volume or weight to proceed with the analytical testing. If insufficient sample volume or weight is received, analysis will not proceed without client approval;
8. All samples that require thermal preservation are considered acceptable if they are received at a temperature within 2°C of the required temperature, or within the method-specified range. For samples with a required temperature of 4°C, samples with a temperature ranging from just above freezing to 6°C are acceptable. Samples that are delivered to the lab on the same day they are collected are considered acceptable if the samples are received on ice. Any samples that are not received at the required temperature will not be processed without prior client approval.
9. For all compliance **drinking water** samples, analyses will be rejected at the time of receipt if they are not received in a secure manner, are received in inappropriate containers, are received outside the required temperature range, are received outside the recognized holding time, are received with inadequate identification on sample containers or COC, or are improperly preserved (with the exception of VOA samples- tested for pH at time of analysis).
10. Some specific clients may require custody seals. **For these clients**, samples or coolers that are not received with the proper custody seals will not be processed without prior client approval.

Attachment II – Example Chain-of-Custody Form

CHAIN-OF-CUSTODY Analytical Request Document

Pace Analytical

Chain-of-Custody is a LEGAL DOCUMENT - Complete all relevent fields

LAB USE ONLY- Affix Workorder/Login Label Here or List Pace Workorder Number or MTJL Log-in Number Here

ALL SHADED AREAS are for LAB USE ONLY

Company:	Billing Information:
Address:	
Report To:	Email To:
Copy To:	Site Collection Info/Address:
Customer Project Name/Number:	State: County/City: Time Zone Collected: / [ ]PT [ ]MT [ ]CT [ ]ET
Phone: Email:	Site/Facility ID #: — Compliance Monitoring? [ ] Yes [ ] No
Collected By (print):	Purchase Order # : Quote #: — DW PWS ID #: DW Location Code:
Collected By (signature):	Turnaround Date Required: — Immediately Packed on Ice: [ ] Yes [ ] No
Sample Disposal: [ ] Dispose as appropriate [ ] Return [ ] Archive: _____ [ ] Hold:	Rush: [ ] Same Day [ ] Next Day [ ] 2 Day [ ] 3 Day [ ] 4 Day [ ] 5 Day (Expedite Charges Apply) — Field Filtered (if applicable): [ ] Yes [ ] No Analysis:

* Matrix Codes (Insert in Matrix box below): Drinking Water (DW), Ground Water (GW), Wastewater (WW), Product (P), Soil/Solid (SL), Oil (OL), Wipe (WP), Air (AR), Tissue (TS), Bioassay (B), Vapor (V), Other (OT)

Container Preservative Type **

Lab Project Manager:

** Preservative Types: (1) nitric acid, (2) sulfuric acid, (3) hydrochloric acid, (4) sodium hydroxide, (5) zinc acetate, (6) methanol, (7) sodium bisulfate, (8) sodium thiosulfate, (9) hexane, (A) ascorbic acid, (B) ammonium sulfate, (C) ammonium hydroxide, (D) TSP, (U) Unpresreved, (O) Other _____

Analyses

Lab Profile/Line:

Lab Sample Receipt Checklist:
Custody Seals Present/Intact Y N NA
Custody Signatures Present Y N NA
Collector Signature Present Y N NA
Bottles Intact Y N NA
Correct Bottles Y N NA
Sufficient Volume Y N NA
Samples Received on Ice Y N NA
VOA –Headspace Acceptable Y N NA
USDA Regulated Soils Y N NA
Samples in Holding Time Y N NA
Residual Chlorine Present Y N NA
Cl Strips: _____
Sample pH Acceptable Y N NA
pH Strips: _____
Sulfide Present Y N NA
Lead Acetate Strips: _____

LAB USE ONLY:
Lab Sample # / Comments:

Customer Sample ID	Matrix *	Comp / Grab	Collected (or Composite Start) Date	Collected (or Composite Start) Time	Composite End Date	Composite End Time	Res Cl	# of Ctns

Customer Remarks / Special Conditions / Possible Hazards:

Type of Ice Used: Wet Blue Dry None

Packing Material Used:

Radchem sample(s) screened (<500 cpm): Y N NA

SHORT HOLDS PRESENT (<72 hours): Y N N/A

Lab Tracking #:

Samples received via: FEDEX UPS Client Courier Pace Courier

LAB Sample Temperature Info:
Temp Blank Received: Y N NA
Therm ID#: _____
Cooler1 Temp Upon Receipt: __oC
Cooler1 Therm Corr. Factor: ___oC
Cooler1 Corrected Temp: _____oC
Comments:

Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:	MTJL LAB USE ONLY Table #:
Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:	Acctnum: Template: Prelogin: PM: PB:
Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:	Trip Blank Received: Y N NA HCL MeOH TSP Other; Non Conformance(s): YES / NO; Page: _____ of: _____

Attachment III – Example Sample Condition Upon Receipt Form

Pace Analytical

SAMPLE CONDITION UPON RECEIPT FORM

Project #: _____ **Date/Time and Initials of person examining**

Courier: ☐ Fed Ex ☐ UPS ☐ USPS ☐ Client ☐ Commercial ☐ Pace ☐ Other _____

Tracking #: _____

Custody Seal on Cooler/Box Present: ☐ Yes ☐ No **Seals Intact:** ☐ Yes ☐ No

Packing Material: ☐ Bubble Wrap ☐ Bubble Bags ☐ None ☐ Other _____

Thermometer: 1 2 3 4 5 6 A B C D E F Ice Type: ☐ Wet ☐ Blue ☐ None | Samples collected today and on ice ☐ Yes ☐ No ☐ N/A

Cooler Temperature: _____ Ice Visible in Sample Containers?: ☐ Yes ☐ No ☐ N/A

(Initial/Corrected) Temp should be above freezing to 6°C If temp. is Over 6°C or under 0°C, was the PM Notified?: ☐ Yes ☐ No ☐ N/A

All discrepancies will be written out in the comments section below.

	Yes	No		Yes	No	N/A
Are samples from West Virginia? Document any containers out of temp.			checked?: **exceptions: VOA, coliform, LLHg, O&G, and any container with a septum cap or preserved with HCl.**			
USDA Regulated Soils? (ID, NY, WA, OR,CA, NM, TX, OK, AR, LA, TN, AL, MS, NC, SC, GA, FL, or Puerto Rico)			All containers needing preservation are found to be in compliance with EPA recommendation (<2, >9, >12) unless otherwise noted.			
Chain of Custody Present:			Circle: HNO3 H2SO4 NaOH NaOH/ZnAc			
Chain of Custody Filled Out:			Dissolved Metals field filtered?:			
Short Hold Time Analysis (<72hr)?: Analysis:			Headspace Wisconsin Sulfide			
Time 5035A TC placed in Freezer or Short Holds To Lab:				Present	Absent	N/A
			Residual Chlorine Check (SVOC 625 Pest/PCB 608)			
			Residual Chlorine Check (Total/Amenable/Free Cyanide)			
Rush TAT Requested:			Headspace in VOA Vials (>6mm):			
Containers Intact?:			Trip Blank Present?:			
Sample Labels Match COC?: Except TCs, which only require sample ID			Trip Blank Custody Seals?:			

Comments:

F-IN-Q-290-rev.16,5Mar2018

Attachment IV – Example Sample Container Count Form

CLIENT: _____

COC PAGE ____ **of** ____

COC ID# _____ Project # _____

Sample Line Item	DG9H	VG9H	AG0U	AG1H	AG1U	AG2U	AG3S	WGFU	SP5T	BP1U	BP2N	BP2S	BP2U	BP3B	BP3N	BP3S	BP3U	SBS Bulk Kit R	DI			Matrix SI/Wt/NAL (Soil/Water/Non-Aqueous Liquid)	pH <2	pH >9	pH>12
1																									
2																									
3																									
4																									
5																									
6																									
7																									
8																									
9																									
10																									
11																									
12																									

Container Codes

Glass

DG9B	40mL Na Bisulfate amber vial	AG0U	100mL unpreserved amber glass
DG9H	40mL HCL amber voa vial	AG1H	1 liter HCL amber glass
DG9M	40mL MeOH clear vial	AG1S	1 liter H2SO4 amber glass
DG9P	40mL TSP amber vial	AG1T	1 liter Na Thiosulfate amber glass
DG9S	40mL H2SO4 amber vial	AG1U	1liter unpreserved amber glass
DG9T	40mL Na Thio amber vial	AG2N	500mL HNO3 amber glass
DG9U	40mL unpreserved **amber** vial	AG2S	500mL H2SO4 amber glass
VG9H	40mL HCL clear vial	AG2U	500mL unpreserved amber glass
VG9T	40mL Na Thio. clear vial	AG3S	250mL H2SO4 glass amber
VG9U	40mL unpreserved **clear** vial	AG3U	250mL unpreserved amber glass
VGFX	40mL w/hexane wipe vial	BG1H	1 liter HCL clear glass
VSG	Headspace septa vial & HCL	BG1S	1 liter H2SO4 clear glass
WGKU	8oz unpreserved clear jar	BG1T	1 liter Na Thiosulfate clear glass
WGFU	4oz clear soil jar	BG1U	1 liter unpreserved glass
JGFU	4oz unpreserved amber wide	BG3H	250mL HCl Clear Glass
		BG3U	250mL Unpreserved Clear Glass

Plastic / Misc.

BP1A	1 liter NaOH, Asc Acid plastic	BP3U	250mL unpreserved plastic
BP1N	1 liter HNO3 plastic	BP3Z	250mL NaOH, Zn Ac plastic
BP1S	1 liter H2SO4 plastic		
BP1U	1 liter unpreserved plastic	AF	Air Filter
BP1Z	1 liter NaOH, Zn, Ac	C	Air Cassettes
BP2A	500mL NaOH, Asc Acid plastic	R	Terra core kit
BP2N	500mL HNO3 plastic	SP5T	120mL Coliform Na Thiosulfate
BP2O	500mL NaOH plastic	U	Summa Can
BP2S	500mL H2SO4 plastic	ZPLC	Ziploc Bag
BP2U	500mL unpreserved plastic		
BP2Z	500mL NaOH, Zn Ac		
BP3B	250mL NaOH plastic		
BP3N	250mL HNO3 plastic		
BP3S	250mL H2SO4 plastic		

Document Information

Document Number: ENV-SOP-IND1-0005 **Revision:** 00

Document Title: Subcontracting Samples

Department(s): Client Services

Previous Document Number: S-IN-C-003-rev.05

Date Information

Effective Date: 02 Oct 2017

Next Review Date: 02 Oct 2019 **Last Review Date:**

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Pace Analytical Services
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Indianapolis, IN 46268
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STANDARD OPERATING PROCEDURE

SUBCONTRACTING SAMPLES

Reference Methods: N/A

Local SOP Number:	S-IN-C-003-rev.05
Effective Date:	October 2, 2017
Supersedes:	S-IN-C-003-rev.04
SOP Template Number:	SOT-ALL-C-003-rev.07

APPROVALS

General Manager — September 19, 2017 Date

Quality Manager — September 19, 2017 Date

Client Services Manager — September 19, 2017 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

This is **COPY#** _____ Distributed on _____ by _____ and is ____ **CONTROLLED**

S-IN-C-003-rev.05

Table of Contents

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to establish a uniform system in the event that samples must be transferred to another laboratory for analysis. The following procedures are intended to prevent any negative impact on data quality or turnaround time, maintain accurate records of shipped samples, and ensure proper revenue allocation.

2. Summary of Method

2.1. Samples are subcontracted to a Pace network laboratory or to an outside laboratory when the analysis cannot be performed by the owner region/laboratory. Samples are subcontracted only with the consent and approval of the client. The subcontracted laboratory must maintain current NELAC/TNI, or other federal program certification or other primary state accreditation for the state the samples originated from unless prior approval from the client is received to use an alternate laboratory. Whenever possible, arrangements for a subcontracted analysis must be made prior to start of the project.

2.2. Sample analysis may be subcontracted when senior lab management determines that the present workload of the laboratory prohibits the analysis of samples within the required hold times or project due date, the requested method/parameter has not been developed, or when the required certification or accreditation is not current.

2.3. All revenue must be properly allocated through the Laboratory Information Management System (LIMS) or alternate system. In the case of a new project with tests that must be subcontracted, the Account Executives should identify the subcontract labs during the quoting process.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP apply to all personnel involved in the process of subcontracting samples to another lab.

3.2. This SOP is applicable to all samples requiring transfer to another laboratory in order to meet holding time, certification, or method requirements.

3.3. **Parameters**: Not applicable to this SOP.

4. Applicable Matrices

4.1. Not applicable to this SOP.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Not applicable to this SOP.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Samples that will be subcontracted will be checked in using the same process as samples remaining in the owning lab. Adjustment of sample pH will be done by the work lab.

7.2. Samples to be shipped to another laboratory for analyses must be shipped according to the handling and preservation requirements of the analysis to be performed.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Quality Manual, Glossary Section.

8.2. **Sending Region** – This is the laboratory that originally received the samples and will be producing the invoice.

8.3. **Receiving Region –** This is the laboratory that receives the samples from another Pace laboratory.

8.4. **SI (Sub in) Code -** Subcontracting code used to define which area in the laboratory will receive the payment. This may have a different name depending on which LIMS is used.

8.5. **SO (Sub out) code** – Subcontracting code used to define that the samples were sent to a laboratory outside the Pace network. This may have a different name depending on which LIMS is used.

8.6. **Analysis code -** This is a group of data which describes a specific analysis. It is comprised of all the data necessary to perform procedures and report results.

8.7. **Sample Acceptance Form (SAF)**: form generated by LIMS system after a project is logged in and reviewed by the Project Manager. This form is sent to the client electronically. This may have a different name depending on which LIMS is used.

8.8. **Sample Receipt Form (SRF):** form generated by LIMS system after a project is logged in. Contains sample and project information. This may have a different name depending on which LIMS is used.

9. Equipment and Supplies

Table 9.1

Equipment/Supplies	Description/ Comments
Sample Labels	
Sample Containers and/or kits	
Coolers	
Plastic bags	
Blank Chains-of-Custody	
Bottle Order Database	
Preservatives	
Disposable pipettes	
Bubble wrap	
Absorbent Sheets or other packing materials	
USDA labels	

10. Reagents and Standards

10.1. Not applicable to this SOP.

11. Calibration and Standardization

11.1. Not applicable to this SOP.

12. Procedure

12.1. When it is determined that a Pace laboratory cannot perform an analysis, the Project Manager (PM) or Project Coordinator (PC) associated with those samples must locate and secure the services of another facility.

12.1.1. If the analysis is routine to the sending region and the sample must be shipped (e.g., due to capacity issues, equipment failure, etc.), then the department manager is responsible for notifying the PM that the samples must be shipped.

12.2. The PM/PC must obtain client approval before subcontracting the samples.

12.3. Contractual obligations must be considered in the decision of where to send samples. Client permission may be obtained verbally, but must be received via e-mail, facsimile, and/or writing prior to the submission of results. **Note:** Copies of telephone logs may be used as a form of documentation and should be copied into the project file.

12.3.1. All subcontract laboratories must submit proof of applicable accreditation prior to receiving samples from a Pace lab. There must also be a subcontract lab information form and proof of insurance on file.

12.3.2. Only pre-approved subcontract labs will be used unless a client requires Pace to use a specific subcontract lab.

12.3.3. If Pace wants to add another subcontract lab to the approved list of labs, refer to the procedures listed in SOP **S-IN-Q-027, Evaluation and Qualification of Vendors.**

12.3.4. If the subcontract laboratory is not approved to perform the work, Pace can either refrain from sending samples or initiate a formal inspection of the proposed facility.

12.3.5. The sending lab must communicate any extra information necessary for the subcontract lab to perform the work properly (i.e., technical specifications involved, specific storage requirements needed, etc.).

12.4. When subcontracting samples to another laboratory, the PM/PC must discuss the following information with the subcontracting laboratory:

12.4.1. Analyses/Methods;

12.4.2. Number of samples;

12.4.3. Matrix;

12.4.4. Receipt Date;

12.4.5. Due Date;

12.4.6. Dry weight for soil samples;

12.4.7. Holding Time Constraints;

12.4.8. Required reporting limits;

12.4.9. QC Deliverables;

12.4.10. Certification requirements;

12.4.11. USDA Soil Permit requirements (as necessary);

12.4.12. Required sample volumes and preservatives.

12.5. If samples are sent to another Pace laboratory (inter-regionally), the sending region will perform the following tasks:

12.5.1. Log the samples into the LIMS using the appropriate 'Sub-In' analysis codes inherent to the lab's LIMS, however named.

12.5.2. Obtain an Inter-Laboratory Work Order (IRWO) form (example Attachment I) or similar form, depending on the LIMS used.

12.5.3. Assign Inter-Laboratory Work Order (IRWO) number and complete some form of Interregional Sub-out log (this is optional).

12.5.4. Enter the following information into the IRWO Form (example Attachment I) or similar form. Keep a copy in the project file.

12.5.4.1. Today's date in the space marked "Date prepared" and the date the results are due to the sending region is noted in "Requested Completion Date".

12.5.4.2. Sending region, receiving region, state of sample origin, the type of QC deliverable, external client and sending Project Manager must be filled in on the IRWO form.

12.5.4.3. Sending Project number/ Work Order Number– assigned by LIMS in sending laboratory.

12.5.4.4. Check off what type of work is being sent, the requested reportable units, and whether to report the data moisture corrected (dry weight).

12.5.4.5. Enter method description, container type, quantity of containers, preservative, quantity of samples, and unit price.

12.5.4.5.1. Total Price, which is split between the two laboratories. The system will default to 80/20 for all tests (except for dioxin which defaults to a 90/10 split); if different enter the correct split. This means that 80% of the revenue goes to the work region and 20% of the revenue goes to the owner region.

12.5.4.5.2. Mark if the samples are to be returned to the sending laboratory; if checked no, the receiving laboratory is responsible for final disposition of the remaining sample volume.

12.5.4.5.3. Mark the matrix of the samples.

12.5.5. Attach a copy of the sub-in COC printed from LIMS (if applicable) and mark the appropriate box on the IRWO form.

12.5.6. Attach a copy of the Sample Condition Upon Receipt (SCUR) form that was completed during the sample staging process.

12.5.7. A copy of the Inter-Regional Work Order (or IRWO/Sub-COC) form must be placed in the project folder.

12.5.8. If sending extracts, include prep batch logs and standards prep information. Include compound list and reporting limits when clients request a special list.

12.5.9. All paperwork being shipped must be placed in a sealable bag, and may be emailed or faxed prior to shipment.

12.5.10. Once the samples are received in the receiving region, the following information is entered into the LIMS:

12.5.10.1. Project number – this will be the receiving lab's project number and is assigned by LIMS.

12.5.10.2. Sample number(s) - must be the sending lab's sample number. These numbers must appear on the report run from LIMS by the sending lab.

12.5.10.3. Client ID – from the sending region.

12.5.10.4. Receipt date – must be the date received by the receiving lab, not that of the original sending lab.

12.5.10.5. Split between the two labs. System will default to 80/20; if different enter the correct split. The percent entered should be the receiving region's share of the revenue.

12.5.10.6. Full charge for the work being completed.

12.5.10.7. Analysis code - will be the receiving lab's method specific analysis code.

12.5.11. Project completion- Receiving Region:

12.5.11.1. Deliver results to the sending lab.

12.5.11.2. Enter a Ship Date in the Project Edit screen, this closes out the project.

12.5.11.3. Sends the IRWO form to the ABM and may keep a copy in the project file.

12.5.12. Project completion- Sending Region:

12.5.12.1. Batch the interregional schedules (analysis codes) and validate, thus forcing them to completion.

12.6. If samples are sent outside of Pace, the following tasks must be performed once the subcontract laboratory has been approved:

12.6.1. Create new COC in LIMS using Client project and sample identifications but do not put Client name on owner COC (example Attachment II). Retain copy of COC and file with PM/PC paperwork.

12.6.2. Note: Attach Compound List and Reporting Limits if clarification is needed.

12.7. Once the reports are received from the subcontract labs (internal or external labs), the reports are collated with any information from the sending laboratory. All information pertaining to the analysis of the samples is fully disclosed to the client.

12.7.1. The subcontract lab must be noted clearly somewhere on the final report to the client (e.g., the cover letter). A comment may be added to the final report with wording such as "The samples were subcontracted to <Full Name and Address of the Subcontracted Laboratory> for <specific tests> analysis. Results of this analysis are reported on the <Full Lab Name> final report".

12.7.2. At a minimum, the subcontract lab must provide Pace with a method blank and LCS for all target analytes, where applicable to the test. This is the minimum amount of quality control necessary to evaluate the subcontract lab data.

12.8. The sending lab must make all pertinent sample receipt information available to the lab performing the actual sample analysis. If the sending lab has already performed sample receipt activities (e.g., preservation checks, etc.), this must be fully documented on the COC or SCUR that is sent to the lab running the samples. Adjustment of sample pH will be done by the work lab.

13. Quality Control

13.1. Minimum data review requirements: The sending lab must review the following information when receiving a final report from a subcontract lab. If any of these items is incorrect or lacking information, the PM/PC must contact the subcontract lab to obtain the correct information or to obtain a revised final report:

13.1.1. Verify analytical tests are correct per sample number;

13.1.2. Verify analyte lists are correct per test;

13.1.3. Verify that the minimum amount of quality control has been completed for each test (method blank and LCS).

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. Not applicable to this SOP.

23. Waste Management

23.1. Not applicable to this SOP.

24. Pollution Prevention

24.1. Not applicable to this SOP.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. The NELAC Institute (TNI) Standard- 2003 and 2009.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: Example Inter-Regional Work Order (IRWO).

26.2. Attachment II: Example Chain of Custody.

27. Revisions

Document Number	Reason for Change	Date
S-IN-C-003-rev.02	1. Cover page: removed reference to SOP Template. Revised format to Periodic Review from Annual Review format. Updated copyright information. 2. Table of Contents: removed reference to attachments. 3. Section 7 Responsibilities and Distribution removed because this information is contained in the Quality Manual. Removal caused section numbering to change. 4. Section 11 Procedure (previously Section 12): reorganized entire section and simplified the information in old section 12.5.4. 5. Section 15: added TNI reference. 6. Section 16: updated list of attachments. 7. Attachments: updated attachment versions and added two new attachments.	14Jun2011
S-IN-C-003-rev.03	1. Cover Page: added address to upper right corner of page 2. Table of Contents: added new Section 14, Method Modifications 3. New Section 14 added, Method Modifications.	17Jun2013
S-IN-C-003-rev.04	1. Cover page: changed phone number 2. Section 11.6.4: added as requirement for sub lab QC. 3. Attachment 1: updated	10Sep2015
S-IN-C-003-rev.05	1. Adapted from SOT-ALL-C-003-rev.07. 2. Section 25.2: added years 2003 and 2009 to TNI reference.	18Sep2017

Attachment I- Example Inter-Regional Work Order

Pace Analytical™

INTER-LABORATORY WORK ORDER #_____
(To be completed by sending lab)

Sending Project No:	
Receiving Project No:	
Check Box for Consolidated Invoice:	☐
Date Prepared:	
REQUESTED COMPLETION DATE:	

Sending Region		Sending Project Mgr.	
Receiving Region		External Client	
State of Sample Origin		QC Deliverable	

All questions should be addressed to sending project manager.

Type of Work: Analytical ☐ Other (Identify) _____
Requested Reportable Units _____ Report Wet or Dry Weight? _____

WORK REQUESTED

Method Description	Container Type (Include volume)	Quantity of containers	Preservative	Quantity of Samples	Unit Price	Amount
						$ -
						$ -
						$ -
						$ -
						$ -
						$ -
					TOTAL	$ -

Special Requirements: _____

Receiving Region Department	Acctg. Code	Totals from above	Revenue Allocation	
			Receiving Region (80%)	Client Services Dept. Sending Region (20%)
Microbiology	17		$ -	$ -
Metals	20		$ -	$ -
Wet Chem.	21		$ -	$ -
ICPMS	22		$ -	$ -
SV GCMS	30		$ -	$ -
SV GC & LC	31		$ -	$ -
V GC	33		$ -	$ -
V GCMS	34		$ -	$ -
Dioxin* (Includes Coplanar PCBs & PBDEs)	35		$ -	$ -
Radiation*	38		$ -	$ -
Air	39		$ -	$ -
Asbestos	60		$ -	$ -
Other(Specify)			$ -	$ -
Total			$ -	$ -

*Revenue Allocation (Receiving Region (90%) and Sending Region (10%))

FOR ANALYTICAL WORK COMPLETE THIS SECTION ALSO

Chain of Custody Included: ☐ Yes ☐ No Return Samples to Sending Region: ☐ Yes ☐ No

Matrix: ☐ Soil ☐ Water ☐ Air ☐ Other (Identify) _____

CONFIRMATION OF WORK COMPLETED

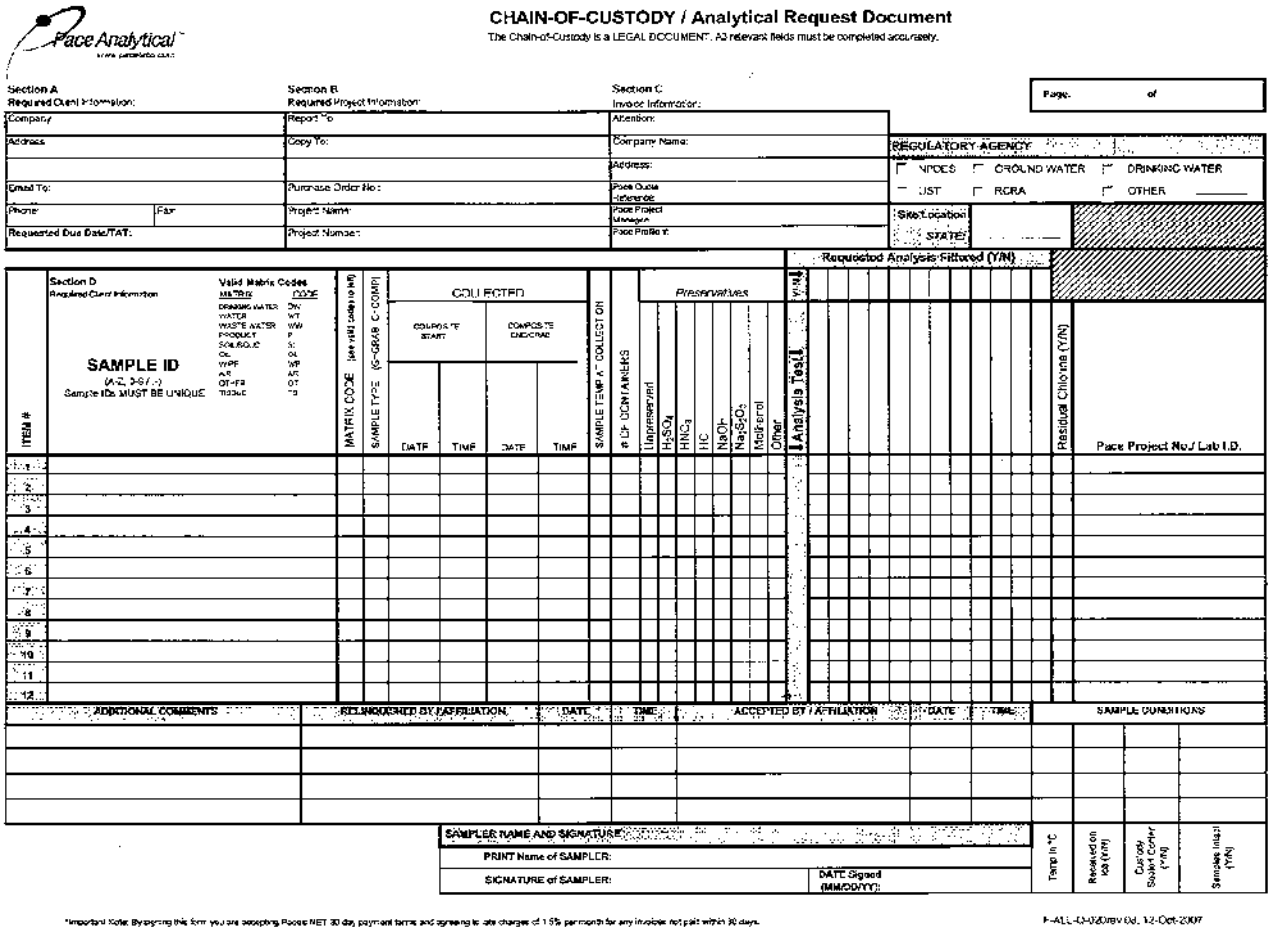
Date Completed: _____ Receiving Project Manager: _____

DISPOSITION of FORM

Original sent to the receiving lab - Copy kept at the sending lab.
When work completed: Original sent to the ABM at the receiving laboratory. Copies are made to corporate as needed.

FALLC002rev.07, 2December2009

Attachment II- Example Chain-of-Custody



Pace Analytical

CHAIN-OF-CUSTODY / Analytical Request Document

The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately.

Section A — Required Client Information: Company; Address; Email To:; Phone: Fax; Requested Due Date/TAT:

Section B — Required Project Information: Report To; Copy To:; Purchase Order No.:; Project Name:; Project Number:

Section C — Invoice Information: Attention:; Company Name:; Address:; Pace Quote Reference:; Pace Project Manager:; Pace Profile #:

Page: of

REGULATORY AGENCY: NPDES; GROUND WATER; DRINKING WATER; UST; RCRA; OTHER

Site Location: STATE:

Requested Analysis Filtered (Y/N)

ITEM #	Section D Required Client Information — SAMPLE ID (A-Z, 0-9 / , -) Sample IDs MUST BE UNIQUE	MATRIX CODE (see valid codes to left)	SAMPLE TYPE (G=GRAB C=COMP)	COLLECTED: COMPOSITE START DATE	COMPOSITE START TIME	COMPOSITE END/GRAB DATE	COMPOSITE END/GRAB TIME	SAMPLE TEMP AT COLLECTION	# OF CONTAINERS	Preservatives: Unpreserved	H_2SO_4	HNO_3	HCl	NaOH	$Na_2S_2O_3$	Methanol	Other	Analysis Test (Y/N)	Residual Chlorine (Y/N)	Pace Project No./ Lab I.D.
1																				
2																				
3																				
4																				
5																				
6																				
7																				
8																				
9																				
10																				
11																				
12																				

ADDITIONAL COMMENTS	RELINQUISHED BY / AFFILIATION	DATE	TIME	ACCEPTED BY / AFFILIATION	DATE	TIME	SAMPLE CONDITIONS

SAMPLER NAME AND SIGNATURE

PRINT Name of SAMPLER:

SIGNATURE of SAMPLER: DATE Signed (MM/DD/YY):

Temp in °C | Received on Ice (Y/N) | Custody Sealed Cooler (Y/N) | Samples Intact (Y/N)

*Important Note: By signing this form you are accepting Pace's NET 30 day payment terms and agreeing to late charges of 1.5% per month for any invoices not paid within 30 days.

F-ALL-Q-020rev.04, 12-Oct-2007

Document Information

Document Number: ENV-SOP-IND1-0008 **Revision:** 00

Document Title: Bottle Preparation

Department(s): Client Services

Previous Document Number: S-IN-C-004-rev.05

Date Information

Effective Date: 08 Jan 2018

Next Review Date: 08 Jan 2020 **Last Review Date:**

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Pace Analytical Services, LLC
7726 Moller Road
Indianapolis, IN 46268
Phone: 317.228.3100
Fax: 317.872.6189

STANDARD OPERATING PROCEDURE

BOTTLE PREPARATION

Reference Methods: N/A

Local SOP Number:	S-IN-C-004-rev.05
Effective Date:	January 8, 2018
Supersedes:	S-IN-C-004-rev.04
SOP Template Number:	SOT-ALL-C-004-rev.06

APPROVALS

General Manager — January 2, 2018 Date

Quality Manager — December 28, 2017 Date

Sample Receiving Supervisor — December 28, 2017 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

S-IN-C-004-rev.05

Table of Contents

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to outline the procedures involved with bottle preparation and shipment.

2. Summary of Method

2.1. Bottle orders are prepared according to client needs and are purchased with or without preservatives only from approved vendors. All bottles are stored appropriately to avoid contamination.

2.2. Bottles, preservatives, field blanks, and trip blanks are prepared, packaged, labeled, and shipped following DOT regulation and client requests. An information packet is included with each box or cooler.

2.3. Bottles must be stored under specific conditions and in specific locations, typically by type of preservative or container. Bottles must be segregated from potential sources of contamination, including target analytes.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP apply to all personnel involved in the preparation and shipment of bottles used for sample collection.

3.2. **Parameters**: Not applicable to this SOP.

4. Applicable Matrices

4.1. Not applicable to this SOP.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Not applicable to this SOP.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Acceptable sample preservation, containers, and hold times are listed in Attachment II of this SOP. They may also be located in the Pace Quality Assurance Manual, the laboratory's method SOPs or in the applicable test method. Samples are stored separately from all standards and reagents and any known highly contaminated samples.

7.2. **NOTE**: To avoid contamination, no food or drink products can be located near the areas where samples are unpacked, labeled, or staged or where outgoing bottles are prepared.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual.

8.2. **Chain-of-Custody (COC):** a form used to record the field identification of samples collected, analyses requested, date and time of collection, sample preservation used, and traceability of samples from time of collection until delivery to the laboratory. This is a legal document.

8.3. **Laboratory Information Management System (LIMS):** a computer system used to manage the flow and traceability of environmental samples and associated data within the laboratory.

8.4. **Matrix:** the bulk characteristics of a sample. See Table 8.1 below.

8.5. **Safety Data Sheet (SDS):** contains information on chemicals used in the laboratory.

8.6. **Sample Custody:** a sample is considered to be in someone's custody if:

8.6.1. It is in one's physical possession;

8.6.2. It is in someone's view, after being in someone's physical possession;

8.6.3. It is kept in a secured area, restricted to authorized personnel only.

8.7. **Sample Condition Upon Receipt (SCUR) form:** a form used to record the condition of samples received in the laboratory.

8.8. **Sample Receipt Form (SRF):** form generated by LIMS system after a project is logged in. Contains sample and project information.

8.9. **UN Number -** identification numbers preceded by the letters UN are associated with proper shipping names considered appropriate for international and domestic transportation. These shipping names along with the identification numbers are located in the Federal Register (49CFR172.101).

Table 8.1

NELAC/TNI defined matrix	Pace Analytical defined matrix
Aqueous: any liquid sample not defined as drinking water. Includes surface water, groundwater, effluents, TCLP, and other extracts.	Waters: includes groundwater, wastewaters, drinking waters, effluents, and any free-flowing liquids.
Drinking water: any aqueous sample that has been designated as potable or potentially potable.	Not assigned as a separate matrix, but samples are assigned to drinking water methods.
Non-aqueous liquid: any organic liquid with <15% settleable solids.	Other or Non-aqueous Liquid: Assigned as a separate matrix from waters.
Biological tissue: any sample from a biological origin such as fish tissue or plant material.	Tissue: would include tissue and plant samples.
Solids: includes soils, sediments, sludges and other matrices with >15% settleable solids	Soils: includes soils, sediments, sludges; other solid materials such as wood, metal, etc. may fall under another heading.
Chemical waste: a product or by product of an industrial process that results in a matrix not defined above.	Other or Non-aqueous Liquid: Assigned as a separate matrix from waters.
Air: vapor samples including those contained within sorbent tubes, filters or other devices.	Air: vapor samples including those contained within sorbent tubes, filters, or other devices.
No corresponding matrix to wipe; wipes would be included in with solids.	Wipe: includes wipe samples or swabs taken to check for surface contamination.

9. Equipment and Supplies (Including Computer Hardware and Software)

Table 9.1

Equipment/Supplies	Description/ Comments
Sample Labels	
Sample Containers and/or kits	
Coolers	
Plastic bags	
Blank COCs	
Bottle Order Program	
Preservatives	
Disposable pipettes	
Bubble wrap	
Absorbent Sheets or other packing materials	
LIMS Computer System	Epic Pro

10. Reagents and Standards

10.1. All reagents used in this procedure must be labeled with:

10.1.1. Laboratory reagent identification number;

10.1.2. Unless otherwise noted, the name and concentration of the reagent;

10.1.3. Date the reagent was received, opened and, as needed, prepared;

10.1.4. Person preparing reagent;

10.1.5. Expiration date.

10.2. **Reagents: Table 10.1**

Reagent	Formula	Concentration
Sulfuric Acid	H_2SO_4	1:1
Nitric Acid	HNO_3	20%
Hydrochloric Acid	HCl	1:1
Sodium Hydroxide	NaOH	50% or Pellets
Sodium Thiosulfate	$Na_2S2O_3 \cdot 5H_2O$	
Zinc Acetate Solution (for sulfide)		
Methanol	MeOH	Purge and Trap Grade
Ascorbic Acid (for cyanide)		
Sodium Bisulfate		
Hexane for PCB Wipes		Pesticide Grade

10.3. For acids, bases and other reagents obtained from other laboratory departments, this information is located in the department reagent preparation log. In the event that these reagents are managed within the Sample Receiving group, the department must maintain its own reagent preparation log.

10.4. Some Pace labs use pre-preserved sample containers. In this case, documentation from the vendor must be maintained for bottleware and preservation traceability.

11. Calibration and Standardization

11.1. Pipettes and other equipment used for measuring volumes must be calibrated according to S-IN-Q-157, **Support Equipment** or its equivalent revision or replacement.

12. Procedure

12.1. A Bottle Order Request form is completed after it is determined what the client needs for a specific project or field event.

12.2. The bottle order form is delivered electronically to the bottle prep area and printed on the day the bottle kit is to be assembled and shipped.

12.2.1. If the order needs to be shipped out or picked up within 24 hours, or if the order is very large, the Project Manager (PM) should tell the bottle prep personnel that the order will require immediate attention and enter the bottle order into the bottle order database as a RUSH order.

12.2.2. If the order does not require expedited handling, the order is entered into the bottle order database using the date the bottle order is due to the customer.

12.3. Sample management personnel will review the bottle order to determine if there is a sufficient stock of bottles to fill the order as written, and to clarify any special instructions listed.

12.3.1. Any problems or questions should be directed to the person who completed the bottle order or a PM or the Client Services Manager (CSM) if they are not available.

12.3.2. Each bottle order is assigned a unique ID number to use for future tracking of bottles and reagents used.

12.4. Purchasing the bottles or containers:

12.4.1. Only pre-cleaned, new, certified bottles are used to fill orders for containers, where available. These must be purchased from an approved vendor.

12.4.2. Containers can be purchased by the following two options: 1) Pre-preserved by the supplier, and 2) Unpreserved.

12.4.3. Where certified bottles are not available, the lab may be required to demonstrate that the containers are free from interferences and contamination when compared to the analytes of interest. This demonstration will be dependent on the regional or client driven quality assurance requirements. If the laboratory staff is unsure of these requirements, consult the local Senior Quality Manager (SQM)/Quality Manager (QM) for more information.

12.4.4. Containers that have been returned from clients must not be reused to prepare bottle orders unless the COC seal has not been broken on the outer container box. The packing material must not be reused. If the containers are returned to the laboratory outside of the sealed box and the COC seal on the individual bottles has not been broken, they may be reused only when clearly segregated for the client returning the bottles.

12.4.5. The Certificate of Analysis (COA) for each bottle lot is filed in the appropriate folder for future reference. Record the lot number for each bottle type used in the bottle kit on the bottle order form.

12.5. Sample Container Labels:

12.5.1. Sample labels can be the standard Pace Analytical blank roll or sheet labels, or can be preprinted using the laboratory's label printing procedure.

12.5.2. Sample labels may be affixed to each container or provided unattached depending on the needs of the client. When unspecified by the client, do not attach the labels to the bottles:

12.5.2.1. When sending the labels attached to the container, affix a sample label to each container before the preservative is added or, as the bottles are prepared for shipment or delivery.

12.5.2.2. Always place the label on the bottle as close to the bottom of the bottle as possible. Make sure the label is not wrinkled or creased, and that it is as straight as possible.

12.5.2.3. If a client requests that labels be shipped separate from the bottles, make sure the bottles are marked with the preservative used.

12.6. Absorbent Material – Shipments being prepared with one or more preservative (Table 10.1) must have an absorbent sheet placed on the bottom of the cooler, in order to absorb all the hazardous materials in case of a spill. **This is a DOT requirement.**

12.7. Container Preparation with Preservative **-** Containers requiring the addition of preservatives prior to shipment must be preserved according the preservation chart listed in Attachment II.

12.7.1. Purchase the required preservatives at the appropriate concentrations from an approved vendor, or prepare the appropriate reagents from stock solutions according to the specifications in Table 10.1.

12.7.1.1. Each new bottle of reagent must be recorded in the Sample Receiving Reagents and Standards Logbook or in the relevant department reagent logbook.

12.7.1.2. Remove the lids from the containers to be preserved, taking care to place the lids on the counter with the inside facing up.

12.7.1.3. Add the appropriate amount of preservative to each bottle, and replace the lid. Make sure the lid is tight.

12.7.1.4. Wipe any excess preservative that remains on the outside of the container using a paper towel. Discard the towel after use.

12.7.1.5. Containers with corrosive preservatives require a positive means of securing the lid or cap to prevent leakage (e.g., tape over cap). **This is a DOT requirement.**

12.8. Preparation for Preservation at time of Sample Collection **-** A client may also request that the preservatives be shipped separately from the bottles, for preservation at the time of sample collection. This is not the preferred approach for Pace Analytical and the client should be discouraged from doing so wherever possible. Nevertheless, if the client insists on using this approach, prepare the container kit as follows:

12.8.1. Prepare the preservatives for shipping by pouring them into an appropriate shipping container (consult the laboratory DOT trained shipping specialist), labeling the container with the contents, the date filled and the initials of the person preparing the solution. Also include the appropriate equipment (e.g., disposable pipettes) for field preparation.

12.8.2. Include any instructions for adding the preservatives to the sample containers in the field.

12.8.3. Laboratory personnel cannot add more than **30mL** of preservative to any containers due to the rules for small quantity exception. **This is a DOT requirement.**

12.9. Select the prepared bottles needed to fill the bottle order and gather them on the counter.

12.9.1. Group the bottles by bottle type, or by sampling location, depending on the request on the bottle order.

12.9.2. If there are preprinted sample labels provided, affix them to the appropriate bottles. These can be placed over unmarked labels if the bottles are already pre-labeled.

12.10. Field Blank Preparation

12.10.1. Prepare a set of empty bottles defined on the bottle order form.

12.10.2. Include enough reagent grade laboratory water to fill all of the bottles requested for the field blank. This should be shipped in separate approved containers, per method, labeled with date prepared.

12.11. Trip Blank Preparation

12.11.1. Prepare a set of empty bottles defined on the bottle order form.

12.11.2. Aqueous trip blank samples are usually provided only for volatile analyses. However, clients may request a trip blank for all bottle types that they are using in the field.

12.11.2.1. For aqueous trip blanks, fill each of the bottles with reagent grade laboratory water and label them with the following information: LABORATORY TRIP BLANK – DO NOT OPEN – RETURN WITH SAMPLES. Volatile vials must be filled so that there is no headspace in the vials.

12.11.3. Methanol trip blanks may be prepared to document the transport of methanol preserved volatile samples. These may be taken directly from the same kit or source that the sample containers are taken from.

12.11.4. Mark the date that the bottles were filled at the laboratory on each bottle and affix a custody seal on the vials to assure the bottles are not tampered with.

12.11.5. The shelf life for trip blanks preserved in the laboratory will be consistent with the shelf life of the sample vials (see corresponding expiration date on the COA), or 1 year, whichever is sooner for aqueous trip blanks, or 3 months, whichever is sooner for methanol trip blanks.

12.11.6. The holding time for trip blanks will be based on the date of sample collection from the first sample collected in that project, unless the client has documented a date on the COC.

12.11.7. The preservation for trip blanks must be consistent with the preservatives utilized in sample collection.

12.12. Wrap all containers in appropriate packing material to prevent breakage, typically foam, bubble bags, or more bubble wrap. When shipping glass containers in the original box, provide sufficient bubble bags or bubble wrap for the return of samples.

12.13. Select a shipping container for the samples:

12.13.1. If a box is requested, pack the samples as firmly as possible into the box. The contents of the box should not move around when shaken.

12.13.2. If a cooler is requested, the cooler must be large enough to allow room for the sample containers to be returned with enough ice to cool the samples to $\leq 6^{o}$ during return shipment.

12.13.3. Choose a cooler that is clean and dry.

12.14. Pack the containers for shipment or delivery to the client:

12.14.1. Place a layer of absorbent sheet material on the bottom of the cooler. Place a layer of bubble wrap on top of the absorbent sheet.

12.14.2. Open a large trash bag and line the cooler with it. All sample containers should be placed inside the trash bag liner in the cooler.

12.14.3. If the bottles are to be packed by sampling location (i.e., well, outfall, etc.), select the requested number of each type of bottle for each sample and bag them in a Ziploc bag.

12.14.3.1. If the bottles are pre-labeled with the location, make sure that all of the bottles chosen have the same client ID. Place glass containers inside bubble bags before packing the cooler.

12.14.3.2. Mark the bag with the location ID if requested.

12.14.3.3. Place the bag in the cooler, making sure that any bottles containing preservative are upright to avoid spillage.

12.14.3.4. Add additional sets of bottles to the cooler, as space will allow.

12.14.4. If the bottles are to be packed by bottle type, pack the cooler or box with the bottles. If the bottles contain preservatives, pack the bottles upright to help prevent spillage. If the bottles are to be packed by bottle type, pack the cooler or box with the bottles.

12.14.5. Allow room for the sample containers to be returned with enough ice to cool the samples. This space should be filled with extra packing material to prevent breakage during shipment of the empty containers.

12.15. Place a temperature blank in the cooler.

12.15.1. Temperature blanks are prepared by filling a small plastic bottle with tap water and replacing the cap.

12.15.2. The bottle should be labeled "LABORATORY TEMPERATURE BLANK – RETURN WITH SAMPLES – DO NOT OPEN". A brightly colored label should be used to call the sampler's attention to the temperature blank.

12.16. Add an information packet to the cooler or box which contains the following information in a Ziploc bag:

12.16.1. COC Forms (F-ALL-Q-020) (number specified on the bottle request form);

12.16.2. Additional sample labels, if required;

12.16.3. Cooler Custody Seals, if required;

12.16.4. Sampling instructions, if required;

12.16.5. 'Tips for Packing Your Cooler' sheet;

12.16.6. Pace Analytical return address label;

12.16.7. Appropriate description of contents of sample containers (e.g., preservatives);

12.16.8. Copy of the bottle request form;

12.16.9. Pre-paid return shipping label, if required;

12.16.10. Sample Acceptance Policy (F-ALL-C-002).

12.16.11. Short Hold/RUSH stickers as needed.

12.17. Seal the cooler or box with packing tape or bands for shipment:

12.17.1. Tape the lid down tightly or band the cooler or box with an auto band-sealer so that it will not come open during shipment.

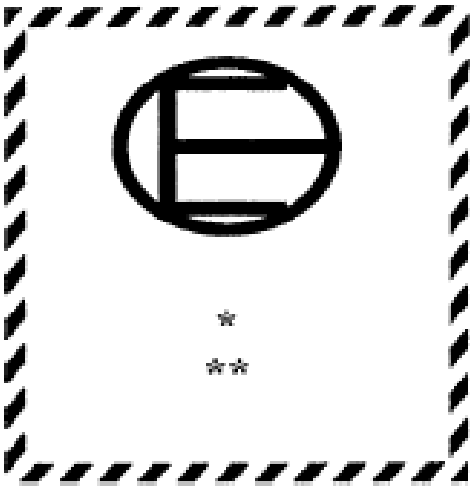
12.17.2. Wrap a continuous tape strip completely around the cooler (or use an auto band sealer).

12.17.3. If using tape, seal the cooler with one custody seal if requested by the client, and sign and date the seal.

12.18. Label the outside of the cooler with appropriate client information, i.e., project name, project manager's name, delivery date, etc. If the cooler is being shipped all necessary information should be present on the shipping label.

12.19. Preservatives are able to be shipped without hazardous material labeling or restrictions so long as 49 CFR 173.4 and 49 CFR 173.4a are obeyed (regulations commonly referred to as Small Quantity Exemptions). These regulations include restrictions already discussed such as having a positive means of securing the cap (Section 12.7.1.5) and volume limit of 30mL per container (Section 12.8.3). These shipments must also be labeled according to these regulations to properly designate the containers as exempt from DOT regulations.

12.19.1. All preservative shipments designated for air transport must have the following label:



12.19.1.1. The "*" must be replaced by the primary hazard class, or when assigned, the division of each of the hazardous materials contained in the package. The "**" must be replaced by the name of the shipper or consignee if not shown elsewhere on the package. Refer to Attachment I for Hazard Classes.

12.19.1.2. This label must be not less than 100mm (3.9inches) x 100mm (3.9inches) and must be durable and clearly visible.

12.19.2. Preservative shipments are able to be sent without hazardous material restrictions or hazardous material labeling because steps are taken to ensure that the package conforms to 49CFR 173.4a (the exception for limited quantities). When preparing a preservative shipment, the shipper must understand 49 CFR 173.4 and obey all parts of the regulation. See Attachment III for a list of these rules. All preservative shipments are designated for ground transport only and must have a label that states, "**This package conforms to 49 CFR 173.4 for domestic highway or rail transport only".** Here is an example:

12.20. Drop shipment of sample containers:

12.20.1. If a drop shipment of sample containers is required by a client, that is if the bottles are not going to be prepared and shipped from the laboratory, Pace Analytical will order the sample containers from a certified vendor. The vendor will ship the preserved containers directly to the client along with a Certificate of Analysis for the containers.

12.20.2. **Note: Nitric acid preserved containers drop-shipped by air must contain nitric acid at a concentration less than 20%.**

12.21. Courier Delivery:

12.21.1. Place the bottle kit in the appropriate location for courier deliveries, and notify the courier of the scheduled delivery date, contact, and location.

12.21.2. A label is affixed to the top of the cooler with the delivery information or the information is documented and placed in a specific location for the courier to know where to go and what to pick up.

12.22. Outside Carrier Shipments:

12.22.1. Schedule the package shipment and affix the shipping label to the container to be shipped.

12.22.2. Place the cooler or package to be shipped in the appropriate area for pickup by the outside carrier.

13. Quality Control

13.1. All supporting documentation related to sample custody must be retained by the laboratory. This includes; memorandums, fax transmissions, all paperwork received copies of email transmissions.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. Hazards and Precautions - Use extreme caution in preparing bottles with preservatives (i.e. nitric acid) as they may be hazardous. Each reagent and chemical used in this method should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats, safety glasses and ventilation hoods. SDS are on file and available to all personnel.

22.2. All personnel involved in bottle preparation and shipment are responsible for complying with OSHA and DOT regulations. These regulations pertain to the safe handling and/or shipping of the chemicals specified in this procedure. A reference file of SDSs is available to all personnel. Refer to the Sample Control Supervisor for any questions or concerns related to the safe handling and shipment of hazardous materials.

22.3. Other laboratory safety requirements are contained in the Chemical Hygiene Plan/Safety Manual. Immediate questions can also be addressed with the local Safety Officer.

23. Waste Management

23.1. Not applicable to this SOP.

24. Pollution Prevention

24.1. Not applicable to this SOP.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. The NELAC Institute (TNI); "Quality Systems"- 2003 and 2009.

25.3. Chapter 3, "Inorganic Analytes;"SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA, Rev. 3, 1996.

25.4. Code of Federal Regulations, Chapter 40, Part 136.3, Table II.

25.5. American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1995, Standard Methods for the Examination of Water and Wastewater, A.E. Greenberg, L.W. Clesceri, A.D. Eaton and M.A.H. Franson, eds., 19th ed., American Public Health Association, Washington D. C.

25.6. U.S. Environmental Protection Agency, 1983, Methods for Chemical Analysis of Water And Wastes, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

25.7. U.S. Environmental Protection Agency, 1996, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Office of Solid Waste and Emergency Response, Washington D.C.

25.8. U.S. Environmental Protection Agency, 1988, Methods for Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I – List of Preservatives and Hazard Classes.

26.2. Attachment II – Sample Containers, Preservation, and Holding Time

26.3. Attachment III – Regulation 49 CFR 173.4.

26.4. Attachment IV – Regulation 49 CFR 173.4a.

27. Revisions

Document Number	Reason for Change	Date
S-IN-C-004-rev.04	1. Adapted from Corporate SOT-ALL-C-004-rev.05 2. Cover page: added lab address and revised document control format 3. Table 10.1: added hexane 4. Section 12.4.5: added requirement that only one CofA from each bottle lot be maintained. 5. Section 12.5: removed recommendation to place the label as low as possible on the bottle and added instructions for printing pre-printed labels. 6. Section 12.11.3: added Terracore and bulk supply to clarify. 7. Attachment II: added Indiana RISC and Ohio VAP allowance for preservation of water for Hexavalent Chromium analysis.	03Dec2015
S-IN-C-004-rev.05	1. Adapted from Corporate SOT-ALL-C-004-rev.06. 2. Table 8.1: removed saline matrix and revised Pace matrix for non-aqueous liquids and chemical waste. 3. Table 10.1: revised to match Pace Indy reagents. 4. Section 12: updated to reflect electronic bottle order database. 5. Section 12.14: updated to match Pace Indy cooler packing procedures. 6. Section 12.15: added that brightly colored temperature blank labels should be used. 7. Section 12.16: added short hold/rush stickers. 8. Section 25: added years 2003 and 2009 to TNI reference. 9. Attachment I: updated.	26Dec2017

Attachment I – List of Preservatives and Hazard Classes

CHEMICAL	CLASS/DIVISION	UN NUMBER
Acetone	3	1090
Hexane	3	1208
Methanol	3	1230
Hydrochloric Acid	8	1789
Nitric Acid	8	2031
Sodium Bisulfate	8	2837
Sodium Hydroxide	8	1824
Sulfuric Acid	8	1830
Trisodium Phosphate	8	3262
Sodium thiosulfate	none	none

Class 3 = Flammable liquid
Class 8 = Corrosive material

UN Number - Identification numbers preceded by the letters UN are associated with proper shipping names considered appropriate for international transportation as well as domestic transportation.

Attachment II – Sample Containers, Preservation, and Holding Times

THE HOLDING TIME INDICATED IN THE CHART BELOW IS THE MAXIMUM ALLOWABLE TIME FROM COLLECTION TO EXTRACTION AND/OR ANALYSIS PER THE ANALYTICAL METHOD. FOR METHODS THAT REQUIRE PROCESSING PRIOR TO ANALYSIS, THE HOLDING TIME IS DESIGNATED AS 'PREPARATION HOLDING TIME/ANALYSIS HOLDING TIME'.

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Acid Base Accounting	Sobek	Solid	Plastic/Glass	None	N/A
Acidity	SM2310B	Water	Plastic/Glass	≤ 6°C	14 Days
Acid Volatile Sulfide	Draft EPA 1629	Solid	8oz Glass	≤ 6°C	14 Days
Actinides	HASL-300	Water	Plastic/Glass	pH<2 HNO_3	180 Days
Actinides	HASL-300	Solid	Plastic/Glass	None	180 Days
Alkalinity	SM2320B/310.2	Water	Plastic/Glass (NY requires separate bottle filled to the exclusion of air)	≤ 6°C	14 Days
Alkylated PAHs		Water	1L Amber Glass	≤ 6°C; pH<2 1:1 HCl (optional)	14/40 Days preserved; 7/40 Days unpreserved
Alkylated PAHs		Solid	8oz Glass	≤ 10°C	1 Year/40 Days
Anions (Br, Cl, F, NO_2, NO_3, o-Phos, SO_4, bromate, chlorite, chlorate)	300.0/300.1/SM4110B	Water	Plastic/Glass	≤ 6°C; EDA if bromate or chlorite run	All analytes 28 days except: NO_2, NO_3, o-Phos (48 Hours); chlorite (immediately for 300.0; 14 Days for 300.1). NO_2/NO_3 combo 28 days.
Anions (Br, Cl, F, NO_2, NO_3, o-Phos, SO_4, bromate, chlorite, chlorate)	300.0	Solid	Plastic/Glass	≤ 6°C	All analytes 28 days except: NO_2, NO_3, o-Phos (48 hours); chlorite (immediately). NO_2/NO_3 combo 28 days.

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Anions (Br, Cl, F, NO_2, NO_3, o-Phos, SO_4	9056	Water/ Solid	Plastic/Glass	≤ 6°C	48 hours
Aromatic and Halogenated Volatiles (see note 1)	8021	Solid	5035 vial kit	See note 1	14 days
Aromatic and Halogenated Volatiles	602/8021	Water	40mL vials	pH<2 HCl; ≤ 6°C; $Na_2S_2O_3$ if Cl present	14 Days (7 Days for aromatics if unpreserved)
Asbestos	EPA 600/R-93/116	Solid	Plastic/Glass; bulk- 2" square; popcorn ceiling- 2tbsp; soil- 4oz	None (handling must be done in HEPA filtered fume hood; drying may be required)	N/A
Bacteria, Total Plate Count	SM9221D	Water	Plastic/WK	≤ 6°C; $Na_2S_2O_3$	24 Hours
Base/Neutrals and Acids	8270	Solid	8oz Glass	≤ 6°C	14/40 Days
Base/Neutrals and Acids	625/8270	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Base/Neutrals, Acids & Pesticides	525.2	Water	1L Amber Glass	pH<2 HCl; ≤ 6°C; Na sulfite if Cl present	14/30 Days
Biomarkers		Water	≤ 6°C; pH<2 1:1 HCl (optional)	14/40 Days preserved; 7/40 Days unpreserved	≤ 6°C; pH<2 1:1 HCl (optional)
Biomarkers		Solid	≤ 10°C	1 Year/40 Days	≤ 10°C
BOD/cBOD	SM5210B	Water	Plastic/Glass	≤ 6°C	48 hours
Boiling Range Distribution of Petroleum Fractions	ASTM D2887-98	Product	10mL glass vials	≤ 6°C	N/A
BTEX/Total Hydrocarbons	TO-3	Air	Summa Canister	None	28 Days
BTEX/Total Hydrocarbons	TO-3	Air	Tedlar Bag or equivalent	None	72 Hours
Carbamates	531.1	Water	Glass	$Na_2S_2O_3$, Monochloroacetic acid pH <3; ≤ 6°C	28 Days
Carbamates	8318	Water	Glass	Monochloroacetic acid pH 4-5; ≤ 6°C	7/40 Days
Carbamates	8318	Solid	Glass	≤ 6°C	7/40 Days
Carbon Specific Isoptope Analysis (CSIA)	AM24	Water	40mL clear VOA vial with TLS	≤ 6°C, trisodium phosphate or HCl	N/A

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Cation/Anion Balance	SM1030E	Water	Plastic/Glass	None	None
Cation Exchange	9081	Solid	8oz Glass	None	unknown
Cations (Ferrous Iron, Ferric Iron, Divalent Manganese)	7199 modified	Water	40mL clear VOA vials with mylar septum	≤ 6°C; HCl	48 Hours
Chloride	SM4500Cl-C,E	Water	Plastic/Glass	None	28 Days
Chlorinated Hydrocarbons in Vapor	AM4.02	Vapor	20cc vapor vial with flat septum	None	N/A
Chlorine, Residual	SM4500Cl-D,E,G/330.5/Hach 8167	Water	Plastic/Glass	None	15 minutes
Chlorophyll	SM10200H	Water	Opaque bottle or aluminum foil	≤ 6°C	48 Hours to filtration
COD	SM5220C, D/410.4/Hach 8000	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Coliform, Fecal	SM9222D	Water	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	8 Hours
Coliform, Fecal	SM9222D	Solid	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	24 Hours
Coliform, Fecal	SM9221E	Water	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	8 Hours
Coliform, Fecal	SM9221E	Solid	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	24 Hours
Coliform, Total	SM9222B	Water	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	8 Hours
Coliform, Total	SM9221B	Solid	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	8 Hours
Coliform, Total, Fecal and E. coli	Colilert/ Quanti-tray	Water	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	8 Hours
Coliform, Total and E. coli	SM9223B	Drinking Water	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	30 Hours
Color	SM2120B,E	Water	Covered Plastic/Acid Washed Amber Glass	≤ 6°C	48 Hours
Condensable Particulate Emissions	EPA 202	Air	Solutions	None	180 Days
Cyanide, Reactive	SW846 chap.7	Water	Plastic/Glass	None	28 Days
Cyanide, Reactive	SW846 chap.7	Solid	Plastic/Glass	None	28 Days
Cyanide, Total and Amenable	SM4500CN-A,B,C,D,E,G,I,N/9010/ 9012/335.4	Water	Plastic/Glass	pH≥12 NaOH; ≤ 6°C; ascorbic acid if Cl present	14 Days (24 Hours if sulfide present-SM4500CN only)
Diesel Range Organics- Alaska DRO	AK102	Solid	8oz Glass	≤ 6°C	14/40 Days
Diesel Range Organics-Alaska DRO	AK102	Water	1L Glass	pH<2 HCl; ≤ 6°C	14/40 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Diesel Range Organics- TPH DRO	8015	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Diesel Range Organics- TPH DRO	8015	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Diesel Range Organics- TPH DRO	8015	Tissue	1L Amber Glass	≤ - 10°C	1 Year if frozen/40 Days
Diesel Range Organics- TPH DRO	TO-17	Air	Thermal desorption tubes via SKC Pocket Pumps or equivalent	≤ 6°C but above freezing	28 Days
Diesel Range Organics- NwTPH-Dx	Nw-TPH-Dx	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Diesel Range Organics- NwTPH-Dx	Nw-TPH-Dx	Water	1L Amber Glass	pH <2 HCl; ≤ 6°C	14/40 Days; 7 Days from collection to extraction if unpreserved
Diesel Range Organics- Wisconsin DRO	WI MOD DRO	Solid	Tared 4oz Glass Jar	≤ 6°C	10/47 Days
Diesel Range Organics- Wisconsin DRO	WI MOD DRO	Water	1L Amber Glass	≤ 6°C; pH <2 HCl	14/40 Days
Dioxins and Furans	1613B	Solid	8oz Glass	≤ 6°C	1 year
Dioxins and Furans	1613B	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	1 year
Dioxins and Furans	1613B	Fish/ Tissue	Aluminum foil	≤ 6°C	1 year
Dioxins and Furans	8290	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	30/45 Days
Dioxins and Furans	8290	Solid	8oz Glass	≤ 6°C	30/45 Days
Dioxins and Furans	8290	Fish/ Tissue	Not specified	< -10°C	30/45 Days
Dioxins and Furans	TO-9	Air	PUF	None	7/40 Days
Diquat/Paraquat	549.2	Water	Amber Plastic	≤ 6°C; $Na_2S_2O_3$	7/21 Days
EDB/DBCP (8011) EDB/DBCP/1,2,3-TCP (504.1)	504.1/8011	Water	40mL vials	≤ 6°C; $Na_2S_2O_3$ if Cl present	14 Days
Endothall	548.1	Water	Amber Glass	≤ 6°C; $Na_2S_2O_3$	7/14 Days
Enterococci	EPA 1600	Water	100mL Plastic	≤ 10°C	8 Hours
Enterococci	Enterolert	Water	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	8 Hours
Explosives	8330/8332	Water	1L Amber Glass	≤ 6°C	7/40 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Explosives	8330/8332	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Extractable Petroleum Hydrocarbons (aliphatic and aromatic)	NJ EPH	Water	1L Amber Glass	pH < 2 HCl; ≤ 6°C	14/40 Days
Extractable Petroleum Hydrocarbons (aliphatic and aromatic)	NJ EPH	Solid	4oz Glass Jar	≤ 6°C	14/40 Days
Extractable Petroleum Hydrocarbons (aliphatic and aromatic)	MA-EPH	Water	1L Amber Glass	pH<2 HCl; ≤ 6°C	14/40 Days
Extractable Petroleum Hydrocarbons (aliphatic and aromatic)	MA-EPH	Solid	4oz Glass Jar	≤ 6°C	7/40 Days
Fecal Streptococci	SM9230B	Water	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	8 Hours
Ferrous Iron	SN3500Fe-D; Hach 8146	Water	Glass	None	Immediate
Flashpoint/ Ignitability	1010	Liquid	Plastic/Glass	None	28 Days
Florida PRO	FL PRO DEP (11/1/95)	Liquid	Glass, PTFE lined cap	≤ 6°C; pH <2 H_2SO_4 or HCl	7/40 Days
Fluoride	SM4500Fl-C,D	Water	Plastic	None	28 Days
Gamma Emitting Radionuclides	901.1	Water	Plastic/Glass	pH<2 HNO_3	180 days
Gasoline Range Organics	8015	Water	40mL vials	pH<2 HCl	14 Days
Gasoline Range Organics	8015	Solid	5035 vial kit	See note 1	14 days
Gasoline Range Organics (C3-C10)	8260B modified	Water	40mL vials	≤ 6°C; HCl	14 Days
Gasoline Range Organics (C3-C10)	8260B modified	Solid	4oz Glass Jar	≤ 6°C	14 Days
Gasoline Range Organics- Alaska GRO	AK101	Solid	5035 vial kit	See 5035 note*	28 Days if GRO only (14 Days with BTEX)
Gasoline Range Organics- Alaska GRO	AK101	Water	40mL vials	pH<2 HCl; ≤ 6°C	14 Days
Gasoline Range Organics- NwTPH-Gx	Nw-TPH-Gx	Water	40mL vials	pH<2 HCl; ≤ 6°C	7 Days unpreserved; 14 Days preserved

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Gasoline Range Organics- NwTPH-Gx	Nw-TPH-Gx	Solid	40mL vials	≤ 6°C; packed jars with no headspace	14 Days
Gasoline Range Organics- Wisconsin GRO	WI MOD GRO	Water	40mL vials	pH<2 HCl; ≤ 6°C	14 Days
Gasoline Range Organics- Wisconsin GRO	WI MOD GRO	Solid	40mL MeOH vials	≤ 6°C in MeOH	21 Days
Glyphosate	547	Water	Glass	≤ 6°C; $Na_2S_2O_3$	14 Days (18 Months frozen)
Grain Size	ASTM D422	Solid	Not specified	Ambient	N/A
Gross Alpha (NJ 48Hr Method)	NJAC 7:18-6	Water	Plastic/Glass	pH<2 HNO_3	48 Hrs
Gross Alpha and Gross Beta	9310/900.0	Water	Plastic/Glass	pH<2 HNO_3	180 Days
Gross Alpha and Gross Beta	9310	Solid	Glass	None	180 Days
Haloacetic Acids	552.1/552.2	Water	40mL Amber vials	NH_4Cl; ≤ 6°C	14/7 Days if extracts stored ≤ 6°C or 14/14 Days if extracts stored at ≤ -10°C
Hardness, Total ($CaCO_3$)	SM2340B,C/130.1	Water	Plastic/Glass	pH<2 HNO_3	180 Days
Heterotrophic Plate Count (SPC/HPC)	SM9215B	Water	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	8 Hours
Heterotrophic Plate Count (SPC/HPC)	SimPlate	Water	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	8 Hours
Herbicides, Chlorinated	8151	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Herbicides, Chlorinated	8151	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Herbicides, Chlorinated	515.1/515.3	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	14/28 Days
Hexavalent Chromium	7196/218.6/ SM3500Cr-B, C	Water	Plastic/Glass	≤ 6°C	24 Hours (see note 4)
Hexavalent Chromium	218.6/SM3500Cr-B, C	Water	Plastic/Glass	Ammonium Buffer to pH 9.3-9.7 Refer to local SOP	28 Days (see note 4)
Hexavalent Chromium	218.6/218.7	Drinking Water	Plastic/Glass	Ammonium Buffer pH >8	14 Days (see note 4)
Hexavalent Chromium	7196 (with 3060)	Solid	Glass	≤ 6°C	30 Days from collection to extraction and 7 days from extraction to analysis

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Hydrocarbons in Vapor	AM4.02	Vapor	20cc vapor vial with flat septum	None	N/A
Hydrogen by Bubble Strip	SM9/AM20GAx	Water	20cc vapor vial with stopper septum	None	14 Days
Hydrogen Halide and Halogen Emissions	EPA 26	Air	Solutions	None	6 Months
Ignitability of Solids	1030	Non-liquid Waste	Plastic/Glass	None	28 Days
Lead Emissions	EPA 12	Air	Filter/Solutions	None	6 Months
Light Hydrocarbons by Bubble Strip	SM9/AM20GAx	Water	20cc vapor vial with stopper septum	None	14 Days
Light Hydrocarbons in Vapor	AM20GAx	Vapor	20cc vapor vial with flat septum	None	14 Days
Lipids	Pace Lipids	Tissue	Plastic/Glass	≤ -10°C	1 Year if frozen
Mercury, Low-Level	1631E	Solid	Glass	None	28 Days
Mercury, Low-Level	1631E	Water	Fluoropolymer bottles (Glass if Hg is only analyte being tested)	12N HCl or BrCl	48 Hours for preservation or analysis; 28 Days to preservation if sample oxidized in bottle; 90 Days for analysis if preserved
Mercury, Low-Level	1631E	Tissue	Plastic/Glass	≤ - 10°C	28 Days if frozen
Mercury	7471	Solid	8oz Glass Jar	≤ 6°C	28 Days
Mercury	7470/245.1/245.2	Water	Plastic/Glass	pH<2 HNO_3	28 Days
Mercury	7471/245.6	Tissue	Plastic/Glass	≤ - 10°C	28 Days if frozen
Metals (GFAA)	7000/200.9	Water	Plastic/Glass	pH<2 HNO_3	180 Days
Metals (ICP)	NIOSH 7300A/7303	Air	Filters	None	180 Days
Metals (ICP/ICPMS)	6010/6020	Solid	8oz Glass Jar	None	180 Days
Metals (ICP/ICPMS)	6010/6020/200.7/200.8	Water	Plastic/Glass	pH<2 HNO_3	180 Days
Metals (ICP/ICPMS)	6020	Tissue	Plastic/Glass	≤ -10°C	180 Days if frozen

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Methane, Ethane, Ethene	8015 modified	Water	40mL vials	HCl	14 Days
Methane, Ethane, Ethene	RSK-175; PM01/AM20GAx	Water	20mL vials	HCl; or trisodium phosphate or benzalkonium chloride and ≤ 6°C	14 Days; 7 Days unpreserved
Methane, Ethane, Ethene	EPA 3C	Air	Summa Canister	None	28 Days
Methane, Ethane, Ethene	EPA 3C	Air	Tedlar Bag or equivalent	None	5 Days
Methanol, Ethanol	8015 modified	Water	40mL vials	≤ 6°C	14 Days
Methanol, Ethanol	8015 modified	Solid	2oz Glass	≤ 6°C	14 Days
Methyl Mercury	1630	Water	Teflon/ fluoropolymer	Fresh water- 4mL/L HCl; Saline water- 2mL/L H_2SO_4 (must be preserved within 48 hours of collection)	6 months
Methyl Mercury	1630	Tissue	2-4oz glass jar	≤ 0°C	28 Days; ethylated distillate 48 hours
Nitrogen, Ammonia	SM4500NH3/350.1	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Nitrogen, Total Kjeldahl (TKN)	351.2	Solid	Plastic/Glass	≤ 6°C	28 Days
Nitrogen, Total Kjeldahl (TKN)	SM4500-Norg/351.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Nitrogen, Nitrate	SM4500-NO3/352.1	Water	Plastic/Glass	≤ 6°C	24 Hours preferred
Nitrogen, Nitrate & Nitrite combination	353.2	Solid	Plastic/Glass	≤ 6°C	28 Days
Nitrogen, Nitrate & Nitrite combination	SM4500-NO3/353.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Nitrogen, Nitrite or Nitrate separately	SM4500-NO2/353.2	Water	Plastic/Glass	≤ 6°C	48 Hours
Nitrogen, Organic	SM4500-Norg/351.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Non-Methane Organics	EPA 25C	Air	Summa Canister	None	28 Days
Non-Methane Organics	EPA 25C	Air	Tedlar Bag or equivalent	None	72 Hours
Odor	SM2150B	Water	Glass	≤ 6°C	24 Hours
Oil and Grease/HEM	1664A/SM5520B/9070	Water	Glass	pH<2 H_2SO_4 or HCl; ≤ 6°C	28 Days
Oil and Grease/HEM	9071	Solid	Glass	≤ 6°C	28 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Oil Range Organics	8015	Solid	Glass	≤ 6°C	14/40 Days
Oil Range Organics	8015	Water	Glass	≤ 6°C	7/40 Days
Organic Matter	ASA 29-3.5.2	Solid	Plastic/Glass	None; samples air-dried and processed prior to analysis	N/A
Oxygen, Dissolved (Probe)	SM4500-O	Water	Glass	None	15 minutes
Oxygenates on Product (GCMS SIM)	1625 modified	Product	10mL glass vial	≤ 6°C	14 Days (7 Days from extraction)
PBDEs	1614	Water	1L Amber Glass	≤ 6°C	1 Year/1 Year
PBDEs	1614	Solid	Wide Mouth Jar	≤ 6°C	1 Year/1 Year
PBDEs	1614	Tissue	Aluminum Foil	≤ -10°C	1 Year/1 Year
PCBs and Pesticides, Organochlorine (OC)	TO-4/TO-10	Air	PUF	None	7/40 Days
PCBs and Pesticides, Organochlorine (OC)	608	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	Pest: 7/40 Days; PCB: 1 Year/1 Year
PCBs, Pesticides (OC), Herbicides	508.1	Water	Glass	Na2SO3; pH<2 HCl; ≤ 6°C	14/30 Days
PCBs, total as Decachlorobiphenyl	508A	Water	1L Glass, TFE lined cap	≤ 6°C	14/30 Days
Perchlorate	331	Water	Plastic/Glass	≥0-6°C, field filtered with headspace	28 Days
Permanent Gases (O2, N2, CO2)	RSK-175; PM01/AM20GAx	Water	40mL vials	benzalkonium chloride and ≤ 6°C	14 Days
Permanent Gases by Bubble Strip	SM9/AM20GAx	Water	20cc vapor vial with stopper septum	None	14 Days
Permanent Gases in Vapor	AM20GAx	Vapor	20cc vapor vial with flat septum	None	14 Days
Pesticides, Organochlorine (OC)	8081	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Pesticides, Organochlorine (OC)	8081	Solid	8oz Glass Jar	≤ 6°C	14/40 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Pesticides, Organochlorine (OC)	8081	Tissue	8oz Glass Jar	≤ -10°C	1 Year if frozen/40 Days
Pesticides, Organophosphorous (OP)	8141	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Pesticides, Organophosphorous (OP)	8141	Water	1L Amber Glass	pH 5-8 with NaOH or H_2SO_4; ≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
PCBs (Aroclors)	8082	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	1 Year/1 Year
PCBs (Aroclors)	8082	Solid	8oz Glass Jar	≤ 6°C	1 Year/1 Year
PCBs (Aroclors)	8082	Tissue	Plastic/Glass	≤ -10°C	1 Year if frozen/1 Year
PCB Congeners	1668A	Water	1L Amber Glass	≤ 6°C but above freezing	1 Year/1 Year
PCB Congeners	1668A	Solid	4-8oz Glass Jar	≤ 6°C but above freezing	1 Year/1 Year
PCB Congeners	1668A	Tissue	4-8oz Glass Jar	≤ -10°C	1 Year/1 Year
Paint Filter Liquid Test	9095	Water	Plastic/Glass	None	N/A
Particle Size	ASA 15-5 modified	Solid	Plastic/Glass (100g sample)	None	N/A
Particulates	PM-10	Air	Filters	None	180 Days
Permanent Gases	EPA 3C	Air	Summa Canister	None	28 Days
Permanent Gases	EPA 3C	Air	Tedlar Bag or equivalent	None	5 Days
pH	SM4500H+B/9040	Water	Plastic/Glass	None	15 minutes
pH	9045	Solid	Plastic/Glass	None	7 Days
Phenol, Total	420.1/420.4/9065/9066	Water	Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Phosphorus, Orthophosphate	SM4500P/365.1/365.3	Water	Plastic	≤ 6°C	Filter within 15 minutes, Analyze within 48 Hours
Phosphorus, Total	SM4500P/ 365.1/365.3/365.4	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Phosphorus, Total	365.4	Solid	Plastic/Glass	≤ 6°C	28 Days
Polynuclear Aromatic Hydrocarbons (PAH)	TO-13	Air	PUF	None	7/40 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Polynuclear Aromatic Hydrocarbons (PAH)	TO-17	Air	Thermal desorption tubes via SKC Pocket Pumps or equivalent	≤ 6°C but above freezing	28 Days
Polynuclear Aromatic Hydrocarbons (PAH)	8270 SIM	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Polynuclear Aromatic Hydrocarbons (PAH)	8270 SIM	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Polynuclear Aromatic Hydrocarbons (PAH)	8270 SIM	Tissue	Plastic/Glass	≤ -10°C	1 Year if frozen/40 Days
Purgeable Organic Halides (POX)	9021	Water	Glass; no headspace	≤ 6°C	14 Days
Radioactive Strontium	905.0	Water	Plastic/Glass	pH<2 HNO_3	180 days
Radium-226	903.0/903.1	Water	Plastic/Glass	pH<2 HNO_3	180 days
Radium-228 (see note 3)	9320/904.0	Water	Plastic/Glass	pH<2 HNO_3	180 days
Radium-228 (see note 3)	9320	Solid	Plastic/Glass		
Residual Range Organics- Alaska RRO	AK103	Solid	8oz Glass	≤ 6°C	14/40 Days
Saturated Hydrocarbons		Water	≤ 6°C; pH<2 1:1 HCl (optional)	14/40 Days preserved; 7/40 Days unpreserved	≤ 6°C; pH<2 1:1 HCl (optional)
Silica, Dissolved	SM4500Si-D	Water	Plastic	≤ 6°C	28 Days
Solids, Settleable	SM2540F	Water	Glass	≤ 6°C	48 Hours
Solids, Total	SM2540B	Water	Plastic/Glass	≤ 6°C	7 Days
Solids, Total	SM2540G	Solid	Plastic/Glass	≤ 6°C	7 Days
Solids, Total (FOC, OM, Ash)	ASTM D2974	Solid	Plastic/Glass	≤ 6°C	7 Days
Solids, Total Dissolved	SM2540C	Water	Plastic/Glass	≤ 6°C	7 Days
Solids, Total Suspended	SM2540D/USGS I-3765-85	Water	Plastic/Glass	≤ 6°C	7 Days
Solids, Total Volatile	160.4/SM2540E	Water	Plastic/Glass	≤ 6°C	7 Days
Solids, Total Volatile	160.4	Solid	Plastic/Glass	≤ 6°C	7 Days
Specific Conductance	SM2510B/9050/120.1	Water	Plastic/Glass	≤ 6°C	28 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Stationary Source Dioxins and Furans	EPA 23	Air	XAD Trap	None	30/45 Days
Stationary Source Mercury	EPA 101	Air	Filters	None	180 Days, 28 Days for Hg
Stationary Source Metals	EPA 29	Air	Filters	None	180 Days, 28 Days for Hg
Stationary Source PM10	EPA 201A	Air	Filters	None	180 Days
Stationary Source Particulates	EPA 5	Air	Filter/Solutions	None	180 Days
Sulfate	SM4500SO4/9036/ 9038/375.2/ASTM D516	Water	Plastic/Glass	$\leq 6^{o}C$	28 Days
Sulfide, Reactive	SW-846 Chap.7	Water	Plastic/Glass	None	28 Days
Sulfide, Reactive	SW-846 Chap.7	Solid	Plastic/Glass	None	28 Days
Sulfide, Total	SM4500S/9030	Water	Plastic/Glass	pH>9 NaOH; ZnOAc; $\leq 6^{o}C$	7 Days
Sulfite	SM4500SO3	Water	Plastic/Glass	None	15 minutes
Surfactants (MBAS)	SM5540C	Water	Plastic/Glass	$\leq 6^{o}C$	48 Hours
Total Alpha Radium (see note 3)	9315/903.0	Water	Plastic/Glass	pH<2 HNO_3	180 days
Total Alpha Radium (see note 3)	9315	Solid	Plastic/Glass	None	180 days
Total Inorganic Carbon (TIC)	PM01/AM20GAx	Water	40mL VOA vial with mylar septum	$\leq 6^{o}C$	14 Days
Total Organic Carbon (TOC)	SM5310B,C,D/9060	Water	Glass	pH<2 H_2SO_4 or HCl; $\leq 6^{o}C$	28 Days
Total Organic Carbon (TOC)	9060/Walkley Black/Lloyd Kahn	Solid	Glass	$\leq 6^{o}C$	14 Days
Total Organic Halogen (TOX)	SM5320/9020	Water	Glass; no headspace	$\leq 6^{o}C$	14 Days
Total Petroleum Hydrocarbons (aliphatic and aromatic)	TPHCWG	Water	40mL vials	pH<2 HCl, no headspace, $\leq 6^{o}C$	7 Days
Total Petroleum Hydrocarbons (aliphatic and aromatic)	TPHCWG	Solid	Glass	$\leq 6^{o}C$	14 days
Tritium	906.0	Water	Glass	None	180 days
Turbidity	SM2130B/180.1	Water	Plastic/Glass	$\leq 6^{o}C$	48 Hours
Total Uranium	908.0/ASTM D5174-97	Water	Plastic/Glass	pH<2 HNO_3	180 days
UCMR Metals	200.8	Water	Plastic or glass	pH<2 HNO_3	28 Days
UCMR Hexavalent Chromium	218.7	Water	HDPE or propylene	Na_2CO_3/$NaHCO_3$/ $(NH_4)_2SO_4$; pH>8	14 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
UCMR Chlorate	300.1	Water	Plastic or glass	EDA	28 Days
UCMR Perfluorinated Compounds	537	Water	Polypropylene	Trizma	14 Days
UCMR 1, 4 Dioxane	522	Water	Glass	Na_2SO_3, $NaHSO_4$; pH<4	28 Days
UV254	SM5910B	Water	Glass	≤ 6°C	48 Hours
Vermiculite	EPA 600/R-93/116	Solid	Plastic/Glass	None (handling must be done in HEPA filtered fume hood; drying may be required)	N/A
Volatile Fatty Acids	AM21G	Water	40mL clear VOA vials	≤ 6°C	21 Days
Volatile Fatty Acids (low level)	AM23G	Water	40mL clear VOA vials	≤ 6°C with benzalkonium chloride	14 Days
Volatiles	8260	Solid	5035 vial kit	See note 1 (analyze for acrolein and acrylonitrile per local requirements)	14 days
Volatiles	8260	Water	40mL vials	pH<2 HCl; ≤ 6°C; $Na_2S_2O_3$ if Cl present (preserve and analyze for acrolein and acrylonitrile per local requirements)	14 Days
Volatiles	8260	Conc. Waste	5035 vial kit or 40mL vials	≤ 6°C	14 Days
Volatiles	624	Water	40mL vials	pH<2 HCl; ≤ 6°C; $Na_2S_2O_3$ if Cl present (or unpreserved if run within 7 days of collection) (preserve and analyze for acrolein and acrylonitrile per local requirements)	14 Days (7 Days for aromatics if unpreserved)
Volatiles (see note 2)	524.2	Water	40mL vials (in duplicate)	pH<2 HCl; ≤ 6°C; Ascorbic acid or $Na_2S_2O_3$ if Cl present[2]	14 Days

[1] **5035/5035A Note**: 5035 vial kit typically contains 2 vials water, preserved by freezing **or**, 2 vials aqueous sodium bisulfate preserved at 4°C, **and** one vial methanol preserved at ≤6°C **and** one container of unpreserved sample stored at ≤6°C.

[2] Method 524.2 lists ascorbic acid as the preservative when residual chlorine is suspected, unless gases or Table 7 compounds are NOT compounds of interest and then sodium thiosulfate is the preservative recommended.

[3] Methods 9315 and 9320 both state that if samples are unpreserved, the samples should be brought to the lab within 5 days of collection, preserved in the lab, and then allowed to sit for a minimum of 16 hours before sample preparation/analysis.

[4] The holding time for hexavalent chromium may be extended by the addition of the ammonium buffer listed in EPA 218.6 per the 2012 EPA Method Update Rule. Although Method 218.6 stipulates a different pH range (9.0 to 9.5) for buffering, this method requirement was modified in the Method Update Rule to a pH range of 9.3 to 9.7.For non-potable waters, adjust the pH of the sample to 9.3 to 9.7 during collection with the method required ammonium sulfate buffer to extend the holding time to 28 days. For potable waters, addition of the buffer during collection will extend the holding time for 14 days per EPA 218.7 and the EPA UCMR program.

Attachment III – Shipping Exemption Regulation 49 CFR 173.4 "Small quantities for highway and rail"

(a) When transported domestically by highway or rail in conformance with this section, quantities of Division 2.2 (except aerosols with no subsidiary hazard), Class 3, Division 4.1, Division 4.2 (PG II and III), Division 4.3 (PG II and III), Division 5.1, Division 5.2, Division 6.1, Class 7, Class 8, and Class 9 materials are not subject to any other requirements when—

(1) The maximum quantity of material per inner receptacle or article is limited to—

(i) Thirty (30) mL (1 ounce) for authorized liquids, other than Division 6.1, Packing Group I, Hazard Zone A or B materials;

(ii) Thirty (30) g (1 ounce) for authorized solid materials;

(iii) One (1) g (0.04 ounce) for authorized materials meeting the definition of a Division 6.1, Packing Group I, Hazard Zone A or B material; and

(iv) An activity level not exceeding that specified in §§ 173.421, 173.424, 173.425 or 173.426, as appropriate, for a package containing a Class 7 (radioactive) material.

(v) Thirty (30) mL water capacity (1.8 cubic inches) for authorized Division 2.2 materials.

(2) With the exception of temperature sensing devices, each inner receptacle:

(i) Is not liquid-full at 55 °C (131 °F), and

(ii) Is constructed of plastic having a minimum thickness of no less than 0.2 mm (0.008 inch), or earthenware, glass, or metal;

(3) Each inner receptacle with a removable closure has its closure held securely in place with wire, tape, or other positive means;

(4) Unless equivalent cushioning and absorbent material surrounds the inside packaging, each inner receptacle is securely packed in an inside packaging with cushioning and absorbent material that:

(i) Will not react chemically with the material, and

(ii) Is capable of absorbing the entire contents (if a liquid) of the receptacle;

(5) The inside packaging is securely packed in a strong outer packaging;

(6) The completed package, as demonstrated by prototype testing, is capable of sustaining—

(i) Each of the following free drops made from a height of 1.8 m (5.9 feet) directly onto a solid unyielding surface without breakage or leakage from any inner receptacle and without a substantial reduction in the effectiveness of the package:

(A) One drop flat on bottom;

(B) One drop flat on top;

(C) One drop flat on the long side;

(D) One drop flat on the short side; and

(E) One drop on a corner at the junction of three intersecting edges; and

(ii) A compressive load as specified in § 178.606(c) of this subchapter.

*Note to paragraph (**a**)(6):Each of the tests in paragraph (a)(6) of this section may be performed on a different but identical package; i.e., all tests need not be performed on the same package.*

(7) Placement of the material in the package or packing different materials in the package does not result in a violation of § 173.21;

(8) The gross mass of the completed package does not exceed 29 kg (64 pounds);

(9) The package is not opened or otherwise altered until it is no longer in commerce; and

(10) The shipper certifies conformance with this section by marking the outside of the package with the statement "**This package conforms to 49 CFR 173.4 for domestic highway or rail transport only**."

(b) A package containing a Class 7 (radioactive) material also must conform to the requirements of § 173.421(a)(1) through (a)(5) or § 173.424(a) through (g), as appropriate.

(c) Packages which contain a Class 2 (other than those authorized in paragraph (a) of this section), Division 4.2 (PG I), or Division 4.3 (PG I) material conforming to paragraphs (a)(1) through (10) of this section may be offered for transportation or transported if approved by the Associate Administrator.

(d) Lithium batteries and cells are not eligible for the exceptions provided in this section.

Attachment IV – Shipping Exemption Regulation 49CFR 173.4a "Excepted quantities"

Title 49: Transportation
PART 173—SHIPPERS—GENERAL REQUIREMENTS FOR SHIPMENTS AND PACKAGINGS

II. § 173.4a Excepted quantities.
(a) Excepted quantities of materials other than articles transported in accordance with this section are not subject to any additional requirements of this subchapter except for:
(1) The shipper's responsibilities to properly class their material in accordance with §173.22 of this subchapter;
(2) Sections 171.15 and 171.16 of this subchapter pertaining to the reporting of incidents; and
(3) For a Class 7 (Radioactive) material the requirements for an excepted package.

(b) ***Authorized materials***. Only materials authorized for transport aboard passenger aircraft and appropriately classed within one of the following hazard classes or divisions may be transported in accordance with this section:
(1) Division 2.2 materials with no subsidiary hazard;
(2) Class 3 materials;
(3) Class 4 (PG II and III) materials except for self-reactive materials;
(4) Division 5.1 (PG II and III);
(5) Division 5.2 materials only when contained in a chemical kit or a first aid kit;
(6) Division 6.1, other than PG I, Hazard Zone A or B material;
(7) Class 7, Radioactive material in excepted packages
(8) Class 8 (PG II and III), except for UN2803 (Gallium) and UN2809 (Mercury); and
(9) Class 9, except for UN1845 (Carbon dioxide, solid or Dry ice), and lithium batteries and cells.

(c) ***Inner packaging limits***. The maximum quantity of hazardous materials in each inner packaging is limited to:
(1) 1 g (0.04 ounce) or 1mL (0.03 ounce) for solids or liquids of Division 6.1, Packing Group I or II or other materials that also meet the definition of a toxic material;
(2) 30 g (1 ounce) or 30mL (1 ounce) for solids or liquids other than those covered in paragraph (c)(1) of this section; and
(3) For gases a water capacity of 30mL (1.8 cubic inches) or less.

(d) ***Outer packaging aggregate quantity limits***. The maximum aggregate quantity of hazardous material contained in each outer packaging must not exceed the limits provided in the following paragraphs. For outer packagings containing more than one hazardous material, the aggregate quantity of hazardous material must not exceed the lowest permitted maximum aggregate quantity. The limits are as follows:
(1) For other than a Division 2.2 or Division 5.2 material:
(i) Packing Group I—300g (0.66 pounds) for solids or 300mL (0.08 gallons) for liquids;
(ii) Packing Group II—500g (1.1 pounds) for solids or 500mL (0.1 gallons) for liquids;
(iii) Packing Group III—1 kg (2.2 pounds) for solids or 1L (0.2 gallons) for liquids;
(2) For Division 2.2 material, 1L (61 cubic inches); or
(3) For Division 5.2 material, 500g (1.1 pounds) for solids or 250mL (0.05 gallons) for liquids.

(e) ***Packaging materials***. Packagings used for the transport of excepted quantities must meet the following:
(1) Each inner receptacle must be constructed of plastic, or of glass, porcelain, stoneware, earthenware or metal. When used for liquid hazardous materials, plastic inner packagings must have a thickness of not less than 0.2 mm (0.008 inch).

(2) Each inner packaging with a removable closure must have its closure held securely in place with wire, tape or other positive means. Each inner receptacle having a neck with molded screw threads must have a leak proof, threaded type cap. The closure must not react chemically with the material.
(3) Each inner packaging must be securely packed in an intermediate packaging with cushioning material in such a way that, under normal conditions of transport, it cannot break, be punctured or leak its contents. The intermediate packaging must completely contain the contents in case of breakage or leakage, regardless of package orientation. For liquid hazardous materials, the intermediate packaging must contain sufficient absorbent material that:
(i) Will absorb the entire contents of the inner packaging. In such cases, and
(ii) Will not react dangerously with the material or reduce the integrity or function of the packaging materials.
(iii) The absorbent material may be the cushioning material.
(4) The intermediate packaging must be securely packed in a strong, rigid outer packaging.
(5) Placement of the material in the package or packing different materials in the package must not result in a violation of §173.21.
(6) Each package must be of such a size that there is adequate space to apply all necessary markings.
(7) The package is not opened or otherwise altered until it is no longer in commerce.
(8) Overpacks may be used and may also contain packages of hazardous material or other materials not subject to the HMR subject to the requirements of §173.25.

(f) ***Package tests***. The completed package as prepared for transport, with inner packagings filled to not less than 95% of their capacity for solids or 98% for liquids, must be capable of withstanding, as demonstrated by testing which is appropriately documented, without breakage or leakage of any inner packaging and without significant reduction in effectiveness:
(1) Drops onto a solid unyielding surface from a height of 1.8 m (5.9 feet):
(i) Where the sample is in the shape of a box, it must be dropped in each of the following orientations:
(A) One drop flat on the bottom;
(B) One drop flat on the top;
(C) One drop flat on the longest side;
(D) One drop flat on the shortest side; and
(E) One drop on a corner at the junction of three intersecting edges.
(ii) Where the sample is in the shape of a drum, it must be dropped in each of the following orientations:
(A) One drop diagonally on the top chime, with the center of gravity directly above the point of impact;
(B) One drop diagonally on the base chime; and
(C) One drop flat on the side.

(2) A compressive load as specified in §178.606(c) of this subchapter. Each of the tests in this paragraph (f) of this section may be performed on a different but identical package; that is, all tests need not be performed on the same package.

(g) ***Marking***. Excepted quantities of hazardous materials packaged, marked, and otherwise offered and transported in accordance with this section must be durably and legibly marked with the following marking:

(1) The "*" must be replaced by the primary hazard class, or when assigned, the division of each of the hazardous materials contained in the package. The "**" must be replaced by the name of the shipper or consignee if not shown elsewhere on the package.
(2) The symbol shall be not less than 100 mm (3.9 inches) x 100 mm (3.9 inches), and must be durable and clearly visible.

(h) ***Documentation***.
(1) For transportation by highway or rail, no shipping paper is required.
(2) For transport by air, a shipping paper is not required, except that, if a document such as an air waybill accompanies a shipment, the document must include the statement "Dangerous Goods in Excepted Quantities" and indicate the number of packages.
(3) For transport by vessel, a shipping paper is required and must include the statement "Dangerous Goods in Excepted Quantities" and indicate the number of packages.

(i) ***Training***. Each person who offers or transports excepted quantities of hazardous materials must know about the requirements of this section.

(j) ***Restrictions***. Hazardous material packaged in accordance with this section may not be carried in checked or carry-on baggage.

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ENV-SOP-IND1-0019 Chemical Oxygen Demand

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	11 Apr 2019, 08:10:06 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Sarah Potts (007977)	Manager - Lab Services	15 Apr 2019, 09:09:13 AM	Approved
Steven Sayer (004775)	General Manager	15 Apr 2019, 11:31:07 AM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining Chemical Oxygen Demand (COD) of aqueous samples while meeting the requirements specified in EPA Method 410.4, Revision 2.0.

2. Summary of Method

2.1. Samples, method blanks and standards are placed in sealed tubes and heated in a block digestor in the presence of dichromate at 150°C. After 2 hours, the tubes are removed, cooled, and measured spectrophotometrically at 420nm for low range samples or 600nm for high range samples.

2.2. Reduced volume versions of this method that use the same reagents and molar ratios are acceptable provided they meet the quality control and performance requirements stated in the methods.

3. Scope and Application

3.1. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.2. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of COD analysis equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable to the measurement of COD in groundwater, surface waters and domestic and industrial wastewaters.

5. Limits of Detection and Quantitation

5.1. The default reporting limit is 10mg/L. Refer to the LIMS for method detection limit.

6. Interferences

6.1. Chlorides are quantitatively oxidized by dichromate and therefore represent a possible positive interference. Mercuric sulfate is added to the digestion tubes to complex with the chlorides.

6.2. Method interferences may be caused by contaminants in the reagent water, reagents, glassware and other sample processing apparatus. Method blanks are analyzed to check for these possible interferences.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	250mL in plastic or glass container	H_2SO_4 to pH<2	Cool to ≤6°C	Samples must be analyzed within 28 days of collection.

Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation

Equipment	Description / Comments
COD Reactor	Capable of maintaining temp of 150°C
Spectrophotometer	Thermo AquaMate+ or equivalent, capable of reading 420nm and 600nm
Touch mixer	Vortex mixer or equivalent

9.2. General Supplies

Item	Description
Auto-Pipettes	Eppendorf or equivalent, various sizes
Volumetric flasks	Class A, various volumes
Kimwipes	Or equivalent wipe for cleaning tubes.

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
Low range COD vials	Chemetrics/ catalog #K7355; 10-150mg/L, or equivalent COD vials
High range COD vials	Chemetrics/ catalog #K7365; 50-1500mg/L, or equivalent COD vials

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	ICAL
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This solution contains all target analytes and should be prepared from a different source than the calibration standards.	This solution is used for the LCS and MS.

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock High-Range COD Calibration Standard	Aqua Solutions COD Standard, catalog #TEN152; 10,000mg/L, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working High-Range COD Calibration Standards	Refer to Section 10.2.3.1	Must be prepared fresh daily.	Not applicable
Stock Low-Range COD Calibration Standard	Hach catalog #22539-29; 1000mg/L, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Low-Range COD Calibration Standards	Refer to Section 10.2.3.2	Must be prepared fresh daily.	Not applicable
Stock High-Range COD ICV/Spiking Standard	Environmental Express catalog #B1031; 10,000mg/L, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working High-Range COD ICV/LCS Standard	Refer to Section 10.2.3.3	Must be prepared fresh daily.	Not applicable
Stock Low-Range COD ICV/Spiking Standard	Ricca Spectro Pure catalog #SP069170500; 1000mg/L, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Low-Range COD ICV/LCS Standard	Refer to Section 10.2.3.4	Must be prepared fresh daily.	Not applicable

10.2.3. Standard Preparation Procedures

10.2.3.1. Working High-Range COD Calibration Standards

Prepare a series of standards covering the desired range by diluting appropriate volumes of the Stock High-Range COD Calibration Standard (10,000mg/L) in reagent water. Examples of calibration standards for high-range COD are as follows but may vary:

Standard ID	Amt. of Stock Calibration Std. Used	Final Volume	Final Concentration
CAL0	0.0mL	10mL	0 mg/L
CAL1	0.125mL	25mL	50 mg/L
CAL2	0.25mL	25mL	100 mg/L
CAL3	0.30mL	10mL	300 mg/L
CAL4 (CCV)	0.5mL	10mL	500 mg/L
CAL5	1.0mL	10mL	1000 mg/L
CAL6	1.5mL	10mL	1500 mg/L

10.2.3.2. Working Low-Range COD Calibration Standards

Prepare a series of standards covering the desired range by diluting appropriate volumes of the Stock Low-Range COD Calibration Standard (1000mg/L) in reagent water. Examples of calibration standards for low-range COD are as follows but may vary:

Standard ID	Amt. of Intermediate Calibration Std. Used	Final Volume	Final Concentration
CAL0	0.0mL	10mL	0 mg/L
CAL1	0.25mL	25mL	10 mg/L
CAL2	0.25mL	10mL	25 mg/L
CAL3 (CCV)	0.50mL	10mL	50 mg/L
CAL4	1.0mL	10mL	100 mg/L
CAL5	1.5mL	10mL	150 mg/L

10.2.3.3. Working High-Range COD ICV/LCS Standard Preparation

Dilute 0.5mL of the Stock High-Range COD ICV/Spiking Standard (10,000mg/L) to 10mL with reagent water for a final concentration of 500mg/L.

10.2.3.4. Working Low-Range COD ICV/LCS Standard Preparation

Add 0.5mL of Stock Low-Range COD ICV/Spiking Standard (1000mg/L) to 10mL with reagent water for a final concentration of 50mg/L.

11. Calibration

11.1. **Initial Calibration:** A minimum of a blank and 5 calibration standards is required for each COD range. The lowest calibration standard for Low-Range COD must be at or below the reporting limit. New initial calibrations must be analyzed every 6 months at a minimum. Refer to the Quality Manual for more information regarding calibration curves.

11.2. **Linear Calibration:** For Low-Range analysis at 420nm, zero the spectrophotometer using reagent water. For High-Range analysis at 600nm, zero the spectrophotometer using an undigested reagent blank. Use the instrumentation software to prepare a standard curve by plotting absorbance versus concentration of each calibration blank and standard. The analyst may employ a regression equation that does not pass through the origin. The regression will produce the slope and intercept terms for a linear equation.

11.3. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be ≥ 0.995.

11.4. **Initial Calibration Corrective Action:** If the curve does not meet the acceptance criteria, then a new calibration curve must be analyzed. If the second curve attempt does not meet the acceptance criteria, the analyst must consult the department manager and instrument maintenance and/or preparation of new standards must be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.5. **Initial Calibration Verification (ICV):** In addition to meeting the linearity requirement, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known value of the standard. This step is referred to as Initial Calibration Verification. The ICV is analyzed immediately following an initial calibration curve. Acceptable recovery range for the ICV is 90-110%.

11.6. **ICV Corrective Action:** If the ICV is not acceptable, another ICV may be analyzed. If the second ICV fails, then a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICV must be reanalyzed. Exception: If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.7. **Initial Calibration Blank (ICB):** The ICB consists of reagent water for Low-Range analysis or an undigested reagent blank for High-Range analysis. An ICB must be analyzed after each ICV. If the ICB result is above the reporting limit, sample analysis cannot proceed. Samples associated with a failed ICB must be reanalyzed. Exception: If the ICB is >RL, associated samples determined to be <RL are reportable.

11.8. **Continuing Calibration Verification (CCV):** When an ICAL is not analyzed, the calibration must be verified by analyzing a CCV at the beginning of the analytical sequence. In all cases, a CCV must also be analyzed after every 10 samples and at the end of the analytical sequence to verify the system is still calibrated. The CCV should be from the same material as the curve standards. The acceptable recovery range for the CCV is 90-110%.

11.9. **CCV Corrective Action:** If a CCV fails the acceptance criteria, another CCV may be analyzed. If the second CCV fails, then a new initial calibration curve must be analyzed. Samples must be bracketed by acceptable CCVs in order to be reportable. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable.

11.10. **Continuing Calibration Blank (CCB):** The CCB consists of reagent water for Low-Range analysis or an undigested reagent blank for High-Range analysis. A CCB must be analyzed after each ICV or CCV. If the CCB result is above the reporting limit, another CCB may be analyzed. If the second CCB fails, then a new calibration curve must be analyzed. Samples associated with a failed CCB must be reanalyzed. **Exception**: If the CCB is >RL, associated samples determined to be <RL are reportable.

12. Procedures

12.1. Turn on the COD reactor and heat to 150°C.

12.2. While holding a fresh COD vial at an angle, carefully pipette 2mL of blank, standard or sample into the vial. If any reagent is spilled, discard the tube and use another one. CAUTION: the reagents inside the COD tubes are hazardous due to corrosivity and toxicity – see Section 22. Avoid contact of vial contents with skin and use caution with samples that are pH >7 due to potential reactivity. Waste vials must be disposed of properly – see Section 23.

12.3. Replace the cap and tighten securely. Mix on touch mixer for 10 seconds.

12.4. Prepare a method blank by pipetting 2mL of reagent water into a vial.

12.5. LCS Preparation:

12.5.1. Low-Range: Pipette 2mL of the Working Low-Range COD ICV/Spiking Standard into a low-range vials for an LCS concentration of 50mg/L.

12.5.2. High-Range: Pipette 2mL of the Working High-Range COD ICV/Spiking Standard into a high-range vial for an LCS concentration of 500mg/L.

12.6. MS/MSD Preparation:

12.6.1. Low-Range: Dilute 0.5mL of the Stock Low-Range COD ICV/Spiking Standard (1000mg/L) to 10mL with sample and mix well. Pipette 2mL of this spiked sample into a low-range vial for a spike concentration of 50mg/L.

12.6.2. High-Range: Dilute 0.5mL of the Stock High-Range COD ICV/Spiking Standard (10,000mg/L) to 10mL with sample and mix well. Pipette 2mL of this spiked sample into a high range vial for a spike concentration of 500mg/L.

12.7. Place the mixed sample vials in the preheated COD reactor. Check the vials after approximately 15 minutes. If any of the low-range COD vials has turned green, re-preparation of the sample in the high-range COD vial will be required. Heat the vials for a total of two hours at 150°C. Turn off the reactor and allow the vials to cool for about 20 minutes to 120°C.

12.8. While still warm, carefully invert the vial several times to mix the contents. Place the vials in a test tube rack to cool completely.

12.9. Turn on the spectrophotometer, adjust the wavelength to 420nm for Low-Range vials or to 600nm for High-Range vials and allow it to warm up. For Low-Range analysis at 420nm, zero the spectrophotometer using reagent water. For High-Range analysis at 600nm, zero the spectrophotometer using an undigested reagent blank.

12.10. Wipe all vials clean using a Kimwipe and read the absorbance of each. Record the absorbance once stabilized.

12.11. Compute sample concentration by comparing sample response with the standard curve. Multiply derived concentration by appropriate dilution factor.

12.12. Any sample that exceeds the concentration range of the Low-Range COD vials must be diluted by a maximum of 2x and reanalyzed using a Low-Range COD vial or reanalyzed using a High-Range COD vial. Any sample that exceeds the concentration range of the High-Range COD vials must be diluted and reanalyzed using a High-Range COD vial. Any sample having a concentration <50mg/L analyzed using the High-Range COD vials must be reanalyzed using the Low-Range COD vials.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples.	Target analyte must be less than the method detection limit (MDL).	Wipe down the method blank tube and reanalyze. If method blank is still >MDL, re-prepare and reanalyze associated samples or qualify samples >MDL with B0. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples.	90-110% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, re-prepare and reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analyte	One MS/MSD set per batch plus an additional MS if >10 samples in the batch.	90-110% Recovery ≤20% RPD	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

$$\text{Aqueous Sample (mg/L)} = \frac{(X_s)(V_f)}{(V_i)}$$

Where X_s = COD concentration from instrument in mg/L
V_f = Final volume of sample in Liters
V_i = Initial volume of sample in Liters

14.2. LCS equation:

R = (C/S) * 100

Where R = percent recovery
C = observed LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation:

$$R = \frac{(Cs - C)}{S} * 100$$

Where R = percent recovery
Cs = observed spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. MDLs must be determined per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Commercially-prepared COD vials pre-filled with digestion solution are used for consistency.

19.2. Method has been modified for manual spectrophotometric analysis of commercially-prepared COD vials for consistency and safety.

19.3. Method has been modified to include commercially-prepared low-range COD vials that are read at 420nm for improved accuracy at lower concentrations.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP.

23.2. After COD analysis is complete, return used COD vials to an original shipping container of used COD vials. When the original shipping container is full, transfer all used COD vials to the COD vial drum in the waste disposal area.

23.3. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. EPA EMSL Method 410.4, Revision 2.0, 1993.

25.2. Standard Methods, 5220 Chemical Oxygen Demand (COD), 1997, editorial revisions 2011.

25.3. Pace Analytical Quality Manual; latest revision.

25.4. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-012-rev.09	1. Table of Contents: added new Section 14, Method Modifications 2. Section 3.2: reference to MDL added. 3. Table 9.3: updated standard information 4. Section 9.2.3: updated standard preparation information 5. Sections 11.5 and 11.7: updated standard references. 6. Section 11.8: added process for checking vials after 15 minutes in block digestor. 7. Section 11.10: added reference to Table 1 and Table 2. 8. Section 11.11: added procedure for handling over range samples. 9. Sections 11.12 and 11.13: removed previous tables and calculations and added reference to Table 1 and Table 2 for determining sample concentrations. 10. Table 12.1: updated Method Blank corrective action. 11. New Section 14, Method Modifications added 12. Section 15.1: updated SOP reference. 13. Section 17: added references to Table 1 and Table 2. 14. Table 1 and Table 2 added	06May2013
S-IN-I-012-rev.10	1. Cover: replaced Hach 8000 reference with 410.4. 2. Section 1: changed Hach 8000 reference to 410.4. 3. Section 2: changed 620nm wavelength to 600nm. 4. Table 8.1: updated spectrophotometer reference 5. Section 9: updated standard references and preparation 6. Section 10: updated calibration procedure for multi-point curves, removed CAL0, updated zeroing procedure for spectrophotometer and updated what is used for the ICB/CCB. 7. Section 11: updated procedure for spiking and for zeroing the spectrophotometer. 8. Section 15: added special disposal instructions for used COD vials. 9. Section 16: replaced Hach 8000 method reference with EPA 410.4 reference and added reference to SM5220. 10. Section 17: removed concentration tables.	10Aug2015
S-IN-I-012-rev.11	1. Converted to 27 section format. 2. Table 7.1: revised storage temperature format. 3. Table 10.3: updated details of ICV standard 4. Table 13.1: updated corrective actions for LCS and removed Duplicate. 5. Section 14.1: added calculation for final concentration. 6. Section 25.4: added years 2003 and 2009 to TNI reference.	06Aug2017
ENV-SOP-IND1-0019-rev.01	1. Removed cover, table of contents and headers for use in Master Control. 2. Section 9.2: added Kimwipes. 3. Section 10.2.3.1: added CAL0 to table. 4. Section 10.2.3.2: added CAL0 to table. 5. Section 11.1: added blank to curve requirement. 6. Section 12.2: updated references to other sections, clarified hazard of COD tubes, and added a caution for samples with pH >7. 7. Section 12.10: specified use of a Kimwipe to wipe tubes before reading. 8. Table 13.1: updated method blank criteria to be <MDL and updated corrective action. 9. Section 23.2: updated storage and disposal of used COD vials.	10Apr2019

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ENV-SOP-IND1-0046 Ammonia Nitrogen

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	30 Jul 2019, 01:08:11 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Sarah Potts (007977)	Manager - Lab Services	30 Jul 2019, 03:21:38 PM	Approved
Steven Sayer (004775)	General Manager	31 Jul 2019, 01:45:28 PM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining Ammonia Nitrogen in aqueous samples while meeting the requirements specified in EPA method 350.1, revision 2.0 and Standard Method 4500-NH_3 G, 2011.

2. Summary of Method

2.1. Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside and measured colorimetrically at 630nm.

3. Scope and Application

3.1. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.2. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of ammonia nitrogen analysis equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable for the measurement of ammonia nitrogen in potable water, ground water, surface and saline waters, domestic and industrial wastes and soils.

5. Limits of Detection and Quantitation

5.1. The default reporting limit for aqueous samples is 0.1mg/L (standard level) and 0.02mg/L (low level) and for soil samples is 5mg/kg. Refer to LIMS for method detection limits.

6. Interferences

6.1. Calcium and magnesium ions may precipitate if present in sufficient concentration. Tartrate or EDTA is added to the sample in-line in order to prevent this.

6.2. Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent at the pH of 9.5 at which distillation is carried out.

6.3. Residual chlorine must be removed by pretreatment of the sample prior to distillation/analysis.

6.4. Interferences due to turbidity may be filtered out of undistilled samples by means of 0.45 um filter prior to analysis. Aqueous samples with a significant amount of solids should be distilled prior to analysis.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	250mL in plastic or glass container	H_2SO_4 to pH<2	Cool to ≤6°C	Analysis must be completed within 28 days of collection.
Solid	50g in a glass jar	none	Cool to ≤6°C	Analysis must be completed within 28 days of collection.

Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation

Equipment	Vendor	Description / Comments
Autoanalyzer	Lachat Quikchem 8500 or equivalent	Equipped with autosampler, heating unit, flow cell spectrophotometer for use at 630nm and data reduction system. Must use PVC pump tubing for this method.
Distillation apparatus	Lachat Micro-Dist Unit or equivalent	21 place micro-distillation unit, self contained, temperature controlled
Balance	OHaus, Mettler or equivalent	Capable of weighing to 0.1g.

9.2. General Supplies

Item	Description
Automatic-pipettors	Various sizes, Eppendorf or equivalent
Distillation tubes	Micro Dist Tubes, Lachat or equivalent
Distillation tube press	Wine bottle corker or equivalent to seal distillation tubes
Volumetric flasks	Class A, various sizes
Disposable Beakers	50mL or equivalent
Syringe filter	0.45um, Environmental Express or equivalent
Balance	Capable of weighing to 0.1g
Chlorine test strips	HF Scientific Micro Check low-range, or equivalent
pH test paper	Fisher narrow-range for pH 8-9.5, or equivalent
Autosampler tubes	Glass or plastic, for use with Lachat autosampler
Parafilm	Fisher or equivalent for capping stored distillates

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II
Simulated Soil Matrix	Ottawa sand or equivalent.
Phenol	Reagent grade crystals
Sodium Hydroxide	Reagent grade pellets
Sulfuric Acid	Concentrated, reagent grade
Sodium Phenolate solution	Dissolve 83g phenol crystals in 500mL of reagent water in small increments. Cautiously add, while stirring, 32g of sodium hydroxide pellets. Periodically cool flask under water faucet. When cooled completely, dilute to 1L with reagent water. Expires one week from date of preparation.
Sodium Hypochlorite solution	Dilute 250mLof commercial bleach solution (5.25%) to 500mL reagent water. Must be prepared fresh daily.
Disodium ethylenediamine tetraacetate (EDTA)	Reagent grade crystals
EDTA Buffer solution (5%)	Dissolve 50g of EDTA crystals and 5.5g sodium hydroxide pellets in 1L of reagent water. Expires one month from date of preparation.
Sodium Nitroprusside Dihydrate	Reagent grade crystals
Sodium Nitroprusside solution (0.35%)	Dissolve 3.5g of sodium nitroprusside crystals into 1L of reagent water. Expires two weeks from date of preparation.
1N Sodium Hydroxide solution	Dissolve 20g sodium hydroxide pellets in 500mL of reagent water.
Trapping solution (0.016M H_2SO_4)	Dilute 0.444mL concentrated sulfuric acid to 500mL with reagent water. Expires 6 months from date of preparation.
Borate Buffer	Ricca cat #1040-32 or equivalent Observe manufacturer's expiration date
Sodium Thiosulfate	Fisher cat #S445-500 or equivalent Observe manufacturer's expiration date
Sodium Thiosulfate 0.025N (Dechlorinating Reagent)	Dissolve 1.75g of Sodium Thiosulfate in 500mL of reagent water. Expires one week from date of preparation.
Antifoam	Silicon emulsion Fisher 02-002-333 or equivalent

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions and vendors

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	ICAL
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This standard is used for spiking MS/MSD sets.	Same solution can be used for the LCS and MS/MSD

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Ammonia Calibration Standard	Hach; catalog # 24065-49; 100mg/L Ammonia as N, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Ammonia Calibration Standards	Refer to Section 10.2.3.1	Must be prepared fresh daily.	Not Applicable
Stock Ammonia ICV Standard	SPEX; catalog # AS-NH3N9-2Y; 1000mg/L Ammonia as N, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate Ammonia ICV/Spiking Standard	Refer to Section 10.2.3.2	Expires 1 month from date of preparation or on expiration date of stock standard, whichever comes first.	Same as stock standard.
Working Ammonia ICV Standard	Refer to Section 10.2.3.3	Must be prepared fresh daily.	Not Applicable

10.2.3. Preparation Procedures

10.2.3.1. Working Ammonia Calibration Standard Preparation

Working calibration standards must be prepared fresh daily by diluting the Stock Ammonia Calibration Standard (100mg/L) to 100mL with reagent water. Examples of possible calibration standards for the standard level analysis and low level analysis are as follows:

Standard Level (Water and Soil)

Standard ID	Amount of Stock Std.	Final Volume	Final Concentration
CAL0	0mL	100mL	0mg/L
CAL1	0.1ml	100mL	0.10mg/L
CAL2	0.25mL	100mL	0.25mg/L
CAL3	0.50mL	100mL	0.50mg/L
CAL4	1.0mL	100mL	1.0mg/L
CAL5	2.5mL	100mL	2.5mg/L
CAL6 (CCV)	5.0mL	100mL	5.0mg/L
CAL7	10mL	100mL	10mg/L

Low Level (Water only)

Standard ID	Amount of Stock Std.	Final Volume	Final Concentration
CAL0	0mL	100mL	0mg/L
CAL1	0.02ml	100mL	0.02mg/L
CAL2	0.05mL	100mL	0.05mg/L
CAL3	0.2mL	100mL	0.2mg/L
CAL4 (CCV)	0.8mL	100mL	0.8mg/L
CAL5	2.0mL	100mL	2.0mg/L

10.2.3.2. Intermediate Ammonia ICV/Spiking Standard Preparation

Dilute 5mL of the Stock Ammonia ICV Standard (1000mg/L) to 50mL with reagent water for a concentration of 100mg/L.

10.2.3.3. Working Ammonia ICV Standard Preparation

Standard Level ICV: Dilute 5mL of the Intermediate Ammonia ICV standard (100mg/L) to 100mL with reagent water for a concentration of 5mg/L. This standard must be prepared fresh daily.

Low Level ICV: Dilute 0.3mL of the Intermediate Ammonia ICV standard (100mg/L) to 100mL with reagent water for a concentration of 0.3mg/L. This standard must be prepared fresh daily.

11. Calibration

11.1. **Initial Calibration:** Initial calibration consists of a minimum of five standards and a calibration blank that are analyzed in decreasing order of concentration. The lowest calibration standard must be at or below the reporting limit. A new initial calibration curve is run on each working day. Refer to the Quality Manual for more information regarding calibration curves.

11.2. **Linear Calibration**: Using the Lachat software, prepare a standard curve by plotting peak area of standard versus the ammonia concentration. The analyst may employ a regression equation that does not pass through the origin. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be ≥ 0.995.

11.3. Back calculate the concentration of each calibration point. Acceptable recovery range for back-calculated calibration standards is 90-110%. Acceptable recovery for the lowest calibration standard is 50-150%.

11.4. **Initial Calibration Corrective Action:** If the curve does not meet the acceptance criteria, then a new calibration curve must be analyzed. If the second curve attempt does not meet the acceptance criteria, the analyst must consult the department manager and instrument maintenance and/or preparation of new standards must be considered.

11.5. **Initial Calibration Verification (ICV):** In addition to meeting the linearity requirement, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known value of the standard. This step is referred to as Initial Calibration Verification. The ICV is analyzed immediately after an initial calibration curve. The acceptable range for this standard is +/-10% Difference, which is equivalent to 90-110% Recovery.

$$\% \text{ Difference} = \frac{(\text{Calculated concentration} - \text{Theoretical concentration})}{\text{Theoretical concentration}} \times 100$$

$$\% \text{ Recovery} = \frac{\text{Calculated concentration}}{\text{Theoretical concentration}} \times 100$$

11.6. **ICV Corrective Action:** If the ICV is not acceptable, another ICV may be analyzed. If the second ICV fails, then a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICV must be reanalyzed. **Exception:** If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.7. Initial Calibration Blank (ICB): The ICB consists of reagent water. An ICB must be analyzed after each ICV. If the ICB result is above the reporting limit, sample analysis cannot proceed. Samples associated with a failed ICB must be reanalyzed. Exception: If the ICB is >RL, associated samples determined to be <RL are reportable.

11.8. Continuing Calibration Verification (CCV): A CCV must be analyzed after every 10 samples and at the end of the analytical batch to verify the system is still calibrated. The CCV should be from the same material as the curve standards. The acceptable range for these standards is +/-10% Difference, which is equivalent to 90-110% Recovery.

11.9. CCV Corrective Action: If a CCV fails the acceptance criteria, another CCV may be analyzed. If the second CCV fails, then a new initial calibration curve must be analyzed. Samples must be bracketed by acceptable CCVs in order to be reportable. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable.

11.10. Continuing Calibration Blank (CCB): The CCB consists of reagent water. A CCB must be analyzed after each CCV. If any CCB result is above the reporting limit, sample analysis must be stopped. Samples associated with a failed CCB must be reanalyzed. **Exception**: If the CCB is >RL, associated samples determined to be <RL are reportable.

12. Procedures

12.1. Sample Distillation (if applicable)

12.1.1. Water samples associated with an NPDES permit must be distilled prior to analysis, unless a comparative analysis is conducted for equivalency of results for undistilled samples, as described in 40CFR Part 136, Table IB, footnote 6. All soil samples must be distilled prior to analysis. Method Blank and LCS must also be distilled if associated samples are distilled.

12.1.2. Water Sample Distillation:

12.1.2.1. Sample preparation Step 1: Transfer approximately 50 mL aliquot of sample into a clean disposable beaker and check for residual chlorine using a Chlorine Test Strip. If chlorine is present, add 0.025N Sodium Thiosulfate dropwise until no chlorine is indicated by subsequent test strips.

12.1.2.2. Sample preparation Step 2: Using the same 50 mL aliquot of sample, add 1N NaOH dropwise to adjust pH to 9.5. Measure pH by means of narrow range pH paper or pH meter. Alternatively, sample may be placed on auto-titrator to adjust pH to 9.5 with 1N NaOH.

12.1.2.3. Set Distillation unit to 120° C. Allow heater to warm up to set temperature. This will take approximately 30 minutes.

12.1.2.4. Measure 6 mL of sample into a labeled sample tube.

12.1.2.5. Prepare a Method Blank by measuring 6 mL of reagent water into a labeled sample tube.

12.1.2.6. Prepare an LCS by diluting 0.10 mL of the Intermediate Ammonia ICV Standard (100mg/L) to 6mL with reagent water for a concentration of 1.7 mg/L.

12.1.2.7. Prepare a Matrix Spike by diluting 0.10 mL of the Intermediate Ammonia ICV Standard (100mg/L) to 6mL with sample for a concentration of 1.7 mg/L.

12.1.2.8. Add 1.0 mL of Borate Buffer into each tube.

12.1.2.9. Dispense 1.0 mL of 0.016 M sulfuric acid trapping solution into 'M' end of distillation tube and seal the top with a membrane and distillation cap.

12.1.2.10. Immediately press the 'D' end of the distillation tube over the sample tube and place assembly into the press and seal the sample tube by applying downward pressure.

12.1.2.11. Put assembled distillation tube into the pre-heated hot block and set the timer for 30 minutes.

12.1.2.12. After 30 minutes, while wearing heat resistant gloves, immediately remove the sample tube from the distillation tube and roll tube to collect all sample condensate into the 'M' end of distillation tube.

12.1.2.13. Break the distillation tube at the constricted portion of the tube and fill to 6mL mark with reagent water. Analyze immediately or cap with parafilm until analysis can be performed.

12.1.3. Soil Sample Distillation:

12.1.3.1. Set Distillation unit to 120° C. Allow heater to warm up to set temperature. This will take approximately 30 minutes.

12.1.3.2. Add 0.5 g of sample into a labeled sample tube and add 5 mL of reagent water.

12.1.3.3. Prepare a Method Blank by adding 0.5g Ottawa Sand into a labeled sample tube and add 5 mL of reagent water.

12.1.3.4. Prepare an LCS by adding 0.1 mL of the Intermediate Ammonia ICV Standard (100mg/L) to a labeled sample tube with 0.5g Ottawa Sand and 5mL reagent water for a spike concentration of 20mg/Kg after distillation and volume adjustment to 10 mL.

12.1.3.5. Prepare a Matrix Spike by adding 0.1 mL of the Intermediate Ammonia ICV Standard (100mg/L) to a labeled sample tube with 0.5g sample and 5mL reagent water for a spike concentration of 20mg/Kg after distillation and volume adjustment to 10 mL.

12.1.3.6. Add 1.0 mL of Borate Buffer into each tube.

12.1.3.7. Dispense 1.0 mL of 0.016 M sulfuric acid trapping solution into 'M' end of distillation tube and seal the top with a membrane and distillation cap.

12.1.3.8. Immediately press the 'D' end of the distillation tube over the sample tube and place assembly into the press and seal the sample tube by applying downward pressure.

12.1.3.9. Put assembled distillation tube into the pre-heated hot block and set the timer for 30 minutes.

12.1.3.10. After 30 minutes, while wearing heat resistant gloves, immediately remove the sample tube from the distillation tube and roll tube to collect all sample condensate into the 'M' end of distillation tube.

12.1.3.11. Break the distillation tube at the constricted portion of the tube and fill to 10 mL mark with reagent water. Analyze immediately or cap with parafilm until analysis can be performed

12.2. Undistilled Samples

12.2.1. Prepare a Method Blank by measuring 10 mL of reagent water into a labeled disposable beaker.

12.2.2. Prepare an LCS by diluting 0.10 mL of the Intermediate Ammonia ICV Standard (100mg/L) to 10mL with reagent water for a concentration of 1.0 mg/L.

12.2.3. Prepare a Matrix Spike by diluting 0.10 mL of the Intermediate Ammonia ICV Standard (100mg/L) to 10mL with sample for a concentration of 1.0 mg/L.

12.3. Configure the instrument according to manufacturer's instructions. Allow the heating unit, colorimeter and recorder to warm up. Run a baseline with all reagents, using reagent water to flush the tubing. Whenever new tubing is used, allow ample time to flush residual compounds from the tubing.

12.4. Filter any samples that contain suspended solids using a 0.45um syringe filter. If any samples in a batch are filtered, the Method Blank and LCS must also be filtered.

12.5. Establish initial calibration as described in Sections 11.1 through 11.7.

12.6. Once initial calibration is established, analyze each sample, Method Blank, LCS and MS/MSD. An example sequence may be as follows:

Initial calibration standards
ICV
ICB
Method blank
LCS
Client samples
CCV
CCB
Client samples
CCV
CCB

12.7. Sample concentrations exceeding the linear range must be diluted and reanalyzed, or result must be qualified as an estimated concentration. If sample was distilled, re-distillation at a dilution may be needed.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples.	Target analyte must be less than reporting limit.	Reanalyze method blank. If target compound is still >RL in method blank reanalyze all associated samples *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples.	90-110% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, re-prepare and reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analyte	One MS/MSD set per batch plus an additional MS if >10 samples in the batch.	90-110% Recovery ≤20% RPD	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

Undistilled Aqueous Sample (mg/L) = $(X_s)(D)$

Distilled Aqueous Sample (mg/L) = $\frac{(X_s)(V_f)(D)}{(V_i)}$ Solid Sample (mg/Kg) = $\frac{(X_s)(V_f)(D)}{(W_s)}$

Where: X_s = Ammonia concentration, mg/L
V_f = Final sample volume of distillate, L
D = Dilution factor
V_i = Initial sample volume distilled, L
W_s = Weight of solid sample distilled, Kg

Moisture corrected concentration = $\frac{\text{(Final concentration as received)}}{\text{(100- \%Moisture)}} \times 100$

14.2. LCS equation:

$$R = (C/S) * 100$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation:

$$R = \frac{(Cs - C)}{S} * 100$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. Method Detection Limits (MDLs): MDLs must be determined per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Procedure modified for use of Lachat Micro-Dist system.

19.2. Samples which are distilled are distilled into a sulfuric acid solution per SM4500-NH3 B for use with the phenate method and not distilled into a boric acid solution.

19.3. Procedure modified for analysis of soils.

19.4. Calibration standards are not distilled.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP.

24. Pollution Prevention

24.1. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24.2. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. USEPA, Method 350.1, "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, Revision 2.0, August 1993.

25.2. Standard Methods for the Examination of Water and Wastewater; Method 4500-NH_3 G, 2011.

25.3. Lachat Method No. 10-107-06-1-K and J

25.4. Pace Analytical Quality Manual; latest revision.

25.5. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-043-rev.12	1. Cover page: Added SM4500NH3G method reference and updated document control format. 2. Section 1.0: Added SM4500NH3G method reference. 3. Section 2: Added potable water matrix, low-level RL and reference to LIMS for MDLs. 4. Section 4.3: clarified that chlorine is removed prior to distillation/analysis. 5. Table 8.1: updated Lachat model number and added heating unit. Specific that PVC tubing must be used. 6. Table 8.2: updated chlorine test strips and added narrow-range pH paper. 7. Table 9.1: updated expiration of phenolate, buffer and nitroprusside solutions. 8. Table 9.3: updated expiration of intermediate ICV/Spiking standard. 9. Section 9.2.3: Added low level curve and ICV. 10. Section 10.1: Added calibration blank. 11. Section 10.2: Changed absorbance to peak height. 12. Section 14: added modification for use with Lachat Micro-Dist system and use of sulfuric acid solution instead of a boric acid solution for the distillation. 13. Section 16: Added SM4500NH3G and Lachat method references.	30Sep2015
S-IN-I-043-rev.13	1. Converted to 27-section format. 2. Cover page: added 2011 Standard Method reference. 3. Section 1.1: added 2011 Standard Method reference. 4. Table 7.1: revised storage conditions format. 5. Section 9.2: added tube press and parafilm. 6. Section 10.1: added conc. H2SO4, antifoam and sodium thiosulfate dry reagent. 7. Section 11: added requirement for back-calculation of curve points. 8. Section 12.6: added option to re-distill sample at a dilution. 9. Section 14.1: updated units so that equations are in like terms and added separate equations for distilled and undistilled aqueous samples. 10. Section 25: added 2011 Standard Method reference and added years 2003 and 2009 to TNI reference.	20Jun2017
ENV-SOP-IND1-rev.01	1. Removed cover page, table of contents, and headers for use in Master Control. 2. Section 6.4: added 3. Section 9.1: added balance to list of instrumentation. 4. Section 12: added section for preparation of undistilled samples. 5. Table 13.1: updated corrective action for method blank. 6. Section 18: updated MDL procedure reference.	30Jul2019

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ENV-SOP-IND1-0062 Sulfide

QM Approval

Name/Signature	Title	Date	Meaning/Reason
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Management Approval

Name/Signature	Title	Date	Meaning/Reason
Anne Troyer (008754)	Manager - Lab Services	15 Mar 2019, 04:39:02 PM	Approved
Steven Sayer (004775)	General Manager	18 Mar 2019, 07:39:10 AM	Approved

1. Purpose

1.1. The purpose of this SOP is to provide a laboratory specific procedure for determining sulfide in aqueous samples while meeting the requirements specified in Standard Method 4500-S^2-D (2011).

2. Summary of Method

2.1. Sulfide reacts with dimethyl-p-phenylenediamine to produce methylene blue. The intensity of the blue color is proportional to the sulfide concentration. This compound is measured at a wavelength maximum of 665nm.

3. Scope and Application

3.1. Acid insoluble sulfides are not measured by this method. Copper sulfide is the only common sulfide in this class.

3.2. Reporting limits, control limits, volumes used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of sulfide analysis equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable for the measurement of total and dissolved sulfides in ground water, surface water, and saline waters and domestic and industrial wastes

5. Limits of Detection and Quantitation

5.1. The default reporting limit is 0.1mg/L. Refer to the LIMS for the method detection limit.

6. Interferences

6.1. Samples should be taken with minimum aeration and container should be filled with minimal headspace. Sulfide can be volatilized by aeration or converted to a form that is not measurable.

6.2. Color or turbidity may interfere with photometric readings.

6.3. Strong reducing substances such as sulfite, thiosulfate, and hydrosulfite may reduce the blue color or prevent it from developing.

7. Sample Collection, Preservation and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	250mL in plastic container. Fill container completely without overflowing.	pH>9 with 1mL of 1:1 NaOH plus 0.5mL of 1N zinc acetate per 250mL sample.	Cool to ≤6°C	Analysis must be completed within 7 days of collection.

Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation

Equipment	Model / Version	Description / Comments
Spectrophotometer	Thermo Aquamate UV or equivalent	Capable of measuring at 665nm with a light path of 1cm

9.2. General Supplies

Item	Vendor	Description
Test tubes	Fisher or equivalent	Borosilicate glass, 16x100mm
Beakers	Fisher or equivalent	Disposable, 10mL
Erlenmeyer flasks	Fisher or equivalent	500mL
Mechanical Pipettors	Eppendorf or equivalent	Various capacities
Syringe filters	Environmental Express or equivalent	0.45um
Pipets	Fisher or equivalent	10mL, glass, wide-bore

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II
Sulfide 1 Reagent	Hach catalog #1816-49
Sulfide 2 Reagent	Hach catalog #1817-49

10.2. Analytical Standards

10.2.1. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Sulfide Calibration Standard	Absolute catalog #54139, 1000mg/L in single-use ampules, or equivalent	Manufacturer's recommended expiration date. After opening ampule, remainder can be stored in a 20mL vial for up to one week.	Refrigerate
Intermediate Sulfide Calibration Standards	Refer to Section 10.2.2.1	Must be prepared fresh daily, immediately prior to use.	Not applicable
Working Sulfide Calibration Standards	Refer to Section 10.2.2.2	Must be prepared fresh daily, immediately prior to use.	Not applicable
Stock Sulfide ICV Standard	Aqua Solutions catalog #8975, 1000mg/L or equivalent	Manufacturer's recommended expiration date.	Refrigerate
Intermediate Sulfide ICV Standard	Refer to Section 10.2.2.3	Must be prepared fresh daily, immediately prior to use.	Not applicable
Working Sulfide ICV Standard	Refer to Section 10.2.2.4	Must be prepared fresh daily, immediately prior to use.	Not applicable

10.2.2. Standard Preparation

10.2.2.1. Intermediate Sulfide Calibration Standard Preparation

Bring Stock Sulfide Calibration Standard in ampule to room temperature prior to opening. Dilute 1.0mL of the Stock Sulfide Calibration Standard (1000mg/L) to 100mL with reagent water for a concentration of 10mg/L. This standard must be prepared fresh daily, immediately prior to use.

10.2.2.2. Working Sulfide Calibration Standard Preparation

Working calibration standards are prepared using the Intermediate Sulfide Calibration Standard (10mg/L) and must be prepared fresh daily in reagent water immediately prior to use. Examples of possible calibration standards are as follows:

Standard	Int. Std. Volume	Final Volume	Final Conc.
CAL0	0.0mL	5mL	0.0mg/L
CAL1	0.05mL	5mL	0.1 mg/L
CAL2	0.125mL	5mL	0.25 mg/L
CAL3 (CCV)	0.25mL	5mL	0.5 mg/L
CAL4	0.375mL	5mL	0.75 mg/L
CAL5	0.5mL	5mL	1.0 mg/L

10.2.2.3. Intermediate Sulfide ICV Standard Preparation

Bring Stock Sulfide ICV Standard to room temperature prior to opening. Dilute 1.0mL of the Stock Sulfide ICV Standard (1000mg/L) to 100mL with reagent water for a concentration of 10mg/L. This standard must be prepared fresh daily, immediately prior to use.

10.2.2.4. Working Sulfide ICV Standard Preparation

Dilute 0.25mL of the Intermediate Sulfide ICV Standard (10mg/L) to 5mL with reagent water for a concentration of 0.5mg/L. This standard must be prepared fresh daily, immediately prior to use.

11. Calibration and Standardization

11.1. **Initial Calibration:** A minimum of 5 calibration standards is required. The lowest calibration standard must be at or below the reporting limit. A new initial calibration must be analyzed every 6 months at a minimum. Refer to the Quality Manual for more information regarding calibration curves.

11.2. **Linear Calibration:** After zeroing the spectrophotometer with reagent water, prepare a standard curve by plotting absorbance versus sulfide concentration of each calibration standard. The analyst may employ a regression equation that does not pass through the origin. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be $\geq$ 0.995.

11.3. Back calculate the concentration of each calibration point. Acceptable recovery range for back-calculated calibration standards is 90-110%. Acceptable recovery for the lowest calibration standard is 50-150%.

11.4. **Initial Calibration Corrective Action:** If the calibration does not meet the acceptance criteria, then a

new calibration curve must be analyzed. If the second calibration attempt does not meet the acceptance criteria, the analyst must consult the department manager and instrument maintenance and/or preparation of new standards must be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.5. Initial Calibration Verification (ICV): In addition to meeting the linearity requirement, any new calibration curve must be assessed for accuracy. A single standard from a secondary source must be analyzed and the results obtained must be compared to the known value of the standard. This step is referred to as Initial Calibration Verification. The ICV is analyzed immediately following an initial calibration curve. Acceptable recovery range for the ICV is 90-110%.

11.6. ICV Corrective Action: If the ICV is not acceptable, another ICV may be analyzed. If the second ICV fails, then a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICV must be reanalyzed. Exception: If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.7. Initial Calibration Blank (ICB): The ICB consists of reagent water. An ICB must be analyzed after each ICV. If the ICB result is above the reporting limit, sample analysis cannot proceed. Samples associated with a failed ICB must be reanalyzed. Exception: If the ICB is >RL, associated samples determined to be <RL are reportable

11.8. Continuing Calibration Verification (CCV): When an ICAL is not analyzed, the calibration must be verified by analyzing a CCV at the beginning of the analytical sequence. In all cases, a CCV must also be analyzed after every 10 samples and at the end of the analytical sequence to verify the system is still calibrated. The CCV should be from the same material as the curve standards. The acceptable recovery range for the CCV is 90-110%.

11.9. CCV Corrective Action: If a CCV fails the acceptance criteria, another CCV may be analyzed. If the second CCV fails, then a new initial calibration curve must be analyzed. Samples must be bracketed by acceptable CCVs in order to be reportable. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable.

11.10. Continuing Calibration Blank (CCB): A CCB consists of reagent water. A CCB must be analyzed after each CCV. If the CCB result is above the reporting limit, another CCB may be analyzed. If the second CCB fails, then a new calibration curve must be analyzed. Samples associated with a failed CCB must be reanalyzed. **Exception**: If the CCB is >RL, associated samples determined to be <RL are reportable.

12. Procedures

12.1. Sample Pretreatment for Interferences

12.1.1. If necessary or required by program or client, eliminate interferences due to sulfite, thiosulfate, iodide and other soluble substances by allowing the ZnS precipitate to settle for 30 minutes. Mark the sample volume level on the sample container using a permanent marker. Decant as much supernatant as possible without loss of the precipitate. Refill the bottle to the mark with reagent water, shake to re-suspend the precipitate, and quickly withdraw a sample aliquot for analysis. **NOTE: This step is required for all Marathon samples.**

12.2. Sample Analysis

12.2.1. Using a wide-bore pipet, transfer 5mL of **vigorously shaken** sample into a labeled disposable beaker.

12.2.2. Prepare a Method Blank by transferring 5mL reagent water to a labeled disposable beaker.

12.2.3. Prepare an LCS by diluting 0.25mL of the Intermediate Sulfide ICV Standard (10mg/L) to 5mL with reagent water in a labeled disposable beaker for a spike concentration of 0.5mg/L.

12.2.4. Prepare a Matrix Spike by diluting 0.25mL of the Intermediate Sulfide ICV Standard (10mg/L) to 5mL with sample in a labeled disposable beaker for a spike concentration of 0.5mg/L.

12.2.5. Add 0.25mL of Hach Sulfide 1 reagent and 0.25mL of Hach Sulfide 2 reagent to each disposable beaker. Shake or mix gently. Wait five minutes for color development.

12.2.6. Pour sample into a test tube and wipe the test tube clean prior to determining absorbance.

12.2.7. Adjust the wavelength control of the spectrophotometer to 665nm. Zero the spectrophotometer using the reagent blank.

12.2.8. Measure the absorbance of the standards, blanks and samples. A typical run sequence may be as follows:

ICAL Standards
ICV
(If ICAL not run, CCV would replace the ICAL and the ICV in the sequence)
ICB/CCB
Method blank
LCS
Client samples
CCV
CCB
Client samples
CCV
CCB

12.2.9. If the sample has a significant amount of color, make a dilution or prepare a background correction sample by preparing a second 5mL aliquot of the sample at the same dilution, adding only Sulfide 1 reagent.

12.2.10. From the absorbance or corrected absorbance, determine the concentration of sulfide present using the calibration curve and calculation in Section 14.1. Any sample with a sulfide concentration that exceeds the linear range of the calibration curve must be diluted and reanalyzed, or over range results must be qualified as estimated.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples.	Target analyte must be less than reporting limits	Reanalyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples.	90-110% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, re-prepare and reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analyte	One MS/MSD set per batch plus an additional MS if >10 samples in the batch.	90-110% Recovery ≤20% RPD	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

Aqueous Sample (mg/L) = $(X_s)(D)$

Where: X_s = Sample concentration from calibration curve, mg/L
D = Dilution factor (Final sample volume/Initial sample volume)

14.2. LCS equation:

R = (C/S) * 100

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation:

$$R = \frac{(Cs - C)}{S} * 100$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. MDLs must be determined per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Sample containers are purchased pre-preserved with 1mL 1:1 NaOH plus 0.5mL 1N Zinc Acetate per 250mL.

19.2. A spectrophotometric wavelength of 665 nm is used and spectrophotometer is zeroed using reagent water, not re-zeroed using the background absorbance of each sample.

19.3. Certified standards are purchased and have a short shelf-life. Standard solutions are not standardized prior to use.

19.4. Hach Sulfide 1 and Sulfide 2 reagents are used for analysis.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. Standards and Reagents

The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible. **The Hach Sulfide 2 reagent contains potassium dichromate. The final solution will contain hexavalent chromium at a high level. The excess solution should be disposed of properly.**

22.2. Samples

Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves**,** lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. Standard Methods for the Examination of Water and Wastewater; Sulfide Method 4500 S^{2-} D, 2011.

25.2. Hach Water Analysis Handbook; 4th edition; Method 8131; Methylene Blue method

25.3. Pace Analytical Quality Manual; latest revision.

25.4. TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-076-rev.07	1. Cover page: changed phone number, added year reference to method, changed effective date format and revised document control format. 2. Section 1.1: added method year to reference. 3. Section 8.1: updated instrument information. 4. Section 9.3: updated standard information to reflect purchased certified standards. 5. Section 9.2.2: updated standard preparation information. 6. Section 10: removed standardization procedure for standards due to purchasing certified standards with short shelf life. Added ICB. 7. Section 11.1: added sample volume determination procedure. 8. Section 11.2: changed sample volume to 5mL and changed volume of reagents added. 9. Section 11.3: removed D from calculation. 10. Table 12.1: updated MS/MSD frequency. 11. Section 14: added modification that standards are purchased as certified, short-life solutions and are not standardized. 12. Section 16.1: added method year to reference.	10Nov2015
S-IN-I-076-rev.08	1. Converted to 27-section format. 2. Section 6.1: added that sample container should be filled with minimum headspace. 3. Table 7.1: added that sample container should be filled with minimum headspace, revised storage temperature format. 4. Section 9.1: updated spectrophotometer details. 5. Section 9.2: added syringe filters. 6. Section 10.1: removed all reagents except reagent water, Sulfide 1 and Sulfide 2. 7. Table 10.3: added storage procedure for opened ampule of stock calibration standard. 8. Section 10.2.2: added detail to bring standards to room temperature prior to use. 9. Section 11: added requirement to back-calculate curve standards and acceptance criteria. 10. Table 13.1: revised LCS corrective action. 11. Section 14: updated equation to remove Vi and Vf. 12. Section 25.4: added years 2003 and 2009 to TNI reference.	03Jun2017
ENV-SOP-IND1-0062-rev.01	1. Removed cover, table of contents and headers for use in Master Control. 2. Table 7.1: removed unpreserved option. 3. Section 9.1: updated spec model. 4. Section 9.2: added wide-bore pipets. 5. Section 10.2.2.2: added CAL0 to example calibration. 6. Section 11.2: changed reagent blank to reagent water for zeroing spec. 7. Section 12.2.1: specified use of wide-bore pipet and changed “well mixed” to “vigorously shaken.” 8. Section 12.2.10: added that results are calculated using the calibration curve. 9. Section 14.1: added reference to sample concentration from calibration curve. 10. Section 18.1: updated MDL procedure reference. 11. Section 19: added modification for zeroing spec on reagent water. 12. Section 25.1: updated year of reference method to 2011.	15Mar2019

Document Information

Document Number: ENV-SOP-IND1-0065 **Revision:** 01

Document Title: Measurement of Solids

Department(s): Wet Chemistry

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ENV-SOP-IND1-0065 Measurement of Solids

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	09 May 2019, 04:47:30 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Sayer (004775)	General Manager	10 May 2019, 07:18:04 AM	Approved
Sarah Potts (007977)	Manager - Lab Services	10 May 2019, 09:25:18 AM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining Total Solids (TS), also known as Total Residue, Total Dissolved Solids (TDS), also known as Filterable Residue, Total Suspended Solids (TSS), also known as Non-Filterable Residue, Fixed and Volatile Solids Ignited at 550°C, and Settleable Solids, while meeting the requirements specified in Standard Methods 2540 B, C, D, E and F, 2011.

2. Summary of Method

2.1. For TS, a well-mixed sample is placed into a beaker and evaporated to dryness in an oven.

2.2. For TSS, a well-mixed sample is filtered through a glass fiber filter and the residue remaining on the filter is dried in an oven.

2.3. The filtrate from the TSS analysis can be used for the TDS analysis by evaporating to dryness in an oven.

2.4. For Fixed and Volatile Solids, the residue from Method B is ignited to constant weight at 550°C.

2.5. For Settleable Solids, a well mixed sample aliquot is poured into a graduated Imhoff cone and allowed to settle.

3. Scope and Application

3.1. This method is applicable for the measurement of TDS, TSS, TS, Settleable Solids and Volatile Solids.

3.2. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of solids analysis equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable to drinking water, surface and saline waters and domestic and industrial wastes.

5. Limits of Detection and Quantitation

5.1. The reporting limits for the various forms of solids are shown in the table below. Refer to LIMS for method detection limits.

Parameter	Reporting Limit	Method
Total Solids (TS)	10 mg/L	2540 B
Total Dissolved Solids (TDS)	10 mg/L	2540 C
Total Suspended Solids (TSS)	5 mg/L	2540 D
Total Volatile Solids (TVS)	10 mg/L	2540 E
Settleable Solids	0.1 mL/L/Hr	2540 F

6. Interferences

6.1. Water samples containing significant amounts of calcium, magnesium, chloride or sulfate may require prolonged drying and desiccating time and may require rapid weighing. Samples with high bicarbonate concentration may require prolonged drying time to convert the bicarbonate into carbonate.

6.2. Samples high in TDS, such as saline waters, may be subject to positive interference. The appropriate filtering apparatus and filters should be chosen to minimize this possible interference.

6.3. Floating oil and grease, if present, should be dispersed by mixing and included with the sample.

6.4. Negative errors in the volatiles solids may be produced by loss of volatile matter during drying. Determination of low concentrations of volatile solids in the presence of high fixed solids may be subject to considerable error.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous samples for TS, TDS, TS, or TVS	250-1000mL minimum in a plastic container.	None required	Cool to ≤6°C	Samples must be analyzed within 7 days of collection date.
Aqueous samples for Settleable Solids	1000mL minimum in a plastic container	None required	Cool to ≤6°C	Settleable Solids must be determined within 48 hours of collection.

Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Constant Weight – the process of repeated cycles of drying/igniting, cooling, desiccating and weighing until the weight change is less than 4% of the previous weight or <0.5mg, whichever is less.

8.2. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment

Equipment	Vendor	Description / Comments
Drying Oven	Precision Scientific or equivalent	For TDS, capable of holding temperature at 180°C +/-2°C. For TSS and TS, capable of holding temperature at 103°C to 105°C.
Filter support	Fisher or equivalent	For use with 47mm filters
Suction Flask	Fisher or equivalent	Side-arm flask, 1L capacity or equivalent
Analytical Balance	Mettler, OHaus or equivalent	Capable of weighing to 0.1mg.
Desiccator	Fisher or equivalent	
Vacuum pump		
Muffle furnace		Capable of maintaining 550°C

9.2. General Supplies

Item	Vendor	Description
Filter discs	Whatman 934-AH, Environmental Express F93447MM or equivalent	47mm glass-fiber
Graduated cylinder	Fisher or equivalent	Class A, 100mL capacity
Glass beakers	Fisher or equivalent	100mL capacity
Volumetric flask	Fisher or equivalent	Class A, 1000mL for standard preparation
Tongs or forceps	Fisher or equivalent	For handling of glass fiber filers
Crucibles/Dishes		Porcelain for determining volatile solids, various sizes
Imhoff cones		With stand for determining settleable solids

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for preparing the LCS, as applicable.

Table 10.2 Standard Definitions and Vendors

Standard	Description
Spiking Standard (LCS)	This solution contains all target analytes.

10.2.2. Storage Conditions

Table 10.3 – Analytical Standards and Storage Conditions

Standard Type	Description	Expiration	Storage
Stock TSS Reference Standard	Celite, Fisher catalog #C212-500 or equivalent.	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions.
Working TSS Reference Standard	Refer to Section 10.2.3.1	Standard expires 6 months from date of preparation.	Refrigerate
Stock TS/TDS Reference Standard	Fisher Sodium Chloride; catalog #S271-3 or equivalent.	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions.
Working TS/TDS Reference Standard	Refer to Section 10.2.3.2	Standard expires 6 months from date of preparation.	Ambient

10.2.3. Preparation Procedures

10.2.3.1. Working TSS Reference Standard Preparation

Place 100mg of the Stock TSS Reference Standard into a 1L volumetric flask and dilute to volume with reagent water for a final concentration of 100mg/L. Place prepared solution on a stir plate and stir for a minimum of 24 hours in order to saturate solids with water.

10.2.3.2. Working TS/TDS Reference Standard Preparation

Place 0.3000g of the Stock TS/TDS Reference Standard into a 1L volumetric flask and dilute to volume with reagent water for a final concentration of 300mg/L.

11. Calibration

11.1. Analytical balance must be checked each day of use with Class 1 weights. The balance should be vendor-calibrated and serviced annually, at a minimum.

12. Procedures

12.1. Total Solids (TS) – Method 2540B

12.1.1. Preparation of glass beakers or evaporating dishes: Heat the clean beakers to 103-105ºC for one hour. Cool in desiccator and weigh immediately before use. If volatile solids are to be measured, ignite clean evaporating dish at 550°C for 1 hour in a muffle furnace. Cool in desiccator and weigh immediately before use.

12.1.2. Prepare a Method Blank by transferring 100mL of reagent water into a pre-weighed beaker.

12.1.3. Prepare a Laboratory Control Sample (LCS) by quantitatively transferring 100mL of the Working TS Reference Standard into a pre-weighed beaker.

12.1.4. Allow samples to come to room temperature. Quantitatively transfer 100mL of well mixed sample to a pre-weighed glass beaker. Sample volume may vary and should result in 2.5 – 200mg of residue.

12.1.5. Evaporate the samples to dryness in a drying oven. The oven temperature may need to be lowered initially to prevent splattering.

12.1.6. Continue drying the evaporated sample for at least one hour at 103°-105ºC.

12.1.7. Cool the beaker completely in a desiccator and weigh. Repeat the drying and desiccating cycle until a constant weight is achieved.

12.2. Total Dissolved Solids (TDS) – Method 2540C

12.2.1. Preparation of glass beakers or evaporating dishes: Heat the clean beakers to 180ºC +/- 2ºC for one hour. Cool in desiccator and weigh immediately before use.

12.2.2. Preparation of glass fiber filter disc: Place the glass fiber filter on the filter apparatus. While a vacuum is applied, rinse the disc with three successive 20mL volumes of reagent water. Continue to apply the vacuum until all water has passed through. Discard the rinsate. Alternatively, commercially prepared pre-washed and dried filters may be used.

12.2.3. Prepare a Method Blank by transferring 100mL of reagent water to the filter using a graduated cylinder.

12.2.4. Prepare a Laboratory Control Sample (LCS) by quantitatively transferring 100mL of the Working TDS Reference Standard to the filter using a graduated cylinder.

12.2.5. Allow samples to come to room temperature. Quantitatively transfer 100mL of well mixed sample to the filter using a graduated cylinder. Sample volume may vary and should result in 2.5 – 200mg of residue.

12.2.6. With the vacuum still on, rinse the graduated cylinder, filter and filter holder with three 10mL portions of reagent water, allowing complete drainage in between washings. Continue suction for about 3 minutes.

12.2.7. Transfer the filtrate to a weighed evaporating dish or beaker and evaporate to dryness in the oven at 180°C.

12.2.8. Cool the beaker completely in a desiccator and weigh. Repeat the drying and desiccating cycle until a constant weight is achieved.

12.3. Total Suspended Solids (TSS) – Method 2540D

12.3.1. Preparation of glass fiber filter disc: Place the glass fiber filter on the filter apparatus. While a vacuum is applied, rinse the disc with three successive 20mL volumes of reagent water. Continue to apply the vacuum until all water has passed through. Remove the filter from the apparatus and dry in an oven at 103°-105°C for one hour. Remove the filter from the oven and place in desiccator. Repeat the drying procedure until a constant weight is achieved. Weigh the filter immediately before use. Alternatively, commercially prepared pre-washed and pre-weighed filters may be used.

12.3.2. Assemble the filtering apparatus and begin vacuum suction. Wet the filter with a small amount of reagent water to seat it against the fritted support.

12.3.3. Prepare a Method Blank by transferring 100mL of reagent water to the filter using a graduated cylinder.

12.3.4. Prepare a Laboratory Control Sample (LCS) by quantitatively transferring 100mL of the Working TSS Reference Standard to the filter using a graduated cylinder.

12.3.5. Allow samples to come to room temperature. Shake the sample vigorously and quantitatively transfer 100mL to the filter using a graduated cylinder. Sample volume may vary and should result in 2.5 – 200mg of residue.

12.3.6. With the suction still on, wash the graduated cylinder, filter and filter holder with three 10mL portions of reagent water, allowing complete drainage in between washings. Continue suction for about 3 minutes.

12.3.7. Carefully remove the filter from the filter apparatus. Dry for a minimum of one hour at 103°-105°C.

12.3.8. Cool the filter completely in a desiccator and weigh. If sample is being prepared and reported in the same day, repeat the drying cycle until a constant weight is achieved. Constant weight is not required if sample is dried in the oven over night.

12.4. Fixed and Volatile Solids Ignited at 550°C – Method 2540E

12.4.1. Preheat muffle furnace to 550°C and ignite residue produced by Method 2540B to constant weight. Usually 15-20 minutes ignition is required for 200mg residue.

12.4.2. Transfer the dish to a desiccator for final cooling in a dry atmosphere. Do not overload desiccator.

12.4.3. Weigh dish as soon as it has cooled to balance temperature. Repeat cycle of igniting, cooling, desiccating and weighing until a constant weight is obtained.

12.5. Settleable Solids – Method 2540F

12.5.1. Fill an Imhoff cone to the 1-L mark with a well-mixed sample.

12.5.2. Settle for 45 minutes, gently agitate sample near the sides of the cone with a rod or by spinning.

12.5.3. Settle 15 minutes longer.

12.5.4. Record volume of settleable solids in the cone as milliliters per liter.

12.5.5. If the settled matter contains pockets of liquid between large settled particles, estimate volume of these and subtract from volume of settle solids.

12.5.6. Where a separation of settleable and floating materials occurs, do not estimate the floating material as settleable matter.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples.	Target analyte must be less than reporting limits.	Reanalyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples.	80-120% Recovery	Reanalyze associated samples if original LCS is outside acceptance limits. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Sample Duplicate (DUP)	Sample	One sample duplicate for every 10 or fewer samples analyzed.	≤10% RPD	No corrective action necessary. Qualify data as appropriate. ***Exception:*** 1. Duplicate sample values <5x RL are not evaluated because values at or near the RL provide statistically insignificant RPD results.

14. Data Analysis and Calculations

14.1. Calculate **TS** as follows:

$$\text{Total residue (TS), mg/L} = \frac{(A - B) \times 1000}{C}$$

Where A = weight of sample + dish, in mg
B = weight of dish, in mg
C = mL of sample used

14.2. Calculate **TDS** as follows:

$$\text{Filterable residue (TDS), mg/L} = \frac{(A - B) \times 1000}{C}$$

Where A = weight of dried residue + dish, in mg
B = weight of dish, in mg
C = mL of sample used

14.3. Calculate **TSS** as follows:

$$\text{Non-Filterable residue (TSS), mg/L} = \frac{(A - B) \times 1000}{C}$$

Where A = weight of filter + residue, in mg
B = weight of filter, in mg
C = mL of sample used

14.4. Calculate **volatile solids** as follows:

$$\text{Volatile Solids, mg/L} = \frac{(A - B) \times 1000}{\text{Sample Volume, mL}}$$

$$\text{Fixed Solids, mg/L} = \frac{(B - C) \times 1000}{\text{Sample Volume, mL}}$$

Where A = weight of residue + dish before ignition, mg
B = weight of residue + dish or filter after ignition, mg
C = weight of dish or filter, mg

14.5. LCS equation

$R = (C/S) * 100$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.6. RPD calculations (for duplicates):

$$\textbf{RPD} = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Oven Temperature: If oven is found to be at a temperature that is below the minimum specified temperature for the analysis at the end of the sample drying time, the oven must be returned to the required temperature and samples must remain in the oven for a minimum of one hour.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Oven Temperature: If oven is found to be at a temperature that is greater than the maximum specified temperature for the analysis while samples are drying, the samples must be re-set or the resulting data must be qualified as potentially biased low.

18. Method Performance

18.1. **Demonstration of Capability (DOC)**: Every analyst who performs these methods must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Samples are measure using Class A graduated cylinders, not pipets.

19.2. Samples are shaken, not stirred.

19.3. Constant weight is not determined on samples for TSS dried over night.

19.4. Lab uses $\leq$10% RPD to evaluate duplicates which is roughly equivalent to method recommendation of duplicate sample agreement within 5% of their average weight.

20. Instrument/Equipment Maintenance

20.1. Refer to maintenance log and/or instrument manufacturer's instructions.

21. Troubleshooting

21.1. Refer to maintenance log and/or instrument manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Pollution Prevention

23.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

24. Waste Management

24.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP.

24.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

25. References

25.1. Standard Methods for the Examination of Wastewater and Water; Methods 2540B, C, D, E and F 1997, editorial revisions 2011.

25.2. Pace Analytical Quality Manual; latest revision.

25.3. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-084-rev.06	1. Converted to Corporate 27-section format. 2. Cover page: added 2011 to method reference. 3. Section 1.1: added 2011 to method reference. 4. Table 7.1: updated storage temperature format. 5. Section 10: removed reference to standard for MS/MSD. 6. Sections 12.1, 12.2, 12.3: added instructions for preparation of method blank and LCS. Moved calculations to Section 14. 7. Table 13.1: changed RPD to ≤10%, which is roughly equivalent to +/-5% of the average weight as stated in the method. 8. Section 19: added modification for use of ≤10% RPD for duplicates. 9. Section 25: added 2011 to method reference and added 2003 and 2009 to TNI reference.	1May2017
ENV-SOP-IND1-0065-rev.01	1. Table 7.1: revised minimum volume to a range of 250-1000mL. 2. Section 12.1.4: added minimum residue statement from method. 3. Section 12.1.5: removed minimum residue statement. 4. Section 12.2.1: removed reference to volatile solids. 5. Section 12.2.2: added option to use pre-washed and dried filters. 6. Sections 12.2.3-12.2.5: removed sentence about continuing to apply the vacuum to remove all traces of water. 7. Sections 12.3.3-12.3.5: removed sentence about continuing to apply the vacuum to remove all traces of water. 8. Section 16: added corrective action for low oven temperature. 9. Section 17: added corrective action for high oven temperature.	5May2019

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Document Number: ENV-SOP-IND1-0095 **Revision:** 00

Document Title: Total Organic Carbon

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Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

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STANDARD OPERATING PROCEDURE

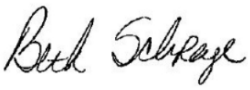
THE DETERMINATION OF TOTAL ORGANIC CARBON (TOC) AND DISSOLVED ORGANIC CARBON (DOC)

REFERENCE METHOD: STANDARD METHOD 5310C (2011)

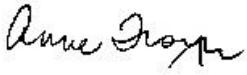
SOP NUMBER:	S-IN-I-169-rev.02
EFFECTIVE DATE:	May 11, 2018
SUPERSEDES:	S-IN-I-169-rev.01

APPROVAL

General Manager — May 9, 2018 Date



Quality Manager — May 9, 2018 Date



Department Manager — May 8, 2018 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

S-IN-I-169-rev.02

Table of Contents

1. Purpose

1.1. The purpose of this SOP is to provide a laboratory specific procedure for determining Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) in aqueous samples while meeting the requirements specified in Standard Method 5310C.

2. Summary of Method

2.1. Organic carbon is oxidized to carbon dioxide by persulfate in the presence of heat or ultraviolet light. The carbon dioxide produced may be purged from the sample, dried and transferred with a carrier gas to a nondispersive infrared (NDIR) analyzer or be coulometrically titrated.

2.2. DOC is the fraction of TOC that passes through a 0.45 um pore diameter filter.

3. Scope and Application

3.1. Reporting limits, control limits, volumes used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.2. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of TOC and DOC analysis equipment and reagents.

4. Applicable Matrices

4.1. This method is applicable to the measurement of TOC or DOC in aqueous samples.

5. Limits of Detection and Quantitation

5.1. The laboratory reporting limit is 1 mg/L. Refer to the LIMS for method detection limit.

6. Interferences

6.1. Insufficient acidification of samples may result in incomplete release of carbon dioxide.

6.2. The intensity of the ultraviolet light reaching the sample may be reduced by highly turbid samples or with aging of the ultraviolet light source, resulting in sluggish or incomplete oxidation.

6.3. Large organic particles or very large or complex organic molecules may be oxidized slowly because persulfate oxidation is rate-limited.

6.4. Persulfate oxidation of organic molecules is slowed in samples containing significant concentrations of chloride.

6.5. With any organic carbon measurement, contamination during sample handling and treatment is a likely source of interference.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous TOC	250 mL amber glass bottle	pH<2 with H_2SO_4 or H_3PO_4	Cool to ≤6°C	Samples must be analyzed within 28 days of collection.
Aqueous DOC	250 mL amber glass bottle	Filtered 0.45um, pH<2 with H_2SO_4 or H_3PO_4	Cool to ≤6°C	Samples must be analyzed within 28 days of collection.

Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions

9. Equipment and Supplies

9.1. Equipment and Instrumentation

Equipment	Description / Comments
TOC Analyzer	Shimadzu TOC-Vwp, Teledyne Tekmar Phoenix 8000, or equivalent, including autosampler and data system.

9.2. General Supplies

Item	Description
Autopipettes	Various volume ranges, calibration checked
Volumetric flasks	Class A, various sizes
Graduated cylinders	Class A, various sizes
Vials	40mL glass with screw cap
Filtration equipment	0.45um pore diameter filters and filtration apparatus for Dissolved Organic Carbon analysis

10. Reagents and Standards

10.1. Reagents

Reagent	Description
Reagent water	ASTM Type II water
Phosphoric acid	Extra pure, 85% solution in water. Acros Organics 29570, or equivalent
Acidified Water	Place about 500mL reagent water into a 1L volumetric flask. Add 8mL Phosphoric acid and bring to 1L with reagent water. Store in amber glass at ambient temperature. Solution expires one month from date of preparation.
Phosphoric acid solution for Shimadzu TOC-Vwp	Place about 500mL reagent water into a 1L volumetric flask. Slowly add 200mL Phosphoric acid while stirring. Allow solution to cool and bring to 1L with reagent water. Store in amber glass at ambient temperature. Solution expires one month from date of preparation.
Phosphoric acid solution for Tekmar Phoenix 8000	Place about 500mL reagent water into a 1L volumetric flask. Slowly add 250mL Phosphoric acid while stirring. Allow solution to cool and bring to 1L with reagent water. Store in amber glass at ambient temperature. Solution expires one month from date of preparation.
Sodium Persulfate	Crystalline, reagent grade. Acros Organics 20202, or equivalent.

Reagent	Description
Sodium Persulfate solution for Shimadzu TOC-Vwp	Place about 500mL reagent water into a 1L volumetric flask. Add 120g Sodium Persulfate and 30mL Phosphoric acid and stir to mix well. Bring to 1L with reagent water. It is recommended that this solution be allowed to stand in a cool dark location for 24 hours before use. Store in amber glass at ambient temperature. Solution expires one month from date of preparation.
Sodium Persulfate solution for Tekmar Phoenix 8000	Place about 500mL reagent water into a 1L volumetric flask. Add 117g Sodium Persulfate and 42mL Phosphoric acid and stir to mix well. Bring to 1L with reagent water. Allow this solution to equilibrate for 12 hours before use. Store in amber glass at ambient temperature. Solution expires one week from date of preparation.

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification standards, second source verification, and for preparing LCS, MS, and MSD samples.

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This solution contains the target analyte and is used to spike MS/MSD sets.	Same solution can be used for both the LCS and MS/MSD.

10.2.2. Storage Conditions

Table 10.2 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock TOC Calibration Standard	Ricca: catalog #1847; 1000mg/L potassium hydrogen phthalate, or equivalent	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions
Working TOC Calibration Standards	Refer to Section 10.2.3.1	Expires one month from preparation.	Same as stock standard.
Stock TOC ICV Standard	AlfaAesar; catalog #42562; 1000mg/L potassium hydrogen phthalate, or equivalent.	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions
Working TOC ICV Standard	Refer to Section 10.2.3.2	Prepare fresh daily.	Same as stock standard.
Stock Inorganic Carbon Standard	Ricca; catalog #1845-16; 1000mg/L, or equivalent	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions

10.2.3. Standard Preparation Procedures

Refer to the standard preparation logbook or database for additional instructions regarding preparation of standards for TOC analysis.

10.2.3.1. Working TOC Calibration Standard Preparation

Working calibration standards must be prepared fresh each day in reagent water. Prepare standards in 100mL volumetric flasks and add 2-3 drops of 85% Phosphoric acid to each flask prior to mixing. Pour standards into labeled 40mL vials for analysis. Examples of possible calibration standards are as follows but may vary:

Standard	Stock TOC Cal. Std. Volume	Final Volume	TOC Final Conc.
Cal Std 0	0 mL	100mL	0 mg/L
Cal Std 1	0.1 mL	100mL	1 mg/L
Cal Std 2	0.5 mL	100mL	5 mg/L
Cal Std 3 (CCV)	1.0 mL	100mL	10 mg/L
Cal Std 4	1.5 mL	100mL	15 mg/L
Cal Std 5	2.0 mL	100mL	20 mg/L

10.2.3.2. Working TOC ICV Standard Preparation

Dilute 1.0 mL of the Stock TOC ICV Standard (1000mg/L) and 2-3 drops of 85% Phosphoric acid to 100mL with reagent water for a final spike concentration of 10 mg/L.

11. Calibration

11.1. **Initial Calibration:** Initial calibration standards are analyzed in increasing order of concentration. The lowest calibration standard must be at or below the reporting limit. A new initial calibration curve is analyzed every six months, at a minimum, or as needed. Refer to the Quality Manual for more information regarding calibration curves.

11.2. **Linear Calibration:** Using the instrument software, construct a standard curve by plotting instrument response versus TOC concentration. The regression calculation will generate a correlation coefficient that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be $\geq$0.995.

11.3. **Initial Calibration Corrective Action**: If the calibration curve does not meet the acceptance criteria, then a new calibration curve must be analyzed. If the second curve attempt does not meet the acceptance criteria, the analyst must consult the department manager and instrument maintenance and/or preparation of new standards must be considered.

11.4. **Initial Calibration Verification (ICV)**: In addition to meeting the linearity requirement, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy of the calibration, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known value of the standard. This step is referred to as Initial Calibration Verification. The ICV is analyzed immediately after an initial calibration curve. The acceptable range for the ICV is 90-110% Recovery.

11.5. **ICV Corrective Action:** If the ICV is not acceptable, another ICV may be analyzed. If the second ICV fails, then a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICV must be

reanalyzed. Exception: If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.6. **Initial Calibration Blank (ICB):** The ICB consists of acidified reagent water. An ICB must be analyzed after each ICV. If the ICB result is >2x MDL, sample analysis cannot proceed. Samples associated with a failed ICB must be reanalyzed. Exception: If the ICB is >2x MDL, associated samples determined to be <RL are reportable.

11.7. **Continuing Calibration Verification (CCV):** When an ICAL is not analyzed, the calibration must be verified by analyzing a CCV at the beginning of the analytical sequence. In all cases, a CCV must also be analyzed after every 10 samples and at the end of the analytical sequence to verify the system is still calibrated. The CCV should be from the same material as the calibration standards. The acceptable recovery range for the CCV is 90-110%.

11.8. **CCV Corrective Action:** If a CCV fails the acceptance criteria, another CCV may be analyzed. If the second CCV fails, then a new initial calibration curve must be analyzed. Samples must be bracketed by acceptable CCVs in order to be reportable. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable.

11.9. **Continuing Calibration Blank (CCB):** A CCB consists of acidified reagent water. A CCB must be analyzed after each CCV. If the CCB result is >2x MDL, another CCB may be analyzed. If the second CCB fails, then a new calibration curve must be analyzed. Samples associated with a failed CCB must be reanalyzed. **Exception**: If the CCB is >2x MDL, associated samples determined to be <RL are reportable.

12. Procedures

12.1. Sample Pretreatment

12.1.1. Allow samples to come to room temperature.

12.1.2. If dissolved organic carbon is to be determined and samples were not filtered in the field, filter sample, Method Blank and LCS through 0.45um filter, taking care to avoid contamination.

12.1.3. Pour well-mixed sample into a labeled 40mL vial.

12.1.4. If the sample is high in solids, invert to mix and allow solids to settle. Decant or pipet the supernatant into a labeled 40mL vial for analysis.

12.1.5. When sample dilution is needed, use acidifed water as the diluent. Dilution should be considered when sample is turbid, high in solids, or has an organic odor.

12.2. Sample Analysis

12.2.1. Set up and calibrate instrument per manufacturer's instructions.

12.2.2. Prepare a Method Blank by filling a labeled 40mL vial with acidified water.

12.2.3. Prepare an LCS by diluting 0.4 mL of the Stock TOC ICV Standard (1000mg/L) to 40mL with acidified water for a final spike concentration of 10 mg/L.

12.2.4. Prepare a Matrix Spike by diluting 0.4 mL of the Stock TOC ICV Standard (1000mg/L) to 40mL with sample for a final spike concentration of 10 mg/L.

12.2.5. Prepare an Inorganic Carbon Check by diluting 0.4 mL of the Stock Inorganic Carbon Standard (1000mg/L) to 40mL with sample for a final spike concentration of 10 mg/L.

12.2.6. Analyze samples per instrument manufacturer's instructions. A typical analytical sequence may be as follows:

ICAL Standards
ICV (If ICAL not analyzed, CCV would replace the ICAL and ICV in the sequence)
ICB/CCB
Method Blank
LCS
Client samples
Inorganic Carbon Check
MS/MSD
CCV
CCB
Client samples
MS
CCV
CCB

12.2.7. Use instrument manufacturer's data system for the determination of sample concentrations. Calculate the final concentration in the sample as follows:

TOC or DOC (mg/L) = $(X_s)(D)$

Where: X_s = Concentration of the analyte in the sample from the curve in mg/L
D = Dilution factor (Final volume/Initial volume)

12.2.8. Replicate measurements should be reproducible to within ±10% RPD. Repeat analysis if replicate measurements are outside of the ±10% RPD criteria.

12.2.9. Samples that exceed the linear range must be reanalyzed at a dilution or over range concentrations must be qualified as estimated.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Acidified water	One per preparation batch of up to 20 samples.	Target analyte must be <2x MDL	Reanalyze method blank. If target compound is still >2x MDL in method blank, reanalyze all associated samples that are >RL. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples.	**TOC:** 90-110% Recovery **DOC:** 90-110% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analyte	One MS/MSD set per batch plus an additional MS if >10 samples in the batch.	80-120% Recovery ≤20% RPD	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Inorganic Carbon Check	Inorganic Carbon spike	One Inorganic Carbon Check per analytical run.	Spiked result should equal the unspiked result within ≤20% RPD.	Instrument maintenance is required.

14. Data Analysis and Calculations

14.1. Use instrument manufacturer's data system for the determination of sample concentrations. Calculate the final concentration in the sample as follows:

$$\text{TOC or DOC (mg/L)} = (X_s)(D)$$

Where: X_s = Concentration of TOC or DOC in the sample from the curve in mg/L
D = Dilution factor (Final volume/Initial volume)

14.2. LCS equation:

$$R = (C/S) * 100$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation:

$$R = \frac{(Cs - C)}{S} * 100$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. MDLs must be conducted per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016, 40 CFR Part 136 Appendix B, effective August 28, 2017.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Stock standards are purchased as certified solutions and are not prepared in the lab from dry chemicals.

19.2. Reagents are prepared per instrument manufacturer's instructions and may differ from those listed in the method.

19.3. Calibration check standard analyzed after every tenth analysis is not made from a source material other than the calibration standards.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling or other relevant SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. Standard Methods for the Examination of Water and Wastewater, Method 5310C, 2000. Editorial revision 2011.

25.2. Shimadzu TOC-Vwp User's Manual, 2004.

25.3. Teledyne Tekmar Phoenix 8000 User's Manual, 14-7045-074 Rev. E, 2003.

25.4. Pace Analytical Quality Manual; latest revision.

25.5. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-169-rev.00	1. Converted to Pace SOP format. 2. Added reagent detail for Shimadzu TOC-Vwp instrument. 3. Removed 9060 reference.	23Sep2015
S-IN-I-169-rev.01	1. Converted to 27 section format. 2. Table 7.1: revised storage temperature format and removed holding time for unpreserved samples. 3. Section 9.2: added graduated cylinders. 4. Section 10.1: added Acidified Water and updated storage of other reagents. 5. Table 10.2: added Stock Inorganic Carbon standard. 6. Section 12.2: updated diluents to acidified water, updated preparation of LCS and MS and added preparation of Inorganic Carbon Check. 7. Table 13.1: updated corrective action for method blank and LCS and added Inorganic Carbon check. 8. Section 25.1: corrected method reference. 9. Section 25.5: added years 2003 and 2009 to TNI reference.	11Oct2017
S-IN-I-169-rev.01	1. Table 7.1: removed “preserved” from hold time language. 2. Section 11.6: updated ICB acceptance criteria. 3. Section 11.9: updated CCB acceptance criteria. 4. Section 12.1: added detail for sample pre-treatment when samples are high in solids or may contain interferences. 5. Table 13.1: updated components and acceptance criteria for Method Blank. 6. Section 18.1: updated reference for MDL procedure. 7. Section 19: added a modification for CCV analyzed after every tenth analysis, not LCS. 8. Section 25.5: added NELAC to reference.	8May2018

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ENV-SOP-IND1-0025 ICP Metals (6010)

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	15 Oct 2019, 03:23:02 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Felicia Walker (005354)	Manager - Lab Services	15 Oct 2019, 04:19:43 PM	Approved
Steven Sayer (004775)	General Manager	16 Oct 2019, 07:24:58 AM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining the concentration of metals in aqueous and solid environmental samples while meeting the requirements specified in SW-846 method 6010B.

2. Summary of Method

2.1. Prior to analysis, samples must be solubilized or digested using appropriate sample preparation methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2. This method describes multielement determinations by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices.

2.3. Background correction may be required to compensate for spectral interferences. Background is measured adjacent to analyte lines at a wavelength selected to be free of spectral interference and which reflects the same change in background intensity as occurs at the wavelength measured. Background correction is not required in cases of line broadening where a correction would actually degrade the analytical result.

3. Scope and Application

3.1. This method is applicable to the determination of most trace elements, including metals, in solution.

3.2. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of ICP systems and interpretation of ICP data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable to groundwater, surface water, wastewater, extract, leachate, soil, sediment, sludge and other solid samples.

5. Limits of Detection and Quantitation

5.1. Refer to Table 1 for the list of metals and reporting limits. Refer to the LIMS for method detection limits.

6. Interferences

6.1. **Spectral interferences:** Overlap of emission lines from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena and stray light can contribute to spectral interferences. These interferences can typically be minimized by careful selection of quantitation wavelengths, inter-element corrections, and background correction.

6.2. **Physical interferences:** Changes in sample viscosity, surface tension, or other effects associated with sample transport and nebulization can produce significant inaccuracies, especially in samples containing high concentrations of dissolved solids and acids. Dissolved solids may build up on the nebulizer tip, altering the sample flow rate and causing instrument drift. These effects can be minimized by sample

dilution or use of a specially designed high-solids nebulizer.

6.3. High Salt Concentrations: high salt concentrations in sample digestates can cause signal suppression and confuse interference tests.

6.4. Chemical interferences: Molecular compound formation, ionization effects, and solute vaporization effects are typically not significant with ICP determinations. If observed, they can be minimized by careful selection of plasma and spectrometer operating parameters.

6.5. Memory interferences: Sample deposition on the nebulizer tubing, spray chamber, and plasma torch can cause apparent sample carryover. Memory interferences can be minimized by flushing the system with rinse blanks between samples. If memory interference is suspected for a sample, the sample must be re-analyzed after a sufficient rinse period.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous - Total	250mL in plastic container	- HNO_3 to pH of <2 - Samples received at pH>2 must be preserved to pH<2 with HNO_3 and equilibrate for 24 hours before being prepared for analysis. Record date/time of preservation in preservation logbook.	Ambient or Cool to ≤6°C	Must be analyzed within 6 months of the collection date.
Aqueous - Dissolved	250mL in plastic container	- Filter; HNO_3 to pH<2	Ambient or Cool to ≤6°C	Must be analyzed within 6 months of the collection date.
Solid	50 grams in glass or plastic container	- No chemical preservation	Ambient or Cool to ≤6°C	Must be analyzed within 6 months of the collection date.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Vendor	Description / Comments
ICP-AES	Thermo-Fisher iCAP6500 or equivalent	Equipped with and autosampler and data system

9.2. General Supplies

Item	Vendor	Description
Volumetric Flasks	Class A	Various capacities
Volumetric Pipettors	Eppendorf or equivalent	Various sizes
Autosampler Vials	Environmental Express or equivalent	
Analytical Balance	Ohaus or eqivalent	Capable of weighing to 0.01g
Graduated Cylinders	Class A	Various capacities
pH strips	Fisher or equivalent	Full range

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II
Argon	High purity, liquefied
Nitric acid	Concentrated, trace metal analyzed or equivalent
Hydrochloric acid	Concentrated, trace metal analyzed or equivalent

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	ICAL
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This solution contains the target analytes and is used to spike MS/MSD sets.	Same solution can be used for the LCS and MS/MSD
Internal Standard	A solution added to all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard is used to adjust response ratios to account for instrument drift.	Yttrium
Interference Check Standards	Prepared to contain a known amount of interfering elements that will provide an accurate test of the interelement correction factors. If the ICP will display overcorrection as a negative number, the additional spiking with interfered elements is not necessary.	ICSA (ICSAB for BP Samples only)

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Calibration Standards	SPEX; catalog #'s MIXSTD1-100; MIXSTD2-100; MIXSTD3-100; MIXSTD4-100; MIXSTD5-100; PLS19-2Y; CLSN2-2Y; CLTI9-2Y; PLLI2-2Y; PLP9-3Y; CLAG2-2Y; PLSR2-2Y or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Calibration Standards	Refer to Section 10.2.3.2	Must be prepared fresh weekly	Same as stock standards
Stock ICV Standard	Inorganic Ventures; catalog #s PA-STD-1B; PA-STD-2B; PA-STD-3B or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working ICV Standard	Refer to Section 10.2.3.4	Must be prepared fresh weekly	Same as stock standard
Working Second Source Spiking Solution	Refer to Section 10.2.3.5	Expires 6 months from date of preparation.	Same as stock standard

Standard Type	Description	Expiration	Storage
Stock Interference Check Standard A	SPEX; catalog # INT-A1 or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Interference Check Standard A (ICSA)	Refer to Section 10.2.3.6	Must be prepared fresh weekly	Same as stock standards
Stock Interference Check Standard AB	SPEX; catalog #INT-A1, XFSMN-26-250A (mix 1B), XFSMN-27-250A (mix 2B), or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Interference Check Standard AB (ICSAB)	Refer to Section 10.2.3.8	Must be prepared fresh weekly	Same as stock standards
Stock CRDL standards	SPEX individual standards for each element; 1000 or 10,000 mg/L, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate CRDL Standard	Refer to Section 10.2.3.11	Expires 6 months from date of preparation.	Same as stock standards
Working CRDL standard	Refer to Section 10.2.3.12	Must be prepared fresh weekly	Same as stock standards
Stock Internal Standard	SPEX; catalog # PLY2-2X; 1000mg/L yttrium or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Internal Standard	Refer to Section 10.2.3.13	Must be prepared fresh weekly	Same as stock standards

10.2.3. Standard Preparation Procedures

10.2.3.1. Stock Calibration Standard Details

The following table shows the seven stock standard mixes that may be used to prepare the initial calibration and calibration check standards:

Analyte	Concentration (mg/L)
Catalog # MIXSTD1-100	
Lead	500
Selenium	200
Cadmium	150
Zinc	150
Manganese	100
Beryllium	50
Catalog # MIXSTD2-100 + strontium PLSR2-2Y	
Iron	10,000
Barium	100
Cobalt	100
Copper	100
Vanadium	100
Strontium	100
Catalog # MIXSTD3-100 + silicon PLSI9-2Y	
Arsenic	500
Molybdenum	100
Silicon	100
Catalog #MIXSTD4-100	
Calcium	1000
Potassium	400

Catalog #MIXSTD4-100 Cont'd	
Aluminum	200
Sodium	200
Chromium	20
Nickel	20
Catalog #MIXSTD5-100	
Magnesium	1000
Antimony	200
Thallium	200
Boron	100
Silver	50
Mix #6(combines: CLSN2-2Y; CLTI9-2Y, PLLI2-2Y, PLP9-3Y)	
Lithium	1000
Phosphorus	10,000
Tin	1000
Titanium	1000
Mix #7- Catalog #CLAG2-2Y	
Silver	1000

10.2.3.2. Working Calibration Standards Preparation

Prepared fresh weekly and diluted from the stock standard mixes listed above, using a reagent water mixture that is 5% nitric acid and 2% hydrochloric acid unless otherwise noted.

Working Std. ID	Stock Standard	Vol. of Stock Std.	Final Volume
Calibration Std. Mix 1	MIXSTD1-100	2mL	100mL
Calibration Std. Mix 2	MIXSTD2-100 Strontium PLSR2-2Y	1mL 0.1mL	100mL
Calibration Std. Mix 3	MIXSTD3-100 Silicon PLSI9-2Y	2mL 0.8mL	100mL
Calibration Std. Mix 4	MIXSTD4-100	5mL	100mL
Calibration Std. Mix 5	MIXSTD5-100	2mL	100mL
Calibration Std. Mix 6	Lithium PLLI-2Y Phosphorus PLP9-3Y Tin CLSN2-2Y Titanium PLTI9-2Y	1mL 0.1mL 1mL 1mL	100mL
Calibration Std. Mix 7	Silver CLAG2-2Y	0.2mL	100mL in 10% HCl solution

10.2.3.3. Stock ICV Standard Details

The following table shows the concentrations of the stock standards purchased from Inorganic Ventures as three mixes:

Analyte	Concentration (mg/L)
Inorganic Ventures PA-STD1B / SPEX XFSMN-26-250A	
Arsenic	200/100
Barium	200/100
Beryllium	200/100
Cadmium	200/100
Cobalt	200/100
Chromium	200/100
Copper	200/100
Manganese	200/100

Inorganic Ventures PA-STD1B Cont'd	
Nickel	200/100
Phosphorus	200/100
Lead	200/100
Selenium	200/100
Thallium	200/100
Lithium	200/100
Strontium	200/100
Vanadium	200/100
Zinc	200/100
Inorganic Ventures PA-STD2B / SPEX XFSMN-27-250A	
Silicon	1000/500
Boron	200/100
Molybdenum	200/100
Antimony	200/100
Tin	200/100
Titanium	200/100
Zirconium	200/100
Silver	100/50
Inorganic Ventures PA-STD3B / SPEX XFSMN-28-250A	
Aluminum	2000/1000
Calcium	2000/1000
Iron	2000/1000
Potassium	2000/1000
Magnesium	2000/1000
Sodium	2000/1000

10.2.3.4. Working ICV Standard Preparation

Add 0.5mL of each Stock ICV Standard mix to a 100mL volumetric flask and dilute to volume with a reagent water solution that is 5% nitric acid and 2% hydrochloric acid. If using SPEX stock standards, add 1.0 mL of each mix.

10.2.3.5. Working Second Source Spiking Solution

Add 25.0 mL of each Stock ICV Standard mix to a 100 mL volumetric flask and dilute to volume with reagent water solution that is 2% nitric acid.

10.2.3.6. Stock Interference Check Standard A (ICSA) Details

SPEX Interference Check Standard A (ICSA), mg/L	
Aluminum	5000
Calcium	5000
Magnesium	5000
Iron	2000

10.2.3.7. Working Interference Check Standard A (ICSA) Preparation

Dilute 10mL of the Stock ICSA Standard to 100mL with a reagent water solution that is 5% nitric acid and 2% hydrochloric acid.

10.2.3.8. Stock Interference Check Standard AB (ICSAB) Details

SPEX INT-A1	
Al, Ca, Mg	5000
Fe	2000
SPEX XFSMN-26-250A (Mix 1B)	
As, Ba, Be, B, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl, V, Zn, Li, P	100
SPEX XFSMN-27-250A (Mix 2B)	
Mo, Sb, Sn, Ti, B	100
Ag	50
Si	500

10.2.3.9. Working Interference Check Standard AB (ICSAB) Preparation

Dilute 10mL of the stock INT-A1 standard and 0.5mLof the stock Mix 1B and Mix 2B to 100mL with a reagent water solution that is 5% nitric acid and 2% hydrochloric acid.

10.2.3.10. Stock CRDL Standards Detail

When specified by client or program requirements, a low-level check standard, also known as a CRDL standard, must be analyzed prior to sample analysis and at the end of each analytical batch to bracket the client samples. Acceptance limits for all target elements is 50-150% recovery. The Stock CRDL standards are as follows:

Element	Conc. (ug/mL)	SPEX Catalog #	Element	Conc. (ug/mL)	SPEX Catalog #
Aluminum	1000	CLAL2-2Y	Manganese	1000	CLMN2-2Y
Antimony	1000	CLSB7-2Y	Molybdenum	1000	CLMO9-2Y
Arsenic	1000	CLAS2-2Y	Nickel	1000	CLNI2-2Y
Barium	1000	CLBA2-2Y	Phosphorus	10,000	PLP9-3Y
Beryllium	1000	CLBE2-2Y	Potassium	10,000	PLK2-3Y
Boron	1000	PLB9-2Y	Selenium	1000	CLSE2-2Y
Cadmium	1000	CLCD2-2Y	Silicon	1000	PLSI9-2Y
Calcium	10,000	PLCA2-3Y	Silver	1000	CLAG2-2Y
Chromium	1000	CLCR2-2Y	Sodium	10,000	PLNA2-3Y
Cobalt	1000	PLCO2-2Y	Strontium	1000	PLSR2-2Y
Copper	1000	CLCU2-2Y	Thallium	1000	CLTL2-2Y
Iron	10,000	PLFE2-3Y	Tin	1000	CLSN2-2Y
Lead	1000	CLPB2-2Y	Titanium	1000	CLTI9-2Y
Lithium	1000	PLLI2-2Y	Vanadium	1000	CLV2-2Y
Magnesium	10,000	PLMG2-3Y	Zinc	1000	CLZN2-2Y

10.2.3.11. Intermediate CRDL Standard Preparation

Dilute the following volumes of the stock CRDL standards to 50mL with a reagent water solution that is 2% nitric acid:

Element	Volume (mL)	Final Conc. (mg/L)	Element	Volume (mL)	Final Conc. (mg/L)
Aluminum	2.5	50	Manganese	0.125	2.5
Antimony	0.075	1.5	Molybdenum	0.125	2.5
Arsenic	0.125	2.5	Nickel	0.125	2.5
Barium	0.125	2.5	Phosphorus	1.25	250
Beryllium	0.05	1	Potassium	1.25	250
Boron	1.25	25	Selenium	0.125	2.5
Cadmium	0.025	0.5	Silicon	2.5	50
Calcium	1.25	250	Silver	0.125	2.5
Chromium	0.125	2.5	Sodium	1.25	250
Cobalt	0.125	2.5	Strontium	0.125	2.5
Copper	0.125	2.5	Thallium	0.125	2.5
Iron	0.125	25	Tin	0.125	2.5
Lead	0.125	2.5	Titanium	0.125	2.5
Lithium	0.25	5	Vanadium	0.125	2.5
Magnesium	1.25	250	Zinc	0.25	5

10.2.3.12. Working CRDL Standard Preparation

Dilute 1mL of the Intermediate CRDL Standard to 250mL with a reagent water solution that is 5% nitric acid and 2% hydrochloric acid. Final concentrations are shown below.

Element	Final Conc. (ug/L)	Element	Final Conc. (ug/L)
Aluminum	200	Manganese	10
Antimony	6	Molybdenum	10
Arsenic	10	Nickel	10
Barium	10	Phosphorus	1000
Beryllium	4	Potassium	1000
Boron	100	Selenium	10
Cadmium	2	Silicon	200
Calcium	1000	Silver	10
Chromium	10	Sodium	1000
Cobalt	10	Strontium	10
Copper	10	Thallium	10
Iron	100	Tin	10
Lead	10	Titanium	10
Lithium	20	Vanadium	10
Magnesium	1000	Zinc	20

10.2.3.13. Working Internal Standard Preparation

Dilute 5mL of yttrium stock standard (1000mg/L) to 1L with a reagent water solution that is 2% nitric acid for a final concentration of 5mg/L.

11. Calibration

11.1. Initial Calibration: Calibrate the ICP each working day according to the instrument manufacturer's recommended procedures. Flush the system with the Calibration Blank solution prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. The calibration curve must consist of a minimum of a calibration blank and a standard.

11.2. Linear Calibration: Using the instrumentation software, prepare a standard curve for each element by plotting absorbance versus concentration. The analyst may employ a regression equation that does not pass through the origin. If a multi-point calibration is performed, the regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be ≥ 0.995.

11.3. Initial Calibration Corrective Action: If the curve does not meet the acceptance criteria, then a new calibration curve must be analyzed. If the second curve attempt does not meet the acceptance criteria, the analyst must consult the department manager and instrument maintenance and/or preparation of new standards must be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.4. Initial Calibration Verification (ICV): In addition to meeting the linearity requirement, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known value of the standard. This step is referred to as Initial Calibration Verification. The ICV is analyzed immediately following an initial calibration curve. Acceptable recovery range for the ICV is 90-110% and the RSD of replicate readings must be <5%.

11.5. ICV Corrective Action: If the ICV is not acceptable, another ICV may be analyzed. If the second ICV fails, then a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICV must be reanalyzed. **Exception:** If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.6. Initial Calibration Blank (ICB): The ICB consists of a reagent water solution that is 5% HNO_3 and 2% HCl. An ICB must be analyzed immediately following the ICV. If the ICB result is above the reporting limit, another ICB may be analyzed. If the second ICB fails, then a new initial calibration curve must be analyzed. Samples associated with a failed ICB must be reanalyzed. **Exception:** If the ICB is >RL, associated samples determined to be <RL are reportable. **If required by client or program, the ICB must be evaluated as follows: If the ICB result exceeds ½ the RL, the ICB is considered to be unacceptable. Only samples determined to be <RL are reportable. If the absolute value of a negative concentration exceeds twice the established MDL, the ICB is considered to be unacceptable. Samples associated with a failed ICB must be re-analyzed unless the concentration of the target analyte is greater than 10 times the absolute value of the ICB result.**

11.7. Continuing Calibration Verification (CCV): A CCV must be analyzed after every 10 samples and at the end of the analytical batch to verify the system is still calibrated. The acceptable recovery range for the CCV is 90-110% and the RSD of replicate readings must be <5%.

11.8. CCV Corrective Action: If a CCV fails the acceptance criteria, another CCV may be analyzed. If the second CCV fails, then a new initial calibration curve must be analyzed. Samples must be bracketed by acceptable CCVs in order to be reportable. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable.

11.9. Contract Required Detection Limit (CRDL) Standard: A CRDL standard must be analyzed with each analytical run, at a minimum, after calibration. Acceptance limits for all target elements is 50-150% recovery. If required by client or program, another CRDL standard must be analyzed after samples – not to exceed 8 hours between CRDL analyses.

11.10. CRDL Corrective Action: Samples associated with a failed CRDL must be re-analyzed unless the concentration of the target has failed high, then the associated samples determined to be <RL are reportable.

11.11. Interference Check Standard A (ICSA): An ICSA must be analyzed at the beginning of each analytical run. ICSA must be 80-120% of the true value for the elements in the mix. Non-ICSA elements must be within +/-2x the reporting limit.

11.12. ICSA Corrective Action: If the ICSA fails the acceptance criteria, another ICSA may be analyzed. If the second ICSA fails, then a new calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICSA must be reanalyzed. **Exception:** If the ICSA is >120% for any element in the mix or if any non-ICSA element is >2x the reporting limit, indicating high bias, associated samples determined to be <RL are reportable.

11.13. Interference Check Standard AB (ICSAB): If required by client or program an ICSAB must be analyzed at the beginning of each analytical run. ICSAB must be 80-120% of the true value for the elements in the mix.

11.14. ICSAB Corrective Action: If an ICSAB is required by client or program and the ICSAB fails the acceptance criteria, another ICSAB may be analyzed. If the second ICSAB fails, then a new calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICSAB must be reanalyzed. **Exception:** If the ICSAB is >120% for any element in the mix, indicating high bias, associated samples determined to be <RL are reportable.

11.15. Continuing Calibration Blank (CCB): The CCB consists of a reagent water solution that is 5% HNO_3 and 2% HCl. A CCB must be analyzed after every 10 samples following the CCV. If the CCB result is above the reporting limit, another CCB may be analyzed. If the second CCB fails, then a new calibration curve must be analyzed. Samples associated with a failed CCB must be reanalyzed. **Exception**: If the CCB is >RL, associated samples determined to be <RL are reportable. **If required by client or program, the CCB must be evaluated as follows: If the CCB result exceeds ½ the RL, the CCB is considered to be unacceptable. Only samples determined to be <RL are reportable. If the absolute value of a negative concentration exceeds twice the established MDL, the CCB is considered to be unacceptable. Samples associated with a failed CCB must be re-analyzed unless the concentration of the target analyte is greater than 10 times the absolute value of the CCB result.**

12. Procedure

12.1. Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges; the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis.

12.2. Configure the ICP per manufacturer's instructions and allow it to become thermally stable.

12.3. Approximately 10mL portions of each standard, Method Blank, LCS, sample and MS/MSD are poured into autosampler tubes for analysis.

12.4. Establish initial calibration as described in Section 11.

12.5. Once initial calibration is established, analyze each sample, Method Blank, LCS and MS/MSD. An example sequence may be as follows:

Initial calibration blank
Mix 1
Mix 2
Mix 3
Mix 4
Mix 5
Mix 6
Mix 7
ICV
ICB
CRDL
ICSA
ICSAB (if required)
Method blank
LCS
Client samples
CCV
CCB
Client samples
CCV
CCB
CRDL (if required)
ICSA (if required)
ICSAB (if required)

12.6. The instrument performs two replicate readings for each analysis and the average of the two readings is used to derive the concentration. For samples, the difference between the two readings must be ≤20% RSD for values that are >4x the reporting limit. If the RSD is >20% for values that are >4x the reporting limit, the sample must be reanalyzed.

12.7. Samples with analyte concentrations above the upper linear range must be diluted and reanalyzed or the over range results must be qualified as estimated.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water or boiling chips	One per preparation batch of up to 20 samples, per matrix.	Target analyte must be less than reporting limits	Reanalyze method blank. Re-digest and reanalyze if target compound is still >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required. 3) If sample concentration is >10x blank level, sample and method blank may be reported, but sample must be qualified. (Not for VAP)
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples, per matrix.	80-120% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, re-prepare and reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified. 3) If the batch's associated MS or MSD recovery falls within LCS acceptance limits, associated samples may be reported. The LCS data must be qualified. (Not applicable to OH VAP projects)
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analyte	One MS/MSD set per preparation batch of up to 20 samples, per matrix.	75-125% Recovery ≤20% RPD	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Internal Standard	Yttrium	Automatically added to each sample, blank, and standard as part of the analysis.	No acceptance criteria – used to monitor interferences. 60-140%	No corrective action required. Sample may be analyzed at a dilution if interference is indicated.

14. Data Analysis and Calculations

14.1. Calculate sample concentrations using the following equation:

$$\text{Aqueous Sample (ug/L)} = \frac{(X_s)(V_f)(D)}{(V_i)} \qquad \text{Solid Sample (ug/kg)} = \frac{(X_s)(V_f)(D)}{(W_i)}$$

Where: X_s = Element concentration, ug/L
V_f = Final volume of digestate, L
D = Dilution factor
V_i = Initial volume of aqueous sample digested, L
W_i = Initial weight of solid sample digested, kg

$$\text{Moisture corrected concentration} = \frac{\text{(Final concentration as received)}}{(100 - \%\text{Moisture})} \times 100$$

14.2. LCS equation:

$R = (C/S) * 100$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation:

$$\mathbf{R = \frac{(Cs - C)}{S} * 100}$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD equation:

$$\mathbf{RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100}$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. **Method Detection Limit (MDL) Study**: An MDL study must be conducted per 40 CFR Part 136, Appendix B.

18.2. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

18.3. **Linear Dynamic Range Study**: A linear dynamic range study must be conducted for each element by analyzing increasing concentrations of at least three, preferably five different concentration standards across the range. One of these should be near the upper limit of the range. The upper range limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Samples determined to be above the upper range limit must be diluted and reanalyzed. New dynamic ranges should be determined whenever there is a significant change in instrument response. For those analytes that periodically approach the upper limit, the range should be checked every six months. Refer to Section 7.2.5.4 of Method 6010B for more information.

18.4. **Interelement Correction Factors** must be verified and updated every 6 months or when an instrumentation change occurs. Refer to Section 3.1 of Method 6010B for more information.

18.5. **Post-Digestion Spike Addition:** An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrument detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

18.6. **Dilution test:** If the analyte concentration is sufficiently high, minimally, a factor of 10 above the instrument detection limit after dilution, an analysis of a 1:5 dilution should agree within +/-10% of the original determination. If not, a chemical or physical interference effect should be suspected.

19. Method Modifications

19.1. Mixed standard solutions are purchased as certified standards.

19.2. Instrument conditions may vary from those stated in the method.

19.3. Calibration blanks are evaluated to the reporting limit and not to three times the IDL.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible. The stock metals standards are toxic and must be handled with extreme care. Also handle concentrated acids with care, making sure to wear appropriate personal protective

equipment.

22.2. **Samples**: Take precautions when handling samples. Samples must always be treated as potentially hazardous "unknowns". The use of personal protective equipment such as gloves**,** lab coats and safety glasses is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment**: Portions of the preparation and analytical equipment operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling or other applicable SOP. All wastes are accumulated, managed and disposed of in accordance with all federal and state laws and regulations.

24. Pollution Prevention

24.1. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24.2. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", EPA SW-846, latest revision, Method 6010B.

25.2. Pace Analytical Quality Manual; latest revision.

25.3. TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Table 1: Target Metals and Default Reporting Limits

26.2. Table 2: Target Metals Wavelengths

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-019-rev.10	1. Section 3.1: added reference to MDLs. 2. Table 9.2: removed reference to Profiling Standard 3. Table 9.3: removed reference to Profiling Standard 4. Section 9.2.3: removed reference to Profiling Standard 5. Section 9.2.3.2: changed to a tabular format 6. Section 10: removed reference to Profiling Standard. 7. Section 11.9: added language that over range results can be reported if qualified as estimated. 8. Table 12.1: revised method blank corrective action. 9. Inserted new Method Modifications section.	19Sep2012
S-IN-M-019-rev.11	1. Converted SOP to Corporate 27-section format. 2. Cover page: changed phone number, changed effective date format and revised document control format. 3. Table 7.1: added requirement to record date/time of preservation. 4. Table 10.3: updated standard sources and added Li and P. 5. Section 10.2.3: updated standard preparation. 6. Section 11: removed linear regression equation, made CRDL a requirement for each analytical batch, and removed BP requirements and replaced with "If required by client or program." 7. Table 1: updated RLs and added Li, Sr, and P.	18Dec2015
S-IN-M-019-rev.12	1. Table 7.1: updated storage temperature format. 2. Table 10.3: update standard IDs. 3. Section 10.2.3: updated standard preparation to match current procedures. 4. Section 11.7: removed "immediately following ICB" language. 5. Section 12.5: updated example sequence order. 6. Table 13.1: updated corrective action for method blank and LCS. 7. Section 14.1: updated equation to be in like terms with instrument output. 8. Section 18: moved PDS and SD from Section 13 to Section 18. 9. Section 25.3: added years 2003 and 2009 to TNI reference. 10. Section 26.1: updated title of Table 1. 11. Table 1: added "Default" to the title and added "subject to change" footnote.	27Dec2017
ENV-SOP-IND1-0025-rev.01	1. Removed cover page, table of contents, and headers for use in Master Control. 2. Section 18.1: update MDL procedure reference. 3. Section 26: added Table 2 for wavelengths. 4. Attachments: added Table 2 for wavelengths.	15Oct2019

Table 1: Target Metals and Default Reporting Limits[1]

Metals	Aqueous (µg/L)	Solid (mg/kg)
Aluminum - Al	200	50
Antimony - Sb	6	1
Arsenic - As	10	1
Barium - Ba	10	1
Beryllium - Be	4	0.5
Boron - B	100	5
Cadmium - Cd	2	0.5
Calcium - Ca	1000	50
Chromium - Cr	10	1
Cobalt - Co	10	1
Copper - Cu	10	1
Iron – Fe	100	50
Lead – Pb	10	1
Lithium – Li	20	5
Magnesium – Mg	1000	50
Manganese – Mn	10	1
Molybdenum - Mo	10	1
Nickel – Ni	10	1
Phosphorus – P	N/A	50
Potassium - K	1000	50
Selenium - Se	10	1
Silver – Ag	10	0.5
Sodium – Na	1000	50
Strontium – Sr	10	1
Thallium - Tl	10	1
Tin – Sn	10	5
Titanium - Ti	10	1
Vanadium - V	10	1
Zinc – Zn	20	1

[1]Subject to change

Table 2: Target Metals Wavelengths[1]

Element	Wavelength
Aluminum - Al	308.215
Antimony - Sb	206.833
Arsenic - As	189.042
Barium - Ba	455.403
Beryllium - Be	313.042
Boron - B	249.678
Cadmium - Cd	228.802
Calcium - Ca	315.887
Chromium - Cr	267.716
Cobalt - Co	228.616
Copper - Cu	324.754
Iron – Fe	271.441
Lead – Pb	220.353
Magnesium – Mg	279.079
Manganese – Mn	257.610
Molybdenum - Mo	202.030
Nickel – Ni	231.604
Phosphorus – P	177.495
Potassium - K	766.490
Selenium - Se	196.090
Silicon – Si	288.158
Silver – Ag	328.068
Sodium – Na	589.592
Strontium - Sr	407.771
Thallium - Tl	190.856
Tin – Sn	189.989
Titanium - Ti	337.280
Vanadium - V	292.464
Zinc – Zn	206.200

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ENV-SOP-IND1-0038 Hardness

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	09 Oct 2019, 02:58:18 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Felicia Walker (005354)	Manager - Lab Services	09 Oct 2019, 03:38:28 PM	Approved
Steven Sayer (004775)	General Manager	15 Oct 2019, 08:35:43 AM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining total hardness in aqueous samples while meeting the requirements specified in Standard Method 2340B, editorial revisions 2011.

2. Summary of Method

2.1. Hardness is computed from the results of separate determinations of calcium and magnesium by ICP analysis.

3. Scope and Application

3.1. This method is applicable for all concentration ranges of hardness.

3.2. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the determination of total hardness. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable for the measurement of total hardness in drinking, surface and saline waters and domestic and industrial wastes.

5. Limits of Detection and Quantitation

5.1. The default reporting limit for hardness is 1mg/L. Refer to the LIMS for calcium and magnesium method detection limits.

6. Interferences

6.1. Not applicable to this SOP.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous - Total	250mL in plastic container	- HNO_3 to pH of <2 - Samples received at pH>2 must be preserved to pH<2 with HNO_3 and allowed to equilibrate for 24 hours before being prepared for analysis.	Ambient or Cool to ≤6°C	Must be analyzed within 6 months of the collection date.

Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation

Equipment	Vendor	Description / Comments
ICP-AES	Thermo-Fisher iCAP6500 or equivalent	Equipped with and autosampler and data system

9.2. General Supplies

Item	Vendor	Description
Refer to SOP for ICP analysis		

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Refer to SOP for ICP analysis	

10.2. Analytical Standards

10.2.1. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Calcium and Magnesium Calibration Standard	Refer to SOP for ICP analysis	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions

11. Calibration

11.1. ICP must be calibrated per applicable SOP.

12. Procedures

12.1. Analyze samples for Calcium and Magnesium per applicable metals digestion and ICP analysis SOPs.

12.2. Hardness is computed from the results of separate determinations of calcium and magnesium:

Calcium hardness as mg $CaCO_3$/L = 2.497[Ca, mg/L]

Magnesium hardness as mg $CaCO_3$/L = 4.118[Mg, mg/L]

Total hardness as mg $CaCO_3$/L = Calcium hardness + Magnesium hardness

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per analytical batch of up to 20 samples	Target analyte must be less than reporting limit.	Reanalyze method blank. If target analyte is still >RL in method blank, re-digest and reanalyze associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Sample Duplicate	Target analytes	One duplicate per batch of 20 or fewer samples.	≤20% RPD	No corrective action necessary. Qualify data as appropriate

14. Data Analysis and Calculations

14.1. Refer to Section 12.2.

14.2. RPD equation:

$$\text{RPD} = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Section 13.

16. Corrective Action for Out-of-Control Data

16.1. Refer to Section 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Section 13.

18. Method Performance

18.1. The analyst must read and understand this procedure with written documentation maintained in his/her training file.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Refer to maintenance log and/or instrument manufacturer's instructions.

21. Troubleshooting

21.1. Refer to maintenance log and/or instrument manufacturer's instructions.

22. Safety

22.1. Standards and Reagents: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. Samples: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. Equipment: Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling and Management or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Standard Methods for the Examination of Water and Wastewater"; method 2340B, 1997, Editorial Revisions 2011.

25.2. Pace SOP for ICP Metals by 6010 and Pace SOP for ICP Metals by 200.7, or their replacements.

25.3. Pace Analytical Quality Manual; latest revision.

25.4. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-032-rev.10	1. Table of Contents: added new Section 14, Method Modifications 2. Section 3.2: added reference to MDLs for Ca and Mg. 3. Table 7.1: copied table from ICP SOPs – includes contingency for underpreserved samples. 4. Table 8.1: replaced with table from ICP SOPs – more specific information regarding ICP equipment. 5. Tables 8.2 and 9.1: added reference to ICP SOPs 6. Table 12.1: updated corrective action for method blank and revised LCS control limit from 90-110% to 80-120% to match ICP SOPs. 7. Added new Section 14, Method Modifications 8. Section 16: added reference to ICP SOPs.	13May2013
S-IN-M-032-rev.11	1. Cover page: updated method reference to include date, changed SOP number to indicate "M" for metals department, updated document control format and changed phone number. 2. Section 11.2: updated calculations to reflect those in Method 2340B 1997, Editorial Revisions 2011 indicating that both Ca and Mg are expressed in mg/L $CaCO_3$. 3. Table 12.1: removed LCS. 4. Section 12: removed LCS equation. 5. Section 15.1: removed specific SOP reference. 6. Section 16.1: updated method reference to include date. 7. Section 16.2: added "or their replacements" regarding specified SOPs.	20Sep2015
S-IN-M-032-rev.12	1. Converted to 27 section format. 2. Section 1.1: added reference to 2011 editorial revisions of method. 3. Table 7.1: revised storage temperature format. 4. Section 25.4: added years 2003 and 2009 to TNI reference.	08Oct2017
ENV-SOP-IND1-0038-rev.01	1. Removed cover page, table of contents, and headers for use in Master Control. 2. Table 13.1: updated corrective action for method blank and frequency of duplicates. 3. Section 25.2: removed SOP numbers from reference.	7Oct2019

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ENV-SOP-IND1-0044 Mercury in Water and Soil

QM Approval

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Elizabeth Schrage (008534)	Quality Manager	20 Jun 2019, 07:57:46 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Felicia Walker (005354)	Manager - Lab Services	21 Jun 2019, 12:01:20 PM	Approved
Steven Sayer (004775)	General Manager	27 Jun 2019, 06:51:42 AM	Approved

1. Purpose

1.1. The purpose of this SOP is to provide a laboratory specific procedure for determining total mercury concentration while meeting the requirements specified in EPA method 7470A for aqueous samples and method 7471A for solid samples.

2. Summary of Method

2.1. Prior to analysis, all samples are digested by heating with appropriate acids and oxidizing agents to dissolve and oxidize mercury contents.

2.2. This cold-vapor method is based on the absorption of radiation at 253.7nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

3. Scope and Application

3.1. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.2. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of mercury analysis equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable for the measurement of mercury in groundwater, surface and saline waters, domestic and industrial wastes, TCLP extracts, soil, sediment, bottom deposits and sludge-type materials.

5. Limits of Detection and Quantitation

5.1. The default reporting limits for mercury are 0.002 mg/L for aqueous samples and 0.20 mg/kg for solid samples. Refer to the LIMS for method detection limits.

6. Interferences

6.1. High concentrations of sulfide may interfere in some water or solid samples. Potassium permanganate is added during digestion to eliminate sulfide interference. Concentrations as high as 20mg/L in water or 20mg/kg in soils have been demonstrated to cause no interference in spiked samples.

6.2. High concentrations of copper have been reported to interfere with mercury determinations. Concentrations as high as 10mg/L in water or 10mg/kg in soil have been demonstrated to cause no interference in spiked samples.

6.3. High concentrations of chloride, present in samples require additional potassium permanganate. The free chlorine produced during digestion should be removed with excess hydroxylamine hydrochloride solution.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous - Total	500 mL in plastic container.	HNO_3 to pH<2 Samples received at pH>2 must be preserved to pH<2 with HNO_3 and be allowed to equilibrate for 24 hours before being prepared for analysis. Record date/time of preservation in preservation logbook.	Ambient	Analysis must be completed within 28 days of collection date.
Aqueous - Dissolved	500 mL in plastic container	Filter; HNO_3 to pH<2	Ambient	Analysis must be completed within 28 days of collection date.
Solid	100g in a 4oz glass container	None	Cool to ≤6°C	Analysis must be completed within 28 days of collection date.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Vendor	Model / Version	Description / Comments
Automated Mercury Analyzer	CETAC/Teledyne Leeman	M-6100, M-7600 or equivalent	To include an atomic absorption spectrophotometer, mercury lamp, absorption cell, air pump, flow meter, drying tube, autosampler and data system.
Hot Block	Environmental Express	56-well or equivalent	Adjustable and capable of maintaining a temperature of 90°C to 95°C.
Balance	OHaus	GT400 or equivalent	Readability to 0.01g

9.2. General Supplies

Item	Vendor	Description
Auto-pipettes	Eppendorf or equivalent	Various sizes
Volumetric flasks	Class A	100mL
Graduated cylinder	Class A	25mL
Digestion cups	Environmental Express or equivalent	50mL capacity, volumetrically certified
Autosampler tubes	Moldpro, Inc or equivalent	17x100 mm
Plunger filters	Environmental Express or equivalent	For use with digestion cups

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II
Hydrochloric acid	Concentrated, trace metal grade or equivalent
Hydrochloric acid (3%)	Dilute 30 mLs of concentrated HCl to 1L with reagent water. Used for dilution preparation.
Nitric acid	Concentrated, trace metal grade or equivalent
Sulfuric acid	Concentrated, trace metal grade or equivalent
Aqua Regia	Carefully add one volume of nitric acid to three volumes of hydrochloric acid. Must be prepared in a hood and must be prepared immediately before use each day.
Stannous Chloride	Crystals, reagent grade
Stannous Chloride solution	Add 100g stannous chloride and 70 mL conc. HCl in reagent water and dilute to 1L. This solution is good for 3 days. Refrigerate when not in use.
Sodium Chloride	Crystals, reagent grade
Hydroxylamine hydrochloride	Crystals, reagent grade
Sodium Chloride/ Hydroxylamine Hydrochloride solution	Dissolve 120g sodium chloride and 120g hydroxylamine hydrochloride in reagent water and dilute to 1L. This solution is good for 6 months from preparation (hydroxylamine sulfate may be substituted for hydroxylamine hydrochloride).
Potassium permanganate solution (5%)	Commercially purchased Mercury-free, 5% solution (w/v)
Potassium persulfate	Crystals, reagent grade
Potassium persulfate solution	Dissolve 50g Potassium persulfate in reagent water and dilute to 1L. Expires 6 months from the date of preparation and can be stored at room temperature.
Rinse/Probe Wash Solution	Add 25mL HNO3 and 10mL HCl to 500mL reagent water and dilute to 1L.
Boiling chips	Or equivalent to be used as a simulated soil matrix.

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Contract Required Detection Limit Standard	A standard prepared at a concentration equivalent to the reporting limit for verification at that level.	CRDL only if required by program or client
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This solution contains the target analyte and is used to spike MS/MSD sets.	Same solution can be used for both the LCS and MS/MSD.

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Mercury Calibration standard	Ricca; catalog # AHG1KN; 1000mg/L or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate Mercury Calibration standard	Refer to Section 10.2.3.1	Solution expires 6 months from date of preparation.	Same as for stock standard.
Daily Spike Mercury Calibration standard	Refer to Section 10.2.3.2	Must be prepared fresh daily.	Not Applicable
Working Mercury Calibration standards	Refer to Section 10.2.3.3	One-time use standards.	Not Applicable
Stock Mercury ICV/Spiking standard	SPEX; catalog # PLHG4-2Y; 1000mg/L or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate Mercury ICV/Spiking standard	Refer to Section 10.2.3.4	Solution expires 6 months from date of preparation.	Same as for stock standard.
Daily Spike Mercury ICV/Spiking standard	Refer to Section 10.2.3.5	Must be prepared fresh daily.	Not Applicable
Working Mercury ICV standard	Refer to Section 10.2.3.6	One-time use standard.	Not Applicable
Working CRDL standard	Refer to Section 10.2.3.3	One-time use standard.	Not Applicable

10.2.3. Standard Preparation Procedures

Refer to the standard preparation logbook or database for specific instructions regarding preparation of standards for Mercury analysis

10.2.3.1 Intermediate Mercury Calibration Standard Preparation

Dilute 1mL of the Stock Mercury Calibration Standard (1000mg/L) to 100mLs with 2% HNO_3 for a final concentration of 10mg/L. This standard is good for 6 months from the date of preparation.

10.2.3.2 Daily Spike Mercury Calibration Standard Preparation

Dilute 1mL of the Intermediate Mercury Calibration Standard (10mg/L) to 100mLs with 2% HNO_3 for a final concentration of 100ug/L. This standard must be prepared fresh daily.

10.2.3.3 Working Mercury Calibration Standards Preparation

Working calibration standards are one-time use and are prepared by diluting the Daily Spike Mercury Calibration Standard (100ug/L) with reagent water. Examples of possible calibration standards are as follows:

Aqueous:

Standard ID	Amount of Daily Spike	Final Volume in reagent water	Final Concentration
CAL1 (CRDL)	0.06mL	30mL	0.2ug/L
CAL2	0.3mL	30mL	1.0ug/L
CAL3	0.6mL	30mL	2.0ug/L
CAL4 (CCV)	1.5mL	30mL	5.0ug/L
CAL5	2.25mL	30mL	7.5ug/L
CAL6	3.0mL	30mL	10.0ug/L

Solid:

Standard ID	Amount of Daily Spike	Final Volume in reagent water	Final Concentration
CAL1 (CRDL)	0.1mL	50mL	0.2ug/L
CAL2	0.5mL	50mL	1.0ug/L
CAL3	1.0mL	50mL	2.0ug/L
CAL4 (CCV)	2.5mL	50mL	5.0ug/L
CAL5	3.75mL	50mL	7.5ug/L
CAL6	5.0mL	50mL	10.0ug/L

10.2.3.4 Intermediate Mercury ICV/Spiking Standard Preparation

Intermediate Mercury ICV Standard: Dilute 1mL of the Stock Mercury ICV/Spiking Standard (1000mg/L) to 100mLs with 2% HNO_3 for a final concentration of 10mg/L. This standard is good for 6 months from the date of preparation.

10.2.3.5 Daily Spike Mercury ICV/Spiking Standard Preparation

Dilute 1mL of the Intermediate Mercury ICV/Spiking Standard (10mg/L) to 100mLs with 2% HNO_3 for a final concentration of 100ug/L. This standard must be prepared fresh daily and is also used to prepare the LCS and MS/MSD.

10.2.3.6 Working Mercury ICV Standard Preparation

Aqueous: Dilute 1.5mL of the Daily Spike Mercury ICV Standard (100ug/L) to 30mL with reagent water for a standard concentration of 5.0ug/L. This standard is a one-time use standard.

Solid: Dilute 2.5mL of the Daily Spike Mercury ICV Standard (100ug/L) to 50mL with reagent water for a standard concentration of 5.0ug/L. This standard is a one-time use standard.

11. Calibration

11.1. Initial Calibration: A minimum of a calibration blank and five calibration standards is required. The lowest calibration standard must be at or below the reporting limit. A new initial calibration curve with freshly prepared standard is analyzed on each working day. Refer to the Quality Manual for more information regarding calibration curves.

11.2. Linear Calibration: Using the instrumentation software, prepare a standard curve by plotting absorbance versus mercury concentration of each calibration standard. The analyst may employ a regression equation that does not pass through the origin. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be ≥ 0.995.

11.3. Initial Calibration Corrective Action: If the curve does not meet the acceptance criteria, then a new calibration curve must be digested analyzed. If the second curve attempt does not meet the acceptance criteria, the analyst must consult the department manager and instrument maintenance and/or preparation of new standards must be considered. Samples associated with a failed initial calibration must be reanalyzed. Refer to Section 11.12 for additional information.

11.4. Initial Calibration Verification (ICV): In addition to meeting the linearity requirement, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known value of the standard. This step is referred to as Initial Calibration Verification. The ICV is

analyzed immediately following an initial calibration curve. Acceptable recovery range for the ICV is 90-110%.

11.5. ICV Corrective Action: If the ICV is not acceptable, another ICV may be analyzed. If the second ICV fails, then a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICV must be reanalyzed. Exception: If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported. Refer to Section 11.12 for additional information.

11.6. Initial Calibration Blank (ICB): The ICB consists of reagent water that is prepared per Section 11. An ICB must be analyzed immediately following the ICV. If the ICB result is above the reporting limit, the ICB may be reanalyzed. If the second ICB fails, then a new initial calibration curve must be analyzed. Samples associated with a failed ICB must be reanalyzed. **Exception:** If the ICB is >RL, associated samples determined to be <RL are reportable. Refer to Section 11.12 for additional information. **For WI DNR 7470A samples:** ICB must be evaluated to the most current MDL (LOD). If the absolute value of an ICB result exceeds the established MDL but is <RL (LOQ), associated samples are reportable but must be qualified to indicate that an associated blank exceeds the MDL (LOD).

11.7. Continuing Calibration Verification (CCV): A CCV must be analyzed after every 10 samples and at the end of the analytical batch to verify the system is still calibrated. The CCV should be from the same material as the curve standards. The acceptable recovery range for the CCV is 90-110%.

11.8. CCV Corrective Action: If a CCV fails the acceptance criteria, another CCV may be analyzed. If the second CCV fails, then a new initial calibration curve must be analyzed. Samples must be bracketed by acceptable CCVs in order to be reportable. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable. Refer to Section 11.12 for additional information.

11.9. Continuing Calibration Blank (CCB): The CCB consists of reagent water that is prepared per Section 11. A CCB must be analyzed after each CCV. If the CCB result is above the reporting limit, the CCB may be reanalyzed. If the second CCB fails, then a new calibration curve must be analyzed. Samples associated with a failed CCB must be reanalyzed. **Exception**: If the CCB is >RL, associated samples determined to be <RL are reportable. Refer to Section 11.12 for additional information. **For WI DNR 7470A samples:** CCB must be evaluated to the most current MDL (LOD). If the absolute value of a CCB result exceeds the established MDL but is <RL (LOQ), associated samples are reportable but must be qualified to indicate that an associated blank exceeds the MDL (LOD).

11.10. Contract Required Detection Limit Standard (CRDL): The CRDL is an optional check standard at or below the concentration of the reporting limit that is only analyzed if required by program or client. If required by client or program, the CRDL must be analyzed at the beginning of an analytical run, after every 20 samples, and at the end of the analytical run. The acceptable recovery range for the CRDL is 50-150%.

11.11. CRDL Corrective Action: If the CRDL is required by client or program and fails the acceptance criteria, another CRDL may be analyzed. If the second CRDL fails, associated samples must be qualified. **Exception:** If the CRDL is required and is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable without qualification.

11.12. Failure of the initial calibration, ICV, CCV, ICB or CCB that is due to improper or inadequate preparation requires the re-digestion and reanalysis of the associated preparation batch(es). Failure of the initial calibration, ICV, CCV, ICB or CCB due to instrument malfunction requires the instrument to be restored to proper working order and the reanalysis of samples associated with the failed QC.

12. Procedures

12.1. Aqueous Sample Preparation

12.1.1 Transfer a 30mL aliquot of well-mixed sample to a labeled 50mL graduated digestion cup.

12.1.2 Prepare a Method Blank by adding 30mL of reagent water to a labeled digestion cup.

12.1.3 Prepare an LCS by adding 1.5mL of the Daily Spike Mercury ICV/Spiking Standard (100ug/L) to a labeled digestion cup and diluting to 30mL with reagent water for a spike concentration of 5.0ug/L.

12.1.4 Prepare an MS and MSD set by transferring 30mL aliquots of well-mixed sample to separate labeled digestion cups and adding 1.5mL of the Daily Spike Mercury ICV/Spiking Standard (100ug/L) for a spike concentration of 5.0ug/L

12.1.5 Add 0.75mL concentrated HNO_3 to each digestion cup then add 1.5mL concentrated H_2SO_4 to each digestion cup, mixing after each addition.

12.1.6 Add 5mL of 5% potassium permanganate solution to each digestion cup. Ensure that equal amounts of permanganate solution are added to Method Blank and LCS. Swirl to mix. If the purple color does not persist after 15 minutes, then start over at Section 12.1.1 using a diluted aliquot of sample.

12.1.7 **For WI DNR samples:** If the purple color does not persist for the entire 2 hour digestion period, start over at step 12.1.1 using a diluted aliquot of the sample.

12.1.8 Add 2.5mL potassium persulfate solution to each digestion cup, cap loosely and heat samples for 2 hours in the Hot Block at 95°C.

12.1.9 Cool samples and add 1.8mL of sodium chloride/hydroxylamine hydrochloride solution to each sample to reduce the excess potassium permanganate. **CAUTION**: perform this addition in a fume hood, as chlorine gas could be produced. Proceed to Section 12.4.

12.2. Solid Sample Preparation

12.2.1 Weigh 0.3g of sample into a labeled 50mL digestion cup. To ensure the sample is representative of the entire container, the analyst should weigh out three 0.1g aliquots from different parts of the same container.

12.2.2 Prepare a Method Blank by placing several boiling chips into a labeled digestion cup.

12.2.3 Prepare an LCS by placing several boiling chips into a labeled digestion cup and adding 1.5mL of the Daily Spike Mercury ICV/Spiking Standard (100ug/L) for a final concentration of 0.5mg/Kg.

12.2.4 Prepare an MS and MSD by weighing 0.3g portions of a sample into separate labeled digestion cups and adding 1.5mL of the Daily Spike Mercury ICV/Spiking Standard (100ug/L) for a spike concentration of 0.5mg/Kg.

12.2.5 Add 5mL of reagent water to each digestion cup.

12.2.6 Add 2.5mL of aqua regia to each digestion cup.

12.2.7 Heat samples for 2 minutes in the Hot Block at 95°C.

12.2.8 Cool samples and add 25mL reagent water then add 7.5mL of 5% potassium permanganate

solution. Swirl to mix and let sample stand at least 15 minutes. If the purple color does not persist after 15 minutes, then start over at Section 12.2.1 using a reduced portion of sample.

12.2.9 Return the samples to the Hot Block and heat for 30 minutes at 95°C.

12.2.10 Cool samples again and add 3mL of the sodium chloride/hydroxylamine hydrochloride solution to each sample to reduce the excess potassium permanganate. **CAUTION**: perform this addition in a fume hood, as chlorine gas could be produced.

12.2.11 Adjust the digestate volumes to 50mL with reagent water and mix. Proceed to Section 12.4. If needed, a plunger filter may be used to filter the digestate. The Method Blank and LCS must also be filtered if any client samples are filtered in the batch.

12.3. Calibration Standard Preparation

12.3.1 Prepare calibration standards in labeled 50mL digestion cups per the instructions in Section 10.2.3.3.

12.3.2 Follow steps in Section 12.1 to prepare calibration standards for aqueous matrix.

12.3.3 Follow steps in Section 12.2 to prepare calibration standards for solid matrix.

12.4. All sample volumes, reagent volumes, spiking standard volumes, standard/reagent ID numbers, hot block ID numbers, hot block temperature, thermometer ID number, and preparation date and time must be recorded in the electronic prep log.

12.5. Determination of Mercury

12.5.1 Configure the mercury analyzer according to manufacturer's instructions. Allow the colorimeter and recorder to warm up. Run a baseline with all reagents, using reagent water to flush the tubing. Whenever new tubing is used, allow ample time to flush the tubing.

12.5.2 Approximately 10mL portions of each standard, Method Blank, LCS, sample and MS/MSD are poured into autosampler tubes for analysis.

12.5.3 Establish initial calibration as described in Sections 11.1 through 11.6.

12.5.4 Once initial calibration is established, analyze each sample, Method Blank, LCS and MS/MSD. An example sequence may be as follows:

Initial calibration standards
ICV
ICB
CRDL (only if required)
Method blank
LCS
Client samples
CCV
CCB
Client samples
CCV
CCB
CRDL (only if required)

12.6. Any sample digestate with a mercury concentration that exceeds the linear range of the calibration curve must be diluted with 3% HCl solution and re-analyzed or over range results must be qualified as estimated. Alternatively, the sample may be re-digested at a dilution and re-analyzed.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water or boiling chips	One per preparation batch of up to 20 samples, per matrix.	Target analyte must be less than reporting limits.	Reanalyze method blank. Re-digest and reanalyze if target compound is still >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples, per matrix.	80-120% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, re-prepare and reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analyte	One MS/MSD set per preparation batch of up to 20 samples, per matrix.	75-125% Recovery ≤20% RPD	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.

14. Data Analysis and Calculations

14.1. Calculations are performed directly by the instrument software. If dilutions were performed, the appropriate factors must be applied.

14.2. The instrument software calculates the amount of Mercury in the sample aliquot as follows:

$$X_s = (y - b)/a$$

Where: X_s = Concentration of the analyte
y = Total area or response of the analyte
a = slope of the line (the coefficient of x)
b = intercept of the line

14.3. Calculate the final concentration in the sample as follows:

$$\text{Aqueous Sample (ug/L)} = \frac{(X_s)(V_f)(D)}{(V_i)} \qquad \text{Solid Sample (mg/kg)} = \frac{(X_s)(V_f)(D)}{(W_s)} \times 1000$$

Where: X_s = Mercury concentration, ug/L
V_f = Final sample volume of digestate, L
D = Dilution factor of the sample digestate
V_i = Initial sample volume digested, L
W_s = Weight of solid sample digested, mg

$$\text{Moisture corrected concentration} = \frac{\text{(Final concentration as received)}}{\text{(100- \%Moisture)}} \times 100$$

14.4. LCS equation:

$$\mathbf{R = (C/S) * 100}$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.5. MS/MSD equation:

$$\mathbf{R = \frac{(Cs - C)}{S} * 100}$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.6. RPD equation:

$$\mathbf{RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100}$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. Method Detection Limit (MDL) Study: MDLs must be determined per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Digestion procedure modified to use digestion cups in a hot block instead of BOD bottles in a water bath.

19.2. Standards and some reagents purchased as certified solutions.

19.3. Stannous Chloride solution not stirred continually because it is a solution and not a suspension.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. Standards and Reagents: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. Samples: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. Equipment: Portions of the preparation and analytical equipment operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP. All wastes are accumulated, managed and disposed of in accordance with all federal and state laws and regulations.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Methods 7470A and 7471A.

25.2. Pace Analytical Quality Manual; latest revision.

25.3. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not Applicable

27. Revisions

Document Number	Reason for Change	Date
S-IN-M-040-rev.14	1. Converted SOP to Corporate 27-section format. 2. Cover page: changed SOP name to reflect "M" for metals department, changed phone number, changed effective date format and changed document control format. 3. Section 9.2: added plunger filters. 4. Section 10.1: revised wash solution recipe. 5. Section 10: updated standard information and changed Intermediate #2 to Daily Spike. 6. Section 11: removed linear regression equation, made RLVS optional unless required by client or program and updated RLVS corrective action. 7. Section 12: changed Intermediate #2 to Daily Spike, updated procedure when permanganate color does not persist for 15 minutes, added optional use of plunger filters, and added requirement to document all information in the prep log.	15Dec2015
S-IN-M-040-rev.15	1. Section 5.1: updated default RL for solids. 2. Table 7.1: revised storage conditions for solids. 3. Section 9.1: updated instrument information. 4. Section 10.1: updated reagent information. 5. Tables 10.2 and 10.3: changed RLVS to CRDL. 6. Section 10.2.3.3: changed RLVS to CRDL. 7. Section 11.1: added requirement for calibration blank to be analyzed. 8. Sections 11.10 and 11.11: changed RLVS to CRDL. 9. Section 12.5.4: changed RLVS to CRDL. 10. Section 12.6: clarified that digestate can be diluted or sample can be re-digested at a dilution. 11. Table 13.1: updated LCS corrective action. 12. Section 14.3: updated units in equations and added x1000 to equation for solids. 13. Section 25: added years 2003 and 2009 to TNI reference.	21Jun2017
ENV-SOP-IND1-0044-rev..01	1. Removed cover page, table of contents and headers for use in Master Control. 2. Sections 11.6, 11.9, and 12.1.7: added WI DNR requirements. 3. Section 12.2: added requirement for persistence of permanganate color for 15 minutes. 4. Section 18.1: updated MDL reference procedure.	18Jun2019

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ENV-SOP-IND1-0106 ICP-MS Metals (6020)

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	15 Oct 2019, 09:22:53 AM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Felicia Walker (005354)	Manager - Lab Services	15 Oct 2019, 09:38:05 AM	Approved
Steven Sayer (004775)	General Manager	16 Oct 2019, 07:24:11 AM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining the concentration of metals in aqueous and solid environmental samples while meeting the requirements specified in SW-846 method 6020.

2. Summary of Method

2.1. Prior to analysis, samples must be solubilized or digested using appropriate sample preparation methods. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples.

2.2. This method describes multi-element determinations by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced into a mass spectrometer. The ions are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier.

2.3. Interferences must be assessed and valid corrections applied or the data flagged. Interference correction must include compensation for background ions contributed by the plasma gas, reagents and constituents of the sample matrix.

3. Scope and Application

3.1. An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant native amounts of the recommended internal standards.

3.2. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of ICP-MS systems and interpretation of ICP-MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable to the determination of low concentrations of a large number of elements in water samples, solid samples, and in waste extracts or digestates. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

5. Limits of Detection and Quantitation

5.1. Refer to Table 1 for the list of target elements and reporting limits. Refer to the LIMS for method detection limits.

6. Interferences

6.1. **Spectral interferences:** Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions of more than one atom or charge, respectively. Most isobaric interferences that could

affect ICP-MS determinations have been identified in the applicable literature. Refer to Method 6020, Section 3.0 for more information regarding spectral interferences.

6.2. Physical interferences: Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers, reducing orifice size and instrument performance. Total solids levels below 0.2% are recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes.

6.3. Memory interferences: When there are large concentration differences between samples or standards analyzed sequentially, memory interferences, or carryover can occur. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences. The rinse period between samples must be long enough to eliminate significant memory interference.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous - Total	250mL in plastic container	- HNO_3 to pH <2 - Samples received at pH>2 must be preserved to pH<2 with HNO_3 and allowed to equilibrate for 24 hours prior to digestion.	Ambient or Cool to ≤6°C	Must be analyzed within 6 months of the collection date.
Aqueous - Dissolved	250mL in plastic container	- Filter, HNO_3 to pH <2 - Samples filtered in the lab are preserved to pH<2 with HNO_3 and allowed to equilibrate for 24 hours prior to digestion.	Ambient or Cool to ≤6°C	Must be analyzed within 6 months of the collection date.
Solid	50 grams in glass or plastic container	- No chemical preservation	Ambient or Cool to ≤6°C	Must be analyzed within 6 months of the collection date.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Description / Comments
ICP-MS	Agilent 7700/7800, or equivalent, equipped with autosampler and data system

9.2. General Supplies

Item	Description
Volumetric Flasks	Class A, various capacities
Volumetric Pipettors	Various sizes
Autosampler Vials	Environmental Express or equivalent
Analytical Balance	Ohaus or equivalent, capable of weighing to 0.01g
Graduated Cylinders	Class A, various capacities
pH strips	Full range

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II
Argon	High purity, liquefied
Nitric acid	Concentrated, trace metal analyzed or equivalent
Nitric acid, 1%	Place approximately 700mL reagent water into a 1L volumetric flask and add10mL concentrated nitric acid. Bring to volume with reagent water and mix well.
Hydrochloric acid	Concentrated, trace metal analyzed or equivalent
Gold solution	Inorganic Ventures CGAUN-1, 1000ug/mL or equivalent for rinse water
Rinse Water	Dilute 200mL concentrated nitric acid, 100mL concentrated hydrochloric acid and 3mL Gold solution (1000ug/mL) to 10L with reagent water. This solution expires 3 months from the date of preparation.
Diluent	Dilute 10mL concentrated nitric acid to 1L with reagent water. Concentration of acids can vary and may match digestate acid concentration.

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions

Standard	Description	Comments
Tuning Standard	A solution containing elements representing all of the mass regions of interest used to verify that the instrument resolution and mass calibration are within specifications and that the instrument has reached thermal stability.	
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	ICAL
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This solution contains the target analytes and is used for the Post Digestion Spike.	PDS
Internal Standards	A solution added to all standards, samples, spikes, control samples, and method blanks prior to analysis. These standards are used to adjust response ratios to account for instrument drift.	
Interference Check Standards	Prepared to contain a known amount of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections being used.	ICSA and ICSAB
CRDL Standard (Optional)	A standard prepared at or below the reporting limit for each element to verify recovery at that level. This standard is not required by Method 6020 but is optional.	CRDL

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Calibration Standards	Inorganic Ventures; catalog #'s HERT-CAL-5, PACE-49, and 2008CAL-1, and SPEX catalog #PLB9-2Y, or equivalent. See Section 10.2.3.1	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate Boron Calibration Standard	Refer to Section 10.2.3.2	Standard is good for 3 months from date of preparation.	Same as stock standard
Working Calibration Standards	Refer to Section 10.2.3.3	Must be prepared fresh weekly	Same as stock standards
Stock ICV Standards	High Purity Standards; catalog #s HP 6997 and HP 7003, or equivalent. See Section 10.2.3.4	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate ICV Standard	Refer to Section 10.2.3.5	Standard is good for 1 month from date of preparation.	Same as stock standards
Working ICV Standard	Refer to Section 10.2.3.6	Must be prepared fresh weekly	Same as stock standard
Stock Interference Check Standard A (ICSA)	SPEX; catalog # CL-INT-A2, or equivalent. See Section 10.2.3.7	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate ICSA Standard	Refer to Section 10.2.3.8	Standard is good for 3 months from date of preparation.	Same as stock standard
Working ICSA Standard	Refer to Section 10.2.3.9	Must be prepared fresh weekly	Same as stock standards
Stock Interference Check Standards AB (ICSAB)	SPEX; catalog # CL-INT-A2 and Inorganic Ventures; catalog # HERT-CAL-2A, HERT-CAL-2B, or equivalent. See Section 10.2.3.10	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate ICSAB Standard	Refer to Section 10.2.3.11	Standard is good for 3 months from date of preparation.	Same as stock standard
Working ICSAB Standard	Refer to Section 10.2.3.12	Must be prepared fresh weekly	Same as stock standards
Stock CRDL Standard (Optional)	Inorganic Ventures; catalog #PACE-55-REV1, or equivalent. See Section 10.2.3.13	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working CRDL Standard (Optional)	Refer to Section 10.2.3.14	Must be prepared fresh weekly	Same as stock standards
Stock Internal Standards	Inorganic Ventures; catalog #HERT-IS-1, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Internal Standard	Refer to Section 10.2.3.16	Must be prepared fresh weekly	Same as stock standards
Stock Tune Standard	Inorganic Ventures; catalog #HERTVAR-TS-MS-REV1, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Tune Standard	Refer to Section 10.2.3.18	Must be prepared fresh weekly	Same as stock standards
Stock Spiking Standard #1	Inorganic Ventures; catalog #HERT-CAL-2A or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Stock Spiking Standard #2	Inorganic Ventures; catalog #HERT-CAL-2B or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions

10.2.3. Standard Preparation Procedures

10.2.3.1. Stock Calibration Standard Details

The following table shows the stock standard mixes that may be used to prepare the initial calibration and calibration check standards:

Analyte	Concentration (ug/mL)
SPEX Catalog # PLB9-2Y	
B	1000
Inorganic Ventures Catalog # 2008CAL-1	
Mo, Sb	20
Inorganic Ventures Catalog #PACE-49	
Al, Se	100
As, Be, Ba, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl, Th, U, V, Zn	20
Inorganic Ventures Catalog # HERT-CAL-5	
B, Sr, Ti, Sn	20

10.2.3.2. Intermediate Boron Calibration Standard Preparation

Dilute 1mL of the PLB9-2Y Stock Boron Standard (1000ug/mL) to 100mL with diluent for a final concentration of 10mg/L.

10.2.3.3. Working Calibration Standards Preparation

Prepared fresh weekly and diluted from the stock standard mixes in diluent, unless otherwise noted. Below are examples of calibration standards, actual standards may vary:

Working Calibration Std. ID	Volume Int. Boron Standard	Volume 2008CAL-1 Standard	Volume PACE-49 Standard	Volume HERT-CAL-5 Standard	Final Volume	Final Nominal Conc.
CAL0	0mL	0mL	0mL	0mL	1000mL	0ug/L
CAL1	0.3mL	0.1mL	0.1mL	0.1mL	1000mL	2ug/L
CAL2 (CCV)	0mL	1mL	1mL	1mL	1000mL	20ug/L
CAL3	0mL	10mL	10mL	10mL	1000mL	200ug/L

10.2.3.4. Stock ICV Standard Details

The following table shows the stock standard mixes that may be used to prepare the initial calibration verification standard:

Analyte	Concentration (ug/mL)
High Purity Standards Catalog #HP 7003	
Al, As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Sr, Tl, Th, U, V, Zn	100
High Purity Standards Catalog #HP 6997	
Sb, Mo, Sn, Ti	100

10.2.3.5. Intermediate ICV Standard Preparation

Dilute 0.5mL of the HP 7003 Stock Standard (100ug/mL) and 0.5mL of the HP 6997 Stock Standard (100ug/mL) to 100mL with diluent for a final concentration of 500ug/L.

10.2.3.6. Working ICV Standard Preparation

Dilute 1mL of the Intermediate ICV Standard (500ug/L) to 10mL with diluent for a final concentration of 50ug/L.

10.2.3.7. Stock Interference Check Standard A (ICSA) Details:

***SPEX CL-INT-A2* (ug/mL)**	
Al, Ca, Fe, Mg, P, K, Na, S	1000
C	2000
Chloride	10000
Mo, Ti	20

10.2.3.8. Intermediate ICSA Standard Preparation

Dilute 1mL of the Stock ICSA Standard (1000ug/mL nominal) to 10mL with diluent for a final nominal concentration of 100ug/mL.

10.2.3.9. Working ICSA Standard Preparation

Dilute 2mL of the Intermediate ICSA Standard (100ug/mL nominal) to 10mL with 1% nitric acid solution for a final nominal concentration of 20ug/mL.

10.2.3.10. Stock Interference Check Standard AB (ICSAB) Details:

***SPEX CL-INT-A2* (ug/mL)**	
Al, Ca, Fe, Mg, P, K, Na, S	1000
C	2000
Chloride	10000
Mo, Ti	20
***Inorganic Ventures HERT-CAL-2A* (ug/mL)**	
Si	20
Mo, Sb, Sn, Ti, Zr	2
***Inorganic Ventures HERT-CAL-2B* (ug/mL)**	
Al, Ca, Fe, K, Mg, Na	20
Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sr, Th, Tl, U, V, Zn	2

10.2.3.11. Intermediate ICSAB Standard Preparation

Dilute 1mL of the CL-INT-A2 standard, 0.2mL of the HERT-CAL-2A standard and 0.2mL of the HERT-CAL-2B standard to10mL with diluent for a final nominal concentration of 40ug/L.

10.2.3.12. Working ICSAB Standard Preparation

Dilute 2mL of the Intermediate ICSAB Standard (40ug/L nominal) to 10mL with 1% nitric acid solution for a final nominal concentration of 8ug/L.

10.2.3.13. Stock CRDL Standard Details (Optional):

Inorganic Ventures PACE-55-REV1 ug/L	
Al	1000
B	500
Zn	300
Cr	200
As, Ba, Co, Cu, Mn, Mo, Pb, Sb, Se, Sn, Sr, Th, Ti, Tl, V	100
Ag, Ni	50
Be, Cd, U	20

10.2.3.14. Working CRDL Standard Preparation (Optional)

Dilute 1mL of the Stock CRDL Standard (20-1000ug/L) to 100mL with a 1% nitric acid solution for a final concentration as shown below:

Working CRDL Standard Concentration, ug/L	
Al	10
B	5
Zn	3
Cr	2
As, Ba, Co, Cu, Mn, Mo, Pb, Sb, Se, Sn, Sr, Th, Ti, Tl, V	1
Ag, Ni	0.5
Be, Cd, U	0.2

10.2.3.15. Stock Internal Standard Details:

Stock Internal Standard Concentration, ug/mL	
Bismuth	1000 (0.1%)
Indium	1000 (0.1%)
6-Lithium	1000 (0.1%)
Scandium	1000 (0.1%)
Terbium	1000 (0.1%)
Yttrium	1000 (0.1%)

10.2.3.16. Working Internal Standard Preparation

Dilute 1mL of Stock Internal Standard (1000ug/mL) to 1L with a 2% nitric acid solution for a final concentration of 1ug/mL (0.0001%).

10.2.3.17. Stock Tune Standard Details:

Stock Tune Standard Concentration, ug/mL	
Ba, Be, Ce, Co, In, Li, Mg, Pb, Th, Tl, U, Y	10

10.2.3.18. Working Tune Standard Preparation

Dilute 0.1mL of the Stock Tune Standard (10ug/mL) to 1L with a 1% nitric acid solution for a final concentration of 1ug/L.

11. Calibration and Standardization

11.1. Follow the instrument manufacturer's instructions for setup, tuning, calibration and operation of the ICP-MS. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. Rinse between samples using rinse water.

11.2. Tuning: The ICP-MS tuning standard must be analyzed to verify that the instrument has reached thermal stability and that resolution and mass calibration are within the required specifications. The tuning standard is analyzed at least five times and the relative standard deviation (RSD) must be ≤5% for all analytes contained in the tuning standard. Conduct mass calibration and resolution checks in the mass regions of interest. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be <0.9 amu full width at 5% peak height.

11.3. Initial Calibration: Calibrate the ICP-MS each working day according to the instrument manufacturer's recommended procedures. Flush the system with the Calibration Blank solution prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. The calibration curve must consist of a minimum of a calibration blank and three non-zero standards. Use the average of at least three integrations for both calibration and sample analyses.

11.4. Linear Calibration: Using the instrumentation software, prepare a standard curve for each element by plotting absorbance versus concentration. The analyst may employ a regression equation that does not pass through the origin. When a multi-point calibration is performed, the regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be ≥ 0.995.

11.5. Initial Calibration Corrective Action: If the curve does not meet the acceptance criteria, then a new calibration curve must be analyzed. If the second curve attempt does not meet the acceptance criteria, the analyst must consult the department manager and instrument maintenance and/or preparation of new standards must be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.6. Initial Calibration Verification (ICV): In addition to meeting the linearity requirement, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known value of the standard. This step is referred to as Initial Calibration Verification. The ICV is analyzed immediately following an initial calibration curve. Acceptable recovery range for the ICV is 90-110%.

11.7. ICV Corrective Action: If the ICV is not acceptable, another ICV may be analyzed. If the second ICV fails, then a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICV must be reanalyzed. **Exception:** If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.8. Initial Calibration Blank (ICB): An ICB must be analyzed immediately following the ICV. If the ICB result is above the reporting limit, another ICB may be analyzed. If the second ICB fails, then a new initial calibration curve must be analyzed. Samples associated with a failed ICB must be reanalyzed. **Exception:** If the ICB is >RL, associated samples determined to be <RL are reportable. **For WI DNR**, the ICB must also be evaluated as follows: If the absolute value of an ICB result exceeds the established MDL but is <WI LOQ, associated samples are determined to be reportable but must be qualified to indicate that an associated blank exceeds the MDL concentration for the analyte.

11.9. Continuing Calibration Verification (CCV): A CCV followed immediately by a CCB must be analyzed after every 10 samples and at the end of the analytical batch to verify the system is still calibrated. The acceptable recovery range for the CCV is 90-110%.

11.10. CCV Corrective Action: If a CCV fails the acceptance criteria, another CCV may be analyzed. If the second CCV fails, then a new initial calibration curve must be analyzed. Samples must be bracketed by acceptable CCVs in order to be reportable. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable.

11.11. Continuing Calibration Blank (CCB): A CCB must be analyzed immediately following each CCV. If the CCB result is above the reporting limit, another CCB may be analyzed. If the second CCB fails, then a new initial calibration curve must be analyzed. Samples associated with a failed CCB must be reanalyzed. Exception: If the CCB is >RL, associated samples determined to be <RL are reportable. . **For WI DNR**, the CCB must also be evaluated as follows: If the absolute value of a CCB result exceeds the established MDL but is <WI LOQ, associated samples are determined to be reportable but must be qualified to indicate that an associated blank exceeds the MDL concentration for the analyte.

11.12. Interference Check Standard A (ICSA): An ICSA must be analyzed at the beginning of each analytical run or once every 12 hours. The ICSA must be 80-120% of the true value for the elements in the mix. All other analytes not included in the ICSA standard must be within +/-2x the reporting limit.

11.13. ICSA Corrective Action: If the ICSA fails the acceptance criteria, another ICSA may be analyzed. If the second ICSA fails, then a new calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICSA must be reanalyzed. **Exception:** If the ICSA is >120% for any element in the mix or if any non-ICSA element is >2x the reporting limit, indicating high bias, associated samples determined to be <RL are reportable.

11.14. Interference Check Standard AB (ICSAB): An ICSAB must be analyzed at the beginning of each analytical run or once every 12 hours. The ICSAB must be 80-120% of the true value for the elements in the mix.

11.15. ICSAB Corrective Action: If the ICSAB fails the acceptance criteria, another ICSAB may be analyzed. If the second ICSAB fails, then a new calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICSAB must be reanalyzed. **Exception:** If the ICSAB is >120% for any element in the mix, indicating high bias, associated samples determined to be <RL are reportable.

11.16. CRDL Standard (Optional): A CRDL standard may be analyzed prior to sample analysis and also at the end of each analytical batch to bracket the associated samples. Advisory range for all target elements is 50-150% recovery. No corrective action is required if the CRDL recovery is outside the advisory range.

12. Procedure

12.1. Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges; the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis.

12.2. Configure the ICP-MS per manufacturer's instructions and allow it to become thermally stable. Tune and calibrate the instrument per the manufacturer's instructions and the requirements outlined in Section 10.

12.3. Approximately 10mL portions of each standard, Method Blank, LCS, sample and MS/MSD are poured into autosampler tubes for analysis.

12.4. Once tuning and initial calibration have been established, analyze each sample, Method Blank, LCS and MS/MSD. Rinse between samples using rinse water. An example sequence may be as follows:

Tuning Standard x 5
Calibration Blank (CAL0)
CAL1
CAL2
CAL3
Blank
ICV
ICB
CRDL (Optional)
ICSA
ICSAB
Method blank
LCS
Client samples
CCV
CCB
Client samples
CCV
CCB

12.5. The instrument performs three replicate readings for each analysis and the average of the three readings is used to derive the concentration. For samples, the difference between the three readings must be ≤20% RSD for values that are >4x the reporting limit. If the RSD is >20% for values that are >4x the reporting limit, the sample must be reanalyzed.

12.6. If dilutions were performed, the appropriate factors must be applied to sample values. Samples with analyte concentrations above the upper linear range must be diluted and reanalyzed or the over range results must be qualified as estimated.

12.7. Calculations must include appropriate interference corrections, internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for Lead.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water or resin chips	One per preparation batch of up to 20 samples, per matrix.	Target analyte must be below the reporting limit.	Reanalyze method blank. If target compound is still >RL in method blank, re-digest and reanalyze associated samples. **For WI DNR:** if the method blank is >MDL but <2.2x the MDL, result must be qualified with B0. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analyte	One per preparation batch of up to 20 samples, per matrix.	80-120% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, re-digest and reanalyze all associated samples. *Exceptions:* 1) A matrix spike that passes LCS criteria may be used in place of a failed LCS for batch acceptance. 2) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 3) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analyte	One MS/MSD set per preparation batch of up to 20 samples, per matrix.	75-125% Recovery ≤20% RPD	If the MS/MSD fails, perform a Post Digestion Spike on the same sample used for the MS/MSD, as described in Section 12.5.
Internal Standards	Lithium, Scandium, Yttrium, Indium, Terbium, Bismuth	Automatically added to each sample, blank, and standard as part of the analysis.	**ICB/CCB/ICS:** 80-120% of CAL0 response. **All Others:** 30-120% of CAL0 response **For WI DNR**: 70-125% of CAL0 response.	When the internal standard response of the ICB, CCB, ICSA or ICSAB fails, recalibration and reanalysis of affected samples is required. When the internal standard response of other samples fails, the sample must be diluted fivefold or greater and reanalyzed.

13.2. Post-Digestion Spike Addition: If the MS/MSD recoveries are unacceptable, the sample from which the MS/MSD was performed should also be spike with a post digestion spike. Otherwise, another sample from the same preparation batch should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 75-125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the reporting limit. If this spike fails, then the dilution test should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed. Post digestion spike is prepared by diluting 0.1mL of HERT-CAL-2A (2ug/mL) and 0.1mL of HERT-CAL-2B (2-20ug/mL) to 10mL with sample for a final concentration of 2ug/L (20ug/L for Al).

13.3. Dilution test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the reporting limit after dilution), an analysis of a 1:5 dilution should agree within +/-10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

14. Data Analysis and Calculations

14.1. Calculate the sample concentration using the following equations:

$$\text{Aqueous Sample (ug/L)} = \frac{(X_s)(V_f)(D)}{(V_i)} \qquad \text{Solid Sample (ug/kg)} = \frac{(X_s)(V_f)(D)}{(W_s)}$$

Where: X_s = Element concentration, ug/L
V_f = Final volume of digestate, L
D = Dilution factor
V_i = Initial sample volume digested, L
W_s = Weight of solid sample digested, kg

$$\text{Moisture corrected concentration} = \frac{\text{(Final concentration as received)}}{(100 - \%\text{Moisture})} \times 100$$

14.2. LCS equation:

$$\mathbf{R = (C/S) * 100}$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation:

$$\mathbf{R = \frac{(Cs - C)}{S} * 100}$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD equation:

$$\mathbf{RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100}$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. Method Detection Limits (MDLs): MDLs must be determined per 40 CFR Part 136, Appendix B.

18.2. Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Samples are analyzed for Boron, Molybdenum, Strontium, Thorium, Tin, Titanium, and Uranium in addition to the elements listed in Method 6020.

19.2. Tuning criteria observed is more stringent than required by the method so that the same criteria can be used for both methods 6020 and 200.8.

19.3. Rinse water contains a small amount of gold as recommended by instrument manufacturer to prevent plating of some elements in the sample introduction system.

20. Instrument/Equipment Maintenance

20.1. Refer to maintenance log and/or instrument manufacturer's instructions.

21. Troubleshooting

21.1. Refer to maintenance log and/or instrument manufacturer's instructions.

22. Safety

22.1. Standards and Reagents: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. Samples: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. Equipment: Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling or other applicable SOP. All wastes are accumulated, managed and disposed of in accordance with all federal and state laws and regulations.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", EPA SW-846, latest revision, Method 6020.

25.2. Pace Analytical Quality Manual; latest revision.

25.3. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Table 1: Target Elements and Reporting Limits

26.2. Table 2: Characteristic Masses and Internal Standard Assignments

27. Revisions

Document Number	Reason for Change	Date
S-IN-M-180-rev.00	1. Converted to Pace SOP format. 2. Added detailed tune criteria. 3. Separated Method 200.8 into its own SOP.	23Sep2015
S-IN-M-180-rev.01	1. Converted to 27-section format. 2. Table 7.1: revised storage temperature format. 3. Table 10.2: added "optional" to CRDL. 4. Table 10.3: revised stock ICSA, stock CRDL and stock tune information. 5. Section 10.2.3: revised stock ICSA, stock CRDL and stock tune information. 6. Section 11: reworded CCV and CCB sections for clarity. 7. Table 13.1: updated LCS corrective action and Internal Standard Acceptance Criteria and Corrective Action. 8. Section 13.2: changed acceptance criteria to 75-125% recovery. 9. Section 14.1: updated calculations to be in like terms with instrument output. 10. Section 25.3: added years 2003 and 2009 to TNI reference. 11. Table 1: updated barium RLs and added subject to change.	09Oct2017
ENV-SOP-IND1-0106-rev.01	1. Removed cover page, table of contents, and headers for use in Master Control. 2. Section 9.1: updated instrument model numbers. 3. Section 10.1: updated diluent details. 4. Section 10.3: updated ICV stock source. 5. Sections 10.2.3.4 and 10.2.3.5: updated ICV stock source information. 6. Sections 11.8 and 11.11: added WI requirements for ICB and CCB. 7. Table 13.1: updated method blank and internal standard to include WI requirements. 8. Section 18.1: updated MDL procedure reference.	8Oct2019

Table 1: Target Elements and Reporting Limits[1]

Element	Aqueous RL (µg/L)	Solid RL (mg/kg)
Aluminum - Al	10	1
Antimony - Sb	1	0.1
Arsenic - As	1	0.1
Barium - Ba	1	0.5
Beryllium - Be	0.2	0.05
Boron - B	5	0.5
Cadmium - Cd	0.2	0.05
Chromium - Cr	2	0.2
Cobalt - Co	1	0.1
Copper - Cu	1	0.05
Lead – Pb	1	0.1
Manganese – Mn	1	0.1
Molybdenum - Mo	1	0.1
Nickel – Ni	0.5	0.05
Selenium - Se	1	0.1
Silver – Ag	0.5	0.05
Strontium – Sr	1	0.1
Thallium - Tl	1	0.1
Thorium – Th	1	0.1
Tin – Sn	1	0.1
Titanium - Ti	1	0.1
Uranium – U	1	0.1
Vanadium - V	1	0.05
Zinc – Zn	3	0.5

[1]Reporting limits are subject to change.

Table 2: Characteristic Masses and Internal Standard Assignments

Element	Characteristic Mass(es)	Internal Standard
Aluminum - Al	27	^{45}Sc
Antimony - Sb	121	^{115}In
Arsenic - As	75	^{89}Y
Barium - Ba	137	^{159}Tb
Beryllium - Be	9	^{6}Li
Boron - B	11	^{6}Li
Cadmium - Cd	114	^{115}In
Chromium - Cr	52	^{45}Sc
Cobalt - Co	59	^{45}Sc
Copper - Cu	65	^{45}Sc
Lead – Pb	206,207,208	^{209}Bi
Manganese – Mn	55	^{45}Sc
Molybdenum - Mo	98	^{89}Y
Nickel – Ni	60	^{45}Sc
Selenium - Se	78	^{89}Y
Silver – Ag	107	^{115}In
Strontium – Sr	88	^{89}Y
Thallium - Tl	205	^{209}Bi
Thorium – Th	232	^{209}Bi
Tin – Sn	118	^{115}In
Titanium - Ti	48	^{45}Sc
Uranium – U	238	^{209}Bi
Vanadium - V	51	^{45}Sc
Zinc – Zn	66	^{45}Sc

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QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	01 Feb 2019, 08:29:51 AM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Sayer (004775)	General Manager	01 Feb 2019, 08:33:46 AM	Approved
Rachel Wrede (008235)	Manager - Lab Services	01 Feb 2019, 09:51:33 AM	Approved

1. Purpose

1.1. This Standard Operating Procedure (SOP) documents the procedures used by Pace Analytical Services – Indianapolis to determine the concentration of Volatile Organic Compounds (VOCs) in environmental samples. The laboratory utilizes purge-and-trap GC/MS and bases these documented procedures on those listed in SW-846 Method 8260C, 5030A, 5030B, and 5035A.

2. Summary of Method

2.1. Volatile organic compounds are introduced into the gas chromatograph by a purge-and trap method. The analytes are purged from a sample aliquot or extract using an inert gas. The purged analytes are collected on an absorbent trap. At the completion of the purge time, the trap is rapidly heated and back flushed to drive out the trapped analytes. The analytes are transferred into the inlet of a capillary gas chromatography column. The carrier gas flow through the column is controlled and the temperature is increased according to a set program to achieve optimum separation of purged analytes. The mass spectrometer is operated in a repetitive scan mode. Analytes are identified by the GC/MS retention times and by a comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected primary ion relative to an internal standard against a calibration curve.

3. Scope and Application

3.1. This method is applicable to most organic compounds that have boiling points below 200 ºC and are insoluble or slightly soluble in water. Volatile water-soluble compounds may also be determined although quantitation limits are typically higher due to their hydrophilic properties (e.g. ketones, oxygenates).

3.2. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable to most water and solid samples, regardless of moisture content. Matrices are groundwater, surface water, soil, sediment and waste. Procedures may need to be adapted to address limitations in the method or equipment that might hinder or interfere with sample analysis.

5. Limits of Detection and Quantitation

5.1. The list of target compounds and reporting limits is found in Table 1. Refer to the LIMS for method detection limits.

6. Interferences

6.1. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the absorbent trap. Many common solvents, most notably acetone and methylene chloride, are frequently found in laboratory air at low levels. The use of polytetrafluoroethylene (PTFE, Teflon) as thread sealants, tubing, or in flow controllers is highly recommended since other materials can be sources of contamination which may concentrate in the trap during the purging.

6.2. A common source of interfering contamination is carryover. This may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive action to this condition is rinsing the purging apparatus and sample syringes with organic free water between samples. Analyze one or more blanks to check for contamination prior to sample analysis. If the sample immediately following the high concentration sample does not contain the compounds present in the high level sample, freedom from carryover contamination has been established.

6.3. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

6.4. Since methylene chloride and acetone are common laboratory solvents, special precautions must be taken. The volatiles analysis and sample storage area must be located as far as possible from areas where these solvents are used or stored. Where possible, the volatiles analysis and sample storage area should be served by a separate HVAC system and maintained under positive pressure to prevent intrusion of contaminants. Laboratory clothing previously exposed to methylene chloride fumes during extraction procedures can contribute to sample contamination.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
5030B Aqueous	Minimum (3) VOA vials Additional sample is required if MS/MSD is requested	Acidified w/ 1:1 HCl to pH<2, no headspace	Cool to ≤6°C	pH>2: Analysis must be completed within 7 days of collection date. pH <2: Analysis must be completed within 14 days of collection date. (pH determined post analysis)
5035A Solid Terra Core Kits (Preferred)	One (1) 2-4 oz. wide mouth jar for % moisture **AND** Two (2) 5-g portions in vials with magnetic stir bar and 5.0mL reagent water plus one (1) 5 g portion in a vial with 5.0mL methanol. Additional sample is required if MS/MSD is requested.	Either no preservative or Methanol as a preservative.	Cool to ≤6°C for no more than 48 hours from collection then freeze at -7°C to -20°C. Methanol vials may be stored at 0° to 6°C.	Analysis must be completed within 48 hours if samples are not frozen or preserved with methanol prior to the expiration of the 48 hour period. The holding time may be extended to 14 days if the sample is frozen or preserved with methanol prior to the expiration of the 48 hour period.
5035A Solid Coring Devices (Alternate)	One (1) 2-4 oz. wide mouth jar for % moisture **AND** Two (2) EnCore, TerraCore or similar sampling tubes. Additional sample is required if MS/MSD is requested.	No preservative Sample is extruded into a vial with a magnetic stir bar and 5.0mL reagent water.	Freeze at -7°C to -20°C within 48 hours of collection.	Analysis must be completed within 14 days of collection date.
5030A Solid Bulk Jars	One (1) 2-4 oz. wide mouth jar for % moisture **AND** One bulk sample jar, usually 4 oz. or 8oz.	No preservative Sample is weighed into a vial with a magnetic stir bar and 5.0mL reagent water.	Cool to ≤6°C	Analysis must be completed within 14 days of collection date.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation

Equipment	Vendor	Model / Version	Description / Comments
Gas Chromatographs	Agilent	Lab uses models 6850 and 6890	Or equivalent system
P&T Concentrators	EST Analytical, Tekmar, OI	Tekmar 3000 series, Encon, Encon Evolution, and 4660 Eclipse	Or equivalent system
Data Systems	Agilent	Chemstation	Or equivalent system
Autosamplers	EST Analytical	EST 8100, Centurion, Centurion WS, 4551	Or equivalent system
Mass Spectrometers	Agilent	5973 and 5975	Or equivalent system

9.2. Chromatography Supplies

Item	Vendor	Model / ID	Description
Analytical Columns	Agilent	J&W Scientific DB-624	20m x 0.18mm x 1um or equivalent
Trap	Supelco	Trap K and OI #10	Or equivalent

9.3. General Supplies

Item	Description	Vendor/ Item # / Description
Gas tight syringes	Various sizes	Hamilton or equivalent
Syringe valves	2-way with Luer ends	Supelco or equivalent
Standard vials	stop/go vials, various sizes	Supelco or equivalent
Balance, Analytical/Top Load	Able to measure to nearest 0.001g/0.01g	Mettler, OHaus or equivalent
Sample vials	40mL vials; pre-cleaned	Eagle Picher, QEC, or equivalent

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
Methanol	Purge-and trap grade or equivalent
Sand	Or equivalent material to be used as a simulated soil matrix.

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification, and for preparing LCS, MS, and MSD sample

Table 10.1 Standard Definitions

Standard	Description	Comments
Tune Standard	4-Bromofluorobenzene (BFB) solution used to verify ion response ratios prior to analysis	Must inject between 5 and 50ng
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This solution contains required spiking compounds, at a minimum, and is used to prepare MS/MSD sets.	Same solution can be used for the LCS, MS/MSD and CCV.

10.2.2. Storage Conditions

Table 10.2 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock VOA calibration standards	Restek; catalog #31283, #30265, #30006, #30293, #572444, and #572941, 1000/2000/5000ug/mL or equivalent standards.	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions
Stock Gas calibration standards	Restek; catalog #30439, #30216, and #30646, 200/2000/5000ug/mL, or equivalent standards.	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions
Intermediate VOA calibration standard	Refer to Section 10.2.3.1.	Solution good for 1 month from preparation	Same as stock standard.
Intermediate Gas calibration standard	Refer to Section 10.2.3.2.	Solution good for 1 week from preparation	Same as stock standard
Working VOA calibration standards	Refer to Section 10.2.3.3.	One-time use	Not applicable
Stock VOA ICV/Spiking standards	o2si; catalog #121092-02-SS; 250-5000ug/mL and #121091-06-SS, 250-5000ug/mL or equivalent	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions
Intermediate VOA ICV/Spiking standard	Refer to Section 10.2.3.4.	Solution good for 1 month from preparation	Same as stock standard
Working ICV/Spiking standard	Refer to Section 10.2.3.5.	One-time use	Not applicable
Stock VOATune/ Surrogate standard	Restek; catalog #30240, 2500ug/mL or equivalent	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions
Stock VOA Internal standards	Restek; catalog #30241, 2500ug/mL or equivalent	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions
Working Tune/Surrogate/Internal standard mix	Refer to Section 10.2.3.6.	Solution good for 1 month from preparation	Stored on autosampler under pressure in a 5mL vial.

10.2.3. Preparation Procedures

10.2.3.1. Intermediate VOA Calibration Standard Preparation (Example)

Dilute 1000uL of Restek #572941 (250-2000ug/mL) plus 1000uL of Restek #30293 (2000ug/mL) plus 1000uL of Restek #572444 (250-5000ug/mL) plus 250uL of Restek #30006 (5000ug/mL) plus 250uL of Restek #30265 (2000ug/mL) plus 250uL of Restek #31283 (1000ug/mL) to 5.0mL with Methanol for a final nominal concentration of 50mg/L.

10.2.3.2. Intermediate Gas Calibration Standard Preparation (Example)

Dilute 400uL of Restek #30216 (2000ug/mL) plus 800uL of Restek #30646 (5000ug/mL) plus 1000uL of Restek #30439 (200ug/mL) to 4.0mL with Methanol for a final nominal concentration of 50ug/mL.

10.2.3.3. Working VOA Calibration Standards Preparation

Refer to Tables 10.3a and 10.3b for examples of possible one-time use calibration standards.

Table 10.3a – Working Calibration Standards – Regular Level (examples only)

Standard	Int. VOA Cal. Standard amount	Int. Gas Cal. Standard amount	Final Total Volume	Nominal Final Concentration
CAL1	3uL	3uL	200mL	0.75 ug/L
CAL2	2uL	2uL	50mL	2 ug/L
CAL3	5uL	5uL	50mL	5 ug/L
CAL4	10uL	10uL	50mL	10 ug/L
CAL5	2uL	2uL	5mL	20 ug/L
CAL6 (CCV)	5uL	5uL	5mL	50 ug/L
CAL7	15uL	15uL	5mL	150 ug/L
CAL8	30uL	30uL	5mL	300 ug/L

Table 10.3b – Working Calibration Standards – Low Level (examples only)

Standard	Int. VOA Cal. Standard amount	Int. Gas Cal. Standard amount	Final Total Volume	Nominal Final Concentration
CAL1	2uL	2uL	200mL	0.5 ug/L
CAL2	2uL	2uL	100mL	1 ug/L
CAL3	4uL	4uL	100mL	2 ug/L
CAL4	10uL	10uL	100mL	5 ug/L
CAL5	20uL	20uL	100mL	10 ug/L
CAL6 (CCV)	100uL	100uL	100mL	50 ug/L
CAL7	300uL	300uL	100mL	150 ug/L
CAL8	600uL	600uL	100mL	300 ug/L

10.2.3.4. Intermediate VOA ICV/Spiking Standard Preparation (Example)

Dilute 1.0mL of o2si #121091-06-SS (250-5000ug/mL) plus 1.0mL of o2si #121092-02-SS (250-5000ug/mL) to 5.0mL with Methanol for a final nominal concentration of 50ug/mL.

10.2.3.5. Working ICV/Spiking Standard Preparation (Example)

Add 5uL of the Intermediate ICV standard per 5mL water for a final ICV concentration of 50ug/L.

10.2.3.6. Working Tune/Surrogate/Internal Standard Preparation (Examples only, may vary)

Centurion/Centurion WS Autosamplers: Dilute 100uL of Restek #30240 plus 100uL of Restek #30241 to 5mL with Methanol for a final concentration of 50mg/L.

8100 Soil Autosamplers: Dilute 500uL of Restek #30240 plus 500uL of Restek #30241 to 5mL with Methanol for a final concentration of 250mg/L.

11. Calibration and Standardization

11.1. Tune Verification: At the beginning of each analytical sequence, prior to the analysis of any standards or samples, the mass spectrometer must be hardware tuned by injecting 5-50ng BFB. This is done by analyzing a standard containing BFB. The BFB and calibration verification standard may be combined as long as both tuning and calibration verification acceptance criteria are met without interferences. Use the BFB mass intensity criteria in the table below as tuning acceptance criteria. Alternate tuning criteria may be used provided that method performance is not adversely affected.

Mass (m/z)	Ion Abundance criteria
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	<2% of m/z 174
174	>50% of m/z 95
175	5 to 9% of m/z 174
176	95 to 101% of m/z 174
177	5 to 9% of m/z 176

The mass spectrum of BFB may be obtained by averaging three scans, the peak apex scan and the scans immediately preceding and following the apex. Background subtraction is required using this approach and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other approaches suggested below:

1. A single scan within the BFB peak with background subtraction of a single scan no more than 20 scans prior to the elution of BFB.
2. An average of multiple scans within the BFB peak with background subtraction of a single scan no more than 20 scans prior to the elution of BFB.

If the ratios do not meet the criteria above, reanalyze the BFB tune. If the BFB still fails the criteria, instrument maintenance and/or preparation of new standards must be considered.

11.2. Initial Calibration: Initial Calibration standards are introduced into the GC/MS from the lowest to highest concentration of each working calibration standard. The lowest calibration standard must be at or below the required reporting limit. Five calibration points, at a minimum, are analyzed to evaluate linearity. Refer to the Quality Manual for more information regarding calibration curves. The response factor (RF) is calculated for each compound for each calibration standard as follows:

$$RF = \frac{(A_x)(C_{IS})}{(A_{IS})(C_x)}$$

where: A_x = Area of the quantitation ion for the compound being measured
A_{IS} = Area of the quantitation ion for the internal standard.
C_{IS} = Concentration of the internal standard
C_x = Concentration of the compound being measured.

11.3. The average response factor (RF_{avg}) is determined by averaging the response factors at the different concentrations for each target analyte

11.4. The percent relative standard deviation (%RSD) is calculated as follows:

$$\%RSD = \frac{(SD)}{RF_{avg}} \times 100$$

where: SD = Standard deviation of average RF for a compound
RF_{avg} = Mean of RFs for a compound

11.5. The %RSD should be $\leq$20% for each target analyte.

11.6. For each calibration standard, all reported compounds that appear in Table 3 must meet the minimum response factor criteria shown.

11.7. If the percent relative standard deviation (%RSD) of the RFs for a compound is $\leq$20% over the calibration range, then linearity through the origin is assumed and the RF_{avg} may be used to determine sample concentrations.

11.7.1. If the % RSD for any compound is >20%, the analyst may employ a linear regression equation, non-weighted or weighted 1/x or $1/x^2$, that does not pass through the origin. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be $\geq$ 0.99. Refer to Method 8000C for additional information regarding calibration.

11.8. When calculating the calibration curve using the linear regression model, a minimum quantitation check on the viability of the calibration standard that corresponds to the reporting limit should be performed by re-fitting the response from the calibration standard that corresponds to the reporting limit back into the curve. The recalculated concentration of the reporting limit standard should be within +/-30% of the standard's true concentration. Compounds that fail this criterion and are reported at a concentration that is <2x the reporting limit in associated samples must be qualified as estimated. Alternatively, the reporting limit can be raised to the level of a calibration standard that meets the criteria when re-fitted against the curve.

11.9. Non-linear or quadratic calibration: A non-linear or quadratic calibration model can only be used if the compound(s) have historically exhibited a non-linear response and cannot be used to extend the calibration range for any compound that normally exhibits a linear response in a narrower range. The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of: $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be used and the origin cannot be included as one of the points. Because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. The "goodness of fit" of the polynomial equation is evaluated by calculating the coefficient of the determination (COD) or r^2. The COD or r^2 from the regression equation must be $\geq$0.99. Refer to Method 8000C for additional information regarding calibration.

11.10. If compounds fail to meet the criteria in Sections 11.5-11.9, the calibration fit must be set to average response factor and associated samples concentrations may be determined but they must be reported as estimated. In order to report non-detects, the compound must have been detected with a response greater than zero in the initial calibration standard that corresponds to the reporting limit.

11.11. Initial Calibration Corrective Action: If more than 10% of the compounds included with the initial calibration exceed the ≤20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternative curve fits, then the chromatographic system is considered too imprecise for analysis to begin. Instrument maintenance and/or preparation of new calibration standards must be considered prior to repeating the initial calibration procedure.

11.12. Each day that analysis is performed, the calibration standards and/or check standard(s) should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Are the retention times consistent over the range of calibration for each compound? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably. Additionally, examination of signal-to-noise ratio of analytes in low-level standards may be a useful diagnostic tool to monitor instrument performance. Signal-to-noise ratio is defined as the ratio of the analyte signal to the noise measured on a blank. It is recommended but not required that the signal-to-noise ratio be at least three to confirm detection.

11.13. Initial Calibration Verification (ICV): The initial calibration curve should be verified immediately after performing the standard analysis using a second source standard (ICV) that is prepared using standards from a different source than the calibration standards, with a concentration near the midpoint of the calibration range. The acceptance limits for the ICV are 70-130% recovery for all reported compounds, with the following exceptions:

Acetone	50-150%
Acrolein	50-150%
Bromomethane	50-150%
Iodomethane	50-150%
Methyl acetate	50-150%

11.14. ICV Corrective Action: If the ICV fails the criteria, another ICV may be analyzed. If the second ICV fails, a new initial calibration curve may be analyzed. Instrument maintenance and/or preparation of new calibration standards must also be considered. Quantitative sample analysis should not proceed for those analytes that fail in the ICV or associated results must be qualified as estimated if analysis continues. **Exception:** If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported. Alternatively, the allowance for use of the ICV when the criterion is not met is documented and is at the discretion of the Department Manager, Quality Manager, General Manager or designee.

11.15. Continuing Calibration Verification: The initial calibration is verified every 12 hours by analyzing a BFB tune that must meet the criteria in Section 11.1, followed by a Continuing Calibration Verification (CCV) standard. The CCV is normally prepared using the same standard solution used for the initial calibration but an ICV/LCS can be used as a CCV if it passes the required criteria for a CCV.

11.16. All target compounds in the CCV must be evaluated using a +/-20% variability criterion. Use percent difference when the average RF model calibration has been used. Use percent drift when a regression fit model has been used.

$$\%\ \text{Difference (\%D)} = \frac{\text{Calculated amount of standard} - \text{Expected amount of standard}}{\text{Expected amount of standard}} \times 100$$

$$\%\ \text{Drift} = \frac{\text{Calculated concentration} - \text{Theoretical concentration}}{\text{Theoretical concentration}} \times 100$$

11.17. If the percent difference or percent drift for a compound is ≤20%, then the initial calibration for that compound is considered to be valid and sample analysis can continue. If the criterion is not met for more than 20% of the compounds included in the calibration, then corrective action must be taken prior to sample analysis.

In cases where compounds are >20% difference or drift, they may still be reported as non-detects if the compound was detected with a response greater than zero in the initial calibration standard that corresponds to the reporting limit. For situations when the failed compound is present in samples at or above the reporting limit, reported concentrations must be qualified as estimated values. Alternatively, the sample may be reanalyzed and reported for the compounds in question with a CCV that meets the criteria.

11.18. All compounds that are reported and that appear in Table 3 must meet the minimum response factor criteria shown. If the minimum response factors are not met, the system should be evaluated and corrective action should be taken before sample analysis begins.

11.19. The internal standard areas in the CCV must be between 50%-200% of the internal standard areas of the corresponding standard in the initial calibration. In addition, the retention time of the internal standards in the CCV cannot shift by more than 10 seconds from the corresponding standard in the initial calibration. Failure in either of these two areas requires the analyst to evaluate their system and perform maintenance if necessary.

11.20. CCV Corrective Action: If a CCV fails the acceptance criteria, check the instrument operating conditions, and if necessary, restore them to the original settings, and analyze another CCV. Alternatively, an ICV/LCS may be used as a CCV if it passes the CCV acceptance criteria. If the response still fails the acceptance criteria, then a new initial calibration must be prepared. Samples associated with a failed CCV must be reanalyzed. Exception: If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

12. Procedures

12.1. Configure the purge & trap system and GC/MS system per manufacturer's instructions. All samples must be analyzed at room temperature and the system must be calibrated and free of contamination before samples are analyzed.

12.2. Sample Preparation and Handling

12.2.1. Aqueous Samples

Water samples to be analyzed using the Centurion autosampler require no sample preparation and are loaded as full 40mL VOA vials, unless they require a dilution. Refer to Section 7 for additional information regarding sample handling.

Water samples to be purged on the Archon/8100 autosampler are prepared by quickly measuring a 5mL aliquot of the sample using a 5mL gastight syringe and transferring it to a 40mL VOA vial. This is done as quickly as possible to minimize analyte loss. The syringe is thoroughly rinsed inside and out with reagent water before measuring each sample.

Dilutions on aqueous samples must be prepared in a volumetric fashion. Sample aliquots are measured in either a volumetric pipet or gas-tight syringe and brought to volume in either a volumetric flask or gas-tight syringe.

After analysis, check the residue in the vial using pH paper. The pH should be <2 if HCl-preserved vials were used. Holding time for water samples with pH >2 is 7 days. Appropriately qualify on the sequence log and in LIMS any sample not meeting the pH requirement and/or holding time requirement.

12.2.1.1. Aqueous Method Blank Preparation

12.2.1.1.1. Aqueous Method Blank on Archon autosamplers: The Method Blank consists of a 40mL VOA vial containing 5mL reagent water.

12.2.1.1.2. Aqueous Method Blank on Centurion autosamplers: The Method Blank consists of an HCl-preserved 40mL VOA vial filled completely with reagent water.

12.2.1.2. Aqueous LCS Preparation: add 5uL of the Intermediate ICV/Spiking standard per 5mL reagent water for a nominal LCS concentration of 50ug/L.

12.2.1.3. Aqueous MS Preparation: add 5uL of the Intermediate ICV/Spiking standard per 5mL sample for a nominal MS concentration of 50ug/L.

12.2.2. Soil Samples

12.2.2.1. Low-Level Soils

Preferably, samples received for low level analysis should be contained in pre-weighed Terra Core vials with reagent water. Prior to analysis the sample weight must be determined and recorded by weighing the vial and recording the weight. Subtract the tare weight indicated on the vial and correct for the label weight to determine the sample weight. The sample is ready for analysis. Refer to Section 7 for additional information regarding sample handling.

Alternatively, samples received in coring devices, such as Encore, must be extruded into a pre-weighed VOA vial either with or without 5mL reagent water and a stir bar. Record the weight of the vial after the sample has been placed into it. Subtract the tare weight determined initially to determine the sample weight. The sample is ready for analysis.

Samples received in bulk soil jars are sub-sampled into a VOA vial. Place an empty VOA vial on the balance pan and tare the balance. Quickly add 5 +/-0.5g of sample to the vial. Record the sample weight. Add 5mL of reagent water and a stir bar and cap the vial. The sample is ready for analysis.

12.2.2.1.1. Low-Level Soil Method Blank Preparation: The Method Blank consists of a 40mL VOA vial containing 5 +/-0.5g simulated soil matrix and 5mL reagent water and a stir bar.

12.2.2.1.2. Low-Level Soil LCS Preparation: Place 5 +/-0.5g of simulated soil matrix, 5mL reagent water and a stir bar into a vial. Add 5uL of the Intermediate ICV/Spiking standard for a nominal LCS concentration of 50ug/kg.

12.2.2.1.3. Low-Level Soil MS Preparation: Place 5 +/-0.5g of sample, 5mL reagent water and a stir bar into a vial. Add 5uL of the Intermediate ICV/Spiking standard for a nominal MS concentration of 50ug/kg.

12.2.2.2. Medium-Level Soils

Preferably, samples received for medium-level analysis should be received in pre-weighed Terra Core vials with methanol as a preservative. Prior to analysis the sample weight must be determined and recorded by weighing the vial and recording the weight. Subtract the tare weight indicated on the vial and correct for the label weight to determine the sample weight. The sample is mixed well on a vortex mixer and allowed to settle. A maximum of 200uL of the methanol extract per 5mL reagent water is used for analysis. Refer to Section 7 for additional information regarding sample handling.

Alternatively, samples received in coring devices, such as Encore, must be extruded into a pre-weighed VOA vial with 5mL methanol. Record the weight of the vial after the sample has been placed into it. Subtract the tare weight determined initially to determine the sample weight. The sample is mixed well on a vortex mixer and allowed to settle. A maximum of 200uL of the methanol extract per 5mL reagent water is used for analysis.

Samples received in bulk soil jars are sub-sampled into a VOA vial. Place an empty VOA vial on the balance pan and tare the balance. Quickly add 5 +/-0.5g of sample to the vial. Record the sample weight. Add 5mL methanol and cap the vial. The sample is mixed well on a vortex mixer and allowed to settle. A maximum of 200uL of the methanol extract per 5mL reagent water is used for analysis.

12.2.2.2.1. Medium-Level Soil Method Blank Preparation: The Method Blank consists of a 40mL VOA vial containing 4.8mL reagent water and 200uL methanol.

12.2.2.2.2. Medium-Level Soil LCS Preparation: place 4.8mL reagent water and 200uL methanol into a vial. Add 5uL of the Intermediate ICV/Spiking standard for an LCS concentration of 50ug/kg.

12.2.2.2.3. Medium-Level Soil MS Preparation: place a maximum of 200uL methanol sample extract into a vial and add enough reagent water to bring the final volume to 5mL. Add 5uL of the Intermediate ICV/Spiking standard for an LCS concentration of 50ug/kg.

12.3. Qualitative Analysis: Compounds are identified as present when the following criteria are met:

12.3.1. The relative retention time (RRT) of the sample component must compare within +/- 0.06 RRT units of the RRT of the CCV component.

12.3.2. The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Refer to Table 2 for the characteristic ions.

12.3.3. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

12.4. Quantitative Analysis: Quantitation is based on the integrated abundance of the target analyte's quantitation ion using the internal standard technique.

12.5. Refer to the Manual Integrations SOP for guidance on performing and documenting manual integrations.

12.6. If the sample concentration exceeds the linear range of the analysis, the sample must be diluted and reanalyzed or reported as an estimated concentration.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples, per matrix.	Target analytes must be less than reporting limits.	Reanalyze method blank. If target compound is still >RL in method blank and associated samples, reanalyze samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required. 3) If contaminant is present in the sample at a concentration >10x the method blank, sample may be reported with qualification.
Laboratory Control Sample (LCS)	Applicable target analytes	One per preparation batch of up to 20 samples, per matrix.	Lab-generated limits Refer to the LIMS for acceptance limits. Refer to Section 13.2 for allowable marginal exceedances.	Reanalyze the LCS. If LCS is still outside acceptance limits, reanalyze all associated samples. Refer to Section 13.2 for allowable marginal exceedances. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified. 3) If allowed by program or client, an associated matrix spike that passes LCS acceptance limits may be used in place of the LCS. LCS must be reported and qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analytes	One MS/MSD set per preparation batch of up to 20 samples, per matrix.	Lab-generated limits RPD ≤20% Refer to the LIMS for acceptance limits.	No corrective actions necessary for spiked compounds or surrogates. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Sample Duplicate (Dup)	Sample	One sample duplicate per batch of up to 20 samples if no MS/MSD.	RPD ≤20%	No corrective actions necessary. Qualify duplicate appropriately if RPD is out-of-control.
Surrogates	Applicable surrogate compounds	Added to each standard, sample, and method blank.	Lab-generated limits Refer to the LIMS for acceptance limits.	Samples with surrogate failures must be reanalyzed. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported surrogate data must be qualified. 2) If surrogate result is >QC limits, and sample or method blank results are non-detect, the sample or method blank results may be reported without qualifiers. The surrogate must be qualified. 3) If there is obvious visible chromatographic interference with a surrogate, results may be reported but must be qualified.
As required by client only: **Internal Standards**	Applicable Internal Standard compounds	Added to each standard, sample, and method blank.	Sample ISTD areas must be -50% to +100% from CCV. Sample ISTD RTs must be +/-0.5 minutes from CCV.	Samples with internal standard failures must be reanalyzed at the same dilution or more concentrated. *Exception:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified.

13.2. Allowable Marginal Exceedances: If a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside control limits. A marginal exceedance (ME) is defined as being beyond the LCS control limit of +/-3 standard deviations, but within the ME limits of +/-4 standard deviations around the mean. The number of allowable MEs is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and correction action is necessary. If the same analyte exceeds the LCS control limit consecutively, it is an indication of a systemic problem. The source of the error shall be located and corrective action taken.

The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number Allowed as Marginal Exceedances
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

NOTE: As allowed by client or program, the LCS may be outside the control limits but ≥10% recovery for up to four additional volatile compounds with the exception of benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, total xylenes and any requested oxygenate without corrective action.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

Aqueous Sample (ug/L) = $(X_s)(D)$ Solid Sample (ug/kg) = $\frac{(X_s)(V_f)(D)}{(W_s)}$

Where: X_s = On-column concentration of the analyte, ug/L
V_f = Final volume, L
D = Dilution factor
W_s = Weight of solid sample, kg

Moisture corrected concentration = $\frac{\text{(Final concentration as received)}}{\text{(100- \%Moisture)}} \times 100$

14.2. LCS equation:

R = (C/S) * 100

Where: R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation:

$$R = \frac{(Cs - C)}{S} * 100$$

Where: R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where: RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control of Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. MDLs must be determined per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. GC columns and chromatographic conditions may differ from those recommended.

19.2. Calibration solutions are purchased as certified standards.

20. Instrument/Equipment Maintenance

20.1. Refer to maintenance log and/or instrument manufacturer's instructions.

21. Troubleshooting

21.1. Refer to maintenance log and/or instrument manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed Waste Handling, or other applicable SOP. All wastes are accumulated, managed and disposed of in accordance with all federal and state laws and regulations.

24. Pollution Prevention

24.1. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24.2. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Methods 8000C, 8260C, 5030A, 5030B, and 5035A.

25.2. Pace Analytical Quality Manual; latest revision.

25.3. NELAC/TNI Standard; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Table 1: Method 8260C Target Compounds and Reporting Limits
26.2. Table 2: Characteristic Ions and Internal Standard Association of Target Compounds
26.3. Table 3: Minimum Response Factor Criteria

27. Revisions

Document Number	Reason for Change	Date
S-IN-O-029-rev.18	1. Cover: changed 8260B to 8260C and added actual effective date. 2. Section 1.1: changed 8260B to 8260C 3. Section 4: revised to reflect 8260C 4. Table 8.3: revised balance specifications to match practice 5. Table 9.2: revised for standard mixes currently in use. 6. Section 9.2.3: revised recipes for standard mixes currently in use, changed approx. 5g to 5 +/- 0.5g, added batch QC details for medium-level soils, and detailed surrogate prep for both types of autosampler. 7. Section 10.1: added BFB acquisition guidance. 8. Section 10.13: added as guidance for evaluation of ICAL standards. 9. 10.5 - 10.21: revised to comply with Method 8260C, clarified use of LCS as CCV, and clarified requirement to correct vial TC vial weight for the label weight. 10. Section 11.2.2: added that tared soil vials need to be corrected for label weight and changed approx. 5g to 5 +/- 0.5g. 11. Section 11.5: added as a reference to the Manual Integrations SOP. 12. Section 11.6: added to require over range samples be diluted and reanalyzed or qualified as estimated. 13. Section 12.2: added to clarify the requirement for batch QC. 14. Section 12.3.2: clarified that blank is to be prepared using an HCl preserved vial. 15. Section 12.3.3: changed approx. 5g to 5 +/- 0.5g and added stir bar. 16. Section 13.1: added optional LOD/OQ verification. 17. Section 16.1: removed reference to 8000B and 8260A and changed 8260B to 8260C. 18. Section 17: changed 8260B to 8260C and added Table 3 attachment	31Oct2013
S-IN-O-029-rev.19	1. Converted to Corporate 27-section format. 2. Cover page: changed phone number and revised document control format. 3. Table 7.1: updated temperature format and preservation for 5035A. 4. Section 9.1: updated to include OI instrumentation. 5. Section 9.2: updated to include OI instrumentation. 6. Table 10.2: updated to current standards in use. 7. Section 10.2.3: updated to current standard preparation procedures. 8. Section 11: removed equations for different curve fits. 9. Section 11.7: added option of weighted linear. 10. Section 11.10: added requirement to set failing compounds to average fit. 11. Section 12.2.1: added OI and indicated that sample pH should be <2 if HCl vials were used. 12. Table 13.1: added an exception to MB when sample concentration is>10x MB concentration. Added sample duplicate to table and added RPD criteria. 13. Section 14: equations for water and solid final concentration fixed. 14. Table 1: added compounds for consistency between tables. 15. Table 2: added internal standard association and updated 1,2,3-TCP ions. 16. Table 3: revised minimum RF for TCE and PCE.	23Nov2016
ENV-SOP-IND1-0034-Rev.01	1. Removed cover, table of contents and headers for use in Master Control. 2. Table 10.2: updated stock calibration standards. 3. Section 10.2.3: updated preparation of intermediate and working calibration standards. 4. Section 11.7.1: clarified acceptable weighting for linear calibrations. 5. Section 11.8: clarified the term “reported compounds”. 6. Section 11.10: clarified the term “detected”. 7. Section 11.17: specified <20% difference or drift and clarified the term “detected”. 8. Section 12.2: moved batch QC prep from Section 13 and changed min. MeOH to 200uL. 9. Table 13.1: updated corrective action for MB, LCS and surrogates and added reference to LCS for marginal exceedances. 10. Section 18.1: updated reference to new MDL procedure. 11. Section 25.3: added years 2003 and 2009 to NELAC/TNI reference.	31Jan2019

Table 1: Method 8260C Target Compounds and Reporting Limits[1]

Analyte	RL water (ug/L)	RL soil Low-Level (ug/kg)	RL soil Medium-Level (ug/kg)
Dichlorodifluoromethane	5	5	125
Chloromethane	5	5	125
Vinyl Chloride	2	5	125
Bromomethane	5	5	125
Chloroethane	5	5	125
Trichlorofluoromethane	5	5	125
Acrolein	50	100	2500
1,1,2-Trichlorotrifluoroethane	5	5	125
1,1-Dichloroethene	5	5	125
Acetone	100	100	2500
Iodomethane	10	100	2500
Carbon Disulfide	10	10	250
Methylene Chloride	5	20	500
Acrylonitrile	100	100	2500
Methyl tert-butyl ether	4	5	125
trans-1,2-Dichloroethene	5	5	125
Vinyl Acetate	10	100	2500
1,1-Dichloroethane	5	5	125
2-Butanone (MEK)	25	25	625
cis-1,2-Dichloroethene	5	5	125
2,2-Dichloropropane	5	5	125
Bromochloromethane	5	5	125
Chloroform	5	5	125
Cyclohexane	100	100	2500
1,1,1-Trichloroethane	5	5	125
Carbon Tetrachloride	5	5	125
1,1-Dichloropropene	5	5	125
Benzene	5	5	125
1,2-Dichloroethane	5	5	125
Trichloroethene	5	5	125
Methylcyclohexane	50	50	1250
1,2-Dichloropropane	5	5	125
Dibromomethane	5	5	125
Bromodichloromethane	5	5	125
cis-1,3-Dichloropropene	5	5	125
4-Methyl-2-pentanone (MIBK)	25	25	625
Toluene	5	5	125
trans-1,3-Dichloropropene	5	5	125
Ethyl Methacrylate	100	100	2500
1,1,2-Trichloroethane	5	5	125
Tetrachloroethene	5	5	125
1,3-Dichloropropane	5	5	125
2-Hexanone	25	100	2500
Dibromochloromethane (Chlorodibromomethane)	5	5	125
1,2-Dibromoethane (EDB)	5	5	125
Chlorobenzene	5	5	125
1,1,1,2-Tetrachloroethane	5	5	125
Ethylbenzene	5	5	125
m&p-Xylene	5	5	125
o-Xylene	5	5	125

Analyte	RL water (ug/L)	RL soil Low-level (ug/kg)	RL soil Medium-level (ug/kg)
Styrene	5	5	125
Isopropylbenzene	5	5	125
Bromobenzene	5	5	125
trans-1,4-Dichloro-2-butene	100	100	2500
Bromoform	5	5	125
1,1,2,2-Tetrachloroethane	5	5	125
1,2,3-Trichloropropane	5	5	125
n-Propylbenzene	5	5	125
2-Chlorotoluene	5	5	125
1,3,5-Trimethylbenzene	5	5	125
4-Chlorotoluene	5	5	125
tert-Butylbenzene	5	5	125
1,2,4-Trimethylbenzene	5	5	125
sec-Butylbenzene	5	5	125
1,3-Dichlorobenzene	5	5	125
p-Isopropyltoluene	5	5	125
1,4-Dichlorobenzene	5	5	125
n-Butylbenzene	5	5	125
1,2-Dichlorobenzene	5	5	125
1,2-Dibromo-3-chloropropane	10	10	250
1,2,4-Trichlorobenzene	5	5	125
Hexachlorobutadiene	5	5	125
Naphthalene	5	5	125
1,2,3-Trichlorobenzene	5	5	125
2-Methylnaphthalene	10	10	250

[1]Target Compounds and Reporting Limits are subject to change.

Table 2: Characteristic Ions and Internal Standard Association of Target Compounds[2]

Analyte	Primary Ion	Secondary Ion(s)
Group 1 – Fluorobenzene (IS)	**96**	**-**
Dichlorodifluoromethane	85	87
Chloromethane	50	52
Vinyl Chloride	62	64
Bromomethane	94	96
Chloroethane	64	66
Trichlorofluoromethane	101	103
Acrolein	56	55
1,1,2-Trichlorotrifluoroethane	101	151
1,1-Dichloroethene	96	61, 63
Acetone	43	58
Iodomethane	142	127
Carbon Disulfide	76	78
Methylene Chloride	84	86, 49
Acrylonitrile	53	52, 51
Methyl tert-butyl ether	73	57
trans-1,2-Dichloroethene	96	61, 98
Vinyl Acetate	43	86
1,1-Dichloroethane	63	65, 83
2-Butanone (MEK)	43	57, 72
cis-1,2-Dichloroethene	96	61, 98
2,2-Dichloropropane	77	97
Bromochloromethane	49	128
Chloroform	83	85
Dibromofluoromethane (Surr)	113	111
Cyclohexane	56	84, 41
1,1,1-Trichloroethane	97	99, 61
Carbon Tetrachloride	117	119, 121
1,1-Dichloropropene	75	110, 77
Benzene	78	52, 77
1,2-Dichloroethane	62	98, 64
Trichloroethene	95	97, 130, 132
Methylcyclohexane	55	69, 83
1,2-Dichloropropane	63	62, 112
Dibromomethane	93	95, 174
Bromodichloromethane	83	85, 127
Group 2 – Chlorobenzene-d5 (IS)	**117**	**82, 119**
cis-1,3-Dichloropropene	75	77
4-Methyl-2-pentanone (MIBK)	43	58, 85
Toluene-d8	98	99, 100
Toluene	91	92
trans-1,3-Dichloropropene	75	77
Ethyl Methacrylate	69	99, 114
1,1,2-Trichloroethane	83	97, 85
Tetrachloroethene	166	129, 168
1,3-Dichloropropane	76	78
2-Hexanone	43	58, 100
Dibromochloromethane (Chlorodibromomethane)	129	127
1,2-Dibromoethane (EDB)	107	109
Chlorobenzene	112	77, 114

Analyte	Primary Ion	Secondary Ion(s)
Group 2 – Chlorobenzene-d5 (IS) Continued	**117**	**82, 119**
1,1,1,2-Tetrachloroethane	131	133, 119
Ethylbenzene	106	91
m&p-Xylene	106	91
o-Xylene	106	91
Styrene	104	78
Isopropylbenzene	105	120
4-Bromofluorobenzene (Surr)	95	174, 176
Bromobenzene	77	156, 158
trans-1,4-Dichloro-2-butene	53	88, 75
Group 3 – 1,4-Dichlorobenzene-d4 (IS)	**152**	**115, 150**
Bromoform	173	175, 254
1,1,2,2-Tetrachloroethane	83	131, 85
1,2,3-Trichloropropane	110	75, 77
n-Propylbenzene	91	120
2-Chlorotoluene	91	126
1,3,5-Trimethylbenzene	105	120
4-Chlorotoluene	126	91
tert-Butylbenzene	119	91, 134
1,2,4-Trimethylbenzene	105	120
sec-Butylbenzene	105	134
1,3-Dichlorobenzene	146	111, 148
p-Isopropyltoluene	119	134, 91
1,4-Dichlorobenzene	146	111, 148
n-Butylbenzene	91	92, 134
1,2-Dichlorobenzene	146	111, 148
1,2-Dibromo-3-chloropropane	155	75, 157
1,2,4-Trichlorobenzene	180	182, 145
Hexachlorobutadiene	225	223, 227
Naphthalene	128	127
1,2,3-Trichlorobenzene	180	182, 145
2-Methylnaphthalene	142	141, 115

[2]Subject to change.

Table 3: Minimum Response Factor Criteria

Analyte	Minimum Response Factor (RF)
Dichlorodifluoromethane	0.100
Chloromethane	0.100
Vinyl Chloride	0.100
Bromomethane	0.100
Chloroethane	0.100
Trichlorofluoromethane	0.100
Methylene Chloride	0.100
1,1-Dichloroethene	0.100
trans-1,2-Dichloroethene	0.100
1,1-Dichloroethane	0.200
cis-1,2-Dichloroethene	0.100
Chloroform	0.200
1,1,1-Trichloroethane	0.100
Cyclohexane	0.100
Carbon Tetrachloride	0.100
Benzene	0.500
1,2-Dichloroethane	0.100
*Trichloroethene	0.100
1,2-Dichloropropane	0.100
Bromodichloromethane	0.200
Toluene	0.400
1,1,2-Trichloroethane	0.100
*Tetrachloroethene	0.100
Dibromochloromethane (Chlorodibromomethane)	0.100
1,2-Dibromoethane (EDB)	0.100
Chlorobenzene	0.500
Ethylbenzene	0.100
m&p-Xylene	0.100
o-Xylene	0.300
Styrene	0.300
Bromoform	0.100
Isopropylbenzene	0.100
1,1,2,2-Tetrachloroethane	0.300
1,3-Dichlorobenzene	0.600
1,4-Dichlorobenzene	0.500
1,2-Dichlorobenzene	0.400
1,2,4-Trichlorobenzene	0.200
trans-1,3-Dichloropropene	0.100
cis-1,3-Dichloropropene	0.200
*Acetone	0.010
*2-Butanone (MEK)	0.010
*4-Methyl-2-pentanone (MIBK)	0.050
*2-Hexanone	0.050
Methyl tert-butyl ether	0.100
Carbon Disulfide	0.100
1,2-Dibromo-3-chloropropane	0.050
Methylcyclohexane	0.100
1,1,2-Trichlorotrifluoroethane	0.100
Methyl acetate	0.100

*Alternate minimum RF criteria based on compound performance.

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Notes

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STANDARD OPERATING PROCEDURE

THE DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBS)

REFERENCE METHOD: EPA SW-846 METHOD 8082A

SOP NUMBER:	S-IN-O-050-rev.16
EFFECTIVE DATE:	May 1, 2018
SUPERSEDES:	S-IN-O-050-rev.15

APPROVAL

General Manager — April 27, 2018 Date

Quality Manager — April 27, 2018 Date

Department Manager — April 26, 2018 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

S-IN-O-050-rev.16

Table of Contents

1. Purpose

1.1. The purpose of this SOP is to provide a laboratory specific procedure for determining the concentration of polychlorinated biphenyls (PCBs) in aqueous and solid samples, including oils and wipes, while meeting the requirements specified in EPA method 8082A.

2. Summary of Method

2.1. Samples are extracted using a technique and solvent system appropriate for the given matrix.

2.2. Cleanup steps may be applied to the extract, if necessary, depending on the nature of the matrix interferences and the target analytes.

2.3. The extract is analyzed by a gas chromatograph fitted with an electron capture detector (ECD). Aroclor identification is confirmed by a secondary column.

3. Scope and Application

3.1. Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards.

3.2. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of GC systems and interpretation of GC PCB data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This procedure is used to determine the concentrations of PCBs as Aroclors in extracts from solid, aqueous, oil and wipe matrices.

5. Limits of Detection and Quantitation

5.1. The list of reporting limits can be found in Table 1. Reporting limits may vary as a function of volume or weight of sample extracted and extract final volume. Refer to LIMS for method detection limits

6. Interferences

6.1. Matrix interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware. These interferences lead to discrete artifacts or elevated baselines in gas chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates, which are easily extracted during lab operations. Avoiding the use of plastics in the lab can best minimize interferences from phthalates.

6.2. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. Cleanup procedures may be used to remove such interferences. Refer to the appropriate cleanup SOPs if extract cleanup to remove interferences is required.

6.3. Equipment

Portions of the preparation and analytical equipment operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage, and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	100mL widemouth amber glass bottle	None required	Cool to ≤6ºC	Extract within 6 months of collection and analyze within 40 days of extraction
Solid	>100 grams in 4 or 8oz glass jar	None required	Cool to ≤6ºC	Extract within 6 months of collection and analyze within 40 days of extraction
Oils	>10 grams in a glass container	None required	Cool to ≤6ºC	Extract within 6 months of collection and analyze within 40 days of extraction
Wipes	One wipe per glass container	None required	Cool to ≤6ºC	Extract within 6 months of collection and analyze within 40 days of extraction

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Vendor	Description / Comments
GC	Agilent, 7890A LTM module optional or equivalent	Equipped with dual ECD Detectors; dual columns, and dual injectors, or equivalent system.
Autosampler	Agilent, 7693 or equivalent	150 position
Data System	Chemstation acquisition; Target integrations	Or equivalent software

Equipment	Vendor	Description / Comments
GC Columns	Restek, DB5-MS or DB35-MS or equivalent RTX-CLP1 and RTX-CLP2 or equivalent	Fused silica; 30 meters, 0.32mm ID, 0.25um film thickness, or equivalent column Fused silica: 30m x0.32mm ID x 0.32um and 30m x 0.32mm x 0.25um, or equivalent
LTM GC Columns	Restek, DB-35-MS LTM or equivalent Restek, DB5-MS LTM or equivalent	Fused silica; 15 meters, 0.32mm ID, 0.25um film thickness, or equivalent column Fused silica; 15 meters, 0.32mm ID, 0.25um film thickness, or equivalent column

9.2. General Supplies

Item	Vendor	Description
Glass syringes	Hamilton or equivalent	Various sizes
Glass vials	Fisher or equivalent	20mL volume with Teflon lined caps
Autosampler vials	Fisher or equivalent	2mL volume with Teflon lined crimp tops
Micro-inserts	Hewlett Packard or equivalent	Various sizes

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Hexane	Pesticide or reagent grade or equivalent

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, initial calibration verification and continuing calibration verification.

Table 10.2 Standard Definitions and vendors

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	ICAL
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for required target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	CCV
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the calibration curve.	ICV

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock PCB Calibration standards	Ultra Scientific 1016 cat#EPA-1282, 1260 cat#EPA-1362, each at 1000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Intermediate PCB Calibration standards	Refer to Section 10.2.3.1	Solution good for 6 months from preparation.	Refrigerate
Working PCB Calibration standards	Refer to Section 10.2.3.2	Solution good for 6 months from preparation.	Refrigerate
Stock PCB ICV standard	Restek 1016/1260 cat#32039, each at 1000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Intermediate PCB ICV standard	Refer to Section 10.2.3.3	Solution good for 6 months from preparation.	Refrigerate
Working PCB ICV standard	Refer to Section 10.2.3.4	Solution good for 6 months from preparation.	Refrigerate
Stock PCB Surrogate standard	Ultra; catalog #ISM-320; TCMX; 200ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock Single Point PCB Calibration Standards	Ultra Scientific 1221 cat #EPA-1292, 1232 cat #EPA-1302, 1242 cat #EPA-1312, 1248 cat #EPA-1342, 1254 cat #EPA-1352, 1262 cat #EPA-1372 and 1268 cat #EPA-1382, each at 1000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Intermediate Single Point PCB Calibration Standards	Refer to Section 10.2.3.5	Solution good for 6 months from preparation.	Refrigerate
Working Single Point PCB Calibration Standards	Refer to Section 10.2.3.6	Solution good for 6 months from preparation.	Refrigerate

10.2.3. Standard Preparation Procedures

10.2.3.1. Intermediate PCB Calibration Standard Preparation

Dilute 100uL of the Stock Aroclor 1016 Calibration standard (1000ug/mL), 100uL of the Stock Aroclor 1260 Calibration standard (1000ug/mL) and 50uL of the Stock PCB Surrogate standard (200ug/mL) to 50mL with Hexane for a final Aroclor 1016/1260 concentration of 2ug/mL and a final surrogate concentration of 0.2ug/mL. This recipe can also be used to prepare an intermediate calibration standard for other Aroclors.

10.2.3.2. Working PCB Calibration Standard Preparation

The following are examples of calibration standard concentrations and could vary based on requirements:

Standard	Intermediate PCB Cal. Std. amount	Final Volume in Hexane	Final PCB Conc, ug/L	Final Surr Conc, ug/L
CAL1	2.5uL	1mL	5	0.5
CAL2	5uL	1mL	10	1
CAL3	25uL	1mL	50	5
CAL4	50uL	1mL	100	10
CAL5 (CCV)	250uL	1mL	500	50
CAL6	300uL	800uL	750	75
CAL7	500uL	1mL	1000	100

10.2.3.3. Intermediate PCB ICV Standard Preparation

Dilute 20uL of the Stock PCB ICV standard (1000ug/mL) and 10uL of the Stock PCB Surrogate standard (200ug/mL) to 20mL with hexane for a final Aroclor 1016/1260 concentration of 1ug/mL and a final surrogate concentration of 0.1ug/mL. This recipe can also be used to prepare an intermediate ICV standard for other Aroclors.

10.2.3.4. Working PCB ICV Standard Preparation

Dilute 500uL of the Intermediate PCB ICV standard (1/0.1ug/mL) to 1mL with hexane for a final Aroclor 1016/1260 concentration of 500ug/L and a final surrogate concentration of 50ug/L.

10.2.3.5. Intermediate Single Point PCB Calibration Standard Preparation

The following are examples of intermediate single point calibration standards and could vary based on requirements:

Standard	Stock Single Point PCB Calibration Standard amount	Stock PCB Surr. amount	Final Volume in Hexane	Final PCB Concentration, ug/mL	Final Surr Concentration, ug/mL
Working 1221/1254	10uL each	5uL	20mL	0.5 each	0.05
Working 1232/1262	10uL each	5uL	20mL	0.5 each	0.05
Working 1242/1268	10uL each	5uL	20mL	0.5 each	0.05
Working 1248	10uL	5uL	20mL	0.5	0.05

10.2.3.6. Working Single Point PCB Calibration Standard Preparation

The following are examples of working single point calibration standards and could vary based on requirements:

Standard	Intermediate Single Point PCB Calibration Standard amount	Final Volume in Hexane	Final PCB Concentration, ug/L	Final Surr Concentration, ug/L
Working 1221/1254	200uL	1mL	100 each	10
Working 1232/1262	200uL	1mL	100 each	10
Working 1242/1268	200uL	1mL	100 each	10
Working 1248	200uL	1mL	100	10

11. Calibration

11.1. Before the initial calibration standards are injected, it is advisable to perform routine injection port and column maintenance due to the sensitivity of the ECD detector.

11.2. **Initial Calibration**: Initial calibration standards are introduced into the GC from the lowest to highest concentration by direct injection. Five calibration points, at a minimum, are analyzed to evaluate linearity. The lowest calibration standard must be at or below the required reporting limit. Refer to the Quality Manual for more information regarding calibration curves.

11.2.1. A mixture of Aroclor 1016 and 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. An initial 5-point calibration is performed using the mixture of Aroclors 1016 and 1260.

11.2.2. Standards of the other Aroclors are necessary for pattern recognition. Assuming that the Aroclor 1016/1260 standards have been used to demonstrate the linearity of the detector, these single standards of the remaining Aroclor may be used to determine a single-point calibration factor for each Aroclor. The standards for these other Aroclors should be analyzed before the analysis of any samples, and before the analysis of the Aroclor 1016/1260 initial calibration curve.

11.2.3. In situations where only one or a few Aroclors are of interest for a specific project, the analyst may employ a five-point initial calibration of each of the Aroclors of interest and not use the 1016/1260 mixture or the pattern recognition standards.

11.3. Record the peak area (or height) for each Aroclor peak to be used for quantitation. A minimum of 3 peaks must be chosen for each Aroclor, preferably 5 peaks are used. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. A book of reference chromatograms for each Aroclor has been created for each instrument. Refer to these books for the preferred peaks used for calibration of each Aroclor.

11.4. Calculate the Calibration Factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the calculation below:

$$CF = \frac{\text{Peak Area or Height in the Standard}}{\text{Mass of the Standard Injected, ng}}$$

Five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the 5 peaks chosen for this mixture. The single standard for each of the other Aroclors will generate at least 3 calibration factors, one for each selected peak.

11.5. The percent relative standard deviation (%RSD) is calculated as follows:

$$\%RSD = \frac{(SD)}{CF_{avg}} \times 100$$

where: SD = Standard deviation of average RF for a compound
CF_{avg} = Mean of CFs for a peak

11.6. If the %RSD of the CFs is $\leq$ 20% over the calibration range, then the slopes of the lines for each standard are sufficiently close to one another and the average CF may be used to determine sample concentrations.

11.7. If any %RSD is >20%, the analyst may employ a regression equation that does not pass through the origin. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be $\geq$ 0.99. Refer to Method 8000C for additional information regarding calibration.

11.8. When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the calibration model chosen for this mixture must be applied to the other 5 Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors, use the calibration factors from those standards to evaluate linearity.

11.9. **Initial Calibration Corrective Action:** If the initial calibration curve does not meet the required criteria to be used for quantitative purposes, a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new calibration standards must also be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.10. Each day that analysis is performed, the calibration standard(s) should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Are the retention times consistent over the range of calibration for each compound? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably. Additionally, examination of signal-to-noise ratio of analytes in low-level standards may be a useful diagnostic tool to monitor instrument performance. Signal-to-noise ratio is defined as the ratio of the analyte signal to the noise measured on a blank. It is recommended but not required that the signal-to-noise ratio be at least three to confirm detection.

11.11. **Initial Calibration Verification (ICV):** In addition to meeting the response and linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known true value. This step is referred to as the Initial Calibration Verification. The ICV must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent recovery (%Rec) of the observed

ICV according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Observed concentration}}{\text{Theoretical concentration}} \times 100$$

The ICV is analyzed immediately following the initial calibration curve. The ICV recoveries are evaluated against a default acceptance range of 70-130% recovery.

11.12. ICV Corrective Action: If the ICV exceeds the acceptance range, another ICV may be analyzed. If the second ICV also exceeds the acceptance range, a new initial calibration should be prepared. Alternatively, the allowance for use of the ICV when the criterion is not met is documented and is at the discretion of the Department Manager, Quality Manager, General Manager or designee.

11.13. Daily and Continuing Calibration: Verify the initial calibration each 12-hour shift by injecting a Continuing Calibration Verification (CCV) standard prior to conducting any sample analyses.

The CCV must also be analyzed at intervals of once every 20 client samples and at the end of the analysis sequence. For Aroclor analyses, the CCV standard should be a mixture of Aroclors 1016 and 1260. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition.

11.14. For initial calibrations that employed average calibration factor, the calibration factor (CF_v) for each analyte calculated from the CCV must not exceed a %Difference (%D) of more than +/-20% when compared to the CF_{avg} from the initial calibration curve. For initial calibrations that employed a linear calibration, the % Drift for each analyte calculated from the CCV must be within +/-20% in order to use the calibration model to quantitate sample results.

$$\% \text{ Drift} = \frac{\text{Calculated concentration} - \text{Theoretical concentration}}{\text{Theoretical concentration}} \times 100$$

11.15. CCV Corrective Action: If a CCV fails the acceptance criteria, check the instrument operating conditions, and if necessary, restore them to the original settings, and analyze another CCV. If the response still fails the acceptance criteria, then a new initial calibration must be prepared. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

12. Procedures

12.1. All sample extracts must be analyzed at room temperature and the system must be tuned and calibrated as per Section 11, and free of contamination before samples are analyzed.

12.2. Gas Chromatography conditions: Configure the GC per manufacturer's instructions.

12.3. Inject aliquots of all sample extracts and quality control into the GC under the same operating conditions as used for the calibration standards. The sample vials are loaded onto the autosampler that is programmed via the data system to inject the necessary volume.

12.4. Qualitative Analysis: Compounds are identified as present when the following criteria are met:

12.4.1. Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows are established on both the primary and the confirmation column to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize

the occurrence of both false positive and false negative results. To establish retention time windows, make three or more injections of a standard over the course of a 72-hour period, at a minimum. Record the retention time in minutes for the major peaks and surrogate to three decimal places. Calculate the mean and standard deviation of the absolute retention times of the standard. The retention time window is defined as +/-3 times the standard deviation of the mean absolute retention time established during the 72-hour period or 0.03 minutes, whichever is greater.

12.4.2. Establish the center of the retention time window for each major peak and surrogate by using the absolute retention time for each major peak and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

12.4.3. It may also be useful to establish the center of the retention time window for single point standards by using the absolute retention time for each major peak and surrogate from the single point standards analyzed at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the single point standards analyzed with the initial calibration.

12.4.4. Tentative identification of a PCB compound is made when peaks from the sample extract fall within the established retention time windows for Aroclor peaks. The results of a single column/single injection analysis may be confirmed, if necessary, on a second, dissimilar, GC column. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a standard of the target analyte at a concentration at least as low as the concentration estimated from the primary analysis. When the dual-column approach is employed, the target Aroclors are identified and confirmed when they meet the identification criteria on both columns. When confirmation is made on a second column, that analysis should meet all of the QC criteria described above for calibration, retention times, etc.

12.4.5. A book of reference chromatograms for each Aroclor has been created for each instrument. Refer to these books for the preferred peaks and ratios between peaks that are characteristic of each Aroclor. When interferences are present, degradation has occurred, or multiple Aroclors are suspected, the following tools are helpful for proper identification:

- Overlays of the sample chromatogram with chromatograms of Aroclor standards
- Comparison of characteristic peak retention times with Aroclor standards
- Comparison of the ratio between characteristic peaks with ratios of Aroclor standards
- Comparison with historical results, if available
- Analyst judgment and consultation with other experienced analysts
- Consistent application of evaluation tools

12.5. Quantitative Analysis

12.5.1. The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

12.5.2. Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen and the calibration model established from the multi-point calibration of 1016/1260. A concentration is determined using each of the characteristic peaks and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor. Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard or calibration standards interspersed within the samples. The results from these bracketing standards must meet the calibration verification criteria in Sections 11.13 through 11.15.

12.5.3. A book of reference chromatograms for each Aroclor has been created for each instrument. Refer to these books for the preferred peaks used for quantitation of each Aroclor. When interferences are present or degradation has occurred, peaks yielding concentrations or areas that are dissimilar to the others may be excluded. When multiple co-eluting Aroclors are suspected, quantitation of Aroclor(s) should be based on the best match with established Aroclor patterns as determined using the tools outlined in Section 12.4.5.

12.5.4. When PCB concentrations exceed the calibration range, the sample extract should be rerun at a dilution or the result must be qualified as estimated.

12.5.5. Refer to the Manual Integrations SOP for guidance on performing and documenting manual integrations.

13. Quality Control

13.1. Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water or sodium sulfate	One per preparation batch of up to 20 samples, per matrix.	Target analytes must be less than reporting limits	Re-extract and re-analyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analytes	One per preparation batch of up to 20 samples, per matrix.	Lab-generated limits Refer to the LIMS for acceptance limits.	Re-extract and re-analyze associated samples if original LCS is outside acceptance limits. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analytes	One MS/MSD set per preparation batch of up to 20 samples, per matrix.	Lab-generated limits Refer to the LIMS for acceptance limits.	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Surrogate	Applicable surrogate compound	Added to each sample, standard and method blank	Lab-generated limits Refer to the LIMS for acceptance limits.	Samples with surrogate failures must be re-extracted and reanalyzed. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported surrogate data must be qualified. 2) If surrogate result is >QC limits, and sample results are non-detect, the sample results may be reported without qualifiers. The surrogate must be qualified. 3) MS/MSD surrogate recovery failures do not constitute the re-extraction or reanalysis of samples but the surrogate data must be qualified.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

Aqueous Sample (ug/L) $= \frac{(X_s)(V_f)(D)}{(V_i)} * 1000$ **Solid Sample (ug/kg)** $= \frac{(X_s)(V_f)(D)}{(W_s)} * 1000$

Where: X_s = On-column concentration of the analyte in ug/mL
V_f = Final volume of extract in Liters
D = Dilution factor of concentrated extract
V_i = Volume of aqueous sample extracted in Liters
W_s = Weight of solid sample extracted in kilograms

Moisture corrected concentration $= \frac{\text{(Final concentration as received)}}{(100 - \%\text{Moisture})} \times 100$

Oil Sample (mg/kg) $= \frac{(X_s)(V_f)(D)}{(W_s)}$ **Wipe Sample (Total ug)** $= (X_s)(V_f)(D)$

Where: X_s = On-column concentration of the analyte in ug/mL
V_f = Final volume of extract in milliliters
D = Dilution factor of concentrated extract
W_s = Weight of solid sample extracted in kilograms

14.2. LCS equation

$R = (C/S) * 100$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation

$R = \frac{(Cs - C)}{S} * 100$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD calculations:

$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. MDLs must be conducted per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability (DOC) study.

19. Method Modifications

19.1. Extracts are not stored in the dark. Sample extracts are analyzed within a few days of extraction and are not exposed to light for an extended period of time.

19.2. A standard of the DDT analogs is not analyzed and evaluated because interference from DDT and its breakdown components is more applicable to congener analysis than Aroclor analysis. Analysis of the DDT analogs is not considered a method requirement.

19.3. Single point Aroclor standards may be combined in the same way that Aroclors 1016 and 1260 are combined.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment.

Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in the Waste Handling or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Wastes", EPA SW-846, methods 8082A, 8000C.

25.2. Pace Analytical Quality Manual; latest revision.

25.3. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Table 1: Analytes and reporting limits for the analysis of PCBs by 8082A.

27. Revisions

Document Number	Reason for Change	Date
S-IN-O-050-rev.13	1. Section 2.1: removed specific method references for extraction procedures. 2. Section 3.1: created a table for reporting limits of each matrix and added 1262, 1268 and Total PCBs. 3. Table 7.1: revised hold time to extraction to 6 months. 4. Table 8.1: updated equipment and columns information. 5. Table 9.3: updated standards in use and storage conditions. 6. Section 9.2.3: updated standards used and preparation. 7. Section 10.2.2: clarified that single points should be analyzed before ICAL. 8. Section 10: removed quadratic curve fit criteria. 9. Section 11: removed calculations for average and linear curve fits. 10. Section 14: clarified method modifications.	10Aug2015
S-IN-O-050-rev.14	1. Converted to 27-section format. 2. Section 5: moved table of reporting limits to Table 1 attachment. 3. Table 7.1: revised storage temperature format. 4. Section 9.1: updated LTM column information. 5. Section 10.2.3: updated standard preparation to reflect current procedures. Added intermediate combined single point standards. 6. Section 14: corrected equations for aqueous and solid samples to put them in like terms with instrument output. Added equations for oil and wipe samples. 7. Section 19: added modification for combination of single point Aroclors. 8. Section 25.3: added years 2003 and 2009 to TNI reference. 9. Section 26: added reference to Table 1. 10. Table 1: added table for reporting limits.	27Jul2017
S-IN-O-050-rev.15	1. Section 8.1: removed reference to Glossary section of QAM. 2. Section 10.2.1: removed reference to LCS and MS/MSD standards. 3. Section 11.3: added language for example chromatograms and preferred Aroclor peaks used to calibration. 4. Section 12.4.5: added language and a list of tools to help in the identification of Aroclors in a complex matrix. 5. Section 12.5.3: added language to help in the quantitation of Aroclors in a complex matrix. 6. Section 18.1: updated MDL language to new EPA procedure.	7Mar2018
S-IN-O-050-rev.16	1. Table 7.1: updated collection per sample for aqueous samples to reflect RVE. 2. Section 9.1: updated GC columns. 3. Section 10.2.3.2: added lower CAL1 to example ICAL. 4. Section 25.3: added NELAC to reference.	26Apr2018

Table 1: Analytes and Reporting limits for PCBs analyzed by 8082A

Analyte	CAS Number	Water Reporting Limit	Soil Reporting Limit	Oil Reporting Limit	Wipes Reporting Limit
PCB-1016 (Aroclor 1016)	12674-11-2	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1221 (Aroclor 1221)	11104-28-2	0.2 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1232 (Aroclor 1232)	11141-16-5	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1242 (Aroclor 1242)	53469-21-9	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1248 (Aroclor 1248)	12672-29-6	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1254 (Aroclor 1254)	11097-69-1	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1260 (Aroclor 1260)	11096-82-5	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1262 (Aroclor 1262)	37324-23-5	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1268 (Aroclor 1268)	11100-14-4	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB, Total (Aroclor)	1336-36-3	0.2 ug/L	100 ug/kg	1 mg/kg	0.5 total ug

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QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	15 Nov 2018, 08:01:43 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Sayer (004775)	General Manager	16 Nov 2018, 07:14:44 AM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for extracting non-volatile and semi-volatile organic compounds from groundwater and surface water samples in a separatory funnel while meeting the requirements specified in SW-846 Method 3510C.

2. Summary of Method

2.1. A measured volume of sample, normally about 1 liter, is serially extracted with solvent in a separatory funnel. Reduced sample volumes may be used providing that the ratio of sample to solvent remains consistent with the ratio indicated in Method 3510C. Reduced sample volume extraction may also be referred to as Reduced Volume Extraction (RVE). Some extractions also require the monitoring and adjusting of the pH of the sample. The extract is separated from the sample and is concentrated, followed by cleanup, if necessary, or analysis.

3. Scope and Application

3.1. Applicable compounds, volumes/weights utilized, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.2. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of separatory funnel equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This procedure is for extracting water insoluble or slightly water soluble organic compounds from groundwater, surface water and other aqueous samples using methylene chloride as the extraction solvent.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Solvents, reagents and glassware can all contribute to compound artifacts or raised baselines; both conditions that can affect chromatography. Analyzing method blanks is therefore crucial in determining the presence of contaminants.

6.2. Phthalate esters are common contaminant products in many products in the lab. All plastic products should be avoided when performing this method.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Amber Glass container with Teflon-lined lid, preferably 1L, 125mL widemouth, or equivalent.	None	Cool to ≤6°C	Samples must be extracted within 7 days of collection date and extracts must be analyzed within 40 days of extraction date. Samples for **PCB** analysis must be extracted within 6 months of collection date and extract must be analyzed within 40 days of extraction date.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Vendor	Description / Comments
N-EVAP concentrator	Organomation	Or equivalent equipment
Zymark concentrator (2) and glassware	Zymark	Or equivalent equipment
Shaker Tables	Glass-Col	Or equivalent equipment

9.2. General Supplies

Item	Description
Separatory Funnels	2L or 125mL, Teflon, with PTFE stopcocks and Teflon lids or equivalent
Glass beakers	400mL Pyrex or equivalent
Autosampler vials	~2mL, clear glass with aluminum crimp-top seals
Micro-syringes	Various sizes
Glass funnels	
Glass wool	
Graduated cylinders	Glass, Class A
Kuderna-Danish Concentrator Sets	250mL or 500mL flask with 10mL concentrator tube and 3-ball Snyder column
Heated water bath	Temperature controlled
Boiling Chips	Teflon or equivalent
Pasteur pipettes	For testing sample pH
pH paper	pH range 1-12
Glass stirring rods	For breaking up emulsions
Glass tubes	Disposable, 20x150mm or equivalent
Filter paper	For filtration of extract
Pipettes	Volumetric, Class A, various sizes

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
Sodium Sulfate	Anhydrous, granular 10-60 mesh, meets ACS specs or equivalent. Rinse thoroughly with methylene chloride and allow it to dry prior to use.
Methylene Chloride	Extraction solvent, pesticide grade or equivalent
Acetone	Extraction solvent, pesticide grade or equivalent
Hexane	Exchange solvent, pesticide grade or equivalent
Sulfuric acid solution (1:1)	Reagent grade
Sodium Hydroxide solution (10N)	Dissolve 400g sodium hydroxide pellets into 1L of reagent water or purchase premade

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for preparing LCS, MS, and MSD samples and for spiking surrogate into all samples.

Table 10.2 Standard Definitions and vendors

Standard	Description	Comments
Surrogate standard	Surrogates are added to each sample and QC sample to monitor extraction efficiency.	
Spiking Standard	This solution contains all target analytes.	Same solution can be used for the LCS and MS/MSD

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock BNA RVE spike standard	1. Restek; catalog # 31004, B/N spike; 1000ug/mL, or equivalent 2. Restek; catalog # 31014, Acid spike; 2000ug/mL, or equivalent 3. Restek; catalog # 561763, Custom PAH spike; 5000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working BNA RVE spike standards	Refer to Section 10.2.3.1	Good for 6 months from preparation date	Refrigerate
Stock/Working BNA RVE surrogate standard	O2si; catalog # 110004-83-1L; 100ug/mL, or equivalent. Use 100uL for each BNA RVE.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock Full-list BNA RVE spike standard	1. SVOA Mega Mix; Restek; cat#31850; 1000ug/mL, or equivalent 2. 8270 Mix 1; Restek; cat#572178, 2000ug/mL, or equivalent 3. 8270 Mix 2: Restek; cat#572448, 2000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working Full-list BNA RVE spike standard	Refer to Section 10.2.3.2	Good for 6 months from preparation date	Refrigerate

Standard Type	Description	Expiration	Storage
Stock PCB RVE spike standard	Restek; catalog #32039, Aroclors 1016/1260; 1000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PCB RVE spike standard	Refer to Section 10.2.3.3	Good for 6 months from preparation date	Refrigerate
Stock PCB/8081 RVE surrogate standard	Restek; catalog#32457, TCMX/DCB mix; 200ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PCB/8081 RVE surrogate standard	Refer to Section 10.2.3.4	Good for 6 months from preparation date	Refrigerate
Stock 8081 RVE spike standard	Restek; catalog #32292, 8-80ug/mL of each compound, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8081 RVE spike standard	Refer to Section 10.2.3.5	Good for 6 months from preparation date	Refrigerate
Stock DRO spike standard	Restek; catalog # 31258, Diesel #2 standard; 50,000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working DRO spike standard	Refer to Section 10.2.3.7	Good for 6 months from preparation date	Refrigerate
Stock DRO surrogate standard	Restek; catalog # 31487, Pentacosane; 10,000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working DRO surrogate standard	Refer to Section 10.2.3.8	Good for 6 months from preparation date	Refrigerate
Stock PAH-SIM RVE spike standard	Restek; catalog # 31622, Cal. Mix 5; 2000ug/mL of each compound, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PAH-SIM RVE spike standard	Refer to Section 10.2.3.9	Good for 6 months from preparation date	Refrigerate
Stock PAH-SIM RVE surrogate standard	Restek; catalog # 31062, B/N surrogate; 5000ug/mL of each compound, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PAH-SIM RVE surrogate standard	Refer to Section 10.2.3.10	Good for 6 months from preparation date	Refrigerate
Stock/Working Scan/SIM Combo RVE spike standard	O2si, catalog #114072-06, 10-100ug/mL or equivalent. Use 100uL for the RVE LCS, MS, and MSD.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Freeze after opening.
Stock/Working Scan/SIM Combo RVE surrogate spike standard	O2si, catalog #114071-06; 10-100ug/mL or equivalent. Use 100uL for the RVE LCS, MS, and MSD.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Freeze after opening.
Stock TCLP BNA RVE spike standard	1. Restek; catalog # 31028, TCLP B/N spike; 2000ug/mL of each compound, or equivalent 2. Restek; catalog # 31027, TCLP Acid spike; 2000ug/mL of each compound, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working TCLP BNA RVE spike standard	Refer to Section 10.2.3.11	Good for 6 months from preparation date	Refrigerate

Standard Type	Description	Expiration	Storage
Stock 8141 spike standard	Ultra; catalog #CUS-12835, 100ug/mL of each compound or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock Dichlorvos spike standard	Ultra; catalog #PST-380H1000, 1000ug/mL or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8141 spike standard	Refer to Section 10.2.3.12	Good for 2 months from preparation date	Refrigerate
Stock 8141 surrogate standard	AccuStandard; catalog #M-507-1S-10X, Triphenylphosphate 5000ug/mL or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8141 surrogate standard	Refer to Section 10.2.3.13	Good for 2 months from preparation date	Refrigerate

10.2.3. Standard Preparation Procedures

10.2.3.1. Working BNA RVE Spike Standard Preparation

Dilute 2.5mL of the stock Acid spike standard (2000ug/mL), 5mL of the stock B/N spike standard (1000ug/mL) and 1mL of the stock Custom PAH spike (5000ug/mL) to 50mL with acetone for a final concentration of 100ug/mL. Add 100uL of this working standard to each BNA RVE LCS, MS and MSD.

10.2.3.2. Working Full-list BNA RVE Spike Standard Preparation

Dilute 5mL of Stock Mega Mix(1000ug/mL), 2.5mL of Stock Mix #1 (2000ug/mL) and 2.5mL of Stock Mix #2 (2000ug/mL) to 50mL in acetone for a final concentration of 100ug/mL. Add 100uL of this working full-list spike standard to each BNA RVE LCS, MS, and MSD.

10.2.3.3. Working PCB RVE Spike Standard Preparation

Dilute 100uL of the Stock PCB standard (1000ug/mL) to 1000mL with acetone for a final concentration of 1ug/mL. Add 500uL of this working spike to each PCB RVE LCS, MS and MSD.

10.2.3.4. Working PCB/8081 RVE Surrogate Standard Preparation

Dilute 5mL of Stock 8081/PCB Surrogate Standard (200ug/mL) to 400mL in acetone for a final concentration of 2.5ug/mL. Add 100uL of this working standard to each PCB/8081 RVE sample, Method Blank, LCS, MS and MSD.

10.2.3.5. Working 8081 RVE Spike Standard Preparation

Dilute 5mL of 8081 Stock Spike Standard (8-80ug/mL) to 20mL in acetone for a final concentration of 2-20ug/mL. Add 50uL of this working spike standard to each 8081 RVE LCS, MS and MSD.

10.2.3.6. Working DRO Spike Standard Preparation

Dilute 10mL of the stock DRO surrogate standard (50,000ug/mL) to 200mL with acetone for a final concentration of 2500ug/mL. Add 1mL of this working spike to each DRO/ERO/OHIO MOD LCS, MS and MSD.

10.2.3.7. Working DRO Surrogate Standard Preparation

Dilute 7.5mL of the stock DRO surrogate standard (10,000ug/mL) to 500mL with acetone for a final concentration of 150ug/mL. Add 1ML of this working surrogate to each DRO/ERO/Ohio mod sample, Method Blank, LCS, MS and MSD.

10.2.3.8. Working PAH-SIM RVE Spike Standard Preparation

Dilute 5mL of the stock PAH-SIM RVE spike standard (2000ug/mL) to 200mL with acetone for a final concentration of 50ug/mL. Add 20uL of this working spike to each PAH-SIM RVE LCS, MS and MSD.

10.2.3.9. Working PAH-SIM RVE Surrogate Standard Preparation

Dilute 5.0mL of the stock PAH-SIM RVE surrogate standard (5000ug/mL) to 500mL with acetone for a final concentration of 50ug/mL. Add 20uL of this working surrogate to each PAH-SIM RVE sample, Method Blank, LCS, MS and MSD.

10.2.3.10. Working TCLP BNA RVE Spike Standard Preparation

Dilute 5mL of the stock TCLP acid spike standard (2000ug/mL) and 5mL of the stock TCLP B/N spike standard (2000ug/mL) to 100mL with acetone for a final concentration of 100ug/mL. Add 100uL of this working spike to each TCLP BNA RVE LCS, MS and MSD.

10.2.3.11. Working 8141 Spike Standard Preparation

Dilute 1mL of the Stock 8141 spike standard (100ug/mL) and 100uL of Stock Dichlorvos standard (1000ug/mL) to 5mL in acetone for a final concentration of 20000ug/L. Add 100uL of this working spike to each 8141 LCS, MS and MSD.

10.2.3.12. Working 8141 Surrogate Standard Preparation

Dilute 1mL of the Stock 8141 Surrogate Standard (5000ug/mL) to 50mL in acetone for a final concentration of 100ug/mL. Add 25uL of this working surrogate standard to each 8141 sample, Method Blank, LCS, MS and MSD.

11. Calibration

11.1. Not applicable to this SOP.

12. Procedures

12.1. Make sure that all glassware and Teflon separatory funnels used for this procedure have been properly washed. All washed glassware must be rinsed prior to use with acetone to remove residual water and rinsed with methylene chloride to remove any residual contaminants.

12.2. Measure the initial pH of each sample using wide range pH paper by dipping a clean disposable Pasteur pipette into each sample and touching the pipette to a piece of pH paper. Record the initial pH in the extraction log.

12.3. A nominal sample volume of 100mL of aqueous sample is routinely extracted for Reduced Volume Extractions (RVE); otherwise, a nominal sample volume of 1L is used. Refer to Table 1 – Extraction Conditions for more information. For samples expected to contain high concentrations of analytes, use

a smaller aliquot of sample diluted to 1L or 100mL with reagent water.

12.4. For each extraction batch of 20 or fewer samples, prepare a method blank by placing 1L or 100mL of reagent water in to a labeled separatory funnel on the black separatory funnel racks, or on the trellis. The method blank will be used to check for contamination in the system.

12.5. For each extraction batch of 20 or fewer samples, prepare an LCS by placing 1L or 100mL of reagent water in to a labeled separatory funnel on the black separatory funnel rack, or on the trellis. Spike the reagent water with the appropriate amount of spike solution. The LCS will be used to determine the efficiency of the extraction method.

12.6. If the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle for later volume determination. If only an aliquot of the sample is needed, measure the desired volume using a Class A graduated cylinder and record the volume in mLs. Transfer the sample from the sample bottle or graduated cylinder into a clean separatory funnel on the rack or the trellis.

12.7. For each extraction batch of 20 or fewer samples, prepare a matrix spike (MS) and matrix spike duplicate (MSD) in separate, labeled separatory funnels whenever available sample volume allows.

12.8. Add the appropriate **surrogate** solution to each method blank, sample, LCS, MS and MSD. Add the appropriate **spiking** solution to the LCS, MS and MSD. Refer to the standard preparation log and the sample preparation log for details regarding the appropriate surrogate and spiking solutions and volumes to be used for each method.

12.9. Adjust the sample pH, if necessary, to the pH indicated in Table 1 using 1:1 Sulfuric Acid or 10N Sodium Hydroxide. The pH is checked by dipping the tip of a disposable glass pipet into each well-mixed sample and placing the tip onto the pH paper to obtain a pH measurement.

12.10. Rinse the sample bottle (or graduated cylinder) with the first 60mL portion of extraction solvent for a 1L sample or the first 6mL portion of extraction solvent for a 100mL sample and transfer the rinsate to the separatory funnel. If the sample was transferred to the separatory funnel directly from the sample bottle, refill the bottle to the mark made in Section 12.6 with water and then measure the volume of sample that was in the bottle using a Class A graduated cylinder and record the volume in mLs as the initial sample volume.

12.11. Seal the separatory funnels with Teflon lids and shake for two minutes with periodic venting. This can be done manually or on an automatic shaker. When using the automatic shaker that holds separatory funnels in an inverted position, the stopcocks of the separatory funnels can be left open as an alternative to periodic venting. **NOTE**: Methylene chloride may cause excessive pressure in the separatory funnel. It is recommended to shake slightly and vent before placing funnels on an automatic shaker.

12.12. Return the 2L separatory funnels to the trellis and allow the solvent layer to separate from the aqueous phase. The 125mL separatory funnels remain in the automatic shaker for draining. If an excessive emulsion is present in the solvent layer, it can be broken up manually by using a clean glass stirring rod. If this is not successful, the sample can be drained into a clean secondary container (i.e. VOA vial) and transferred to a centrifuge tube. The extract can be centrifuged and then decanted into the drying funnel.

12.13. Drain the solvent layer through a drying funnel consisting of a clean funnel containing a plug of clean glass wool topped with a portion of clean sodium sulfate. The solvent should be collected in labeled beakers, labeled KD glassware, or labeled glass tubes.

12.14. Repeat the extraction two additional times with 60mL or 6mL aliquots of solvent added for each extraction. Drain the solvent through the drying funnel after each extraction. After the final solvent extraction has been collected, rinse the funnel with methylene chloride and remove the drying funnel.

12.15. If extraction at a secondary pH is required, add acid or base as necessary and serially extract the sample, as described in Sections 12.11-12.14, at the adjusted pH. Collect all sample extract fractions together for concentration. Refer to Table 1 for extraction conditions.

12.16. **Concentration procedure for 8270 BNA, 8270 Scan/SIM Combo, and TCLP samples:** Pour the extract into a labeled Kuderna-Danish concentrator with a concentrator tube securely attached. Add one or two clean boiling chips to the KD flask and attach a 3-ball Snyder column. Place the KD apparatus on a hot water bath so that the flask is partially immersed in the water. At the proper rate of distillation, the balls of the Snyder column should actively chatter but the chambers should not flood with solvent. Adjustment of the angle of the apparatus and the water temperature may be necessary to make the boiling more efficient. When the apparent volume of the extract reaches 4-6mL, remove the apparatus from the water bath and allow it to cool. Once cooled, carefully disassemble the KD apparatus rinsing each joint into the concentrator tube with a small amount of extraction solvent. Place the concentrator tube into the N-Evap and further concentrate the extract until the apparent volume is slightly below 1mL. Continue to Section 12.20.

12.17. **Concentration of PAH-SIM LVE samples:** Pour the extract into a labeled 20x150mm glass tube and place the tube on the N-Evap concentrator in a warm water bath (about 40°C) and evaporate the solvent volume using a gentle stream of nitrogen. The tube should be positioned so that water will not condense into the sample and the sample should not be allowed to go below 0.5mL, this could lead to losses of semi-volatile compounds.

12.18. **Concentration procedure for all other samples:** Pour the entire sample extract into a labeled Zymark extractor tube and place in the Zymark concentrator apparatus. Adjust the settings per manufacturer's instructions. When the apparent volume is slightly below the intended final volume, remove the concentrator from the apparatus and allow it to cool.

12.19. If a solvent exchange is required, see Table 1, add 50mL of the exchange solvent to the Zymark tube. Concentrate the extract to slightly below the intended final volume, remove from the water bath and allow it to cool.

12.20. If further concentration is necessary for any sample extract, nitrogen blowdown can be performed. For this procedure, place the concentrator tube on the N-Evap concentrator in a warm water bath (about 40°C) and evaporate the solvent volume using a gentle stream of nitrogen. The tube should be positioned so that water will not condense into the sample and the sample should not be allowed to go below 0.5mL, this could lead to the loss of semi-volatile compounds.

12.21. Prepare a calibrated vial by volumetrically dispensing the required volume of the solvent being used into a vial and securely capping the vial to eliminate evaporation. The calibrated vial must be prepared daily using a Class A pipet. Quantitatively transfer the sample extract from the Zymark tube or concentrator tube to a vial. Bring the sample extract in the vial to the required final volume listed in Table 1 by visually comparing the sample extract vial volume to the calibrated vial volume. Securely cap the sample extract vial. Store all extracts in the appropriate storage cooler. For extracts that will not concentrate to the usual final volume, use the procedure described above to bring the extract to the next higher practical volume for which a calibrated vial can be prepared.

12.22. Refer to appropriate cleanup SOPs if extract cleanup is required.

13. Quality Control

13.1. Refer to the SOP for the determinative method for batch quality control acceptance criteria and corrective actions.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. Analysts performing this method must document acceptable accuracy and precision by passing a demonstration of capability study (DOC) on an annual basis.

19. Method Modifications

19.1. Spikes not added to graduated cylinder or sample bottle but instead added to the separatory funnel.

20. Instrument/Equipment Maintenance

20.1. Refer to manufacturer's instructions.

21. Troubleshooting

21.1. Refer to manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods"; EPA SW-846, latest revision. Method 3510 "Separatory Funnel Extraction".

25.2. Pace Analytical Quality Manual; latest revision.

25.3. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Table 1: Extraction Conditions

27. Revisions

Document Number	Reason for Change	Date
S-IN-O-054-rev.13	1. Effective date added to cover page and body header. 2. Table 9.1: added preparation of sodium sulfate for use by solvent rinsing. 3. Section 11: revised to add new process of determining sample volume prior to extraction using Class A graduated cylinder. Removed language referring to the previous method of sample volume determination. Reordered sections to reflect the addition of surrogates and spike prior to the addition of solvent. Added a reference to extract cleanup SOPs. 4. Section 13.1: added optional LOD/LOQ verification. 5. Section 14: removed previous method modification of determining sample volume post extraction.	03Nov2013
S-IN-O-054-rev.14	1. Section 3.2: added Pesticides. 2. Section 9.2.2: added detail for 8081 and 8141 standards 3. Section 9.2.3: added detail for 8081 and 8141 standards 4. Table 1: added detail for 8081 and 8141 extractions.	28Feb2015
S-IN-O-054-rev.15	1. Table 7.1: revised holding time for extraction of samples for PCB analysis. 2. Table 9.3: updated storage conditions for standards and added Combo LVE spike. 3. Section 12: removed equations for LCS, RSD, MS. 4. Section 13: removed MDL study requirement.	02Sep2015
S-IN-O-054-rev.16	1. Converted to 27 section format. 2. Table 7.1: updated storage temperature format. 3. Table 10.3: updated standard descriptions. 4. Section 10.2.3: updated standard preparation where needed. 5. Section 12: separated instructions for method blank, LCS and MS/MSD. Specified "first portion" of solvent used to rinse cylinder or bottle. 6. Section 19: removed modification for some samples getting two extractions at each pH. 7. Section 25.3: added years 2003 and 2009 to TNI reference. 8. Table 1: removed columns for # of extractions.	05Sep2017

S-IN-O-054-rev.17	1. Section 2.1: changed LVE reference to RVE for reduced volume extraction. 2. Section 10.2.1: removed reference to calibration standards. 3. Table 10.3: added Dichlorvos stock standard, changed LVE to RVE in all instances, and removed references to full-volume analysis where needed. 4. Section 10.2.3: updated standard preparation procedures where needed. 5. Section 12: changed LVE to RVE in all instances. Changed ring stand language to separatory funnel rack or trellis. Added language to require a method blank, LCS and MS/MSD for each extraction batch of 20 or fewer samples. Added an alternative to periodic venting for inverted separatory funnels on certain automatic shakers. 6. Section 13: removed table 13.1 and referred to SOP for the determinative method. 7. Section 25.3: added years 2003 and 2009 to TNI reference. 8. Table 1: added nominal sample volume column and changed LVE to RVE in all instances.	26Apr2018
S-IN-O-054-rev.18	1. Section 9.2: added 250mL KD as an option. 2. Table 10.3: updated DRO standards. 3. Section 12.6: added procedure for marking bottle for later initial sample volume determination. 4. Section 12.10: added procedure for initial sample volume determination when entire bottle content is used. 5. Section 25.3: added NELAC to reference. 6. Table 1: updated DRO information.	8Jul2018

Table 1 – Extraction Conditions

Determinative Method	Nominal Sample Volume Extracted	Initial Extraction pH	Secondary Extraction pH	Extraction Solvent	Exchange Solvent	Final Extract Volume (mL)
8015 DRO (includes ERO and Ohio mod)	1000mL	<2	N/A	Methylene Chloride	N/A	1
8081 OC PEST RVE	100mL	5-9	N/A	Methylene Chloride	Hexane	10
8082 PCB RVE	100mL	5-9	N/A	Methylene Chloride	Hexane	10
8141 OP PEST	1000mL	As received	N/A	Methylene Chloride	Hexane	10
8270 PAH-SIM RVE	100mL	>11	N/A	Methylene Chloride	N/A	1
8270 BNA RVE	100mL	<2	>11	Methylene Chloride	N/A	1
8270 BNA Scan/SIM Combo RVE	100mL	<2	>11	Methylene Chloride	N/A	1
8270 TCLP BNA RVE	10mL	<2	>11	Methylene Chloride	N/A	1

Document Information

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Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

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STANDARD OPERATING PROCEDURE

THE DETERMINATION OF SEMI-VOLATILE COMPOUNDS BY GC/MS
REFERENCE METHOD: EPA SW-846 METHOD 8270C

SOP NUMBER:	S-IN-O-068-rev.15
EFFECTIVE DATE:	November 27, 2017
SUPERSEDES:	S-IN-O-068-rev.14

APPROVAL

General Manager — November 22, 2017 Date

Quality Manager — November 22, 2017 Date

Department Manager — November 22, 2017 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

S-IN-O-068-rev.15

Table of Contents

1. Purpose

1.1. The purpose of this SOP is to provide a laboratory specific procedure for determining the concentration of semi-volatile organic compounds in sample extracts while meeting the requirements specified in EPA method 8270C.

2. Summary of Method

2.1. Semi-volatile compounds are introduced into a gas chromatograph by injection of a sample extract onto a narrow-bore capillary column for analysis. The column is temperature programmed to separate the analytes that are then detected with a mass spectrometer. Identification of the analytes is made by comparing their mass spectra with spectra of known standards. Quantitation is accomplished by comparing the response of a major ion relative to the internal standard response using a multi-point calibration curve.

2.2. Method 8270C provides chromatographic conditions for the detection of semi-volatile compounds in organic extracts. Aqueous samples are extracted using SW-846 method 3510 Separatory Funnel Extraction or other applicable method. Solid samples are extracted using SW-846 method 3546 Microwave Extraction or other applicable method.

3. Scope and Application

3.1. This method can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, phenols, and nitrophenols.

3.2. The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent extraction and exhibits poor chromatographic behavior. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosdiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

3.3. The following compounds are analyzed using this procedure but are not 8270C listed compounds: Carbazole, Biphenyl (Diphenyl), Caprolactam, Atrazine, Benzaldehyde, Diethyl Aniline, 2,3-Dichloroaniline, 1-Methylnaphthalene and 4-Chlorobenzotrifluoride.

3.4. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.5. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of GC/MS equipment and the interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This procedure is applicable to extracts prepared from many types of solid waste, soils, air sampling media, and water samples.

5. Limits of Detection and Quantitation

5.1. The list of compounds and reporting limits analyzed for method 8270C is found in Table 1. Other compounds may be reported upon completion of appropriate validation procedures. Refer to the LIMS for method detection limits.

6. Interferences

6.1. Glassware for the preparatory steps for this method should be thoroughly cleaned and rinsed. Soap products can leave phthalates on the glassware that may appear in the analytical data. Hits for phthalates should be closely scrutinized and continuous hits should warrant checking on the glassware cleaning procedure.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Amber Glass container with Teflon-lined lid, preferably 1L or 125mL widemouth, or equivalent.	None required	Cool to ≤6ºC	Samples must be extracted within 7 days of collection date and analyzed within 40 days of extraction date.
Solid	> 200 grams in 4oz or 8oz glass jar	None required	Cool to ≤6ºC	Samples must be extracted within 14 days of collection date and analyzed within 40 days of extraction date.

Samples and sample extracts must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation

Equipment	Description / Comments
Gas Chromatographs	Hewlett Packard/Agilent 6890/7890 or equivalent system
Data Systems	Hewlett Packard/Agilent Chemstation or equivalent system
Autosamplers	Hewlett Packard/Agilent or equivalent system
Mass Spectrometers	Hewlett Packard/Agilent 5973/5975. Or equivalent system.

9.2. Chromatography Supplies

Item	Vendor	Model / ID	Description
Analytical Columns	Restek	Rxi-5 Sil MS	30m x 0.25mm or equivalent column

9.3. General Supplies

Item	Description	Vendor/ Item # / Description
Gas tight syringes	Various sizes	Hamilton or equivalent
Syringe valves	2-way with Luer ends	Supelco or equivalent
Standard vials	2mL stop/go vials (clear vials)	Supelco or equivalent
Autosampler vials	1.8mL clear vials	Or equivalent

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Methylene Chloride	Pesticide grade or equivalent
Acetone	Pesticide grade or equivalent
Methanol	Pesticide grade or equivalent

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification standards, second source verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions and vendors

Standard	Description	Comments
Tuning Standard	Standard used to tune the mass spectrometer	DFTPP solution
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This solution contains method required spiking compounds, at a minimum, and is used for spiking MS/MSD sets.	Same solution can be used for the LCS and MS/MSD

10.2.2. Details and Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock 8270 Mega Mix calibration standard	Restek; catalog #31850, 1000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock 8270 Mix #1 calibration standard	Restek; catalog #572178, 2000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock 8270 Mix #2 calibration standard	Restek; catalog #572448, 2000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.

Standard Type	Description	Expiration	Storage
Intermediate 8270 Calibration standard	Refer to Sections 10.2.3.1	Expires 6 months from date of preparation.	Refrigerate
Working 8270/Intermediate 8270 LVE calibration standards	Refer to Section 10.2.3.2	Expires 6 months from date of preparation	Refrigerate
Working 8270 LVE calibration standards	Refer to Sections 10.2.3.3	Expires 6 months from date of preparation.	Refrigerate
Stock 8270 ICV standard-Stock A	NSI; catalog #C-701, 1000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock 8270 ICV standard-Stock B	NSI; catalog #C-402, 2000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock 8270 ICV standard-Stock C	NSI; catalog #C-639, 2000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock 8270 ICV standard-Stock D	NSI; catalog #541H, 2000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock 8270 ICV standard-Lilly ICV	Cresent; catalog #CCS-2579, 1000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8270/Intermediate 8270 LVE ICV standard	Refer to Section 10.2.3.4	Expires 6 months from date of preparation.	Refrigerate
Working 8270 LVE ICV standard	Refer to Section 10.2.3.5	Same expiration date as Intermediate 8270 LVE ICV standard	Refrigerate
Stock internal standards	Restek; catalog # 31006; 4000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8270 LVE internal standards	Refer to Section 10.2.3.6	Expires 6 months from date of preparation.	Refrigerate
Stock Surrogate standards	Accustandard; catalog #M-8270-SS; 4000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock DFTPP Tuning Standard	O2si; catalog #113000-01, 50ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8270 DFTPP LVE Tuning Standard	Refer to Section 10.2.3.7	Expires 6 months from date of preparation.	Refrigerate

10.2.3. Standard Preparation Procedures

10.2.3.1 Intermediate 8270 Calibration Standard Preparation

Dilute 1000uL of Stock 8270 MegaMix calibration standard (1000ug/mL), 500uL of Stock 8270 Mix #1 (2000ug/mL), 500uL of Stock 8270 Mix #2 (2000ug/mL) and 250uL of Stock Surrogate standard (4000ug/mL) to 5mL with Methylene Chloride for a final concentration of 200ug/mL

10.2.3.2 Working 8270/Intermediate 8270 LVE Calibration Standards

The following are examples of calibration standards and could vary based on requirements:

Standard	Int. 8270 Cal. Std. Amount	Final Volume in Methylene Chloride	Final Nominal Cal Std Concentration	Stock Internal Standard amount added to Cal. Std.	Internal Standard Concentration
8270 Cal Std 1	25uL	1000uL	5ug/mL	10uL	40ug/mL
8270 Cal Std 2	50uL	1000uL	10ug/mL	10uL	40ug/mL
8270 Cal Std 3	100uL	1000uL	20ug/mL	10uL	40ug/mL
8270 Cal Std 4	250uL	1000uL	50ug/mL	10uL	40ug/mL
8270 Cal Std 5	400uL	1000uL	80ug/mL	10uL	40ug/mL
8270 Cal Std 6	500uL	1000uL	100ug/mL	10uL	40ug/mL
8270 Cal Std 7	750uL	1000uL	150ug/mL	10uL	40ug/mL

10.2.3.3 Working 8270 LVE Calibration Standards

Prepare using the Working 8270/Intermediate 8270 LVE Calibration Standards from Section 10.2.3.2. The following are examples of calibration standards and could vary based on requirements:

Standard	Intermediate Cal. Std. ID from Section 10.2.3.2	Intermediate Cal. Std. Amount	Final Volume in Methylene Chloride	Final Calibration Standard Concentration	Internal Standard Concentration
8270 LVE Cal. Std 1	8270 Cal Std 1	100uL	1mL	0.5ug/mL	4ug/mL
8270 LVE Cal. Std 2	8270 Cal Std 2	100uL	1mL	1.0ug/mL	4ug/mL
8270 LVE Cal. Std 3	8270 Cal Std 3	100uL	1mL	2.0ug/mL	4ug/mL
8270 LVE Cal. Std 4	8270 Cal Std 4	100uL	1mL	5.0ug/mL	4ug/mL
8270 LVE Cal. Std 5	8270 Cal Std 5	100uL	1mL	8.0ug/mL	4ug/mL
8270 LVE Cal. Std 6	8270 Cal Std 6	100uL	1mL	10ug/mL	4ug/mL
8270 LVE Cal. Std 7	8270 Cal Std 7	100uL	1mL	15ug/mL	4ug/mL

10.2.3.4 Working 8270/Intermediate 8270 LVE ICV Standard Preparation

Dilute 50uL of 8270 ICV Standard-Stock A (1000ug/mL), 25uL of 8270 ICV Standard-Stock B (2000ug/mL), 25uL of 8270 ICV Standard-Stock C (2000ug/mL), 25uL of 8270 ICV Standard-Stock D (2000ug/mL), 50uL of 8270 ICV Standard-Lilly ICV (1000ug/mL), and 25uL of Stock Surrogate Standard (4000ug/mL) to 1mL with methylene chloride for a final concentration of 50-100ug/mL.

10.2.3.5 Working 8270 LVE ICV Standard Preparation

Dilute 100uL of the Intermediate 8270 LVE ICV Standard (50-100ug/mL) to 1mL with methylene chloride for a final concentration of 5-10ug/mL.

10.2.3.6 Working 8270 LVE Internal Standards Preparation

Dilute 300uL of the Stock internal standards (4000ug/mL) to 3mL with methylene chloride for a final concentration of 400ug/mL.

10.2.3.7 Working DFTPP LVE Tuning Standard Preparation

Dilute 200uL of the Stock DFTPP Tuning Standard (50ug/mL) to 1mL with methylene chloride for a final DFTPP concentration of 10ug/mL.

11. Calibration

11.1. DFTPP Tune Verification: At the beginning of each analytical sequence, prior to the analysis of any standards or samples, the mass spectrometer must be hardware tuned using a 50ng injection of DFTPP. Analysis must not begin until the tuning criteria are met. Use the DFTPP mass intensity criteria in the table below as tuning acceptance criteria. Alternate tuning criteria may be used provided that method performance is not adversely affected. The 12-hour window during which standards and samples may be analyzed begins with the injection of DFTPP. All subsequent standards, samples MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

Mass (m/z)	Ion Abundance criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

If the DFTPP ratios do not meet the criteria, reanalyze the DFTPP tune. If the DFTPP still fails the criteria, autotune adjustment, instrument maintenance, and/or preparation of new standards must be considered.

The mass spectrum of DFTPP may be obtained by averaging three scans, the peak apex scan and the scans immediately preceding and following the apex. Background subtraction is required using this approach and must be accomplished using a single scan no more than 20 scans prior to the elution of DFTPP. Do not background subtract part of the DFTPP peak. Alternatively, the analyst may use other approaches suggested below:

1. A single scan within the DFTPP peak with background subtraction of a single scan no more than 20 scans prior to the elution of DFTPP.
2. An average of multiple scans within the DFTPP peak with background subtraction of a single scan no more than 20 scans prior to the elution of DFTPP.

11.2. Initial Calibration: Initial Calibration standards are introduced into the GC/MS from the lowest to highest concentration of each working calibration standard. The lowest calibration standard must be at or below the required reporting limit. Five calibration points, at a minimum, are analyzed to evaluate linearity. Refer to the Quality Manual for more information regarding calibration curves. The response factor (RF) is calculated for each compound for each calibration standard as follows:

$$RF = \frac{(A_x)(C_{IS})}{(A_{IS})(C_x)}$$

where: A_x = Area of the quantitation ion for the compound being measured
A_{IS} = Area of the quantitation ion for the internal standard.
C_{IS} = Concentration of the internal standard
C_x = Concentration of the compound being measured.

11.3. The average response factor (RF_{avg}) is determined by averaging the response factors at the different concentrations for each target analyte

11.4. The percent relative standard deviation (%RSD) is calculated as follows:

$$\%RSD = \frac{(SD)}{RF_{avg}} \times 100$$

where: SD = Standard deviation of average RF for a compound
RF_{avg} = Mean of RFs for a compound

11.5. The %RSD should be should be ≤15% for each target analyte. However, the %RSD for each individual Calibration Check Compound (CCC) must be ≤30%. If the RSD of any CCC is >30%, then the chromatographic system is too reactive and instrument maintenance or preparation of new standards may be necessary before attempting recalibration. The CCCs are:

Base/Neutral Fraction	**Acid Fraction**
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
Diphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

11.6. System Performance Check Compounds (SPCCs) are checked for a minimum average response factor (RF_{avg}) to determine potential instability and/or degradation caused by deterioration of instrument conditions or standard material. The minimum RF_{avg} for the semivolatile SPCCs are as follows:

N-nitroso-di-n-propylamine	0.050
Hexachlorocyclopentadiene	0.050
2,4-Dinitrophenol	0.050
4-Nitrophenol	0.050

If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Instrument maintenance or preparation of new standards may be necessary. The SPCC criteria must be met for sample analysis to begin.

11.7. If the percent relative standard deviation (%RSD) of the RFs for a compound is ≤15% over the calibration range, then linearity through the origin is assumed and the RF_{avg} may be used to determine sample concentrations.

11.8. If the % RSD for any compound is >15%, the analyst may employ a regression equation that does not pass through the origin. The regression calculation will generate a correlation coefficient (r) that is the measure

of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be $\geq$ 0.99. Refer to Method 8000C for additional information regarding calibration.

11.9. Non-linear or quadratic calibration: A non-linear or quadratic calibration model can only be used if the compound(s) have historically exhibited a non-linear response and cannot be used to extend the calibration range for any compound that normally exhibits a linear response in a narrower range. The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of: $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be available and the origin cannot be included as one of the points. Because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. The "goodness of fit" of the polynomial equation is evaluated by calculating the coefficient of the determination (COD) or r^2. The COD or r^2 from the regression equation must be $\geq$ 0.99. Refer to Method 8000C for additional information regarding calibration.

11.10. Initial Calibration Corrective Action: If the initial calibration curve does not meet the required criteria to be used for quantitative purposes, a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new calibration standards must also be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.11. Each day that analysis is performed, the calibration standard(s) should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Are the retention times consistent over the range of calibration for each compound? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably. Additionally, examination of signal-to-noise ratio of analytes in low-level standards may be a useful diagnostic tool to monitor instrument performance. Signal-to-noise ratio is defined as the ratio of the analyte signal to the noise measured on a blank. It is recommended but not required that the signal-to-noise ratio be at least three to confirm detection.

11.12. Initial Calibration Verification (ICV): In addition to meeting the response and linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known true value. This step is referred to as the Initial Calibration Verification. The ICV must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent recovery (%Rec) of the observed ICV according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Observed concentration}}{\text{Theoretical concentration}} \times 100$$

The ICV is analyzed immediately following the initial calibration curve. The ICV recoveries are evaluated against a default acceptance range of 70-130% recovery. Alternative acceptance limits may be appropriate for some compounds.

11.13. ICV Corrective Action: If the ICV exceeds the acceptance range, another ICV may be analyzed. If the second ICV also exceeds the acceptance range, a new initial calibration should be prepared. Alternatively, the allowance for use of the ICV when the criterion is not met is documented and is at the discretion of the Department Manager, Quality Manager, General Manager or designee.

11.14. Continuing Calibration Verification: The initial calibration is verified every 12 hours by analyzing a DFTPP tune verification as described in Section 10.1, followed by a Continuing Calibration Verification

(CCV) standard.

11.15. If the % difference (%D) or % Drift for each CCC is ≤20%, then the initial calibration is assumed to be valid. The response factors for all SPCCs in the CCV standard must meet the criteria in Section 10.6. The % difference (%D) or % Drift for each non-CCC compound should be ≤40%. If non-CCC compounds fail to meet this criterion, the concentrations above the reporting limit in associated samples must be qualified as estimated.

11.16. The internal standard areas in the CCV must be between 50%-200% of the internal standard areas of the corresponding standard in the initial calibration. In addition, the retention time of the internal standards in the CCV cannot shift by more than 30 seconds from the corresponding standard in the initial calibration. Failure in either of these two areas requires the analyst to evaluate their system and perform maintenance if necessary.

11.17. **CCV Corrective Action:** If a CCV fails the acceptance criteria, check the instrument operating conditions, and if necessary, restore them to the original settings, and analyze another CCV. If the response still fails the acceptance criteria, then a new initial calibration must be prepared. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

12. Procedures

12.1. All sample extracts must be analyzed at room temperature and the system must be tuned and calibrated as per Section 10, and free of contamination before samples are analyzed.

12.2. **Gas Chromatography conditions**: Configure the GC/MS per manufacturer's instructions.

12.3. The 1mL extract obtained from sample preparation for 8270 should be fortified with 10uL of the Stock 8270 internal standard (4000ug/mL) just prior to analysis such that 40ng of internal standard is injected onto the column. The 1mL extract obtained from sample preparation for 8270 LVE should be fortified with 10uL of the Working 8270 LVE internal standard (400ug/mL) just prior to analysis such that 4ng of internal standard is injected onto the column. Analyze each 8270 extract by injecting 2uL onto the column. Analyze each 8270 LVE extract by injecting 4uL onto the column.

12.4. **Qualitative Analysis:** Compounds are identified as present when the following criteria are met:

12.4.1. The relative retention time (RRT) of the sample component must compare within +/- 0.06 RRT units of the RRT of the CCV component.

12.4.2. The intensities of the characteristic ions of a compound must maximize in the same scan or within one scan of each other. Refer to Table 2 for characteristic ions.

12.4.3. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

12.5. **Quantitative analysis:** Quantitation is based on the integrated abundance of the target analyte's quantitation ion using the internal standard technique. Calculations are subject to change based on the data reduction software used. Extract concentrations that exceed the upper calibration range must be diluted and reanalyzed or qualified as estimated. Additional internal standard must be added to the diluted extract to maintain the same concentration as the calibration standards.

12.6. Refer to the Manual Integrations SOP for guidance on performing and documenting manual integrations.

12.7. If the sample concentration exceeds the linear range of the analysis, the sample must be diluted and reanalyzed or reported as an estimated concentration.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples, per matrix.	Target analytes must be less than reporting limits.	Re-extract and re-analyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If the method blank concentration is less than 1/10 of the amount measured in the sample, corrective action is not required, affected data must be qualified. 2) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 3) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analytes	One per preparation batch of up to 20 samples, per matrix.	Lab-generated limits Refer to the LIMS for acceptance limits. Refer to Sections 13.2 and 13.3 for additional information.	Re-extract and re-analyze associated samples if original LCS is outside acceptance limits. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analytes	One MS/MSD set per preparation batch of up to 20 samples, per matrix.	Lab-generated limits Refer to the LIMS for acceptance limits.	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Surrogates	Applicable surrogate compounds	Added to each standard, sample, and method blank.	Lab-generated limits Refer to the LIMS for acceptance limits.	Samples with surrogate failures must be re-extracted and reanalyzed. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported surrogate data must be qualified. 2) If surrogate result is >QC limits, and sample or method blank results are non-detect, the sample or method blank results may be reported without qualifiers. The surrogate must be qualified. 3) If only one surrogate fails and it is >10% recovery, re-extraction is not required but data must be qualified. 4) MS/MSD surrogate recovery failures do not constitute the re-extraction or reanalysis of samples but the surrogate data must be qualified.
As required by client only: **Internal Standards**	Applicable Internal Standard compounds	Added to each standard, sample, and method blank.	Sample ISTD areas must be -50% to +100% from CCV. Sample ISTD RTs must be +/-0.5 minutes from CCV.	Samples with internal standard failures must be reanalyzed undiluted or more concentrated. The laboratory may only dilute a sample prior to reanalysis if matrix interference is present. *Exception:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified.

13.2. The matrix spike may be used in place of the LCS as long as the acceptance criteria are as stringent as for the LCS.

13.3. Allowable Marginal Exceedances: If a large number of analytes are in the LCS, it becomes statistically likely that a few will be outside control limits. A marginal exceedance (ME) is defined as being beyond the LCS control limit of +/-3 standard deviations, but within the ME limits of +/-4 standard deviations around the mean. The number of allowable MEs is based on the number of analytes in the LCS. If more analytes exceed the LCS control limits than is allowed, or if any one analyte exceeds the ME limits, the LCS fails and correction action is necessary. If the same analyte exceeds the LCS control limit consecutively, it is an indication of a systemic problem. The source of the error shall be located and corrective action taken. The number of allowable marginal exceedances is as follows:

Number of Analytes in LCS	Number Allowed as Marginal Exceedances
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

NOTE: As allowed by client, the LCS shall be allowed to be outside the control limits but ≥10% for hexachlorocyclopentadiene, N-nitrosodimethylamine, pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, and 4-chloroaniline without corrective action. The LCS shall be allowed to be outside the control limits but >10% for up to four additional compounds, with the exception of any PAH, without corrective action.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

$$\text{Aqueous Sample (ug/L)} = \frac{(X_s)(V_f)(D)}{(V_i)} \qquad \text{Solid Sample (ug/kg)} = \frac{(X_s)(V_f)(D)}{(W_s)}$$

Where:
X_s = Concentration of the analyte from the instrument, ug/mL
V_f = Final volume of extract, mL
D = Dilution factor of extract
V_i = Volume of aqueous sample extracted, L
W_s = Weight of solid sample extracted, kg

$$\text{Moisture corrected concentration} = \frac{\text{(Final concentration as received)}}{\text{(100- \%Moisture)}} \times 100$$

14.2. LCS equation

R = (C/S) * 100

Where R = percent recovery
C = observed LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation

$$R = \frac{(Cs - C)}{S} * 100$$

Where R = percent recovery
Cs = observed spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD calculations:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. An MDL study and/or LOD/LOQ verification must be conducted annually for each matrix per instrument.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Standards are purchased as certified stock solutions and not prepared from neat materials.

19.2. Microwave Method 3546 is used for the preparation of solid samples for analysis by 8270C.

19.3. Phenol-d5 is used as a surrogate instead of Phenol-d6.

19.4. Extract final volumes, volume of internal standards added to extracts, and volume of extract injected into the instrument may vary from those identified in Method 8270C.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Methods 8000C and 8270C.

25.2. Pace Analytical Quality Manual; latest revision.

25.3. TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Table 1: Target Compounds and Reporting Limits

26.2. Table 2: Characteristic Ions of Target Compounds

27. Revisions

Document Number	Reason for Change	Date
S-IN-O-068-rev.13	1. Cover page: added actual effective date. 2. Sections 10.8 and 10.9: removed SW-846 equations and made reference to Method 8000C. 3. Section 10.11: added as guidance for evaluation of ICAL standards. 4. Section 10.12: added that alternative limits may be appropriate for some ICV compounds. 5. Section 10.15: added criteria of <40% for non-CCC compounds in CCV. 6. Section 11.6: added as a reference to the Manual Integrations SOP. 7. Section 11.7: added to require over range samples be diluted and reanalyzed or qualified as estimated. 8. Sections 11.8-11.10: replaced Target equations with SW-846 equations. 9. Table 12.1: corrected references in LCS acceptance criteria section and removed client-specific reference in internal standard section. 10. Section 12.3 Note: removed client-specific reference. 11. Section 13.1: added optional LOD/LOQ verification. 12. Table 1: updated some soil RLs.	01Nov2013
S-IN-O-068-rev.14	1. Converted to SOT format with 27 sections. 2. Cover page: changed phone number and revised document control format. 3. Section 3: added a list of compounds that are analyzed but not listed in the method. 4. Section 9.2: updated column details 5. Table 10.3: updated standard details and storage conditions. 6. Section 10.2.3: updated several standard preparation procedures. 7. Section 12: removed calculations for curve fit types. 8. Updated Tables 1 and 2.	07Dec2015
S-IN-O-068-rev.15	1. Table 7.1: revised storage temperature format. 2. Table 10.3: updated to current standard IDs. 3. Section 10.2.3: revised some recipes to match current practice. 4. Section 14.1: corrected equations to be in like terms with instrument output. 5. Section 25.3: added years 2003 and 2009 to TNI reference. 6. Table 1: changed 5 ug/L RLs to 10 ug/L.	20Nov2017

Table 1: Target Compounds and Reporting Limits[1]

Analyte	RL water (ug/L)	RL soil (ug/kg)
Phenol	10	330
Bis (2-chloroethyl) ether	10	330
2-Chlorophenol	10	330
1,3-Dichlorobenzene	10	330
1,4-Dichlorobenzene	10	330
Benzyl Alcohol	20	660
1,2-Dichlorobenzene	10	330
2-Methylphenol (o-Cresol)	10	330
Bis (2-chloroisopropyl)ether	10	330
3&4-Methylphenol (m&p-Cresol)	20	660
N-Nitroso-di-n-propylamine	10	330
Hexachloroethane	10	330
Nitrobenzene	10	330
Isophorone	10	330
2-Nitrophenol	10	330
2,4-Dimethylphenol	10	330
Benzoic Acid	50	1600
Bis(2-chloroethoxy)methane	10	330
2,4-Dichlorophenol	10	330
1,2,4-Trichlorobenzene	10	330
Naphthalene	10	330
4-Chloroaniline	20	660
Hexachlorobutadiene	10	330
4-Chloro-3-methylphenol	20	660
1-Methylnaphthalene	10	330
2-Methylnaphthalene	10	330
Hexachlorocyclopentadiene	10	330
2,4,6-Trichlorophenol	10	330
2,4,5-Trichlorophenol	10	330
2-Chloronaphthalene	10	330
2-Nitroaniline	50	1600
Dimethyl phthalate	10	330
Acenaphthene	10	330
Acenaphthylene	10	330
2,4-Dinitrophenol	50	1600
4-Nitrophenol	50	1600
Dibenzofuran	10	330
2,4-Dinitrotoluene	10	330
2,6-Dinitrotoluene	10	330
3-Nitroaniline	50	1600
Diethyl phthalate	10	330
4-Chlorophenyl phenyl ether	10	330
Fluorene	10	330
4-Nitroaniline	50	1600
4,6-Dinitro-2-methylphenol	50	1600
N-Nitrosodiphenylamine	10	330
4-Bromophenyl phenyl ether	10	330

Analyte	RL water (ug/L)	RL soil (ug/kg)
Hexachlorobenzene	10	330
Pentachlorophenol	50	1600
Phenanthrene	10	330
Anthracene	10	330
Di-n-butyl phthalate	10	330
Fluoranthene	10	330
Pyrene	10	330
Butyl benzyl phthalate	10	330
3,3'-Dichlorobenzidine	20	660
Benzo(a)anthracene	10	330
Chrysene	10	330
Bis(2-ethylhexyl)phthalate	10	330
Di-n-octyl phthalate	10	330
Benzo(b)fluoranthene	10	330
Benzo(k)fluoranthene	10	330
Benzo(a)pyrene	10	170
Indeno(1,2,3-cd)pyrene	10	330
Dibenz(a,h)anthracene	10	170
Benzo(g,h,i)perylene	10	330
N-Nitrosodimethylamine	10	330
Pyridine	10	1600
Benzidine	20	330
Acetophenone	10	330
2,6-Dichlorophenol	10	330
1,2-Diphenylhydrazine	10	330
2-Picoline	50	1600
1,2,4,5-Tetrachlorobenzene	10	330
1,3-Dinitrobezene	50	1600
2,3,4,6-Tetrachlorophenol	10	330

[1] Target Compounds and Reporting Limits are subject to change.

Table 2: Characteristic Ions of Target Compounds[2]

Analyte	Primary Ion	Secondary Ion(s)
Group 1 - 1,4-Dichlorobenzene-d4 (IS)	152	150, 115
N-Nitrosodimethylamine	42	74,44
Pyridine	79	52
2-Picoline	93	66, 92
4-Chlorobenzotrifluoride[3]	180	161,182
2-Fluorophenol (S)	112	64
Phenol-d5 (S)	99	71, 42
Benzaldehyde	77	105, 106
Phenol	94	65.66
Aniline	93	66, 65
Bis(2-Chloroethyl) ether	93	63.95
2-Chlorophenol	128	64,130
n-Decane[3]	57	43, 142
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
Benzyl alcohol	108	79, 77
1,2-Dichlorobenzene	146	148, 111
Bis(2chloro1methylethyl) ether[3]	45	77, 121
Bis(2-chloroisopropyl) ether	45	77, 121
3&4-methylphenol (m&p cresol)	108	107,77
Acetophenone	105	77, 120
N-Nitroso-di-n-propylamine	70	130, 101
Hexachloroethane	117	201, 199
Group 2 - Naphthalene-d8 (IS)	136	68
Nitrobenzene-d5 (S)	82	128, 54
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	109, 65
2,4-Dimethylphenol	122	107, 121
Bis(2-chloroethoxy) methane	93	95, 123
Benzoic Acid	105	122, 77
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 102
Apha-Terpineol	59	93, 121
2-Chloroaniline	127	65, 92
Hexachlorobutadiene	225	223, 227
Caprolactam	113	55, 56
Diethyl Aniline[3]	134	106, 77
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141, 115
1-Methylnaphthalene[3]	142	141, 115

Analyte	Primary Ion	Secondary Ion(s)
Group 3 - Acenaphthene-d10 (IS)	164	160, 162
Hexachlorocyclopentadiene	237	235, 272
1,2,4,5-Tetrachlorobenzene	216	179, 108
2,3-Dichloroaniline[3]	161	163, 90
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Fluorobiphenyl (S)	172	171
2-Chloronaphthalene	162	127, 164
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
1,3-Dinitrobenzene	168	76, 50
2,6-Dinitrotoluene	165	63, 89
Acenaphthylene	152	150, 153
3-Nitroaniline	138	108, 92
Biphenyl (Diphenyl)	154	153, 152
Acenaphthene	153	154, 152
2,4-Dinitrophenol	184	154, 63
4-Nitrophenol	109	139, 65
2,4-Dinitrotoluene	165	63, 89
Dibenzofuran	168	139, 169
2,3,4,6-Tetrachlorophenol	232	131, 230
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluroene	166	165, 139
4-Nitroaniline	138	108, 65
Group 4 - Phenanthrene-d10 (IS)	188	80,94
4,6-Dinitro-2-methylphenol	198	51,105
N-Nitrosodiphenylamine	169	168, 167
Azobenzene[3]	77	182, 105
1,2-Diphenylhydrazine	77	105, 182
2,4,6-Tribromophenol (S)	330	332, 141
4-Bromophenyl-phenyl ether	248	250, 141
Hexachlorobenzene	284	142, 249
Atrazine	200	215, 202
Pentachlorophenol	266	264, 268
n-Octadecane[3]	57	43, 71
Phenanthrene	178	179, 176
Anthracene	178	176, 179
Carbazole[3]	167	166, 139
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 203
Benzidine	184	92, 185
Group 5 - Chysene-d12 (IS)	240	120, 236
Pyrene	202	101, 203
p-Terphenyl-d14 (S)	244	122, 212
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Bis(2-Ethylhexyl) phthalate	149	167, 279
Benzo(a)athracene	228	229, 226
Chrysene	228	226, 229

Analyte	Primary Ion	Secondary Ion(s)
Group 6 - Perylene-d12 (IS)	264	260, 265
Di-n-ocvtlphthalate	149	279, 43
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluroanthene	252	253, 125
Benzo(a)pyrene	252	253,125
Indeno (1,2,3-cd)pyrene	276	138, 277
Dibenz (a,h) athracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277

[2] Target Compounds are subject to change.
[3] Compound is not listed in Method 8270C.

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1. Purpose/Identification of Method

1.1. The purpose of this SOP is to provide a laboratory specific procedure for determining the concentration of anions in aqueous and solid samples while meeting the requirements specified in EPA Method 300.0, Rev. 2.1 and SW-846 Method 9056A.

2. Summary of Method

2.1. Aqueous samples or solid sample extracts are introduced into an ion chromatograph. The anions of interest are separated and measured using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

3. Scope and Application

3.1. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.2. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of ion chromatograph systems and interpretation of associated data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This procedure is applicable to most drinking water, groundwater, surface water, wastewater, and solids.

5. Limits of Detection and Quantitation

5.1. The table below summarizes the anions that are routinely reported by this method and the current default reporting limits. Refer to the LIMS for method detection limits.

Anion	Reporting Limits-water, (mg/L)	Reporting Limits-soil, (mg/kg)
Bromide	0.05	0.5
Chloride	0.25	2.5
Fluoride	0.1	1
Iodide	0.5	5
Nitrate	0.05	0.5
Nitrite	0.05	0.5
Nitrate-Nitrite	0.1	1
Sulfate	0.25	2.5

6. Interferences

6.1. Interferences can be caused by substances with retention times that are similar to and that overlap those of the anions of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention time.

6.2. The water dip or negative peak that elutes near and can interfere with the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent to 100 mL of each standard and sample.

6.3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

6.4. Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow system.

6.5. The acetate, formate, and other monovalent organic acid anions elute early in the chromatographic run and can interfere with fluoride. The retention times of anions may differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples where acetate is used for pH adjustment.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	One 125mL plastic or glass bottle	No preservative	Cool to ≤6°C Note: Method 300.0 does not require cooling for Bromide, Chloride, or Fluoride.	**Nitrate or Nitrite:** Analysis must be completed within 48 hours of collection date/time. **Other Anions:** Analysis must be completed within 28 days of collection date.
Aqueous NO3+NO2	One 125mL plastic or glass bottle	pH<2 with H_2SO_4 Note: Preservation may interfere with analysis.	Cool to ≤6°C	Analysis must be completed within 28 days of collection date.
Solid	One 4 oz. wide mouth plastic or glass jar	No preservative	Cool to ≤6°C	Analysis must be completed within 28 days of collection date.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation/Equipment

Equipment	Description/Comments
Ion Chromatograph System	Dionex ICS-3000 system or equivalent system that includes autosampler and data system.

9.2. Chromatography Supplies

Item	Description
Guard Column	Dionex AG14 IonPac 4x50mm, or equivalent
Analytical Column	Dionex AS14 IonPac 4x250mm, or equivalent

9.3. General Supplies

Item	Description
Gas tight syringes	Various sizes
Pipets	Class A or calibration-checked variable volume
Volumetric flasks	Class A, various sizes
Graduated cylinders	Class A, various sizes
Beakers	Glass or plastic disposable
Syringe filters	0.45um for filtering samples when required
Filtration apparatus	With 0.45um filter disks for filtration of eluent
Sample vials	120mL plastic with screw top caps
Autosampler vials	1.5mL with screw top septum caps
Balance, Analytical/Top Load	Able to measure to nearest 0.1g
Agitation apparatus	Shaker table, ultrasonic bath or equivalent apparatus for preparation of solids

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
Sodium Bicarbonate	A.C.S grade powder, Fisher S233 or equivalent
Sodium Carbonate, Anhydrous	A.C.S. grade powder, Fisher S263 or equivalent
Stock Eluent	Place 500mL of reagent water into a 1L volumetric flask, add 8.4g of Sodium Bicarbonate and 37.1g of Sodium Carbonate, dissolve and dilute to 1L with reagent water. This solution expires 6 months from the date prepared.
Working Eluent	Place 1000mL of reagent water into a 2L volumetric flask, add 20mL of the Stock Eluent and dilute to 2L with reagent water. This solution should be vacuum filtered through a 0.45um filter prior to use. This solution should be prepared fresh daily.
Simulated soil matrix	Teflon chips, glass beads, plastic beads or other suitable simulated soil matrix.

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification standards, second source verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	ICAL
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify the initial calibration on an ongoing basis.	CCV
Spiking Standard	This solution contains the target analyte and is used to spike MS/MSD sets.	Same solution can be used for both the LCS and MS/MSD.

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
IC Stock Calibration Standard	AccuStandard; catalog #IS-17854-250ML; 100/250/500ug/mL, or equivalent	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions. Refrigerate after opening.
IC Nitrite Stock Calibration Standard	AccuStandard, catalog #IC-NO2-N-10X-1; 1000ug/mL or equivalent	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions. Refrigerate after opening.
IC Intermediate Calibration Standards	See prep directions below in Section 10.2.3.1.	Expires 30 days from date of preparation.	Refrigerate
IC Working Calibration Standards	See prep directions below in Section 10.2.3.2.	Expires one week from date of preparation.	Refrigerate
IC Stock ICV Standard	Inorganic Ventures; catalog # HES-8-REV1; 50/125/250ug/mL, or equivalent.	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions. Refrigerate after opening.
IC Working ICV Standard	See prep directions below in Section 10.2.3.3.	Expires one week from date of preparation.	Refrigerate
IC Iodide Stock Calibration Standard	Environmental Express, catalog #IC-II-M; 1000ug/mL or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
IC Iodide Intermediate Calibration Standard	See prep directions below in Section 10.2.3.4	Expires six months from date of preparation.	Refrigerate
IC Iodide Working Calibration Standards	See prep directions below in Section 10.2.3.5	Expires six months from date of preparation.	Refrigerate
IC Iodide Stock ICV Standard	O2Si, catalog #062013-01-01; 1000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
IC Iodide Working ICV Standard	See prep directions below in Section 10.2.3.6	Expires six months from date of preparation.	Refrigerate

10.2.3. Standard Preparation Procedures

10.2.3.1. IC Intermediate Calibration Standard Preparation

Dilute 50mL of the IC Stock Calibration Standard (100/250/500ug/mL) and 5mL of the IC Nitrite Stock Calibration Standard (1000ug/mL) to 100mL with reagent water. Final concentration of anions:

Anion	Int. Std. Conc., ug/mL
Bromide	50
Chloride	125
Fluoride	50
Nitrate as N	50
Nitrite as N	50
Sulfate	250

10.2.3.2. IC Working Calibration Standards Preparation

Working Calibration Standards are prepared in reagent water from the IC Intermediate Calibration Standard (50/125/250ug/mL). Actual calibration concentrations may vary.

IC Working Calibration Standards (examples only)

Standard	IC Int. Cal. Std volume	Final Volume in reagent water
Calibration Std 0	0mL	100mL
Calibration Std 1	0.1mL	100mL
Calibration Std 2	0.4mL	100mL
Calibration Std 3 (CCV)	1mL	100mL
Calibration Std 4	2mL	100mL
Calibration Std 5	4mL	100mL
Calibration Std 6	10mL	100mL

Final concentrations in each working calibration standard as prepared above:

mg/L	CAL 0	CAL1	CAL2	CAL3	CAL4	CAL5	CAL6
Bromide	0	0.05	0.2	0.5	1.0	2.0	5.0
Chloride	0	0.125	0.5	1.25	2.5	5.0	12.5
Fluoride	0	0.05	0.2	0.5	1.0	2.0	5.0
Nitrate as N	0	0.05	0.2	0.5	1.0	2.0	5.0
Nitrite as N	0	0.05	0.2	0.5	1.0	2.0	5.0
Sulfate	0	0.25	1.0	2.5	5.0	10	25

10.2.3.3. IC Working ICV Standard Preparation

Dilute 0.1mL of the IC Stock ICV Standard (50/125/250ug/mL) to 10mL with reagent water. Final concentration of anions:

Anion	ICV Std. Conc., mg/L
Bromide	0.5
Chloride	1.25
Fluoride	0.5
Nitrate as N	0.5
Nitrite as N	0.5
Sulfate	2.5

10.2.3.4. IC Iodide Intermediate Calibration Standard Preparation

Dilute 10mL of the IC Iodide Stock Calibration Standard (1000ug/mL) to 100mL with reagent water for a final concentration of 100ug/mL.

10.2.3.5. IC Iodide Working Calibration Standards Preparation

Working Iodide Calibration Standards are prepared in reagent water from the IC Iodide Intermediate Calibration Standard (100ug/mL). Actual calibration concentrations may vary.

IC Iodide Working Calibration Standards (examples only)

Standard	Iodide Stock Standard volume	Final Volume in reagent water	Final Iodide Conc., mgL
Calibration Std 0	0mL	100mL	0
Calibration Std 1	0.5mL	100mL	0.5
Calibration Std 2 (CCV)	1.0mL	100mL	1
Calibration Std 3	5mL	100mL	5
Calibration Std 4	10mL	100mL	10
Calibration Std 5	25mL	100mL	25

10.2.3.6. IC Iodide Working ICV Standard

Dilute 0.05mL of the IC Iodide Stock ICV Standard (1000ug/mL) to 10mL with reagent water for a final concentration of 5mg/L.

11. Calibration and Standardization

11.1. Initial Calibration

11.1.1. Set up and warm up the ion chromatograph to establish a stable baseline per manufacturer's instructions.

11.1.2. For initial calibration, analyze a blank and a minimum of three concentrations of calibration standard for each analyte of interest. The lowest calibration standard must be at or below the required reporting limit. Analyze calibration standards in order of increasing concentration. Document the peak area response and retention time for each analyte. A new initial calibration must be performed every six months, at a minimum.

11.1.3. Using the manufacturer's data system software, establish the individual analyte calibration curves by plotting the peak area response against the corresponding concentrations. Use a least squares linear regression to calculate the calibration curve formula. A weighted least squares regression may also be performed using 1/concentration or $1/(\text{concentration})^2$ as the weighting factor. In either case, the correlation coefficient must be 0.995 or greater to be used for quantitation. In situations where the analyst knows the instrument response does not follow a linear model over a sufficiently wide working range, or when other approaches have not met the acceptance criteria, a non-linear or quadratic calibration model may be employed. In order to use a quadratic calibration for quantitation of sample results, a minimum of six calibration standards must be used and the coefficient of determination (COD) or r^2 must be greater than or equal to 0.99. Refer to Method 8000C for additional guidance on calibration procedures.

11.1.4. **Initial Calibration Corrective Action:** If the initial calibration curve does not meet the required criteria to be used for quantitative purposes, a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new calibration standards must also be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.1.5. Each day that analysis is performed, the calibration standard(s) should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Are the retention times consistent over the range of calibration for each compound? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably.

11.1.6. **Initial Calibration Verification (ICV)**: The initial calibration must be verified through the analysis of an Initial Calibration Verification (ICV) standard. The ICV is prepared from an independent source at or near the mid-range of the calibration curve and analyzed immediately following the initial calibration curve. Acceptable recovery range for the ICV is +/-10% of its true value or 90-110% recovery.

11.1.7. **ICV Corrective Action:** If the ICV fails the criteria, another ICV may be analyzed. If the second ICV fails, a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new calibration standards must also be considered. Samples associated with a failed ICV must be reanalyzed. **Exception:** If the ICV fails and is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.2. Calibration Verification

11.2.1. The initial calibration must be verified daily with the analysis of a Continuing Calibration Verification Standard (CCV) at or near mid-range concentration at the beginning of the analytical sequence, after every 10 samples, and at the end of the analytical sequence, as a minimum requirement. If a quadratic curve fit is used, the calibration must be verified at two concentration

levels using at the beginning, after every 10 samples and at the end of each sequence. Acceptable recovery range for the CCV is +/-10% of its true value or 90-110% recovery. The retention time for each analyte must not vary by more than +/-10% from its expected value.

11.2.2. CCV Corrective Action: If a CCV fails the acceptance criteria, check the instrument operating conditions, and if necessary, restore them to the original settings, and analyze another CCV. If the response still fails the acceptance criteria, then a new initial calibration must be prepared. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

12. Procedure

12.1. Set up and warm up the ion chromatography system to establish a stable baseline per manufacturer's instructions and equivalent to the conditions used for initial calibration. All samples must be analyzed at room temperature and the system must be calibrated and free of contamination before samples are analyzed.

12.2. Sample Preparation and Handling

12.2.1. Aqueous Samples

Filter any samples that contain particles larger than 0.45um using a syringe filter. Fill a labeled autosampler vial with a minimum of 1mL of sample. An initial rinse of the vial with sample is recommended. Screw on the septum cap and the sample is ready for analysis. If filtration is necessary, the associated Method Blank, LCS and MS/MSD (if associated with filtered sample) must also be filtered. **NOTE:** Samples that are received acid preserved for NO3+NO2 must be diluted prior to analysis due to the sulfate interference presented by the sulfuric acid preservative.

12.2.1.1.1. Aqueous Method Blank: consists of reagent water.

12.2.1.1.2. Aqueous LCS: Dilute 0.1mL of the IC Stock ICV Standard (50/125/250ug/mL) to 10mL with reagent water. Spike concentrations are the same as the Working ICV.

12.2.1.1.3. Aqueous MS: Dilute 0.1mL of the IC Stock ICV Standard (50/125/250ug/mL) to 10mL with sample. Spike concentrations are the same as Working ICV.

12.2.1.1.4. Aqueous Method Blank - Iodide: consists of reagent water.

12.2.1.1.5. Aqueous LCS - Iodide: Dilute 0.05mL of the IC Iodide Stock ICV Standard (1000ug/mL) to 10mL with reagent water for a final concentration of 5mg/L.

12.2.1.1.6. Aqueous MS - Iodide: Dilute 0.05mL of the IC Iodide Stock ICV Standard (1000ug/mL) to 10mL with sample for a final concentration of 5mg/L.

12.2.2. Soil Samples

Weigh 10 +/-0.5g of sample into a 120mL sample vial and add 100mL of reagent water. Agitate for 10 minutes then allow the slurry to settle. Fill a labeled autosampler vial with a minimum of 1mL of the supernatant. Filter all samples, the associated Method Blank, LCS and MS/MSD. An initial rinse of the autosampler vial with the filtrate is recommended. Screw on the septum cap and the sample is ready for analysis.

12.2.2.1.1. Soil Method Blank: place 10 +/-0.5g of simulated soil matrix and 100mL reagent water into a 120mL sample vial, secure the cap. Agitate for 10 minutes then allow the slurry to settle.

12.2.2.1.2. Soil LCS: place 10 +/-0.5g of simulated soil matrix, 1.0mL of the IC Stock ICV Standard (50/125/250ug/mL) and dilute to100mL with reagent water in a 120mL sample vial, secure the cap. Agitate for 10 minutes then allow the slurry to settle. Spike concentrations are the same as the Working ICV.

12.2.2.1.3. **Soil MS**: place 10 +/-0.5g of sample, 1.0mL of the IC Stock ICV Standard (50/125/250ug/mL) and dilute to100mL with reagent water in a 120mL sample vial, secure the cap. Agitate for 10 minutes then allow the slurry to settle. Spike concentrations are the same as the Working ICV. If filtration is necessary, Method Blank and LCS must also be filtered.

12.2.2.1.4. **Soil Method Blank - Iodide:** place 10 +/-0.5g of simulated soil matrix and 100mL reagent water into a 120mL sample vial, secure the cap. Agitate for 10 minutes then allow the slurry to settle.

12.2.2.1.5. **Soil LCS - Iodide**: place 10 +/-0.5g of simulated soil matrix, 0.5mL of the IC Iodide Stock ICV Standard (1000ug/mL) and dilute to100mL with reagent water in a 120mL sample vial, secure the cap. Agitate for 10 minutes then allow the slurry to settle. Spike concentration is 50mg/kg.

12.2.2.1.6. **Soil MS - Iodide**: place 10 +/-0.5g of sample, 0.5mL of the IC Iodide Stock ICV Standard (1000ug/mL) and dilute to100mL with reagent water in a 120mL sample vial, secure the cap. Agitate for 10 minutes then allow the slurry to settle. Spike concentration is 50mg/kg. If filtration is necessary to remove suspended particles, Method Blank and LCS must also be filtered.

12.3. Inject a suitable volume of sample or QC standard into the IC instrument per manufacturer's instructions. The volume of sample injected must be consistent with the volume used for initial calibration standards. Record the resulting analyte peak areas as well as the peak retention times. A typical run sequence may be as follows:

Instrument Blank
ICAL Standards
ICV
ICB
(If ICAL not run, CCV would replace the ICAL and the ICV in the sequence)
CCV
CCB
Method blank
LCS
Client samples
CCV
CCB
Client samples
CCV
CCB

12.4. Sample concentrations are calculated by comparing response data with the initial calibration. The width of the retention time window used to identify analytes in samples should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window for each analyte. The experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.5. If sample response exceeds the limits of the initial calibration range, dilute the sample with reagent water and reanalyze or the over range result must be qualified as estimated.

12.6. Refer to the Manual Integrations SOP for guidance on performing and documenting manual integrations

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples, per matrix.	**300.0:** Target analytes should be less than the MDL. **9056A:** Target analytes should be <10% of the reporting limit or <10% of the lowest sample conc., whichever is greater.	Reanalyze method blank. If method blank is still does not meet criteria, reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Target analytes	One per preparation batch of up to 20 samples, per matrix.	**300.0:** 90-110% recovery **9056A:** 80-120% recovery	Reanalyze LCS. If LCS is still does not meet criteria, reanalyze all associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified. 3) An associated matrix spike that passes LCS acceptance criteria can be used in place of a failing LCS.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Target analytes	**300.0:** One MS per a minimum of 10% of samples. **9056A:** One MS/MSD set per batch of up to 20 samples, per matrix.	80-120% recovery ≤15% RPD	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Sample Duplicate (DUP)	Sample	One duplicate sample analysis per batch if no MS/MSD performed	≤15% RPD	No corrective actions necessary. RPD outside acceptance criteria must be qualified appropriately.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

$$\text{Aqueous Sample (mg/L)} = (X_s)(D) \qquad \text{Solid Sample (mg/kg)} = \frac{(X_s)(V_f)(D)}{(W_s)}$$

Where: X_s = Concentration of the analyte in the sample from the curve in mg/L
D = Dilution factor of aqueous sample or solid extract
V_f = Final volume of solid extract in Liters
W_s = Weight of solid sample purged or extracted in kilograms

$$\text{Moisture corrected concentration} = \frac{\text{(Final concentration as received)}}{(100 - \%\text{Moisture})} \times 100$$

14.2. LCS equation:

$$\mathbf{R = (C/S) * 100}$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation:

$$\mathbf{R = \frac{(Cs - C)}{S} * 100}$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD equation:

$$\mathbf{RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100}$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. MDLs must be determined per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Method modified for the determination of Iodide.

19.2. Columns and chromatographic conditions may differ from those recommended and are based on instrument manufacturer's specifications.

19.3. Eluent is filtered through 0.45um filter disks instead of 0.2um filter disks.

19.4. Soil extraction procedure found in Method 300.0, revision 2.1, Section 11.7 is also used for Method 9056A. Shaker table or ultrasonic bath is used for agitation of soils instead of magnetic stir bars.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. Standards and Reagents

The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. The use of gloves, lab coats and safety glasses is required. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. Samples

Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment such as gloves**,** lab coats and safety glasses is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

23. Pollution Prevention and Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Methods 9056A and 8000C.

25.2. Environmental Protection Agency, USEPA Method 300.0, Revision 2.1, August 1993.

25.3. Pace Analytical Quality Manual; latest revision.

25.4. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-IN-O-170-rev.01	1. Table 9.3: added Iodide standards 2. Section 9.2.3: added preparation of Iodide standards. 3. Section 10.2.1: corrected CCV control limits to 90-110% recovery 4. Table 12.1: corrected LCS control limits for Method 300.0 to 90-110% recovery.	20Jul2015
S-IN-O-170-rev.02	1. Converted to 27-section format. 2. Table 7.1: revised storage temperature format and clarified holding time for Nitrate or Nitrite. 3. Section 10.1: updated filter used for eluent preparation. 4. Table 10.3: revised storage conditions. 5. Section 10.2.3: clarified preparation/final volume of batch QC for solids. 6. Section 14.1: corrected units in final concentration equations. 7. Section 25.4: added years 2003 and 2009 to TNI reference.	19Jul2017
S-IN-O-170-rev.03	1. Section 2.1: added analytical column. 2. Section 12.3: removed ICVA/CCVA and language about quadratic. 3. Table 13.1: updated acceptance criteria for method blank.	06Feb2018
ENV-SOP-IND1-0096-rev.01	1. Removed cover page, table of contents and headers for use in Master Control. 2. Table 7.1: added notes for aqueous storage and NO3+NO2 preservation. 3. Section 11.2.1: changed frequency of CCVs from every 10 determinations to every 10 samples. 4. Section 12.2: moved preparation of batch QC from Section 10.2.3 to Section 12.2 and added requirement to filter all soil extracts and associated QC. 5. Table 13.1: updated corrective action for MB and LCS to include reanalysis. 6. Section 18.1: updated reference for MDL procedure. 7. Section 25.4: added NELAC to reference.	17Jan2019

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Review: ENV-SOP-IND1-0004 00 Waste Handling and Management

Review

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	10 Feb 2019, 07:49:17 PM	Reviewed

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STANDARD OPERATING PROCEDURE

WASTE HANDLING AND MANAGEMENT

Reference Methods: N/A

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Supersedes:	S-IN-S-002-Rev.02
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APPROVALS

Laboratory General Manager — March 28, 2017 Date

Laboratory Quality Manager — March 24, 2017 Date

Laboratory Waste Coordinator — March 27, 2017 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

S-IN-W-002-Rev.03

Table of Contents

1. Purpose/Identification of Procedure

1.1. Pace Analytical Services (Pace) acknowledges its obligation to the responsible management of the environment and its resources. Pace senior management is committed to operating in such a way that meets or exceeds the state and federal laws governing waste management and encourages the use of best practices to reduce, reuse and recycle waste material where possible. This Standard Operating Procedure (SOP) documents the systems, processes and procedures that this location uses to manage generated wastes.

1.2. It is Pace's policy to minimize the amount of hazardous waste it produces and to reduce the hazardous properties of those wastes whenever practical within regulatory compliance. This can be achieved by periodic auditing of all processes producing hazardous waste; reduction of sample volume delivered by the client; return of excess sample material to clients whenever practical and economical; investigation of new technologies that might require smaller volumes of sample, or produce fewer or less hazardous by-products; implementation of lab cleaning procedures that reduce the volume of cleaning residue; recycling of hazardous materials; and investigation of new treatment technologies that are comprehensively destructive or are effective in reducing the volume or hazardous qualities of the wastes produced.

2. Summary of Method

2.1. Pace facilities that generate waste must initially contact the EPA to obtain an ID number. Each unique type of generated waste is classified and characterized into waste streams according to procedures in 40 CFR 261. The amount of waste the facility generates determines the Generator Status of a lab, which in turn determines how long and how much waste can accumulate. Pace is ultimately responsible for the waste it generates, and is required to obey any and all regulations during the process of creating, accumulating, disposing, and releasing waste to a TSDF for final disposal. Documentation is kept to prove all regulations have been obeyed.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel responsible for all aspects of waste handling and management.

3.2. This SOP is applicable to all processes that involve generated waste, and is designed to assist its operations in adhering to regulations set forth in the following federal statutes: Resource Conservation and Recovery Act (RCRA), Clean Water Act (CWA), Toxic Substances Control Act (TSCA), and DOT Title 49, and Transportation (parts 100-199). Particular attention is given to local pretreatment standards covering discharges to publicly owned treatment works (POTW) when performing elementary neutralization on acidic and basic waste. The local standards are based in part upon provisions in the National Pretreatment Standards and Prohibited Discharge Standards.

3.3. The degree to which RCRA regulations apply to Pace facilities is dependent upon the generator status of the operation. Under the federal rules (state requirements may be more stringent or give the classes a slightly different name) there are three different classes of hazardous waste generators based upon the amount of waste generated in a month to month time frame.

3.4. **Waste Generator Class Limits (federal categories, some locations may have different titles):**

Hazardous Waste Generator Class	Quantity of Hazardous Waste Generated per Month	Generated Monthly Acute Hazardous Waste	Maximum Allowable Hazardous Waste Quantity on-site	Maximum Permitted Waste Accumulation Time
Cond. Exempt Small Quantity	<100kg	<1 kg	<1000kg	Unlimited
Small Quantity	100-1000kg	<1 kg	<6000kg	180 days (270 days if the waste must be sent >200 miles to TSDF)
Large Quantity	>1000kg	>1kg	Unlimited	90 days

3.5. **Parameters**: Not applicable to this SOP.

4. Definitions

4.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

4.2. **Acutely Hazardous Waste** - A waste which is hazardous as identified with an (H) Hazard Code in the lists of Hazardous Waste in 40 CFR Part 261, Subpart D, Sections 261.30, 261.31 and 261.33.

4.3. **Animal and Plant Health Inspection Service (APHIS)** - an agency of the USDA responsible for protecting animal health, animal welfare, and plant health. APHIS is the lead agency for collaboration with other agencies to protect U.S. agriculture from invasive pests and diseases.

4.4. **Clean Air Act** - The Federal Clean Air Act, 42 U.S.C. 7401, and amendments thereto amending 42 U.S.C. 1857 et.seq.

4.5. **Conditionally Exempt Small Quantity Generator** - A generator who produces no more than 100 kilograms of hazardous waste or one kilogram of acutely hazardous waste (or a total of 100 kilograms of any residue or contaminated soil, waste or other debris resulting from the cleanup of a spill, into or on any land or water, or any acute hazardous waste) in a calendar month. The total amount of hazardous waste which may be accumulated on-site is 1000 kilograms.

4.6. **Confined Space** – A space that is large enough and so configured that an employee can bodily enter and perform assigned work; and has limited or restricted means for entry or exit (for example, tanks, vessels, silos, storage bins, hoppers, vaults, and pits are spaces that may have limited means of entry); and is not designed for continuous employee occupancy.

4.7. **Container** - Any device material is stored, transported, treated, disposed of, or otherwise handled.

4.8. **Contingency Plan** - A document setting out an organized, planned, and coordinated course of action to be followed in case of fire, explosion, or release of hazardous waste or hazardous waste constituents which could threaten human health or the environment.

4.9. **Designated Hazardous Waste Storage Area** - Area used to hold hazardous waste for a temporary period, at the end of which the hazardous waste is treated, disposed of, or stored elsewhere. This is the storage area into which hazardous waste from the laboratory (e.g., satellite waste) is moved.

4.10. **DOT** - The United States Department of Transportation.

4.11. **DTSC** – Department of Toxic Substances Control.

4.12. **Elementary Neutralization Unit** – A device which: (1) is used for neutralizing wastes which are hazardous only because they exhibit the corrosivity characteristic defined in 40 CFR 261.22 or are listed in Subpart D of Part 261; and (2) meets the definition of tank, container, transport vehicle, or vessel in 40 CFR 260.10.

4.13. **EPA** - The United States Environmental Protection Agency.

4.14. **EPA Hazardous Waste Number** - The EPA number assigned to each EPA hazardous waste identified in 40 CFR Part 260, Subpart D - Lists of Hazardous Wastes.

4.15. **EPA Identification Number** - The site-specific number assigned to each generator, transporter, and TSDF upon approval of a notification form.

4.16. **Federal Clean Water Act** - 33 U.S.C. 1251, et. Seq.

4.17. **Foreseeable Emergency** - Any fire, explosion, or sudden or non-sudden release of hazardous waste or hazardous waste constituents to the air, soil, or surface water, which could threaten human health or the environment.

4.18. **Generator** - Any person, by site who owns or operates a facility where hazardous waste is generated, i.e. Pace.

4.19. **Hazardous Waste Coordinator** - The Pace employee responsible for creating, guiding, and implementing all hazardous waste management operations.

4.20. **Hazardous Waste** - As defined in 40 CFR Part 261, Subparts B and C, a solid, semi-solid, liquid or contained gaseous waste, or any combination of these wastes.

4.20.1. Which, because of either quantity, concentration, physical, chemical, or infectious characteristics may:

4.20.2. Cause or contribute to an increase in mortality or an increase in irreversible or incapacitating reversible illness; or

4.20.3. Pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, disposed of or otherwise mismanaged.

4.20.4. Or which has been identified as having a characteristic of hazardous waste by the EPA using the criteria established under 40 CFR Part 261, Subpart C, or as listed under Sections 261.31, 261.32, 261.33, and 261.34. Such wastes include, but are not limited to, those which are reactive, toxic, corrosive, ignitable, irritants, strong sensitizers or which generate pressure through decomposition, heat or other means. Such wastes do not include radioactive substances that are regulated by the Atomic Energy Act of 1954, as amended. A waste is considered hazardous if it is listed or it fits into one of four categories. These categories are as follows:

4.20.4.1. Ignitable – (40 CFR 261.21, Waste Code D001) A flash point of less than 60^{o}C/140^{o}F.

4.20.4.2. Corrosive – (40 CFR 261.22, Waste Code D002) A pH of less than 2.0 or greater than 12.5.

4.20.4.3. Reactive – (40 CFR 261.23, Waste Code D003) Reactive wastes exhibit one or more of the following characteristics:

4.20.4.3.1. It is unstable and can undergo a violent change without detonating.

4.20.4.3.2. It can react violently with water.

4.20.4.3.3. When mixed with water it can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.

4.20.4.3.4. It is cyanide or sulfide bearing waste that, when exposed to pH conditions between 2.0 and 12.5, can generate gases, vapors, or fumes that can present a danger to human health or the environment.

4.20.4.3.5. It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

4.20.4.3.6. It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.

4.20.4.3.7. It is a forbidden explosive as defined in 49 CFR 173.51, or a Class A explosive as defined in 49 CFR 173.53, or a Class B explosive as defined in 49 CFR 173.88.

4.20.4.4. Toxic – (40 CFR 261.24, Waste Codes D004-D043) A solid waste that contains a toxic concentration of a contaminant listed in 40 CFR 261.24, Table 1. A toxic waste is given any and all D-codes that apply to the particular material.

4.21. **Hazardous Waste Constituent** - A substance, compound, or element listed as hazardous waste in EPA 40 CFR 261.

4.22. **Lab Pack Material** - A hazardous waste that does not match a listed Pace waste stream category.

4.23. **Large Quantity Generator (LQG)** - Any generator who generates at a rate greater than 1000 kilograms of hazardous waste per month.

4.24. **Manifest** - As defined in 40 CFR Part 262, Subpart B, namely "the form used for identifying the origin, quantity composition, routing and destination of hazardous waste".

4.25. **Plant Protection and Quarantine (PPQ)** – A program within APHIS which attempts to safeguard agriculture and natural resources in the U.S. against the entry, establishment, and spread of animal and plant pests and noxious weeds.

4.26. **Regulated Soil** – Soil from foreign countries, U.S. territories and areas within states that are under Federal quarantine that can be moved into or through continental U.S. only if conditions and safeguards prescribed by the USDA and APHIS are met.

4.27. **Sample** - Except as provided below in 4.27.2.2.3, any solid waste, water, soil, or air that is collected for the sole purpose of being tested to determine its characteristics or composition.

4.27.1. Samples are not subject to any requirements of 40 CFR Part 261.5 or Parts 262 through 267 or Part 270 or Part 124 or to the notification requirements of Section 3010 of RCRA, when:

4.27.1.1. The sample is being transported to a laboratory for the purpose of testing; or

4.27.1.2. The sample is being transported back to the sample collector after testing; or

4.27.1.3. The sample is being stored by the sample collector before transport to a laboratory for testing; or

4.27.1.4. The sample is being stored in a laboratory before testing; or

4.27.1.5. The sample is being stored in a laboratory after testing but before it is returned to the sample collector; or

4.27.1.6. The sample is being stored temporarily in the laboratory after testing for a specific purpose (for example, until conclusion of a court case or enforcement action where further testing of the sample may be necessary).

4.27.2. In order to qualify for the exemption in 4.27.1.1 and 4.27.1.2 above, a sample collector shipping samples to a laboratory and a laboratory returning samples to a sample collector must:

4.27.2.1. Comply with U.S. Department of Transportation (DOT), U.S. Postal Service (USPS), or any other applicable shipping requirements; or

4.27.2.2. Comply with the following requirements if the sample collector determines that DOT, USPS, or other shipping requirements do not apply to the shipment of the sample:

4.27.2.2.1. Assure that the following information accompanies the sample:

4.27.2.2.1.1. The sample collector's name, mailing address, and phone number;

4.27.2.2.1.2. The laboratory's name, mailing address, and phone number;

4.27.2.2.1.3. The quantity of the sample;

4.27.2.2.1.4. The date of shipment; and

4.27.2.2.1.5. A description of the sample.

4.27.2.2.2. Package the sample so that it does not leak, spill, or vaporize from its packaging.

4.27.2.2.3. This exemption does not apply if the laboratory determines that the waste is hazardous but the laboratory is no longer meeting any of the conditions stated in 4.27.1 above.

4.28. **Satellite Waste or Laboratory Satellite Waste** - Hazardous waste generated by Pace that is at or near any point of generation and under the control of the operator. Satellite accumulation provisions allow generators to accumulate up to 55 gallons of hazardous waste (or 1 quart of acute hazardous waste) in containers without starting the storage clock as described in Section 3.4.

4.29. **Satellite Waste Container** - Any portable device used to accumulate laboratory generated waste prior to transfer to the hazardous waste storage area.

4.30. **Small Quantity Generator(SQG)** - A generator who produces no more than 1000 kilograms of hazardous waste (or a total of 1000 kilograms of any residue or contaminated soil, waste or other debris resulting from the cleanup of a spill, into or on any land or water, or any acute hazardous waste) in a calendar month. The total amount of hazardous waste which may be accumulated on-site is 6000 kilograms.

4.31. **TSDF** - A Treatment/Storage/Disposal Facility.

4.32. **Universal Waste** – Commonly used items that are hazardous but can be recycled. These include fluorescent lights, computer monitors, etc.

4.33. **Waste Stream** - The generic profile of chemical and physical properties that satellite wastes exhibit.

5. Procedure

5.1. All Pace facilities that generate hazardous waste must have a Generator's US EPA Identification Number. The ID number is obtained through the applicable EPA region's office by completing EPA form 8700-12, and must be completed before generating any hazardous waste.

5.1.1. Pace only utilizes transporters and treatment, storage, or disposal facilities (TSDFs) that have EPA identification numbers for hazardous waste handling and meet the TSDF transfer requirements.

5.1.2. A new ID number is necessary when changing locations as the number is tied to the facility address.

5.1.3. This facility's US EPA Identification Number is IND984874206.

5.2. The laboratory generates wastes originating from several source types: materials and chemicals used to prepare and analyze samples (e.g., solvents, acids), unconsumed liquid and solid samples, certain types of batteries, mercury from lamps and broken thermometers and automobile waste. Unconsumed samples may include laboratory-contaminated sample residue (both liquid and soil) generated as part of digestion, extraction, etc., procedures used to prepare samples for analysis.

5.2.1. Based on table 3.4, this facility is classified as a Small Quantity Generator.

5.3. Hazardous waste classification is the most critical step in establishing an effective, compliant waste-handling program. Laboratory wastes are classified using the criteria set forth under RCRA for ascertaining non-hazardous versus hazardous status, and this criterion is listed in the definition of hazardous waste in 4.20.

5.4. The following are the waste streams resulting from materials and chemicals used in the laboratory operation. Applicable information for each is given pertaining to packing, labeling, or listing on a manifest. A description of how the wastes are created, and the preferred method of final disposal for each, is included. The overriding principle in hazardous waste classification is application of a conservative formula based on all known or suspected hazards related to a waste material. While this formula may result in some materials being disposed as hazardous when in fact, they are non-hazardous (e.g., false positive), the formula will not be compromised in the interest of reducing the amount of waste produced. This will minimize any risk of a material being disposed of erroneously as non-hazardous when it, by definition, is a hazardous waste.

5.4.1. **Corrosive waste** is generated in the majority of the departments in the laboratory. This waste stream consists primarily of spent or excess aqueous reagent solutions generated from preservatives, acid digestions of metals, impinger solutions or other corrosive solutions generated in the course of analysis. The predominant corrosives include hydrochloric acid, nitric acid and sulfuric acid, but corrosives also include bases. Varying concentrations of metals may be present dependent upon the composition of the reagents added. This waste stream only has the hazardous quality of being corrosive; therefore, if a waste has any additional hazardous waste quality (e.g., Toxic or Ignitable) it cannot be mixed with this stream. This stream is most commonly treated onsite.

Corrosive Waste	
DOT Shipping Name	RQ Waste, Corrosive Liquid, N.O.S (i.e. corrosive material)
EPA Waste #	D002
Container	LIST CONTAINER
Average pH	<2.0,>12.5
Disposal Method	Treatment by Neutralization onsite
Label	Corrosive

5.4.2. The **Chlorinated Waste Stream** consists primarily of methylene chloride with a very small amount of other organic solvents derived from extraction procedures performed on samples and from rinsing glassware. As a best practice, effort is made to have this waste stream as pure as possible in order to offer for recycling.

Chlorinated Solvents	
DOT Shipping Name	RQ Hazardous Waste, Toxic Liquid, N.O.S (i.e. dichloromethane, acetone, methanol)
EPA Hazard Codes	U080, F001/F002
Container	55 gallon drum
Average pH	7.0
Disposal Method	Removed by licensed waste handler
Label	Toxic, Chlorinated

5.4.3. **COD Waste** is specific waste that results from COD analysis. This waste comes from used and expired COD vials of samples and reagent. This stream has sulfuric acid, mercuric sulfate, potassium dichromate, and silver sulfate.

COD Waste	
DOT Shipping Name	NAME
EPA Waste #	D002, D007, D009, D011
Container	COD vial box
Average pH	<2
Disposal Method	Lab-packed by licensed waste handler
Label	Corrosive, Toxic

5.4.4. **PCB Waste** is specific waste that results from PCB analysis. This waste is generated from the preparation of standard solutions used for PCB analysis and may include pipets, vials and other disposable glassware that is contaminated with PCBs. Environmental samples containing 50ppm or more of PCBs are included in this waste stream for disposal by incineration.

PCB Waste	
DOT Shipping Name	UN3432, Polychlorinated Biphenyls
EPA Waste #	N/A
Container	55 gallon drum
Average pH	N/A
Disposal Method	Incineration by licensed waste handler
Label	PCB Waste

5.4.5. **Methanol Waste** is specific waste that results from the analysis of soils for VOCs. This waste comes from soil samples that are preserved in the vial with methanol and the waste stream will include glass vials with plastic lids along with the soil and methanol.

Methanol Waste	
DOT Shipping Name	UN1230, Waste Methanol
EPA Waste #	F003
Container	55 gallon drum
Average pH	N/A
Disposal Method	Removed by licensed waste handler
Label	Methanol Waste

5.4.6. **Miscellaneous Lab Waste** is generated as a result of expired reagents and chemicals, and hazardous samples that cannot be included in another waste stream. This would include waste such as heavy metals waste, solid and aqueous flammable waste, toxic waste and oils. This waste is lab-packed for disposal by a licensed waste handler.

5.5. Some waste can become complicated when attempting to classify as non-hazardous or hazardous due to the list of hazardous constituents contained in sections 40 CFR 261.30-261.35 including a majority of analytes of interest routinely analyzed in Pace laboratories. Definitions have been established for each of the F, K. P, and U lists covering hazardous waste originating from non-specific sources, specific sources and discarded commercial chemical products, off-specification species, container residues, and spill residues. The application of listed hazardous wastes and substances is intended for manufacturing processes involving pure products, by-products, wastes generated as part of the production process and cleanup of materials contaminated from a spill of the listed commercial chemical product or manufacturing chemical intermediate. See Attachment I for common F-listed wastes.

5.5.1. Hazardous waste classification of unconsumed samples by listed hazardous waste criteria is not commonly applied in laboratory operations. Examples of sample types which would be identified as listed hazardous wastes include the following:

5.5.1.1. Samples containing 5% or more (by volume) of halogenated and non-halogenated "spent solvents:" (e.g., drum sample with > 10% TCE);

5.5.1.2. Pure product and two phase solution samples containing a listed chemical product or manufacturing intermediate (e.g., drum sample);

5.5.1.3. Samples from specific sources listed in section 261.32 (e.g., bottom sediment sludge from the treatment of wastewaters from wood-preserving processes that use creosote and/or pentachlorophenol - K001);

5.5.1.4. Samples representing any residue or contaminated soil, water or other debris resulting from the cleanup of a spill into or on any land or water of any commercial chemical product or manufacturing chemical intermediate having a generic name listed in section 261.33, or any residue or contaminated soil, water or other debris resulting from the cleanup of a spill, into or on any land or water, of any off-specification chemical product and manufacturing chemical intermediate which, if it met specifications, would have the generic name listed in section 261.33.

5.5.2. For the wastes listed in 5.5.1.1 and 5.5.1.2, disposal can be achieved by individually lab packing them or combining with other compatible hazardous wastes.

5.5.3. The remaining two sample types in 5.5.1.3 and 5.5.1.4 would also require lab packing for disposal. However, it is important to note that in order for the laboratory to ascertain that the samples were derived from a specific listed source or from a spill of a listed chemical, they must be so informed by the industrial concern or lead agency (e.g., EPA, state regulators) submitting the sample for analysis. If a water or soil sample contains a listed hazardous waste substance whose origin is unknown or uncertain to the lead agency, then that sample is not classified as a listed hazardous waste. Rather in this case, determination of a hazardous waste classification can only be obtained by the waste exhibiting a characteristic of hazardous waste (e.g., hazardous contaminants, ignitability, corrosivity, reactivity).

5.5.4. Due to the fact that the majority of samples analyzed by Pace do not meet the well-defined criteria for identifying "listed" hazardous waste, disposal classification of unconsumed samples will be based upon characteristics of hazardous waste:

5.5.4.1. Non-Hazardous - Analysis results indicate an absence of contaminants; unless contaminants listed under the hazardous disposal categories are parts of the requested sample analysis.

5.5.4.2. Hazardous – Analysis results indicate presence of contaminants (Attachment III) or sample analysis requires hazardous materials and contaminants. Samples in this category are segregated from others and disposed of as hazardous according to laboratory procedures.

5.5.4.3. PCB Waste - Generated exclusively by samples contaminated with greater than trace levels of polychlorinated biphenyls ($\geq$ 50ppm). Samples containing 50ppm (total) or higher of PCBs must be segregated and disposed of as PCB waste.

5.5.4.4. Waste Oil/Paint - Samples which are predominantly of an oil matrix (e.g., highly viscous organic liquid) or paint (solvent and pigment blend) are segregated and disposed in a separate container. Though these samples are defined as nonhazardous, oil samples are a special case and never disposed as nonhazardous. Note: Bottle caps and liners do not typically contain sample residuals and can be disposed of directly through the non-hazardous building refuse.

5.5.5. USDA-APHIS-PPQ Regulated Soils (Regulated Soils) are a special case of sample strictly controlled under quarantine regulations 7 CFR 330 because they can readily provide a pathway for a variety of dangerous organisms throughout the United States. The movement of soil into the United States from foreign sources and from certain regulated areas within the continental U.S. is restricted unless permitted by APHIS under specific conditions and safeguards.

5.5.5.1. Any laboratory that handles Regulated Soils must have an approved Compliance Agreement from USDA-APHIS-PPQ, and labs that handle foreign soils must have an approved Permit to Receive Soil. See updated revision of *USDA Regulated Soil Handling and Disposal S-IN-C-007*for information regarding the handling of these materials.

5.5.6. Though Pace is obligated to ensure nonhazardous discharge complies with requirements set by applicable publicly owned treatment works (POTW) and local regulations, Pace is not obligated to run every available analysis on every sample for proper waste classification. Consequently, samples are characterized according to the preservatives added, the requested analytical testing data, and any knowledge of the sample provided by the client. When sample analysis is canceled/not completed, those untested samples are characterized by the preservatives added and any knowledge of the sample that is obtained by the client.

5.6. Consolidation of wastes from the laboratory proceeds via two distinct routes covering either laboratory-generated hazardous wastes or excess unconsumed samples.

5.6.1. Laboratory Accumulation and Satellite Waste Containers

5.6.1.1. Waste materials from routine lab procedures are collected in containers of appropriate construction, placed in convenient locations at the point of generation. Under RCRA guidelines, these are defined as satellite containers.

5.6.1.2. The amount of hazardous waste stored in the laboratory at the individual satellite areas cannot exceed 55 gallons (liquid) or 550 lbs (solid) per waste stream, for non-acute hazardous waste.

5.6.1.3. Satellite waste containers must be labeled in accordance with all regulations, including:

5.6.1.3.1. Designation of the contents to be hazardous waste with the words “Hazardous Waste” clearly legible.

5.6.1.3.2. The waste stream description (e.g., acid waste).

5.6.1.3.3. A hazard label (e.g., corrosive).

5.6.1.4. The satellite containers must be maintained such that evolution of chemical vapors is precluded. This requires that the container be closed at all times, except when adding or emptying hazardous waste to and from the container.

5.6.1.5. The most critical point in the waste handling system is when a person (e.g., analyst, technician) places a waste material into a satellite container. Here, the characteristics or listing of the waste and the waste stream must both be known to match. For this reason, only material from approved procedures should be placed in the compatible satellite containers. All materials from experimental procedures, unknown or out of the ordinary sources, or from spill cleanups must be characterized and described to the Hazardous Waste Coordinator, who determines the proper method of disposal.

5.6.1.6. Full satellite containers must be transferred to the proper accumulation drum within 3 calendar days. Lab collection containers must not be filled to the top of the opening. Space must be left to prevent splashing of hazardous material when containers are emptied and to allow for expansion and contraction within the drum during transport.

5.6.1.7. Satellite containers for liquid hazardous waste must have secondary containment made of material that could successfully contain the entire satellite container's contents.

5.7. Transferring Satellite Waste to the Waste Storage/Accumulation Area

5.7.1. All transfers of satellite waste to waste drums must be made by the Hazardous Waste Coordinator or designated, trained personnel. When a satellite waste container is full, the Hazardous Waste Coordinator, or designee must be notified. Regular disposal events may be scheduled to dispose satellite waste on a continuous basis.

5.7.2. Find the correct waste drum by referring to the Hazardous Waste placard and hazard label. Mixing solvents that are not compatible could result in a hazardous reaction.

5.7.3. Ensure there is enough capacity in the drum to hold all the content that will be dispensed.

5.7.4. Check to make sure there is a ground connection before opening a solvent waste drum.

5.7.5. Open and slowly pour the contents of the satellite container into the proper waste drum using an appropriate solvent resistant funnel.

5.7.6. Replace the cap on the bunghole and carefully screw the cap on but do not tighten the cap.

5.8. Disposal of Unconsumed Hazardous Samples

5.8.1. Client samples are stored on-site for a defined period of time after the final analytical report is generated and prior to sample disposal. The purpose of sample storage is to provide the client time to review the analytical report and determine if the samples require additional testing or need to be returned to the client. Samples are not considered a waste during this time according to 40 CFR 261.4(d)(1)(vi).

5.8.1.1. During sample storage, the process and sample status must be obvious to employees, customers and auditors. This transparency is imperative to ensure samples are considered active test specimens to be retained until they are categorized as a waste for disposal.

5.8.1.2. Samples which cannot be returned to the client for disposal are characterized according to section 5.4. Samples are characterized by one of three methods:

5.8.1.2.1. Analytical results are evaluated against characterization criteria established for the sample waste stream. The samples which exhibit waste characteristics as previously outlined are segregated and denoted per laboratory/facility policies. A LabTrack ticket is created and then forwarded to the Hazardous Waste Coordinator, who in turn uses the information to coordinate removal of unconsumed samples from active sample storage by the receiving staff.

5.8.1.2.2. The Hazardous Waste Coordinator prints the LabTrack ticket and assigns a client services technician in receiving the task of labeling the sample containers. The number, type and storage locations for the containers are determined form Epic Pro or the COC. An orange dot sticker indicating the hazard (e.g. Lead) is affixed to the top of each container. Non-aqueous liquid samples that are not determined to be hazardous are labeled as Oil/Liquid Non-Hazardous.

5.8.1.2.3. When sample storage areas and/or walk-in coolers are cleared of samples ready for disposal, any samples with orange dot stickers or Oil/Liquid Non-Hazardous labels are placed on a shelf in the disposal area intended for lab-packing. Lab-pack is performed periodically throughout each year by a licensed waste handler.

5.8.1.2.4. PCB and USDA regulated soils are segregated on shelves in the disposal area. The samples are then moved to the PCB hazard drum located in the organic prep lab after they have been retained for greater than 45 days.

5.9. Disposal of Unconsumed Non-Hazardous Samples

5.9.1. Non-hazardous soil/solid samples are placed into the trash compactor destined for incineration.

5.10. Elementary Neutralization

5.10.1. Dilute corrosive solutions (e.g., preserved metals samples) which do not exhibit any hazardous characteristics other than being corrosive, may be neutralized. Elementary neutralization is exempt from RCRA permitting requirements for on-site hazardous waste treatment. While exempt under RCRA guidelines, before utilizing this practice to reduce off-site treatment or disposal of wastes, local pretreatment and discharge standards must be met for publicly owned treatment works (POTW).

5.10.2. The discharges listed below are prohibited under the National Pretreatment Standards and Prohibited Discharge Standards:

5.10.2.1. Pollutants causing fire or explosion (waste with a flashpoint < 60^{o}C);

5.10.2.2. Corrosive wastes with pH less than 2 or greater than 12.5;

5.10.2.3. Solid or viscous pollutants that could potentially block the system;

5.10.2.4. Oxygen-demanding pollutants;

5.10.2.5. Wastes which generate toxic gases.

5.10.3. Dilute corrosive/acidic samples are neutralized in the following procedure:

5.10.3.1. Aqueous samples in glass containers are passed through the glass crusher. The water is pumped from the drum to a neutralization tank/vessel. Refer to Section 6.3 for instructions in the operation of waste disposal equipment.

5.10.3.2. Aqueous samples in plastic containers are poured from the container into a neutralization tank/vessel.

5.10.3.3. As needed, Sodium Hydroxide solution is added to adjust pH to between 6 and 8.

5.10.3.4. Ensure the pH is in the proper range using a pH strip and open the discharge valve from the neutralization tank/vessel and allow neutralized liquid to flow down the drain while flushing with clean water.

5.10.4. Dilute caustic/basic samples are neutralized in the following procedure:

5.10.4.1. Aqueous samples in plastic containers are poured from the container into a neutralization tank/vessel.

5.10.4.2. As needed, Hydrochloric Acid solution is added to adjust pH to between 6 and 8.

5.10.4.3. Ensure the pH is in the proper range using a pH strip and open the discharge valve from the neutralization tank/vessel and allow neutralized liquid to flow down the drain while flushing with clean water.

5.11. Waste Storage Container Requirements

5.11.1. Drums in the hazardous waste storage area are labeled consistent with both DOT and EPA regulations concerning hazardous materials and wastes (see Attachment IV for example of label).

5.11.2. Closure instructions must be available for all containers used to transport hazardous materials. If a container in the accumulation area is the same one the waste will be shipped away in, the Waste Coordinator must obtain the closure instructions from the provider of the containers.

5.11.3. Labels must be easily visible and legible (e.g., a drum must not be labeled and then placed in such a way that the label cannot be seen).

5.11.4. The Accumulation Start Date must be recorded on the drum. The date should reflect the first time waste was added to the drum and not the date when the waste was generated in the laboratory.

5.11.4.1. Once a waste is removed from the point of generation to a hazardous waste staging area, the clock is started for storage time prior to disposal.

5.11.4.2. Drums must be picked up by TSDF for disposal before accumulation time exceeds RCRA requirement for lab's generator status (see section 3.4).

5.11.5. The hazardous waste staging room must be arranged in such a fashion to assure direct access pathways in the event of foreseeable emergency and for safe waste transfer. A minimum aisle space of three feet must be maintained at all times to access hazardous waste containers.

5.11.6. All hazardous waste drums and containers must be securely closed when not in use. All volatile and flammable hazardous waste liquid containers must be securely grounded at all times. Drums containing these liquids should also be manipulated with non-sparking tools and fitted with a drum venting bung, to assure that excess pressure build-ups are safely released.

5.11.7. All liquid waste stream containers must be provided with secondary containment devices. Such containment devices must be made of materials compatible with each waste, and they must be free of leaks. The waste storage room may act as secondary containment as long as the room has been constructed to safely and effectively contain a hazardous waste spill.

5.11.7.1. Secondary containers must exceed the total volume of the largest container stored in each containment device for indoor storage.

5.11.8. Compatibility of wastes must be considered in arranging storage areas. For example, acid waste should never be stored adjacent to basic waste, particularly cyanide wastes. Further examples are outlined in 40 CFR 264, Appendix V.

5.11.9. The hazardous waste staging area is controlled so unauthorized personnel are not able to access the room or contents.

5.11.10. The maximum volume of acutely hazardous waste (e.g., P-listed wastes) that can be accumulated in the laboratory is one quart. The volumetric measurement of one quart is based upon container size in which the waste is stored and not the actual amount (volume) of waste present. An example of how this one quart limit can inadvertently be exceeded involves the disposal of a neat standard of 2,4-dinitrophenol into a one gallon bottle. While the neat standard itself may only constitute 1-2mL, the volume as defined under RCRA would be one gallon, thus the laboratory would be out of compliance.

5.12. Waste Documentation and Reporting

5.12.1. All drums containing hazardous waste are recorded in a database. The information contained in this database is useful when filling out EPA biennial reports and for retaining an accurate description of how much waste has been accumulated. The following information is entered into the logbook/database;

5.12.1.1. The drum number or waste stream identification;

5.12.1.2. The drum capacity (e.g., 55-gallon, etc.);

5.12.1.3. The manifest number associated with the drum's disposal.

5.12.2. The following hazardous waste records must be maintained for a minimum of five years:

5.12.2.1. Drum tracking logs;

5.12.2.2. Sample Reports;

5.12.2.3. Sample disposal information and waste records on computer disc;

5.12.2.4. Analytical records relating to sample waste stream profiling and characterization;

5.12.2.5. Labpack inventory logs;

5.12.2.6. Biennial Reports, Exception Reports, or other reports filed for compliance reasons;

5.12.2.7. Records related to unresolved enforcement action must be retained indefinitely until such a time that the matter is resolved;

5.12.2.8. Facility Certificates of Destruction or Recycling.

5.12.3. A Waste Manifest is the documentation form that must accompany all shipments of hazardous waste while in transit.

5.12.3.1. The manifest for hazardous waste must be signed and dated by a DOT-trained Pace employee responsible for the shipment and by the transporter. The transporter will leavea "two-signature page" copy of the manifest.

5.12.3.2. Within 35 days you will receive a three-signature page (generator, transporter, facility) showing the waste reached its intended destination. Alternatively, the three-signature page will be made available by the waste disposal company through the online account.

5.12.3.3. All manifests must be kept for a minimum of three years.

5.12.4. The central accumulation staging room must have a documented inspection weekly and satellite waste containers must have documented inspection as part of the monthly laboratory inspection. The inspections should ensure all regulations are obeyed.

5.12.4.1. A record of the inspections must be kept in an inspection log or summary.

5.12.4.2. Records must be maintained for at least three years from the date of inspection. At a minimum, the records must indicate:

5.12.4.2.1. The date and time of the inspection;

5.12.4.2.2. The name and signature of the inspector (typically will be Hazardous Waste Coordinator);

5.12.4.2.3. A notation of the observations made (can be in a check-off format, e.g., fire extinguisher: charged _X_ requires recharging __);

5.12.4.2.4. The date and nature of any repairs or other remedial actions.

5.12.5. Annual Generation Reports are required to be filed with the State of Indiana.

6. Training, Expectations, and Supplemental Information

6.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

6.2. **Equipment and Supplies -** The following equipment is mandatory under RCRA guidelines unless otherwise denoted. Periodic review (not to exceed monthly) of availability of equipment and supplies below should be conducted to maintain an adequate and viable supply.

6.2.1. **Chemical Spill Control Neutralizers**: The waste room stores three types of bulk dry spill neutralizers: solvent, acid and base. They may be utilized by placing the dry neutralizer onto a liquid chemical spill. Neutralization is indicated by a prevalent color change.

6.2.2. **Communication Device**: Required for emergency notification of spill, fire, etc.

6.2.3. **Drums**: Common types of waste drums used for storing and shipping hazardous wastes are polyethylene, steel-polyethylene lined, and steel. Sizes are typically 5gal, 15gal, 30gal, and 55gal. Drums used for liquids typically are closed top with an opening to pour the solvent through a funnel, while drums used for solids or lab packs are open-top. The UN rating for all containers must be suitable if the waste is to be transported under DOT regulations.

6.2.4. **Emergency Drench Shower**: Shower should deliver water approximately twenty gallons per minute with a non-interruptible flow. It may be turned on by pulling the shower handle down. It may be turned off by pushing the handle back to the 'off' position.

6.2.5. **Emergency Lighting** (as needed): The waste room is outfitted with emergency lighting that goes on if power fails.

6.2.6. **Exit Signs** (as needed): Exit signs are provided on all waste room doors. These signs are self-illuminating.

6.2.7. **Fire Alarm Pull Station/Evacuation Alarm**: A fire alarm pull station must be in close proximity to the hazardous waste room. The alarm may be activated by pulling the switch. Other alarm systems may be utilized as long as all personnel are trained on the procedures and the process can effectively notify facility employees of an emergency.

6.2.8. **Fire Extinguisher**: An extinguisher with a rating appropriate to the waste being stored in the area must be in close proximity to the hazardous waste room.

6.2.9. **Labels**: A multitude of labels are provided to ensure compliant labeling. They may be purchased or prepared manually.

6.2.10. **Liquid Chemical Neutralizers**: Liquid chemical neutralizers (base and acid) may be used to neutralize a contained hazardous liquid. This may be done by slowly adding the neutralizer to the liquid.

6.2.11. **Spill Control Pads**: Spill pads are used to soak up hazardous liquids. They do not neutralize spills. They are especially effective for cleaning up oily materials. Various pads are available for aqueous and petroleum based liquids.

6.2.12. **Spill Control Pillows**: Spill pillows may be used to soak up large amounts of liquid chemical spills. No neutralization occurs.

6.2.13. **Spill Dikes**: vary depending on the size and type of room: Their purpose is to encircle a spill, barring the spread of a hazardous chemical. They will also absorb liquids, but do not neutralize spills.

6.3. Operation of Waste Disposal Equipment

6.3.1. Specific Safety Warnings

6.3.1.1. **Failure to connect the proper voltages to the equipment may result in personal injury or equipment damage.**

6.3.1.2. **Failure to follow installation instructions may result in personal injury or equipment damage.**

6.3.1.3. **Do not place solid foreign articles such as wood or metal into the glass crusher as they could cause it to malfunction.**

6.3.1.4. **Eye protection and hearing protection must be worn at all times when operating waste disposal equipment.**

6.3.1.5. **Never wear loose fitting clothing, such as neckties, necklaces or scarves when operating waste disposal equipment. Gloves should be worn at all times when operating waste disposal equipment.**

6.3.1.6. **Always keep work area clean. Spills and/or debris on the floor may cause someone to fall against equipment causing personal injury or equipment damage.**

6.3.2. Glass Crusher Operation

6.3.2.1. When placing the glass crusher onto the 55-gallon drum, make sure the drum is stable and level. The drum should be free of defects or holes to insure proper fitting of the crusher. The area chosen for the location of the crusher must allow for airflow around the equipment as well as clearance for the feeding of containers into the machine.

6.3.2.2. The crusher is located in the waste disposal area under a ventilation hood.The unit requires a 115 volt AC receptacle. No lubrication of the equipment is required.

6.3.2.3. The chamber of the glass crusher can be cleaned with water and soap but care must be taken not to put water directly on the electrical controls and the machine should be unplugged before cleaning.

6.3.2.4. To operate, attach the crusher to the drum and plug in the cord. Turn on the motor's power switch and feed waste material into the feeder. If rubber flaps become worn or torn, they should be replaced.

6.3.3. **Trash Compactor Operation**

6.3.3.1. **NOTE: Always stay clear of all moving parts of the compactor.**

6.3.3.2. Carefully raise the overhead door.

6.3.3.3. Open the safety gate and carefully place waste into the receiving compartment of the compactor. Lighter waste items can be added over the top of the safety gate without opening it.

6.3.3.4. Do not overfill the receiving compartment.

6.3.3.5. Ensure that the safety gate is closed and securely latched prior to activating the compactor ram.

6.3.3.6. Press the green Start button to activate the compactor. The unit will make one complete cycle and then stop. Repeat the cycle if necessary.

6.3.3.7. Press the red Stop button to stop the compactor ram in mid-cycle. Press the black Reverse button to reverse the ram.

6.3.3.8. Close the overhead door when compactor is not in use.

6.3.3.9. Contact Republic Services for container removal/disposal when the compactor pressure gauge reads 1100-1300 psi.

6.4. **Attachments**

6.4.1. Attachment I: RCRA Requirements for Labs as a Function of Generator Status.

6.4.2. Attachment II: Hazard Codes for Common F-List Wastes (solvents).

6.4.3. Attachment III: TCLP Contaminant List with Concentration Limits.

6.4.4. Attachment IV: Hazardous Waste Label for Accumulation Drum (example).

6.4.5. Attachment V: Satellite Container Inspection Form (example).

6.4.6. Attachment VI: Waste Accumulation Room Inspection Form (example).

7. References

7.1. Pace Chemical Hygiene/Safety Manual-most current version.

7.2. Pace Quality Assurance Manual- most current version.

7.3. National Environmental Laboratory Accreditation Conference (NELAC) Standard- most current version.

7.4. The NELAC Institute (TNI) Standard- most current version applicable to each lab.

7.5. Department of Defense (DoD) Quality Systems Manual- most current version.

8. Revisions

Document Number	Reason for Change	Date
S-IN-S-002-rev.01	1. Section 8: added sharps containers and pH strips. 2. Section 9: added acid and base for neutralization 3. Section 11: added PCB, non-biohazardous sharps, and miscellaneous lab waste streams. Added neutralization procedure for dilute caustic samples. Added instructions for the operation of waste disposal equipment.	11Jul2011
S-IN-S-002-rev.02	1. Converted to Corporate SOT format. 2. Cover page: added lab header, revised effective date format and revised document control format. 3. Section 9: added dust masks, hearing protection and sharps container. 4. Section 12: added waste stream information for Methanol Water 5. Section 26: removed manifest cover sheet for local version of SOP.	01Jan2016
S-IN-W-002-rev.03	1. Adapted from SOT-ALL-W-002-rev.07. 2. Section 5.1.3: added lab's EPA ID number. 3. Section 5.2.1: added lab's status as a SQG. 4. Section 5.4: added waste stream info for PCBs, Methanol and Miscellaneous. 5. Section 5.8.1.2: added lab's process for identifying hazardous samples. 6. Section 5.9: added lab's process for disposal of non-hazardous solids. 7. Section 5.10.3: described lab's process for neutralizing acidic waste. 8. Section 5.10.4: described lab's process for neutralizing basic waste. 9. Section 5.12.3.2.: added alternative to receiving 3-signature page by mail. 10. Section 6.3: added section to describe operation of waste disposal equipment. 11. Section 6.4: removed Hazardous Waste Manifest Cover Sheet.	23Mar2017

Attachment I: RCRA Requirements for Labs as a Function of Generator Status

Requirement (40CFR)	CESQG	SQG	LQG
Waste Determination (262.11)	Applicable	Applicable	Applicable
Generation Rate Limits (261.5 and 262.34)	<100 kg/mo	100-1,000 kg/mo	1,000 kg/mo or greater
Accumulation Quantity Limit w/o Permit (261.5 and 262.34)	Not to exceed 1,000 kg at any time. Not to exceed 1 kg acute at any time	not to exceed 6,000 kg at any time	No limit
Accumulation Time (261.5 and 262.34)	No limit	180 days or 270 if waste is to be transported over 200 miles.	90 days
EPA ID Number (262.12)	Not required***; possible state requirement	Required	Required
Mark Containers with Start Date (262.34)	Not applicable	Applicable	Applicable
Mark Containers “Hazardous Waste” (262.34(a))	Not applicable	Applicable	Applicable
Air Emission Standards 40 CFR 265 Subpart CC	Not applicable	Not applicable	Applicable
Satellite Accumulation (262.34(c))	Not applicable	Applicable	Applicable
Use Manifests (262, Subpart B)	Not required; possible state requirement	Required	Required
Exception Reporting (262.42)	Not required	Required after 60 days. No TSDF notification requirement.	Required after 45 days. Notification of TSDF within 35 days.
Biennial Report (262.41)	Not required	Not required; possible state requirement	Required
Contingency Plan (265, Subpart D)	Not required, but OSHA (29 CFR 1910.38) requires emergency planning	Basic planning required in accordance with the standards in 262.34(d)(4) and (5) and 265, Subpart C as well as OSHA regulations	Full written plan in accordance with 265 Subpart D, is required by 262.34(a)(4) and OSHA regulations
RCRA Personnel Training (262.34 and 265.16)	Not required, but recommended	Basic training required by 262.34(d)(5)(iii)	Full compliance with the training requirements in 265.16 is required by 262.34(a)(4)
Storage Requirements (without permit) (262.34 and 265)	None, but OSHA regulations under 29 CFR 1910, Subparts H and N, apply, particularly 29 CFR 1910.106	Compliance with technical standards in Part 265, Subparts I and J; for containers and tanks is required by 262.34(d)(2) and (3) and OSHA regulations	Compliance with technical standards in Part 265, Subparts I, J, W, and DD, is required by 262.34(a)(1) and OSHA regulations
Recordkeeping Requirements (262.40)	Waste determinations and generation log required (notification of regulated waste activity, training records, manifests, and land disposal restriction notifications recommended)	Notification of regulated waste activity, waste determinations, generation log, manifests, land disposal restriction notifications, exception reports, and correspondence with local emergency responders (written contingency plan, weekly container inspection & periodic equipment maintenance logs, and RCRA training records recommended)	Notification of regulated waste activity, waste determinations, generation log, manifests, land disposal restriction notifications, exception reports, biennial reports, correspondence with local emergency responders, RCRA training records, and written contingency plan required (weekly container inspection is required & periodic equipment maintenance logs is recommended)
Waste “Designated Facility”	State-approved or RCRA permitted facility or legitimate recycler	RCRA-permitted facility or legitimate recycler	RCRA-permitted facility or legitimate recycler
Land Disposal Restrictions (268.7)	Possible state requirement	Applicable	Applicable

Attachment II: Common F-Listed Solvents

Waste Name	Hazardous Waste Code(s)		Waste Name	Hazardous Waste Code(s)
Acetone	F003		Methylene Chloride	F001, F002
Benzene	F005		Methyl ethyl ketone (MEK)	F005
iso-Butanol	F005		Methyl isobutyl ketone	F003
n-Butyl alcohol	F003		Nitrobenzene	F004
Carbon Disulfide	F005		2-Nitropropane	F005
Carbon Tetrachloride	F001		Orthodichlorobenzene	F002
Chlorobenzene	F002		Pyridine	F005
Chlorinated fluorocarbons (CFC)s	F001		Tetrachloroethylene	F001, F002
Cresols	F004		Toluene	F005
Cresylic acid	F004		1,1,1-Trichloroethane	F001, F002
Cyclohexanone	F003		1,1,2-Trichloeoethane	F002
2-Ethoxyethanol	F005		1,1,2-Trichloro-1,2,2-trifluoroethane	F002
Ethyl acetate	F003		Trichloroethylene	F001, F002
Ethyl benzene	F003		Trichloroflourormethane	F002
Ethyl ether	F003		Xylene	F003
Methanol	F003			

Attachment III: TCLP Contaminant List

Waste ID #	Contaminant	Conc (mg/L)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin	0.02
D013	Lindane	0.4
D014	Methoxychlor	10.0
D015	Toxaphene	0.5
D016	2,4-D	10.0
D017	2,4,5-TP Silvex	1.0
D018	Benzene	0.5
D019	Carbon Tetrachloride	0.5
D020	Chlordane	0.03
D021	Chlorobenzene	100.0
D022	Chloroform	6.0
D023	o-Cresol	200.0
D024	m-Cresol	200.0
D025	p-Cresol	200.0
D026	Cresol	200.0
D027	1,4-Dichlorobenzene	7.5
D028	1,2-Dichloroethane	0.5
D029	1,1-Dichloroethylene	0.7
D030	2,4-Dinitrotoluene	0.13
D031	Heptachlor	0.008
D032	Hexachlorobenzene	0.13
D033	Hexachlorobutadiene	0.5
D034	Hexachloroethane	3.0
D035	Methyl ethyl ketone	200.0
D036	Nitrobenzene	2.0
D037	Pentachlorophenol	100.0
D038	Pyridine	5.0
D039	Tetrachloroethylene	0.7
D040	Trichlorethylene	0.5
D041	2,4,5-Trichlorophenol	400.0
D042	2,4,6-Trichlorophenol	2.0
D043	Vinyl Chloride	0.2

Attachment IV: Hazardous Waste Label for Accumulation Drum (Example)

Attachment V: SatelliteContainer Inspection Form

Waste Container ID	Clearly Labeled as "Hazardous Waste" with Waste Stream	Liquid Waste has Secondary Containment	Closed when not in use
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
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	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No

If any of the above fields are a "NO", please document how the container was brought back into compliance.

Comments: _____

_____

_____

Inspector Signature _____ **Date:** _____

Reviewer Signature _____ **Date:** _____

ATTACHMENT VI: WASTE ACCUMULATION ROOM INSPECTION FORM

Containers closed when not in use	**Labels Easily Seen and Legible**	**Drums have Accumulation Start Date**	**Storage Amounts and Limits Obeyed[1]**	**Secondary Containment** for Liquid Waste	**Adequate Aisle Space**	**Available Emergency Equip. and Materials**	**Signature and Date of Inspection**	**Corrective Action for NO Answers**
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
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Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		

1: Accumulation limits are 90 days for LQG, and 180 days for SQG. SQG may have no more than 6000kg waste at any time.

Document Information

Document Number: ENV-SOP-IND1-0007 **Revision:** 00

Document Title: Waste Management Training Requirements

Department(s): Waste

Previous Document Number: S-IN-W-003-rev.03

Date Information

Effective Date: 10 Apr 2017

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Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-IND1-0007 **Revision:** 00
Title: Waste Management Training Requirements

All dates and times are in Central Time Zone.

Review: ENV-SOP-IND1-0007 00 Waste Management Training Requirements

Review

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	10 Feb 2019, 07:49:03 PM	Reviewed

Pace Analytical Services
7726 Moller Road
Indianapolis, IN 46268
Phone: 317.228.3100
Fax: 317.872.6189

STANDARD OPERATING PROCEDURE

WASTE MANAGEMENT TRAINING REQUIREMENTS

Reference Methods: N/A

SOP Number:	S-IN-W-003-rev.03
Effective Date:	April 10, 2017
Supersedes:	S-IN-S-003-rev.02
SOP Template Number:	SOT-ALL-W-003-rev.05

APPROVALS

Laboratory General Manager — March 28, 2017 Date

Laboratory Quality Manager — March 24, 2017 Date

Laboratory Waste Coordinator — March 27, 2017 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

S-IN-W-003-Rev.03

Table of Contents

1. Purpose

1.1. The purpose of this Standard Operating Procedure (SOP) is to detail the procedures for training all employees in waste management. This SOP outlines the training requirements for each job title with regards to waste management.

2. Summary of Method

2.1. This SOP is intended to provide compliance assistance regarding waste management training. The SOP categorizes the waste management roles into different levels. The level classification of an employee determines the amount of training required.

2.2. Pace Analytical Services designates a Hazardous Waste Coordinator at each location as the qualified person to oversee the waste program of the laboratory. The waste program not only involves the act of correctly classifying and managing waste, but also adequately training all employees involved in waste management. The Hazardous Waste Coordinator must ensure that all applicable county, state, or other local requirements are obeyed.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP apply to all Hazardous Waste Coordinators.

3.2. This SOP relates only to training required for waste management, and obeying this SOP does not guarantee compliance in other areas, such as safety, quality, etc.

3.3. **Parameters**: Not applicable to this SOP.

4. Definitions

4.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

4.2. **Hazardous Waste Coordinator (HWC) –** The Pace employee responsible for creating, guiding, and implementing all hazardous waste management operations at their location.

4.3. **Emergency Coordinator** – The Pace employee responsible for updating and directing the local emergency/contingency plan.

5. Procedure

5.1. Determine waste management training needed by job title and responsibilities.

5.1.1. The job titles and roles for consideration are as follows (these titles include all qualifiers of that position, for example I, II, III, IV, Senior, Intern, Assistant, Lead, etc.):

Laboratory Technician	Sales/Marketing
Laboratory Analyst	Administrative
Supervisor/Managers	Corporate Directors/Officers
Client Services Technicians/Supervisors	Human Resources
Safety Officer	Project Managers/Coordinators
Field Analyst/Field Tech	Information Technology
Hazardous Waste Coordinator	Emergency Coordinator
Environmental Technician	Instrument Services Specialist

5.1.2. **Client Services Technician/Supervisor job description** (with regards to waste management):

5.1.2.1. Waste handling duties to include: labeling containers, understanding storage time limits, proper satellite accumulation, ensure adequate space between waste containers, ensure all waste containers are closed and incompatible materials are stored separately, understand secondary containment, and may include documenting weekly inspections. Other duties may include sample disposal which involves neutralizing and sewering waste, drumming up remaining RCRA and non-RCRA solids, and drumming RCRA Liquids for transport to final disposal facility.

5.1.2.2. Department supervisors and managers related to personnel in sample receiving have the same job description and are responsible for the same job duties.

5.1.3. **Laboratory Technician and Laboratory Analyst job description** (with regards to waste management):

5.1.3.1. Waste handling duties to include: labeling containers, understanding storage time limits, proper satellite accumulation, ensure adequate space between waste containers, ensure all waste containers are closed and incompatible materials are stored separately, understand secondary containment, and may include documenting weekly inspections.

5.1.3.2. Department supervisors and managers related to personnel in each area of the laboratory have the same job description and are responsible for the same duties.

5.1.4. **Emergency Coordinator job description** (with regards to waste management):

5.1.4.1. Duties include maintaining the contingency plan; activating internal alarms and oversee evacuation of entire facility; contact the fire department and/or police and/or ambulance service; notify proper local, state and federal agencies related to emergencies; direct all personnel performing emergency and clean up functions; assemble and direct any on-site emergency responders; maintain all emergency supplies on site; update emergency maps; and other duties outlined in Pace policies and SOP related to safety and other job related duties.

5.1.5. **Hazardous Waste Coordinator job description** (with regards to waste management):

5.1.5.1. Duties include evaluating waste streams; understanding licensing requirements; understanding proper labeling and storage of waste containers; select appropriate transportation and disposal companies; maintain complete and thorough records including manifests and training; implement waste minimization and Pollution Prevention policies; train personnel on the job duties outlined in 5.1.2 and 5.1.3; follow all Pace policies and SOPs related to safety and waste in addition to other responsibilities related to any additional roles held at Pace.

5.2. Determine the level of training required for employee. If an employee has multiple roles or a title that falls between different levels, always take the highest level training requirements. If an employee has a title in one level, but has responsibilities at another level, always assign the highest level training requirements.

5.2.1. Level One – positions that do not require any chemical or hazardous waste contact and do not have a job description related to hazardous waste management:

5.2.1.1. Administrative Positions (including Quality Managers and Senior Quality Managers);

5.2.1.2. Sales/Marketing Positions;

5.2.1.3. Human Resources Positions;

5.2.1.4. Corporate Directors/Officers;

5.2.1.5. Information Technology;

5.2.1.6. Project Managers/Coordinators.

5.2.1.7. Lab General Manager or Assistant General Manager.

5.2.2. Level Two – positions whose jobs require the transferring of wastes from satellite accumulation areas to final accumulation areas, access to a satellite accumulation area, or operating a solvent still, an evaporator or wastewater treatment unit:

5.2.2.1. Laboratory/Environmental Technician;

5.2.2.2. All Specialists, Analysts, and Chemists;

5.2.2.3. Field Analyst/Field Tech;

5.2.2.4. Sample Receiving;

5.2.2.5. Safety Officer;

5.2.2.6. Supervisors/Managers of employees listed in Level Two.

5.2.3. Level Three – positions whose jobs require inspecting accumulation areas/emergency equipment, clean-up to spills, response to emergencies, waste management training of new or relocated employees positions, filling out waste manifests and maintaining waste compliance of the facility:

5.2.3.1. Hazardous Waste Coordinator;

5.2.3.2. Emergency Coordinator.

5.3. Determine the Training Requirements – employees must receive documented training of the following topics:

5.3.1. Level One Training:

5.3.1.1. Read and understand local Pace Analytical Chemical Hygiene/Safety Plan;

5.3.1.2. Receive introductory orientation of facility and familiarization with all safety equipment and procedures for local emergency/contingency plans.

5.3.2. Level Two Training:

5.3.2.1. Everything required in Level One Training (5.3.1);

5.3.2.2. Hazardous Waste Management Training (for general employees). Training must be given within the first 90 days of employment, and annually thereafter. The following topics must be covered at minimum: License requirements; hazardous waste definitions and determination; satellite accumulation requirements and time limits; waste container labeling, inspections, and storage requirements; tank inspections and labeling; general awareness of manifest completion, copy distribution and land disposal restriction notices; record keeping regarding inspections, training, annual reports; waste reduction; and emergency response.

5.3.3. Level Three Training:

5.3.3.1. Everything required in Level Two Training (5.3.2);

5.3.3.2. DOT-HAZMAT Training, with refresher training no more than 3 years after prior training;

5.3.3.3. Hazardous Waste Management Training for Hazardous Waste Coordinators.

6. Training, Expectations, and Supplemental Information

6.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

7. References

7.1. Pace Chemical Hygiene/Safety Manual-most current version.

7.2. Pace Quality Assurance Manual- most current version.

7.3. National Environmental Laboratory Accreditation Conference (NELAC) Standard- most current version.

7.4. The NELAC Institute (TNI) Standard- most current version applicable to each lab.

7.5. Department of Defense (DoD) Quality Systems Manual- most current version.

8. Revisions

Document Number	Reason for Change	Date
S-IN-S-003-rev.01	1. Section 11.1.4: added Safety Officer as optional Emergency Coordinator 2. Section 14: added Method Modifications section per TNI requirements.	01Feb2013
S-IN-S-003-rev.02	1. Re-formatted to Corporate SOT format. 2. Cover page: changed phone number, revised effective date format and revised document control format.	22Dec2015
S-IN-W-003-rev.03	1. Adapted from SOT-ALL-W-003-rev.05. 2. Changed SOP name from a “Safety” SOP to a “Waste” SOP. 3. Cover page: changed phone number and document control format. 4. Added Table of Contents	15Mar2017

Document Information

Document Number: ENV-SOP-IND1-0058 **Revision:** 02

Document Title: Soil and Waste pH

Department(s): Wet Chemistry

Previous Document Number: S-IN-I-069-rev.12

Date Information

Effective Date: 05 Feb 2019

Next Review Date: 05 Feb 2021 **Last Review Date:**

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-IND1-0058 **Revision:** 02
Title: Soil and Waste pH

All dates and times are in Central Time Zone.

ENV-SOP-IND1-0058 Soil and Waste pH

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	05 Feb 2019, 09:33:28 AM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Sayer (004775)	General Manager	05 Feb 2019, 09:48:15 AM	Approved
Anne Troyer (008754)	Manager - Lab Services	05 Feb 2019, 01:14:33 PM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining pH in solid samples while meeting the requirements specified in EPA method 9045C.

2. Summary of Method

2.1. The sample is mixed with reagent water and then the pH of the mixture is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH.

3. Scope and Application

3.1. This method is applicable for the measurement of pH in soils, sludges and solid wastes. If water is present, it must be less than 20% of the total volume of the sample.

3.2. Reporting limits, control limits, volumes used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted for use by, or under the supervision of, analysts experienced in the use of pH analysis equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This procedure is applicable to extracts prepared from many types of solid waste and soil samples.

5. Limits of Detection and Quantitation

5.1. Refer to LIMS for method detection limits.

6. Interferences

6.1. Coatings of oily material or particulate matter on the electrode can impair response. This can be minimized by gently wiping off the electrode or washing with detergent followed by reagent water. An additional treatment with hydrochloric acid (1:9 ratio) may be necessary to remove any remaining film.

6.2. Samples with very low or very high pH may give incorrect readings on the pH meter. This error can be minimized by using a low-sodium-error electrode.

6.3. Temperature can have effects on results. To compensate for temperature interferences, the analyst should always calibrate the pH meter at the same temperature as the samples and they should record the sample temperature and pH at the time of analysis. Alternately, an automatic temperature compensating pH meter can be used.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Solids	>20g in 4oz glass container	None	Ambient	Analyze immediately**

** There is no holding time requirement listed in the method. SW-846 Chapter Three lists the holding time as "analyze immediately." All samples will be qualified as being analyzed outside recommended holding time.
Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation

Equipment	Description / Comments
pH/Ion meter	Accumet AB15 or equivalent equipped with a combination pH probe and temperature sensor.
Analytical balance	OHaus AV212 or equivalent capable of weighing to 0.1g

9.2. General Supplies

Item	Description
Magnetic stirrer	With Teflon coated stir bars. Fisher Brand or equivalent
Disposable beakers	50mL capacity. Fisher Brand or equivalent
Graduated cylinder	Class A for measuring 20mL reagent water volume. Fisher Brand or equivalent
Digestion tubes	50mL capacity with lids. Environmental Express or equivalent
Filter paper	Fisher Brand P4 or equivalent
Tumbling apparatus	

10. Reagents and Standards

10.1. Reagents and Standards

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
pH 2 buffer	Fisher/ catalog # SB-96-1, or equivalent
pH 4 buffer	Fisher/ catalog # SB101-4 or equivalent
pH 7 buffer (CCV)	Fisher/ catalog # SB107-4 or equivalent
pH 10 buffer	Fisher/ catalog # SB115-4 or equivalent
pH 12 buffer	Ricca/ catalog #161532 or equivalent
pH 7 buffer (ICV)	Ricca/ catalog #155141 or equivalent

11. Calibration and Standardization

11.1. Refer to manufacturer's instructions for pH electrode and meter. If using a refillable electrode, uncover the fill hole on the pH electrode and add the appropriate fill solution to the electrode up to the fill hole. The level of the fill solution must always be above the reference junction. The fill hole should remain open when the electrode is in use. Store electrode in KCl filling solution when not in use.

11.2. Each instrument/electrode system must be calibrated on each analysis day with a minimum of two calibration points that bracket the expected pH of the samples. The two points should be at least three pH units apart. Place the appropriate buffer solution into a clean beaker using sufficient volume to cover the sensing elements of the electrodes and to give the magnetic stir bar some clearance to move.

11.3. Press and release the **mode** key until the digital display indicates pH mode.

11.4. Press the **setup** key twice and then press the **enter** key to clear an existing standardization.

11.5. Rinse the electrode with reagent water and immerse the rinsed electrode into the first buffer solution while gently stirring the buffer.

11.6. Press **std** to access Standardization mode. Wait for the reading to stabilize. Press **std** again to initiate standardization. The meter will automatically recognize the buffer and then return to the Measure screen. Record the pH reading of the buffer. Rinse off the electrode with reagent water and gently wipe dry.

11.7. Repeat steps 11.5-11.6 for each of the remaining buffer solutions.

11.8. Do not clear the previous buffers. Readings should be +/-0.1 pH units from the listed values for the buffer solutions. When the three buffers have been standardized, record the slope from the meter. The slope must be 90-102%.

11.9. Check calibration with a second source pH 7 buffer (ICV). Record the pH. Results must be within +/-0.1 pH units of the true value.

11.10. If either of the requirements of steps 11.8 or 11.9 are not met, repeat the meter calibration using fresh buffers. If either of the requirements are still not met, replace electrode filling solution and clean the electrode or replace the electrode.

11.11. Once calibrated, the meter is ready to analyze samples when in the **Measure** mode.

12. Procedures

12.1. Place 20g of sample into a 50mL digestion tube and add 20mL of reagent water. Cap the tube and tumble the suspension continuously for 5 minutes. Additional dilutions are allowed for problematic samples.

12.2. Filter or centrifuge the sample to separate the aqueous phase.

12.3. Decant the aqueous portion of prepared sample or transfer to a disposable beaker.

12.4. Immerse the electrode into the sample and stir gently at a constant rate. Record the sample pH to the nearest 0.1 pH units and record the temperature to the nearest ^{o}C when **STABLE** appears on the screen. For normal use, the pH meter Stability Criteria is set to slow, allowing the highest precision.

12.5. If the pH of the sample exceeds the calibration range (i.e. between 4 and 10), an additional pH buffer solution must be analyzed to confirm the accuracy of the pH meter beyond the calibration range. Results should be within +/-0.1 pH units. If the pH of the additional buffer is not within +/-0.1 pH units, re-standardize the pH meter using buffers that bracket the pH range of the samples and reanalyze the samples.

12.6. Measure and record the pH of the calibration source pH 7 buffer (CCV) at the beginning and ending of each analytical sequence and after every 10 samples. Results should be within +/-0.1 pH units. If the pH reading of the CCV is not within +/-0.1 pH units of the true value, repeat the CCV measurement using fresh CCV. If CCV still fails, replace electrode filling solution and clean the electrode or replace the electrode and repeat calibration per Section 11. Repeat any samples that are not bracketed by acceptable buffer readings.

12.7. Thoroughly rinse and gently blot the electrode between sample measurements.

NOTE 1: Certain customer technical specifications may stipulate that their samples must be analyzed within 4 hours of the calibration.

NOTE 2: For samples originating in West Virginia, the pH meter must be calibrated prior to use with pH buffer standards that bracket the value to be measured.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Sample Duplicate	Sample	One duplicate per every 10 samples analyzed	≤2% RPD	Consult with supervisor to see if another sample should be duplicated.

13.2. RPD equation:

$$\mathbf{RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100}$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

14. Data Analysis and Calculations

14.1. RPD equation:

$$\mathbf{RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100}$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11, 12, and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11, 12, and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11, 12, and 13.

18. Method Performance

18.1. Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

18.2. The analyst must read and understand this procedure with written documentation maintained in his/her training file.

19. Method Modifications

19.1. Samples are gently stirred during pH measurement.

19.2. Acceptance criteria for ongoing calibration buffers is +/-0.1 standard units based on SM4500H+ B recommendations, instead of +/-0.05 standard units recommended in 9045C.

19.3. Buffers are purchased as certified standards.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods"; EPA SW-846, method 9045C.

25.2. Standard Methods for the Examination of Water and Wastewater; Method 4500 H+ B; 2011.

25.3. Accumet AB-15 or equivalent User Manual

25.4. Pace Analytical Quality Manual; latest revision.

25.5. NELAC/TNI Standard; Quality Systems section; 2003, 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-069-rev.10	1. Section 9: tables combined into single Table 9.1 2. Table 9.1: added pH 11 buffer and identified ICV and CCV standards. 3. Section 10: copied Section 10 of pH Waters SOP for consistency. 4. Section 10.5: added (ICV) for clarity. 5. Section 11.6: changed "second source" to "calibration source" and revised criteria to +/-0.05 standard units. 6. Section 16: added reference to the pH meter user manual	30Jul2013
S-IN-I-069-rev.11	1. Table 7.1 and caption: revised holding time to "analyze immediately" and indicated that all sample results would be qualified as outside holding time. 2. Section 11 Note 1: removed specific reference to BP. 3. Section 11 Note 2: added for West Virginia requirements.	29Oct2013
S-IN-I-069-rev.12	1. Cover page: updated phone number and document control format. 2. Converted to 27-section format. 3. Section 9.1: updated pH meter identification. 4. Section 9.2: added tumbling device, digestion tubes and filter paper. 5. Section 10.1: removed pH 11 buffer and updated pH 12 and ICV buffers. 6. Section 11: updated calibration instructions based on current meter in use, added electrode handling information and added corrective actions. 7. Section 12.1: changed procedure for the use of digestion tubes. 8. Section 12.2: changed procedure to filtration for separation of solids from liquid. 9. Table 13.1: changed RPD to $\leq$2%. 10. Section 25: updated user manual reference and TNI reference.	06Feb2017
ENV-SOP-IND1-0058-rev.01	1. Removed cover page, table of contents and headers for use in Master Control.	13Jan2019
ENV-SOP-IND1-0058-rev.02	1. Section 11.8: changed acceptance criterion from +/-0.05 to +/-0.1 pH units. 2. Section 12.6: changed acceptance criterion from +/-0.05 to +/-0.1 pH units. 3. Section 19.2: added modification for new criterion of +/-0.1 pH units. 4. Section 25: added reference to SM4500H+ B.	4Feb2019

Document Information

Document Number: ENV-SOP-IND1-0056 **Revision:** 01

Document Title: Hexavalent Chromium

Department(s): Wet Chemistry

Previous Document Number: S-IN-I-063-rev.12

Date Information

Effective Date: 12 Feb 2019

Next Review Date: 12 Feb 2021 **Last Review Date:**

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-IND1-0056 **Revision:** 01
Title: Hexavalent Chromium

All dates and times are in Central Time Zone.

ENV-SOP-IND1-0056 Hexavalent Chromium

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	12 Feb 2019, 12:08:03 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Sayer (004775)	General Manager	12 Feb 2019, 12:18:39 PM	Approved
Anne Troyer (008754)	Manager - Lab Services	12 Feb 2019, 12:35:56 PM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining Hexavalent Chromium in aqueous and solid samples while meeting the requirements specified in EPA SW-846 method 7196A and Standard Methods 3500-Cr B; 2011.

2. Summary of Method

2.1. Dissolved hexavalent chromium is determined colorimetrically by reaction when diphenylcarbazide in an acid solution. A red-violet color is produced and is measured colorimetrically at 540nm.

3. Scope and Application

3.1. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.2. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of hexavalent chromium analysis equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable for the measurement of hexavalent chromium in groundwater, surface water, soil, sediment and domestic and industrial wastes. Refer to SOP S-IN-I-070 Alkaline Digestion of Solid Samples for Hexavalent Chromium or its replacement for procedures associated with the preparation of solid samples.

5. Limits of Detection and Quantitation

5.1. The default reporting limit for Hexavalent Chromium is 0.01mg/L for aqueous samples and 4mg/kg for solid samples. Refer to the LIMS for method detection limits.

6. Interferences

6.1. The chromium reaction with the diphenylcarbazide is usually free from interferences. However, hexavalent molybdenum and mercury salts also react to form color complexes with the reagent. Vanadium can also interfere, but concentrations up to 10 times that of chromium can be tolerated.

6.2. Iron concentrations greater than 1 mg/L may produce a yellow color that does not normally cause interference at the specified wavelength.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous Unpreserved	250mL in plastic container	None required	Cool to ≤6°C	Analyze samples within 24 hours of collection date/time.
Aqueous Preserved	250mL in plastic container	**Indiana RISC:** 2mL 50% NaOH per 250mL sample. **NPDES:** Ammonium sulfate buffer to pH 9.3-9.7.	Cool to ≤6°C	Analyze samples within 28 days of collection date.
Solid	>100g in a glass or plastic container	None required	Cool to ≤6°C	Digest samples within 30 days of collection date and analyze digestates within 7 days of digestion date.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation

Equipment	Vendor	Description / Comments
Spectrophotometer	Hach DR5000 or equivalent	For use at 540nm with a cell providing a light path of 1cm or longer

9.2. General Supplies

Item	Description
Graduated cylinder	Class A, 50mL
Mechanical pipets	Various sizes, Eppendorf or equivalent
Filter membrane	0.45um, Environmental Express or equivalent
Disposable beakers	20mL
Transfer pipets	Disposable
Volumetric flasks	Class A, various sizes
pH paper	Narrow range 0-3

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II
ChromaVer 3 Chromium reagent powder pillows	Hach cat.#12710-99 or equivalent
Sulfuric Acid, 5N	Aqua Solutions #9109 or equivalent
Sodium Hydroxide (50%)	Fisher cat#SS254-4 or equivalent
Ammonium Sulfate Crystal	Fisher cat#A702-500 or equivalent
Ammonium Hydroxide	Fisher cat#A512-500 or equivalent
Ammonium Sulfate Buffer	Dissolve 33 g of ammonium sulfate in 75 mL reagent water and add 6.5 mL ammonium hydroxide. Dilute to 100 mL with reagent water.

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	ICAL
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration. This standard is used to verify the initial calibration.	CCV
Spiking Standard	This solution contains all target analytes and should be prepared from a different source than the calibration standards.	This solution is used for the LCS, MS/MSD, and post-digestion spikes.

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Cr(VI) Calibration Standard	Ricca catalog #2095-47; 100mg/L or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate Cr(VI) Calibration Standard	Refer to Section 10.2.3.1	Must be prepared fresh daily	Not Applicable
Working Cr(VI) Calibration Standards	Refer to Section 10.2.3.2	Must be prepared fresh daily	Not Applicable
Stock Cr(VI) ICV/LCS Standard	Hach; catalog #810-42H; 50mg/L or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Cr(VI) ICV/LCS Standard	Refer to Section 10.2.3.3	Must be prepared fresh daily	Not Applicable

10.2.3. Standard Preparation Procedures

Refer to the standard preparation logbook or database for additional instructions regarding preparation of standards for Cr(VI) analysis. Instructions for preparation of fresh daily standards are detailed below. Refer to SOP S-IN-I-070 Alkaline Digestion of Solid Samples for Hexavalent Chromium or its replacement for reagents and standards associated with the preparation of solid samples.

10.2.3.1. Intermediate Cr(VI) Calibration Standard Preparation

Dilute 1mL of the Stock Cr(VI) Calibration Standard (100mg/L) to 100mL in a volumetric flask with reagent water for a final concentration of 1.0mg/L.

10.2.3.2. Working Cr(VI) Calibration Standard Preparation

Working calibration standards must be prepared fresh daily by diluting the Intermediate Cr(VI) Calibration Standard (1mg/L) to 10mL with reagent water. Examples of possible calibration standards are as follows:

Standard ID	Amt. of Intermediate Calibration Std. Used	Final Volume	Final Concentration
CAL0	0mL	10mL	0mg/L
CAL1	0.1mL	10mL	0.01mg/L
CAL2	0.5mL	10mL	0.05mg/L
CAL3	1.0mL	10mL	0.10mg/L
CAL4 (CCV)	5.0mL	10mL	0.50mg/L
CAL5	7.5mL	10mL	0.75mg/L
CAL6	10mL	No dilution required	1.0mg/L

10.2.3.3. Working Cr(VI) ICV/LCS Standard Preparation

Dilute 0.1mL of the Stock Cr(VI) ICV/LCS Standard (50mg/L) to 10mL in a volumetric flask with reagent water for a final concentration of 0.50mg/L. This standard must be prepared fresh daily. This standard is also used as the LCS.

11. Calibration and Standardization

11.1. Initial Calibration: A minimum of 5 calibration standards is required. The lowest calibration standard must be at or below the reporting limit. A new initial calibration must be analyzed every 6 months at a minimum. Refer to the Quality Manual for more information regarding calibration curves.

11.2. Linear Calibration: After zeroing the spectrophotometer with reagent water, prepare a standard curve by plotting absorbance versus Cr(VI) concentration of each calibration standard. The analyst may employ a regression equation that does not pass through the origin. The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

where: y = instrument response (peak area)
a = slope of the line (the coefficient of x)
x = concentration of the calibration standard
b = intercept of the line

The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be $\geq$ 0.995.

11.3. Initial Calibration Corrective Action: If the curve does not meet the acceptance criteria, then a new calibration curve must be analyzed. If the second curve attempt does not meet the acceptance criteria, the analyst must consult the department manager and instrument maintenance and/or preparation of new standards must be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.4. Initial Calibration Verification (ICV): In addition to meeting the linearity requirement, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known value of the standard. This step is referred to as Initial Calibration Verification. The ICV is analyzed immediately following an initial calibration curve. Acceptable recovery range for the ICV is 90-110%.

11.5. ICV Corrective Action: If the ICV is not acceptable, another ICV may be analyzed. If the second ICV fails, then a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new standards must also be considered. Samples associated with a failed ICV must be reanalyzed. Exception: If the ICV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.6. Initial Calibration Blank (ICB): An ICB consists of 10mL reagent water. An ICB must be analyzed after each ICV. If the ICB result is above the reporting limit, another ICB may be analyzed. If the second ICB fails, then a new calibration curve must be analyzed. Samples associated with a failed ICB must be reanalyzed. **Exception**: If the ICB is >RL, associated samples determined to be <RL are reportable

11.7. Continuing Calibration Verification (CCV): When an ICAL is not analyzed, the calibration must be verified by analyzing a CCV at the beginning of the analytical sequence. In all cases, a CCV must also be analyzed after every 10 samples and at the end of the analytical sequence to verify the system is still calibrated. The CCV should be from the same material as the curve standards. The acceptable recovery range for the CCV is 90-110%.

11.8. CCV Corrective Action: If a CCV fails the acceptance criteria, another CCV may be analyzed. If the second CCV fails, then a new initial calibration curve must be analyzed. Samples must be bracketed by acceptable CCVs in order to be reportable. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL are reportable.

11.9. Continuing Calibration Blank (CCB): A CCB consists of 10mL reagent water. A CCB must be analyzed after each CCV. If the CCB result is above the reporting limit, another CCB may be analyzed. If the second CCB fails, then a new calibration curve must be analyzed. Samples associated with a failed CCB must be reanalyzed. **Exception**: If the CCB is >RL, associated samples determined to be <RL are reportable.

12. Procedures

12.1. Bring samples to room temperature prior to analysis whenever possible. If samples are turbid, centrifuge samples to remove turbidity. If after centrifugation samples remain turbid, filtration of samples through a 0.45um filter may be performed. Wastewater samples analyzed by Method SM3500Cr B for NPDES compliance must be filtered through 0.45um filter prior to analysis. If any samples in a batch are filtered, the associated Method Blank and LCS must also be filtered.

12.2. Preparation of Batch QC for Aqueous Samples

12.2.1. Prepare a Method Blank: Place 10mL of reagent water into a 20mL disposable beaker and add contents of one Chromaver 3 chromium reagent powder pillow. Swirl or stir for about 30 seconds to dissolve the powder.

12.2.2. Prepare an LCS: Dilute 0.1mL of the Stock Cr(VI) ICV/LCS Standard (50mg/L) to 10mL with reagent water for an LCS concentration of 0.5mg/L. Add the contents of one Chromaver 3 chromium reagent powder pillow. Swirl or stir for about 30 seconds to dissolve the powder.

12.2.3. Prepare a Matrix Spike: Dilute 0.1mL of the Stock Cr(VI) ICV/LCS Standard (50mg/L) to 10mL with sample for a Matrix Spike concentration of 0.5mg/L. Add the contents of one Chromaver 3 chromium reagent powder pillow. Swirl or stir for about 30 seconds to dissolve the powder.

12.3. Unpreserved Aqueous Samples

12.3.1. Place 10mL of sample into a 20mL disposable beaker.

12.3.2. Add contents of one Chromaver 3 chromium reagent powder pillow.

12.3.3. Swirl or stir for about 30 seconds to dissolve the powder.

12.3.4. Check sample pH with narrow range pH paper (0-3). If pH is >2.5, adjust to pH 2 +/-0.5 using 5N sulfuric acid. Alternatively, start over using a diluted samples aliquot.

12.4. Preserved Aqueous Samples and Soil Digestates

12.4.1. Place 10mL of aqueous sample or soil digestate into a 20mL disposable beaker.

12.4.2. Add 0.2mL of 5N sulfuric acid.

12.4.3. Add the contents of one Chromaver 3 chromium reagent powder pillow. Swirl or stir for about 30 seconds to dissolve the powder.

12.4.4. Check sample pH with narrow range pH paper (0-3). If pH is >2.5, start over at step 12.4.1 using a fresh sample aliquot and increase the amount of 5N sulfuric acid added to achieve pH 2 +/-0.5. Alternatively, start over using a diluted samples aliquot.

12.5. Allow 5 to 10 minutes for the color to develop but do not wait beyond 20 minutes to take the reading of the sample on the spectrophotometer. A red-violet color will be observed in the presence of Cr(VI).

12.6. Adjust the wavelength control of the spectrophotometer to 540nm. Zero the spectrophotometer using reagent water. Measure the absorbance of the standards, samples and blanks. A typical run sequence may be as follows:

ICAL Standards
ICV
ICB
(If ICAL not run, CCV/CCB would replace the ICAL, ICV and ICB in the sequence)
Method blank
LCS
Client samples
CCV
CCB
Client samples
CCV
CCB

12.7. To correct for background in samples, use an aliquot of the sample containing all reagents except the Chromaver 3 reagent powder pillow. Aliquot used for background must match pH of sample aliquot used for Cr(VI) determination.

12.8. Any sample with a Cr(VI) concentration that exceeds the linear range of the calibration curve must be diluted and reanalyzed or over range results must be qualified as estimated.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent or Ottawa sand	One per preparation batch of up to 20 samples per matrix.	Target analytes must be <RL	**Water:** Reanalyze method blank. If method blank is still >RL, reanalyze associated samples. **Soils:** Reanalyze method blank. If method blank is still >RL, re-digest and reanalyze associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Cr(VI)	One per preparation batch of up to 20 samples per matrix.	**Water:** 90-110% Recovery **Soil:** 80-120% Recovery	**Water:** Reanalyze LCS. If LCS is still outside acceptance criteria, reanalyze associated samples. **Soils:** Reanalyze LCS. If LCS is still outside acceptance criteria, re-digest and reanalyze associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Aqueous Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Cr(VI)	One MS/MSD set per batch plus an additional MS if >10 samples in the batch.	85-115% Recovery ≤20%RPD	If MS/MSD is out of control but LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Solid Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Cr(VI)	One **soluble** and one **insoluble** MS/MSD set per preparation batch of up to 20 samples.	75-125% Recovery ≤20%RPD	If outside acceptance limits, evaluate sample for pH and Eh and compare to Figure 2 in Method 3060A. If in reducing range, no re-digestion is required. If outside reducing range, re-digestion and reanalysis of entire preparation batch is required. Refer to SOP for pH procedure. Refer to SOP for Eh procedure.
Sample Duplicate (DUP) **Solids only**	Sample	One Sample Duplicate per preparation batch of up to 20 samples.	≤20% RPD	No corrective actions necessary if sample concentration is <4x RL. If sample concentration is ≥4x RL, the RPD must be qualified appropriately.
Post-Digestion Matrix Spike **Solids only**	Cr(VI) at 40mg/kg	One per preparation batch of up to 20 samples.	85-115% Recovery	No corrective actions necessary.

14. Data Analysis and Calculations

14.1. From the corrected absorbance, determine the concentration of chromium present using the calculation below:

$$X = \frac{y - b}{a}$$

Where: X = sample concentration
y = response or absorbance, corrected for background
b = y-intercept
a = slope

14.2. Calculate the final concentration in the sample as follows:

Aqueous Sample (mg/L) = (X)(D)

Solid Sample (mg/kg) = $\frac{(X)(V_f)(D)}{(W_s)}$

Where: X = Measured sample concentration in mg/L
D = Dilution factor (V_f/V_i)
V_f = Final sample volume in L
V_i = Initial sample volume in L
W_s = Weight of solid sample extracted in kilograms

Moisture corrected concentration = $\frac{\text{(Final concentration as received)}}{\text{(100 - \%Moisture)}} \times 100$

14.3. LCS equation:

$R = (C/S) * 100$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.4. MS/MSD equation:

$R = \frac{(Cs - C)}{S} * 100$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.5. RPD equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. Method Detection Limit (MDL) Study: An MDL study must be conducted every 12 months for each matrix per instrument.

18.2. Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Aqueous sample preservation using NaOH is performed as an alternative preservation per IDEM RISC Technical Resource Document, Appendix 2, Analytical Methodology for Risk Assessment table, footnote s(1). Reference is to EPA Method 1669, Section 8.4.5.

19.2. Calibration standards are purchased as certified standards.

19.3. Calibration curve standards for soil analysis are not digested per Method 7196A.

19.4. The lab includes a CAL0 (method blank) in the calibration curve rather than subtracting the absorbance of a method blank from all readings.

19.5. Phosphoric acid is not added prior to color reagent per SM3500Cr B.

19.6. Hach ChromaVer 3 combined reagent is used in place of laboratory prepared H_2SO_4 solution and Diphenylcarbazide solution.

19.7. Method of standard additions is not performed.

19.8. MS/MSD is not performed for every sample matrix analyzed.

20. Instrument/Equipment Maintenance

20.1. Refer to maintenance log and/or instrument manufacturer's instructions.

21. Troubleshooting

21.1. Refer to maintenance log and/or instrument manufacturer's instructions.

22. Safety

22.1. Standards and Reagents: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. Samples: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. Equipment: Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling or other appropriate SOP. All wastes are accumulated, managed and disposed of in accordance with all federal and state laws and regulations.

23.2. Samples determined to have a Cr(VI) concentration $\geq$5 mg/L must be labeled and identified for hazardous waste disposal.

24. Pollution Prevention

24.1. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24.2. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods"; EPA SW-846, latest revision of methods 7196A and 3060A.

25.2. "Standard Methods for the Examination of Waste and Wastewater", Method 3500-Cr B; 2009, Editorial revisions, 2011.

25.3. 40 CFR, Part 136, Table IB and Table II, Method Update Release, 2012

25.4. "Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels", EPA Method 1669, Section 8.4.5, July 1996.

25.5. Pace Analytical Quality Manual; latest revision.

25.6. TNI Standard; Quality Systems section; 2003, 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not Applicable

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-063-rev.11	1. Cover: revised Standard Methods reference from "D" to "B". 2. Section 1.1: revised Standard Methods reference and added a note that SM 3500-Cr B supersedes and is equivalent to SM 3500-Cr D. 3. Section 3.1: added a reference to the alkaline digestion SOP for soil procedures. 4. Section 3.2: added reference to LIMS for MDLs. 5. Table 7.1: updated for water preservation procedure and changed preserved water holding time from 30 days to 28 days. 6. Table 9.1: added reagents for Ammonium Sulfate Buffer 7. Section 9.2.3: added a reference to the alkaline digestion SOP for reagents and standards associated with the preparation of solid samples. 8. Section 11.7: added requirement to qualify over range results 9. Section 11.8: revised/fixed calculation for concentration from curve. 10. Table 12.1: revised method blank corrective actions and added references to pH and Eh procedures for solid sample MS/MSD corrective action. 11. Section 12: added/expanded aqueous LCS preparation. 12. Inserted new Method Modifications section. 13. References: revised Standard Methods reference and added reference to 40 CFR 2012 MUR.	26Sep2012
S-IN-I-063-rev.12	1. Update to 27-section format. 2. Cover page: added year to SM reference, updated phone number and revised effective date and document control format. 3. Section 1.1: added year to SM reference and removed note regarding equivalency to SM3500Cr-D. 4. Section 4: added iron interference. 5. Table 7.1: revised storage temperature format, clarified aqueous preservation by intended use and clarified unpreserved aqueous sample holding time. 6. Section 8.2: added volumetric flasks. 7. Section 9.2: added narrow range pH paper. 8. Table 10.3: added Working ICV/LCS. 9. Section 10.2.3: added daily CCV preparation instructions. 10. Section 11: removed equation for r, added section for ICB and removed ICB from CCB section. 11. Section 12.1: added recommendation to bring samples to room temp., added requirement to filter NPDES samples, added requirement to filter MB and LCS if samples are filtered. 12. Section 12.4: added pH range critera and pH adjustment. 13. Section 12.6: added ICB to example sequence. 14. Table 13.1: updated LCS criteria, aqueous MS/MSD frequency and aqueous MS/MSD corrective action. 15. Section 14: updated equations for concentration. 16. Section 19: updated method modifications. 17. Section 23: added require to identify and properly dispose of samples ≥5 mg/L. 18. Section 25: added year to SM reference and added references to Method 1669.	06Feb2017
ENV-SOP-IND1-0056-rev.01	1. Removed cover page, table of contents and headers for use in Master Control. 2. Section 10.1: changed 1:1 sulfuric to 5N sulfuric. 3. Section 10.2.3.2: updated calibration curve examples to include CAL0 and identify CCV. Removed CCV recipe. 4. Sections11.6 and 11.9: changed contents of ICB and CCB to reagent water only. 5. Section 12.3.4: added pH adjustment details using 5N sulfuric when needed. 6. Section 12.4: changed 1:1 sulfuric to 5N sulfuric and added pH adjustment details. 7. Section 12.6: changed reagent blank to reagent water for zeroing the spec. 8. Table 13.1: updated corrective actions for method blank and LCS. 9. Section 19: added modification for including CAL0 in curve instead of subtracting the method blank from each sample.	10Feb2019

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QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	27 Nov 2018, 08:23:19 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Sayer (004775)	General Manager	28 Nov 2018, 07:33:18 AM	Approved
Timothy Pinckert (003677)	Manager-Lab Services	28 Nov 2018, 11:08:53 AM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining the concentration of 1,2-Dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) in aqueous samples meeting the requirements specified in SW-846 method 8011.

2. Summary of Method

2.1. This method describes the preparation and analysis of 1,2-dibromomethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) in water in accordance with method 8011. These compounds may also be referred to as fumigants or lead scavengers. Preparation is performed by microextraction. Analysis is performed by gas chromatography using dual injection ports, dual columns and dual detectors. This analytical system provides quantitation and confirmation.

3. Scope and Application

3.1. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.2. This method is restricted to use by, or under the supervision of analysts experienced in the technique described. Each analyst performing this method must have demonstrated the ability to perform the described analysis.

4. Applicable Matrices

4.1. This analysis is applicable to drinking water, ground water, and surface water samples.

5. Limits of Detection and Quantitation

5.1. Default reporting limits are: EDB 0.035ug/L and DBCP 0.035ug/L. Refer to LIMS for method detection limits.

6. Interferences

6.1. Impurities that might be present in the extracting solvent may interfere with the analysis. This potential interference is monitored by the use of a method blank. Whenever an interferent is detected in the method blank, it should be reanalyzed. If the interferent is confirmed by reanalysis, the vendor should be contacted and a new lot of extracting solvent should be obtained. Interference-free hexane is defined as having <0.01 ug/L of the analyte. Store hexane in an area known to be free of organochlorine solvents.

6.2. Instances of contamination by diffusion of volatile organics through the septum have been documented. This can be monitored through the use of trip blanks.

7. Sample Collection, Preservation, and Handling

Table 7.1: Sample Collection, Preservation, Storage and Hold time

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	3 - 40 mL glass VOA vials	Sodium thiosulfate 75mg/L, no headspace **OR** 1:1 HCl to pH<2, no headspace	Cool to ≤6°C	Analysis must be completed within 14 days of collection date.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment and General Supplies

Equipment	Vendor	Model / Version	Description / Comments
Gas Chromatograph (GC)	Agilent	7890/LTM with dual ECDs or equivalent equipment	Must be equipped with a data system and autosampler.
Capillary Columns	Agilent	DB-5MS/DB-35MS/DB-XLB or equivalent	Columns must be dissimilar for purposes of confirmation.

9.2. General Equipment and Supplies

Item	Vendor/Description
Glass funnels	
Spatulas	Metal spatula or disposable tongue depressors or equivalent
Analytical Balance	Ohaus EP214C or equivalent
Sample Vials	40mL VOA vials, C&G or equivalent
Volumetric Flasks	Class A, various capacities
Graduated cylinders	Glass, Class A, various sizes
Pipettes	2mL, Class A or equivalent
Disposable pipettes	Or equivalent transfer pipette
Gas tight syringes	Hamilton, various sizes or equivalent
Autosampler vials	2mL with crimp top or equivalent

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent Water	ASTM Type II or equivalent
Sodium Chloride	Meets ACS specs or equivalent
Hexane	JT Baker 9262-03 Ultra Resi-Analyzed or equivalent
Methanol	JT Baker 9263-03 Ultra Resi-Analyzed or equivalent

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification, and for preparing LCS, MS, and MSD samples

Table 10.2 Standard Definitions

Standard	Description	Comments
Surrogate Standard	Surrogates are added to each sample and QC sample to monitor extraction efficiency.	
Spiking Standard	This solution contains method required spiking compounds, at a minimum, and is used for spiking MS/MSD sets.	Same solution can be used for the LCS and MS/MSD
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This standard verifies the accuracy of the calibration curve.	ICV
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify the initial calibration.	CCV

10.2.2. Details and Storage Conditions

Table 10.3 Analytical Standard Details and Storage Conditions

Standard Type	Description	Expiration	Storage
Stock EDB/DBCP Calibration Standard	Restek #30062, 2000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Store in freezer after opening.
Intermediate EDB/DBCP Calibration Standard	Refer to Section 10.2.3.1	Standard is good for one month from preparation date.	Refrigerate
Working EDB/DBCP Calibration Standard	Refer to Section 10.2.3.2	Standard is good for one month from preparation date.	Refrigerate
Stock BFB Surrogate Standard	Restek #30026, 2000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Store in freezer after opening.
Working BFB Surrogate Standard	Refer to Section 10.2.3.3	Standard is good for one month from preparation date.	Refrigerate
Stock EDB/DBCP ICV/CCV Standard	Supelco #48225-U, 2000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Intermediate EDB/DBCP ICV/CCV Standard	Refer to Section 10.2.3.4	Standard is good for one month from preparation date.	Refrigerate
Working EDB/DBCP Spike Standard	Refer to Section 10.2.3.5	Standard is good for one month from preparation date.	Refrigerate
Working EDB/DBCP ICV/CCV Standard	Refer to Section 10.2.3.6	Standard is good for one month from preparation date.	Refrigerate

10.2.3. Standard Preparation Procedures

10.2.3.1. Intermediate EDB/DBCP Calibration Standard

Dilute 6uL of the Stock EDB/DBCP Calibration Standard (2000ug/mL) to 100mL with methanol for a final concentration of 0.12mg/L.

10.2.3.2. Working EDB/DBCP Calibration Standards

The following are examples of calibration standards and could vary based on requirements.

Standard	Int. Cal. Std. Amount	Working BFB Surrogate Std. Amount	Final Volume in Reagent Water	Final Extract Volume	Final Calibration Standard/Surrogate Concentration, ug/mL
CAL1	5uL	5uL	35mL	2mL	0.0003 / 0.0625
CAL2	10uL	10uL	35mL	2mL	0.0006 / 0.125
CAL3	25uL	15uL	35mL	2mL	0.0015 / 0.1875
CAL4	50uL	20uL	35mL	2mL	0.003 / 0.25
CAL5	125uL	50uL	35mL	2mL	0.0075 / 0.625
CAL6	250uL	75uL	35mL	2mL	0.015 / 0.9375
CAL7	500uL	100uL	35mL	2mL	0.03 / 1.25

10.2.3.3. Working BFB Surrogate Standard

Dilute 250uL of the Stock BFB Surrogate Standard (2000ug/mL) to 20mL with methanol for a final concentration of 25mg/L.

10.2.3.4. Intermediate EDB/DBCP ICV Standard

Dilute 25uL of the Stock EDB/DBCP ICV/CCV Standard (2000ug/mL) to 10mL with methanol for a final concentration of 5mg/L.

10.2.3.5. Working EDB/DBCP Spike Standard

Dilute 500uL of the Intermediate #1 EDB/DBCP ICV/CCV Standard (5mg/L) to 10mL with methanol for a final concentration of 0.25mg/L.

10.2.3.6. Working EDB/DBCP ICV/CCV Standard

Dilute 24uL of the Working EBD/DBCP Spike Standard (0.25mg/L) and 20uL of the Working BFB Surrogate Standard (25mg/L) to 35mL with reagent water in a 50mL Class A graduated cylinder. Extract per Section 12.2.

11. Calibration

11.1. Initial Calibration

11.1.1. Calibration standards are extracted and analyzed in the same manner as the samples in order to compensate for possible extraction losses. Calibration standards, check standards, QC samples and blanks are prepared by measuring 35mL of reagent water using a 50mL Class A graduated cylinder and pouring it into a 40mL VOA vial. The appropriate amount of standard and surrogate is then added to the 35mL of reagent water. Each calibration standard is extracted as outlined in Section 12.2.

11.1.2. For initial calibration, analyze a minimum of five concentrations of calibration standard. The lowest calibration standard must be at or below the required reporting limit. Determine the calibration factor (CF) of each standard using the calculation below. Determine the relative standard deviation (RSD) of the calibration factors using the calculation below. If the RSD is $\leq$10% over the working range, linearity through the origin is assumed, and the average calibration factor can be used to calculate sample

concentrations in place of a calibration curve.

$$CF = \frac{\text{Response}}{\text{Concentration}} \qquad RSD = \frac{\text{Std. Dev.}}{\text{Avg. CF}} \times 100$$

11.1.3. If the RSD is >10% over the working range, then linearity through the origin cannot be assumed. A linear regression or weighted linear regression equation that does not pass through the origin can be employed

11.1.4. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be $\geq$0.99. Refer to SW-846 Method 8000C for details regarding equations.

11.1.5. Initial Calibration Corrective Action: If the initial calibration curve does not meet the required criteria to be used for quantitative purposes, a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new calibration standards must also be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.1.6. Initial Calibration Verification (ICV): The initial calibration must be verified through the analysis of an Initial Calibration Verification (ICV) standard. The ICV is analyzed immediately following the initial calibration curve. Acceptable recovery range for the ICV is 60-140%.

11.1.7. ICV Corrective Action: If the ICV fails the criteria, another ICV may be analyzed. If the second ICV fails, a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new calibration standards must also be considered. Samples associated with a failed ICV must be reanalyzed. Exception: If the ICV fails during an overnight run and is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

11.2. Calibration Verification

11.2.1. The initial calibration must be verified daily with the analysis of a Continuing Calibration Verification Standard (CCV) at the beginning of the analytical sequence, after every 20 samples, and at the end of the analytical sequence, as a minimum requirement. Each CCV is extracted as outlined in Section 12.2.

11.2.2. For each CCV, if the calculated concentration of each parameter is within 60-140% recovery, then the initial calibration is considered still valid, and the analyst may continue to use the initial calibration to calculate sample results.

$$\text{Percent Recovery} = (\text{Calculated Conc.} \div \text{Theoretical Conc.}) \times 100$$

11.2.3. CCV Corrective Action: If a CCV fails the acceptance criteria, check the instrument operating conditions, and if necessary, restore them to the original settings, and analyze another CCV. If the response still fails the acceptance criteria, then a new initial calibration must be prepared. Samples associated with a failed CCV must be reanalyzed. Exception: If the CCV is outside of the upper control limit, indicating high bias,

associated samples determined to be <RL may be reported.

11.2.4. Retention Time Windows: Retention time windows must be established for the identification of target analytes. See Section 11.6 of Method 8000C for guidance on establishing retention time windows. The retention time of all analytes in all verification standards must fall within the established retention time windows. If an analyte falls outside the retention time window in a calibration verification standard, new retention time windows must be calculated, unless instrument maintenance corrects the problem.

12. Procedures

12.1. Sample and Batch QC Preparation

12.1.1. Remove 5mL of sample using a disposable pipette. After the 5mL is removed, determine the vial gross weight by weighing the VOA vial and cap to the nearest 0.1g and record the weight. Add 20µL of the Working BFB Surrogate Standard (25mg/L) to the vial for a final BFB concentration of 0.25ug/L.

12.1.2. Prepare a Method Blank by adding 20uL of the Working BFB Surrogate Standard (25mg/L) to 35mL of reagent water in a 40mL VOA vial for a final surrogate concentration of 25ug/L. A Method Blank is required for each batch of 20 or fewer samples.

12.1.3. Prepare a Laboratory Control Sample (LCS) by adding 35µL of the Working EDB/DBCP Spike Standard (0.25mg/L) and 20uL of the Working BFB Surrogate Standard (25mg/L) to 35mL of reagent water in a 40mL VOA vial for a final concentration of 0.25ug/L and 25ug/L, respectively. An LCS is required for each batch of 20 or fewer samples.

12.1.4. Prepare a matrix spike by removing 5mL of sample using a disposable pipette and adding 35µL of the Working EDB/DBCP Spike Standard (0.25mg/L) and 20µL of the Working BFB Surrogate Standard (25mg/L) to the vial for a nominal final spike concentration of 0.25ug/L and 25ug/L, respectively. One MS/MSD set should be prepared for each batch of 20 or fewer samples when sample volume permits.

12.1.5. Extract all prepared samples and QC as outlined in Section 12.2.

12.2. Extraction Procedure

12.2.1. Allow all standards, QC and samples to come to room temperature prior to extraction.

12.2.2. Add approximately 6g sodium chloride to each. Cap and shake until the sodium chloride is dissolved (approximately 10 seconds).

12.2.3. Add 2.0mL hexane to each. Cap and shake for a minimum of 2 minutes. Allow the layers to separate. If storing at this stage, keep the container upside down and refrigerated.

12.2.4. Carefully transfer a sufficient amount of the hexane layer to an autosampler vial for analysis being careful not to include any water.

12.2.5. Determine the vial tare weight by discarding the entire contents of the vial. Weigh the empty vial and cap to the nearest 0.1g and record this weight. Calculate the net weight of sample to the nearest 0.1g by difference using the weight obtained in Section 12.1.1. This net weight is equivalent to the volume of water extracted in mL.

$$\text{Sample Volume (mL)} = \text{Vial Gross Weight (g)} - \text{Vial Tare Weight (g)}$$

12.3. Sample Analysis

12.3.1. All sample extracts must be analyzed at room temperature and the system must be calibrated per Section 11, and free of contamination before samples are analyzed.

12.3.2. Gas Chromatography conditions: Configure the GC per manufacturer's instructions.

12.3.3. Inject equal aliquots of all standard, QC and sample extracts into the GC under the same operating conditions as used for the calibration standards. The sample vials are loaded onto the autosampler that is programmed via the data system to inject the required volume.

12.4. Qualitative Analysis

12.4.1. Analytes are tentatively identified if a peak elutes in the retention time window characteristic of that compound on the primary column. To confirm the presence of that analyte in the sample extract, the peak must also elute in its characteristic retention time window on a second dissimilar column.

12.5. Quantitative Analysis

12.5.1. Use the calibration curve or the calibration factor to directly calculate the uncorrected concentration of each target analyte.

13. Quality Control

Table 13.1. Batch Quality Control Requirements

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples.	Target analytes must be less than reporting limits	Re-extract and re-analyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analytes	One per preparation batch of up to 20 samples.	60-140% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, re-extract and re-analyze associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analytes	One MS/MSD set per preparation batch of up to 20 samples.	60-140% Recovery ≤20% RPD	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Surrogate	Applicable surrogate compound	Added to each sample, standard and method blank	50-150% Recovery	Samples with surrogate failures must be re-extracted and reanalyzed. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported surrogate data must be qualified. 2) If surrogate result is >QC limits, and sample results are non-detect, the sample results may be reported without qualifiers. The surrogate must be qualified. 3) MS/MSD surrogate recovery failures do not constitute the re-extraction or reanalysis of samples but the surrogate data must be qualified.

14. Data Analysis and Calculations

14.1. Calculate the corrected sample concentration using the following equation:

$$\text{Concentration, ug/L} = \frac{(X_s)(V_f)(D)}{(V_i)}$$

Where: X_s = On-column concentration of the analyte, ug/mL
V_f = Final volume of concentrated extract, mL
D = Dilution factor of extract
Vi = Initial sample volume, L

14.2. LCS equation

$$R = (C/S) * 100$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation

$$R = \frac{(Cs - C)}{S} * 100$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD calculations:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. MDLs must be determined per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. Every analyst who performs this method must document acceptable accuracy and precision by passing a demonstration of capability study annually.

19. Method Modifications

19.1. Sodium Chloride is not baked in the muffle furnace because it has been found to be contaminant-free from the vendor.

19.2. Approximately 6g of sodium chloride is added to each sample instead of the 7g indicated in the method in order to allow enough headspace in the vial to facilitate a thorough extraction.

19.3. Samples are shaken for a minimum of 2 minutes instead of the 1 minute indicated in the method to facilitate a more thorough extraction.

19.4. Column type and instrument conditions may vary from those listed in the method.

19.5. Precision limits of ≤20% RPD are observed instead of the 10% RSD indicated in the method.

19.6. Because preservation and holding time requirements for Method 8011 are somewhat ambiguous, preservation to pH<2 with HCl or preservation with sodium thiosulfate as described in Method 504.1 are considered acceptable. Holding time is 14 days from date of collection regardless of preservation.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling, or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention and Waste Management

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. U.S. EPA SW846 Test Methods for Evaluating Solid Waste Method 8011, Revision 0, July 1992

25.2. U.S. EPA SW846 Test Methods for Evaluating Solid Waste, Method 8000C, Revision 3, March 2003.

25.3. U.S. EPA, Method 504.1, Revision 1.1, 1995.

25.4. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Description of Change	Date
S-IN-O-167-Rev.02	1. Converted to 27 section format. 2. Section 6.1: corrected wording regarding hexane contamination. 3. Table 7.1: updated storage temperature format. 4. Table 10.3: separated intermediate standards. 5. Section 11.1: added reference to extraction procedure. 6. Section 11.2: added reference to extraction procedure. 7. Section 12: rearranged to be in the order of the procedure with sample preparation then extraction then analysis. 8. Table 13.1: corrected MS/MSD recovery criteria to match method. 9. Section 14.1: corrected sample concentration calculation to match LIMS. 10. Section 25.3: added years 2003 and 2009 to TNI reference.	13Sep2017
S-IN-O-167-Rev.03	1. Table 7.1: added sodium thiosulfate preservation option and removed shorter holding time for pH>2. 2. Section 11.1.3: added option for weighted linear regression. 3. Section 12.1.1: removed pH determination and instructions for qualifying results if pH>2. 4. Section 18.1: updated MDL procedure reference. 5. Section 19: added preservation options as a modification. 6. Section 25: added reference to Method 504.1. 7. Section 25.4: added NELAC to reference.	8Jul2018
S-IN-O-167-Rev.04	1. Table 10.3: removed intermediate calibration standards 2 and 3 and intermediate ICV standard 2. 2. Section 10.2.3: removed preparation of intermediate calibration standards 2 and 3 and intermediate ICV standard 2 and revised other standard preparations.	30Sep2018
ENV-SOP-IND1-0093-rev.01	1. Removed cover, table of contents and headers for use in Master Control. 2. Table 10.3: revised to reflect current standard-making practice by removing some of the intermediate standards. 3. Section 10.2.3: revised to reflect current standard-making practice by removing some of the intermediate standards. 4. Section 11.1.1: added language to specify the use of a 50mL graduated cylinder for preparation of blanks and standards. 5. Section 12.1.4: clarified preparation of matrix spike. 6. Table 13.1: revised corrective action for LCS to include on reanalysis.	26Nov2018

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STANDARD OPERATING PROCEDURE

THE DETERMINATION OF ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY

REFERENCE METHOD: SW-846 METHOD 8081B

SOP NUMBER:	S-IN-O-173-rev.04
EFFECTIVE DATE:	May 1, 2018
SUPERSEDES:	S-IN-O-173-rev.03

APPROVAL

General Manager — April 27, 2018 Date

Quality Manager — April 27, 2018 Date

Department Manager — April 27, 2018 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

This is **COPY#**_____ distributed on _____ by _____

S-IN-O-173-rev.04

Table of Contents

1. Purpose

1.1. The purpose of this SOP is to provide a laboratory specific procedure for determining the concentration of organochlorine pesticides in sample extracts while meeting the requirements specified in SW-846 Method 8081B.

2. Summary of Method

2.1. Aqueous samples are extracted using Method 3510C, Separatory Funnel Extraction or otherappropriate technique or solvents. Solids are extracted using Method 3546, Microwave Extraction or other appropriate technique or solvents.Non-aqueous wastes are prepared for analysis using Method 3580, Waste Dilution or other appropriate technique or solvents.

2.2. Cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes. Refer to cleanup SOPs for additional details.

2.3. The extract is analyzed by a gas chromatograph fitted with an electron capture detector (ECD). Compound identification is confirmed by a secondary column.

3. Scope and Application

3.1. The list of applicable target compounds and reporting limits determined by method 8081B is found in Table 1. Other compounds may be reported upon completion of appropriate validation procedures. Refer to LIMS for method detection limits.

3.2. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of GC systems and interpretation of GC Pesticide data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This procedure is applicable to organic extracts of groundwater, surface water, soil, sediment and waste.

5. Limits of Detection and Quantitation

5.1. The full list of compounds and reporting limits analyzed by this laboratory for method 8081B is found in Table 1. Other analytes may be reported upon completion of appropriate validation procedures. Refer to LIMS for method detection limits.

6. Interferences

6.1. Matrix interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware. These interferences lead to discrete artifacts or elevated baselines in gas chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates, which are easily extracted during lab operations. Avoiding the use of plastics in the lab can best minimize interferences from phthalates.

6.2. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of

matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. Cleanup procedures may be used to remove such interferences. Refer to the appropriate cleanup SOPs if extract cleanup to remove interferences is required.

6.3. Other halogenated pesticides, industrial chemicals, co-eluting organophosphorous pesticides, chlorophenols and poly chlorinated biphenyls may interfere with target pesticide identification. Multi-component analytes such as toxaphene, chlordane, strobane, and aroclors co-elute with a large number of single peak pesticides. Keponeextracted from samples can cause a broad chromatographic peak that elutes as late as one minute after the retention time of the calibration standards. Method 8081B is not recommended for determining Kepone.

6.4. Co-elution of target analytes may also occur. Common column pair and analyte co-elutions are listed in Method 8081B.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage, and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	100mL widemouth amber glass bottle	None required	Cool to ≤6ºC	Extract within 7 days of collection and analyze within 40 days of extraction.
Solid	200 grams in 4oz. glass jar	None required	Cool to ≤6ºC	Extract within 14 days of collection and analyze within 40 days of extraction.
Non-Aqueous Waste	1 liter in amber glass bottle	None required	Cool to ≤6ºC	Extract within 14 days of collection and analyze within 40 days of extraction.

Sample extracts must be stored refrigerated and in the dark. Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Vendor	Model / Version	Description / Comments
GC	Agilent	7890A or equivalent	Equipped with dual ECD Detectors; dual columns, and dual injectors, autosampler and data system, or equivalent system.
GC Columns	Restek	RTX-CLP1 and RTX-CLP2, or equivalent	Fused silica; 30m x 0.32mm x 0.32um and 30m x 0.32mm x 0.25um, respectively, or equivalent columns

9.2. General Supplies

Item	Vendor	Description
Glass syringes	Hamilton or equivalent	Various sizes
Glass vials	Fisher or equivalent	20mL volume with Teflon lined caps
Autosampler vials	Fisher or equivalent	2mL volume with Teflon lined crimp tops
Micro-inserts	Hewlett Packard or equivalent	Various sizes

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Hexane	Pesticide grade or equivalent

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, initial calibration verification, instrument performance and continuing calibration verification.

Table 10.2 Standard Definitions and vendors

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	ICAL
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for required target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	CCV
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the calibration curve.	ICV
Breakdown Check Standard	A standard injection analyzed to evaluate the reactivity (breakdown) of Endrin and 4,4'-DDT on the chromatography system	PEM

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Pesticide Calibration standard	Restek; Organochlorine Pesticide mix AB#2 Cat #32292, 8-80ug/mL in 1:1 hexane:toluene, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate Pesticide Calibration Standard	Refer to Section 10.2.3.1	Solution good for 6 months from preparation	Same as stock standard
Working Pesticide calibration standards	Refer to Section 10.2.3.2	Solution good for 6 months from preparation.	Same as stock standard.
Stock Pesticide ICV standard	AccuStandard; SW8081 single Column Analyte mix, Cat # M-8081-SC, 1000ug/mL in 1:1 Hexane:Toluene, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Intermediate Pesticide ICV standard	Refer to Section 10.2.3.3	Solution good for 6 months from preparation.	Same as stock standard.
Working Pesticide ICV standard	Refer to Section 10.2.3.4	Solution good for 6 months from preparation.	Same as stock standard.
Stock surrogate standard	Ultra; TCMX & DCB surrogate stock Cat# ISM-320-1, 200ug/mL in acetone, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions

Standard Type	Description	Expiration	Storage
Stock Toxaphene Calibration standard	Ultra; Cat# EPA1161, 1000ug/mL in Methanol, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Toxaphene Calibration Standard	Refer to Section 10.2.3.5	Solution good for 6 months from preparation.	Same as stock standard.
Stock Chlordane(Technical) Calibration standard	Ultra; Cat# PP-150-1, 100ug/mL in Hexane, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Chlordane Calibration Standard	Refer to Section 10.2.3.6	Solution good for 6 months from preparation.	Same as stock standard.
Stock 4,4'-DDT standard	Ultra; Cat# PST280I100A01, 100ug/mL in iso-Octane, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Stock Endrin standard	Ultra; Cat# PP-230-1, 100ug/mL in Methanol, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions
Working Breakdown Check Standard	Refer to Section 10.2.3.7	Solution good for 6 months from preparation.	Same as stock standard.

10.2.3. Standard Preparation Procedures

10.2.3.1. IntermediateCalibration Standard Preparation

Dilute 2.5mL of the Stock Pesticide Calibration standard (8-80ug/mL),200uL of Stock Surrogate standard (200ug/mL)to 25mL in Hexanefor a final concentration of 800-8000ug/L.

10.2.3.2. Working Pesticide Calibration Standard Preparation

The following are examples of calibration standard amounts and could vary based on requirements. Concentrations are listed in Table 2:

Calibration Standard	Volume of Intermediate Calibration Standard	Final Volume in Hexane
CAL1	1uL	800uL
CAL2	5uL	800uL
CAL3	10uL	800uL
CAL4 (CCV)	25uL	1000uL
CAL5	100uL	1600uL
CAL6	100uL	1000uL

10.2.3.3. Intermediate Pesticide ICV Standard Preparation

Dilute 25uL of the Pesticide ICV Standard (1000ug/mL)and 125uL Stock Surrogate Standard to 1mL with Hexane for a final concentration of 25ug/mL.

10.2.3.4. Working Pesticide ICV Standard Preparation

Dilute 20uL of the Intermediate Pesticide ICV standard (25ug/mL)to 10mL in Hexane. Concentrations listed in Table 2.

10.2.3.5. Working Toxaphene Standard Preparation

Dilute 5uL of Stock Toxaphene standard (1000ug/mL) and 2.5uL of Stock Surrogate standard (200ug/mL) to 10mL in Hexane for a final concentration of 500ug/L Toxaphene.

10.2.3.6. Working Chlordane (Technical) Standard Preparation

Dilute 50uL of Stock Chlordane standard (100ug/mL) and 2.5uL of Stock Surrogate standard (200ug/mL) to 10mL in Hexane for a final concentration of 500ug/L Chlordane.

10.2.3.7. Working Breakdown Check Standard Preparation

Dilute 10uLof Stock Endrin standard (100ug/mL) plus 10uL of Stock 4,4'-DDT standard (100ug/mL) plus 2.5uL Stock Surrogate standard (200ug/mL)to 10mL in Hexane for a final concentration of 100ug/L Endrin and 4,4'-DDT.

11. Calibration

11.1. Before the initial calibration standards are injected, it is advisable to perform routine injection port and column maintenance due to the sensitivity of the ECD detector.

11.2. Breakdown Check: A Breakdown Check Standard must be analyzed prior to the start of an analytical sequence and every 12 hours. The breakdown of both 4,4'-DDT and Endrin in the breakdown check standard must be ≤15%. The breakdowns are calculated using peak areas in the following equations:

$$\%\, Breakdown\, DDT = \frac{DDD + DDE}{DDT + DDD + DDE} \times 100$$

$$\%\, Breakdown\, Endrin = \frac{Endrin\, Ketone\, +\, Endrine\, Aldehyde}{Endrin\, +\, Endrin\, Ketone\, +\, Endrin\, Aldehyde} \times 100$$

11.3. Initial Calibration: Initial calibration standards for single peak pesticides are introduced into the GC from the lowest to highest concentration by direct injection. Five calibration points, at a minimum, are analyzed to evaluate linearity. The lowest calibration standard must be at or below the required reporting limit. Refer to the Quality Manual for more information regarding calibration curves.

11.3.1. Calculate the Calibration Factor (CF) for each individual pesticide peak in each of the initial calibration standards using the calculation below:

$$CF = \frac{Peak\ \ Response\ or\ Area}{Concentration}$$

11.3.2. The percent relative standard deviation (%RSD) is calculated as follows:

$$\%\, RSD = \frac{Standard\ Deviation\ of\ Calibration\ Factors}{Average\ of\ Calibration\ Factors}$$

11.4. If the %RSD of the CFs for each analyte is ≤ 20% over the calibration range, then the response of the instrument is considered linear and the average CF may be used to determine sample concentrations.

11.5. If any %RSD is >20%, the analyst may employ a regression equation that does not pass through the origin. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be ≥ 0.99.Refer to Method 8000C for additional information regarding calibration.

11.6. Initial Calibration Corrective Action: If the initial calibration curve does not meet the required criteria to be used for quantitative purposes, a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new calibration standards must also be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.7. Each day that analysis is performed, the calibration standard(s) should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Are the retention times consistent over the range of calibration for each compound? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably. Additionally, examination of signal-to-noise ratio of analytes in low-level standards may be a useful diagnostic tool to monitor instrument performance. Signal-to-noise ratio is defined as the ratio of the analyte signal to the noise measured on a blank. It is recommended but not required that the signal-to-noise ratio be at least three to confirm detection.

11.8. Initial Calibration Verification (ICV): In addition to meeting the response and linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known true value. This step is referred to as the Initial Calibration Verification. The ICV must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent recovery (%Rec) of the observed ICV according to the following equation:

$$\%\,Recovery = \frac{Observed\ Concentration}{Theoretical\ Concentration}$$

The ICV is analyzed immediately following the initial calibration curve. The ICV recoveries are evaluated against a default acceptance range of 70-130% recovery.

11.9. ICV Corrective Action: If the ICV exceeds the acceptance range, another ICV may be analyzed. If the second ICV also exceeds the acceptance range, a new initial calibration should be prepared. Alternatively, the allowance for use of the ICV when the criterion is not met is documented and is at the discretion of the Department Manager, Quality Manager, General Manager or designee.

11.10. Calibration of Multi-component Analytes: Multi-component analytes including Toxaphene and Chlordane are primarily identified by their pattern or fingerprint. These multi-component analytes only require a single calibration standard near the mid-point of the expected calibration range. Use 3-5 major peaks for technical chlordane calibration and 4-6 major peaks for Toxaphene. The Toxaphene pattern may utilize a single total area sum including the characteristic baseline rise or hump of the unresolved mixture. As a routine the lab will calibrate using 5 major peaks each for both compounds. The areas of the peaks selected should be summed and used to determine the concentration. Alternatively, use each peak to calculate a calibration factor for that peak. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample and the resulting 4-6 concentrations are averaged to provide the final result for the sample. A book of reference chromatograms for Toxaphene and

Chlordane has been created. Refer to this book for the preferred peaks used for calibration of Toxaphene and Chlordane.

11.11. Daily and Continuing Calibration: Verify the initial calibration each 12-hour shift by injecting a Continuing Calibration Verification (CCV) standard prior to conducting any sample analyses. The CCV must also be analyzed at intervals of not less than once every 20 client samples and at the end of the analysis sequence.

11.11.1. For initial calibrations that employed average calibration factor, the calibration factor (CF_v) for each analyte calculated from the CCV must not exceed a %Difference (%D) of more than +/-20% when compared to the CF_{avg} from the initial calibration curve.

$$\%\ Difference = \frac{\text{Verification Response Factor}}{Mean\ Calibration\ Response\ Factor}\ x\ 100$$

11.11.2. For initial calibrations that employed a linear calibration, the % Drift for each analyte calculated from the CCV must be within +/-20% in order to use the calibration model to quantitate sample results.

$$\%\ Drift = \frac{\text{Calculated concentration} - \text{Theoretical concentration}}{\text{Theoretical concentration}}\ x\ 100$$

11.12. CCV Corrective Action: If a CCV fails the acceptance criteria, check the instrument operating conditions, and if necessary, restore them to the original settings, and analyze another CCV. If the response still fails the acceptance criteria, then a new initial calibration must be prepared. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

12. Procedures

12.1. All sample extracts must be analyzed at room temperature and the system must be calibrated as per Section 11, and free of contamination before samples are analyzed.

12.2. Gas Chromatography conditions: Configure the GC per manufacturer's instructions.

12.3. Inject 2uL aliquots of all samples and quality control samples into the GC under the same operating conditions as used for the calibration standards. The sample vials are loaded onto the autosampler that is programmed via the data system to inject the necessary volume.

12.4. Qualitative Analysis: Compounds are identified as present when the following criteria are met:

12.4.1. Absolute retention times are used for the identification of organochlorine pesticides. Retention time windows are established on both columns to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. To establish retention time windows, make three or more injections of a standard over the course of a 72-hour period, at a minimum. Record the retention time in minutes for the major peaks and surrogate to three decimal places. Calculate the mean and standard deviation of the absolute retention times of the standard. The retention time window is defined as +/-3 times the standard deviation of the mean absolute retention time established during the 72-hour period. Alternatively, a default retention time window of +/-0.03 minutes may be used.

12.4.2. Establish the center of the retention time window for each major peak and surrogate by using the absolute retention time for each major peak and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

12.4.3. It may also be useful to establish the center of the retention time window for single point standards by using the absolute retention time for each major peak and surrogate from the single point standards analyzed at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the single point standards analyzed with the initial calibration.

12.4.4. Tentative identification of an analyte (either single component or multi-component) is made when a peak from the sample extract falls within the established retention time window for a known target compound. If necessary, analytes identified on a single column may be confirmed on a second dissimilar GC column. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition, the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a standard of the target analyte at a concentration at least as low as the concentration estimated from the primary analysis. When the dual-column approach is employed, the target pesticides are identified and confirmed when they meet the identification criteria on both columns. For multi-component confirmation, pattern recognition is also considered when determining analyte presence. When confirmation is made on a second column, that analysis should meet all of the QC criteria described above for calibration, retention times, etc.

12.4.5. A book of reference chromatograms for each Toxaphene and Chlordane has been created. Refer to this book for the preferred peaks and ratios between peaks that are characteristic of Toxaphene and Chlordane. When interferences are present or degradation has occurred, the following tools are helpful for proper identification:

- Overlays of the sample chromatogram with chromatograms of Toxaphene and Chlordane standards
- Comparison of characteristic peak retention times with Toxaphene and Chlordane standards
- Comparison of the ratio between characteristic peaks with ratios of Toxaphene and Chlordane standards
- Comparison with historical results, if available
- Analyst judgment and consultation with other experienced analysts
- Consistent application of evaluation tools

12.5. Quantitative Analysis

12.5.1. Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard or calibration standards interspersed within the samples. The results from these bracketing standards must meet the calibration verification criteria in Sections 11.11 through 11.12.

12.5.2. A book of reference chromatograms for Toxaphene and Chlordane has been created. Refer to this book for the preferred peaks used for quantitation of Toxaphene and Chlordane. When interferences are present or degradation has occurred, peaks yielding concentrations or areas that are dissimilar to the others may be excluded.

12.5.3. When concentrations exceed the calibration range, the sample extract should be rerun at a dilution or the result must be qualified as estimated.

12.5.4. When the result between a primary and confirmation column disagree by >40% Relative Percent Difference (RPD), the chromatograms should be checked for any obvious reasons for the differences. This could be overlapping or co-eluting peaks, poor baseline integration, or a system more sensitive to interferences in the samples. If no anomalies are noted and there are no chromatographic problems, then SW-846 8000C section 11.10.4.2 advises to report the lower of the two results. The determination to report the lower result or the higher result may rest with the group supervisor or their designee. Where the higher result is reported, the reasoning should be well documented. In either case, the client must be informed of the disparity between the results on the final report.

12.5.5. Refer to the Manual Integrations SOP for guidance on performing and documenting manual integrations.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water or simulated soil matrix	One per preparation batch of up to 20 samples, per matrix.	Target analytes must be less than reporting limits	Re-extract and re-analyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analytes	One per preparation batch of up to 20 samples, per matrix.	Lab-generated limits Refer to the LIMS for acceptance limits.	Re-extract and re-analyze associated samples if original LCS is outside acceptance limits. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analytes	One MS/MSD set per preparation batch of up to 20 samples, per matrix.	Lab-generated limits Refer to the LIMS for acceptance limits.	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Surrogate	Applicable surrogate compound	Added to each sample, standard and method blank	Lab-generated limits Refer to the LIMS for acceptance limits.	Samples with surrogate failures must be re-extracted and reanalyzed. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported surrogate data must be qualified. 2) If surrogate result is >QC limits, and sample results are non-detect, the sample results may be reported without qualifiers. The surrogate must be qualified. 3) MS/MSD surrogate recovery failures do not constitute the re-extraction or reanalysis of samples but the surrogate data must be qualified.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

$$\text{Aqueous Sample (ug/L)} = \frac{(X_s)(V_f)(D)}{(V_i)} \qquad \text{Solid Sample (ug/kg)} = \frac{(X_s)(V_f)(D)}{(W_s)}$$

Where: X_s = Concentration of the analyte from the instrument, ug/L
V_f = Final volume of extract, L
D = Dilution factor of extract
V_i = Volume of aqueous sample extracted, L
W_s = Weight of solid sample extracted, kg

$$\text{Moisture corrected concentration} = \frac{\text{(Final concentration as received)}}{\text{(100 - \%Moisture)}} \times 100$$

14.2. LCS equation:

$$\mathbf{R = (C/S) * 100}$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation:

$$\mathbf{R = \frac{(Cs - C)}{S} * 100}$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD equation:

$$\mathbf{RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100}$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. MDLs must be conducted per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability (DOC) study.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in the Waste Handling or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Wastes", EPA SW-846, methods 8081B and 8000C.

25.2. Pace Analytical Quality Manual; latest revision.

25.3. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Table 1: Target Compounds and Default Reporting Limits

26.2. Table 2: Target Compounds and Surrogate Calibration Concentrations

27. Revisions

Document Number	Reason for Change	Date
S-IN-O-173-rev.00	1. Converted to Pace SOP format. 2. Revised standard solutions for lower final volumes to reduce waste. 3. Added waste dilution reference for preparation of non-aqueous waste.	04Feb2015
S-IN-O-173-rev.01	1. Cover page: revised document control format. 2. Section 2.1: added solids extracted by Method 3546. 3. Table 1: added solid RLs.	24Nov2015
S-IN-O-173-rev.02	1. Converted to 27 section format. 2. Table 7.1: added information for solids and revised storage temperature format. 3. Section 10.2.3: updated recipes for standards to match current practice. 4. Section 12.3: updated injection volume. 5. Section 12.4.1: added use of default RT window as an alternative. 6. Section 14.1: corrected equations to be in like terms with instrument output. 7. Section 25.3: added years 2003 and 2009 to TNI reference.	16Nov2017
S-IN-O-173-rev.03	1. Section 8.1: removed reference to Glossary section of QAM. 2. Section 10.2.1: removed reference to LCS and MS/MSD standards. 3. Table 10.2: added PEM acronym. 4. Section 10.2.3: updated standard preparation to match current procedures. 5. Section 11.10: added language for example chromatograms and preferred Toxaphene and Chlordane peaks used for calibration. 6. Section 12.4.5: added language and a list of tools to help in the identification of Toxaphene and Chlordane in a complex matrix. 7. Section 12.5.2: added language to help in the quantitation of Toxaphene and Chlordane in a complex matrix. 8. Section 18.1: updated MDL language to new EPA procedure.	7Mar2018
S-IN-O-173-rev.04	1. Table 7.1: updated aqueous sample collection to reflect RVE. 2. Section 10.2.3.1: added final concentration range. 3. Section 10.2.3.2: updated ICAL points to reflect RVE. 4. Section 25.3: added NELAC to reference. 5. Table 2: updated ICAL concentrations to reflect RVE.	27Apr2018

Table 1: Target Compounds and Default Reporting Limits[1]

Analyte	CAS#	Reporting Limit Waters (ug/L)	Reporting Limit Solids (ug/kg)
α-BHC	319-84-6	0.05	2.5
β-BHC	319-85-7	0.05	2.5
ɣ-BHC (Lindane)	58-89-9	0.05	2.5
δ-BHC	319-86-8	0.05	2.5
Aldrin	309-00-2	0.05	2.5
Heptachlor	76-44-8	0.05	2.5
Heptachlor Epoxide	1024-57-3	0.05	2.5
(cis)Alpha-chlordane	5103-71-9	0.5	2.5
(trans)Gamma-chlordane[2]	5103-74-2	0.5	2.5
Endosulfan I	959-98-8	0.05	2.5
4,4-DDE	72-55-9	0.1	5
4,4-DDD	72-54-8	0.1	5
4,4-DDT	50-29-3	0.1	5
Endrin	72-20-8	0.1	5
Dieldrin	60-57-1	0.1	5
Endosulfan II	33213-65-9	0.1	5
Endrin Aldehyde	7421-93-4	0.1	5
Endosulfan Sulfate	1031-07-8	0.1	5
Endrin Ketone	53494-70-5	0.1	5
Methoxychlor	72-43-5	0.5	25
Toxaphene	8001-35-2	1.0	50
Chlordane (Technical)	12789-03-6	0.5	50

[1] TargetCompounds and Reporting Limits are subject to change.

[2] SW846-8081A originally identified the compound associated with CAS#5103-74-2 as ɣ-chlordane or *gamma*-chlordane however SW846-8081B along with the reference material providers identifies this as *trans*-chlordane.CAS#5566-34-7 has been assigned to gamma-chlordane however some state agencies, NELAC (TNI), and Proficiency testing providers still associate the CAS#5103-74-2 with gamma-chlordane and certify as that compound.

Table 2: Target Compound and Surrogate Calibration Concentrations [3]

Analyte	CAL1 ug/L	CAL2 ug/L	CAL3 ug/L	CAL4 ug/L	CAL5 ug/L	CAL6 ug/L	ICV ug/L
α-BHC	1	5	10	20	50	80	50
β-BHC	1	5	10	20	50	80	50
ɣ-BHC (Lindane)	1	5	10	20	50	80	50
δ-BHC	1	5	10	20	50	80	50
Aldrin	1	5	10	20	50	80	50
Heptachlor	1	5	10	20	50	80	50
Heptachlor Epoxide	1	5	10	20	50	80	50
alpha-Chlordane	1	5	10	20	50	80	50
gamma-Chlordane	1	5	10	20	50	80	50
Endosulfan I	1	5	10	20	50	80	50
4,4-DDE	2	10	20	40	100	160	50
4,4-DDD	2	10	20	40	100	160	50
4,4-DDT	2	10	20	40	100	160	50
Endrin	2	10	20	40	100	160	50
Dieldrin	2	10	20	40	100	160	50
Endosulfan II	2	10	20	40	100	160	50
Endrin Aldehyde	2	10	20	40	100	160	50
Endosulfan Sulfate	2	10	20	40	100	160	50
Endrin Ketone	2	10	20	40	100	160	50
Methoxychlor	10	50	100	200	500	800	50
DCB (surr)	2	10	20	40	100	160	50
TCMX (surr)	2	10	20	40	100	160	50
Toxaphene			500				50
Chlordane (technical)			500				50

[3] Compounds and concentrations are subject to change.

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QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	19 Feb 2019, 09:40:56 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Sayer (004775)	General Manager	20 Feb 2019, 07:18:06 AM	Approved
Anne Troyer (008754)	Manager - Lab Services	20 Feb 2019, 07:51:38 AM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for determining alkalinity of aqueous and solid samples in while meeting the requirements specified in Standard Method 2320B; 2011.

2. Summary of Method

2.1. An unaltered sample is titrated to a potentiometric endpoint of pH 8.3 and/or pH 4.5. The sample cannot be filtered, diluted, concentrated or altered in any way prior to titration. The titration may be performed manually or using an autotitrator.

3. Scope and Application

3.1. Automated titration is allowable under this method.

3.2. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of alkalinity analysis equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This method is applicable for the measurement of alkalinity in water, wastewater, surface water, ground water, saline waters and domestic and industrial wastes. This method has been modified for the determination of alkalinity in solids.

5. Limits of Detection and Quantitation

5.1. This method is applicable for all ranges of alkalinity, however appropriate aliquots of sample should be used to avoid a titration volume greater than 50mL. The default reporting limit is 2mg/L for water and 100 mg/kg for solids.

6. Interferences

6.1. Substances such as salts of weak organic and inorganic acids may cause interference in the pH measurements.

6.2. Soaps, oily matter, suspended solids or precipitates can coat the pH electrode and cause interference or sluggish response.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Water	250mL in plastic container	No preservation required	Cool to ≤6°C	Samples must be analyzed within 14 days of collection date.
Solids	50g in a glass jar	No preservation required	Cool to ≤6°C	Samples must be analyzed within 14 days of collection date.

Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Instrumentation

Equipment	Vendor/Model / Version	Description / Comments
pH meter	Accumet AR25 or equivalent	Must be capable of reading to 0.1 pH units
Autotitrator	Metrohm 855 Titrosampler or equivalent	To include autosampler and data system
Balance	OHaus or equivalent	Capable of weighing to 0.1g
Magnetic stir plate	Fisher or equivalent	With Teflon-coated stir bars

9.2. General Supplies

Item	Vendor	Description
Graduated cylinders	Fisher or equivalent	Class A, 50 and 100mL capacities
Glass burets	Fisher or equivalent	Class A, 10 and 25mL capacities
Erlenmeyer flasks or beakers	Fisher or equivalent	250mL capacity
Volumetric flask	Fisher or equivalent	Class A, 1L capacity
Plastic sample cups	Fisher or equivalent	100mL with lids
Filter paper	Fisher or equivalent	Medium-fine porosity, Fisher P4 or equivalent
Plastic beads	Environmental Express or equivlanet	Or equivalent for use as a simulated solid matrix

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
Sulfuric Acid solution (0.2N)	Fisher/ catalog # SA218-1 or equivalent. Used for samples with alkalinity >1000mg/L.
Sulfuric Acid solution (0.02N)	Fisher/ catalog # SA226-4 or equivalent
pH 4 buffer	Fisher/ catalog # SB101-4 or equivalent
pH 7 buffer (CCV)	Fisher/ catalog # SB107-4 or equivalent
pH 10 buffer	Fisher/ catalog # SB115-4 or equivalent
pH 7 buffer (ICV)	Ricca/ catalog #1551.4-1 or equivalent

10.2. Analytical Standards

Table 10.2 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Alkalinity standard	Fisher catalog #S263-3, Sodium Carbonate, Anhydrous or equivalent. Dried at 250°C for 4 hours and cooled/stored in a desiccator.	Manufacturer's recommended expiration date.	Stored at room temperature.
Intermediate Alkalinity standard	Sodium carbonate solution, approx. 0.05N: Place 1.25g of dried sodium carbonate into a 500mL volumetric flask and dilute to volume with reagent water.	This solution expires one week from date of preparation.	Stored at room temperature.

11. Calibration

11.1. Refer to manufacturer's instructions for the instrumentation being used. Each instrument/electrode system must be calibrated prior to use using pH 4, pH 7 and pH 10 buffers. The two points should be at least three pH units apart. Place the appropriate buffer solution into a clean beaker using sufficient volume to cover the sensing elements of the electrodes and to give the magnetic stir bar some clearance to move

11.2. The slope must be 90-102% in order to proceed .

11.3. Check the instrument calibration with a second source pH 7 buffer (ICV). Record the pH. Results should be within +/- 0.1 pH units.

12. Procedures

12.1. For samples with <1000mg/L of alkalinity as calcium carbonate, use the 0.02N sulfuric acid titrant and proceed to Section 12.3. For samples with >1000mg/L of alkalinity, use the 0.2N sulfuric acid titrant and proceed to Section 12.4. A preliminary titration is helpful in determining the approximate range of the sample.

12.2. Do not filter, dilute, concentrate, or alter the sample prior to analysis.

12.3. Preparation of Solids

12.3.1. Weigh 10g of sample into a beaker and add 100mL of reagent water. Stir for 30 minutes and then allow the slurry to settle overnight. Filter the sample through filter paper. A 50mL aliquot of the filtrate is analyzed as described below.

12.3.2. Prepare a Method Blank: weigh 10g of plastic beads into a beaker and add 100mL of reagent water. Stir for 30 minutes and then allow the method blank to settle overnight. Filter the method blank through filter paper. A 50mL aliquot of the filtrate is analyzed as described below.

12.3.3. Prepare an LCS by diluting 1mL of the Intermediate Alkalinity standard to 50mL with method blank filtrate. The LCS is analyzed as described below.

12.4. Autotitration:

12.4.1. Configure and calibrate the autotitrator according to manufacturer's instructions.

12.4.2. Prepare a Method Blank by measuring 100mL of reagent water into a labeled plastic cup and set the instrument to the Alk Low method for analysis.

12.4.3. Prepare an LCS by diluting 1mL of the Intermediate Alkalinity standard to 50mL with reagent water in a labeled plastic cup for analysis.

12.4.4. Measure 50mL of aqueous sample or solid sample filtrate into a labeled plastic sample cup for analysis. For samples with low alkalinity (<20 mg/L), use a sample volume of 100mL and set the instrument to the Alk Low method for analysis.

12.4.5. Titrate samples per manufacturer's instructions.

12.4.6. Check the instrument calibration with a pH 7 buffer (CCV) after every 10 samples and at the end of the analytical batch. Record the pH. Results should be within +/- 0.1 pH units. If CCV is outside the criteria, reanalyze samples or qualify affected sample results.

12.4.7. If the alkalinity endpoint is not reached using the autotitrator method, the sample may be reanalyzed using a 25mL sample volume. If the endpoint is still not reached, the sample must be titrated using the manual method and the 0.2N sulfuric acid titrant.

12.5. Manual Potentiometric titration:

12.5.1. Prepare a Method Blank by measuring 100mL of reagent water into a labeled flask or beaker and for analysis. Titrate as described below using the 0.02N sulfuric acid titrant.

12.5.2. Prepare an LCS by diluting 1mL of the Intermediate Alkalinity standard to 50mL with reagent water in a labeled flask or beaker for analysis. Titrate as described below using the 0.02N sulfuric acid titrant.

12.5.3. Measure 50mL of aqueous sample or solid sample filtrate into a labeled flask or beaker and record the volume.

12.5.4. While stirring gently, measure the pH using the pH meter and record the value.

12.5.5. Slowly titrate samples using 0.2N sulfuric acid titrant, being careful to stir thoroughly but gently to allow the meter to obtain a stable reading. Titrate to a pH of 8.3 for samples with an initial pH value greater than 8.3 and record the volume and normality of the acid titrant used. This Phenolphthalein alkalinity (P Alkalinity) endpoint will be required to determine Carbonate and Bicarbonate alkalinity for the sample, if requested. Record volume of titrant to the nearest graduation mark of the buret in use.

12.5.6. Continue titration to a pH of 4.5 and record the total volume and normality of the titrant used.

12.5.7. Check the pH meter calibration with a pH 7 buffer (CCV) after every 10 samples and at the end of the analytical batch. Record the pH. Results should be within +/- 0.1 pH units. If CCV is outside the criteria, reanalyze samples or qualify affected sample results.

12.6. Manual Potentiometric titration of low alkalinity samples:

12.6.1. For alkalinity below 20mg/L, titrate 100mL of aqueous sample or solid sample filtrate as in Section 12.4 using a 10mL microburet and the 0.02N acid solution as the titrant.

12.6.2. Stop the titration when the pH is in the range of 4.3 to 4.7 and record the volume used and the exact pH. Very slowly add titrant to lower the pH exactly 0.3 units and record the additional volume of titrant used.

12.6.3. Check the pH meter calibration with a pH 7 buffer (CCV) after every 10 samples and at the end of the analytical batch. Record the pH. Results should be within +/- 0.1 pH units. If CCV is outside the criteria, reanalyze samples or qualify affected sample results.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per analytical batch of up to 20 samples	Target analyte must be less than reporting limit	Reanalyze method blank. If target compound is still >RL in method blank, reanalyze associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, the sample data may be reported without qualifiers, the method blank must be qualified.
Laboratory Control Sample (LCS)	Target analyte	One per analytical batch of up to 20 samples	90-110% Recovery	Reanalyze LCS. If LCS is still outside acceptance limits, reanalyze associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Sample Duplicate	Target analyte	One duplicate per each 10 samples analyzed	≤20%RPD	No corrective action necessary. Qualify data as appropriate. ***Exception:*** 1) Duplicate sample values <5x RL are not evaluated because values at or near the RL provide statistically insignificant RPD results.

14. Data Analysis and Calculations

14.1. Calculations

14.1.1. Potentiometric titration to pH 4.5 (P alkalinity) or pH 8.3 (T alkalinity):

$$\text{Alkalinity, mg/L of } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{mL sample}}$$

Where: A = mL of standard acid solution used
N = normality of acid solution used

14.1.2. Potentiometric titration of low alkalinity samples:

$$\text{Total Alkalinity, mg/L of } CaCO_3 = \frac{(2B - C) \times N \times 50{,}000}{\text{mL sample}}$$

Where: B = mL of titrant used to reach first recorded pH
C = mL of titrant used to reach 0.3 pH units lower
N = normality of acid solution used

$$\text{Total Alkalinity of Solids, mg/kg} = \frac{\text{Alkalinity, mg/L} \times D}{E}$$

Where D = final volume of solid extract in L
E = initial weight of solid in kg

14.1.3. Determine Total, Carbonate, Bicarbonate, and Hydroxide Alkalinity according to the table below:

Result of Titration	Hydroxide Alk.	Carbonate Alk.	Bicarbonate Alk.
P = 0	0	0	T
P < ½T	0	2P	T – 2P
P = ½T	0	2P	0
P > ½T	2P – T	2(T – P)	0
P = T	T	0	0

Where: P = Phenolphthalein Alkalinity
T = Total Alkalinity

14.2. LCS calculation:

$$\mathbf{R = (C/S) * 100}$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. RPD calculation:

$$\mathbf{RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100}$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11, 12, and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11, 12, and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11, 12, and 13.

18. Method Performance

18.1. Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

19. Method Modifications

19.1. Method modified for use with an autotitrator.

19.2. Method modified for determination of alkalinity in solid samples.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. Standards and Reagents

The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. Samples

Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. Sample containers should be opened in a hood whenever possible.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. Standard Methods for Examination of Water and Wastewater, method 2320B; 2011.

25.2. Pace Analytical Quality Manual; latest revision.

25.3. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-IN-I-003-rev.11	1. Cover: updated method reference with year, changed phone number and revised document control format. 2. Table of Contents: added new section Method Modifications. 3. Section 1: updated method reference with year. 4. Section 2: added option of using an autotitrator. 5. Section 8.1: added autotirator 6. Section 8.2: added plastic sample cups 7. Section 9.1: added pH buffers 8. Section 9.2: revised standard preparation 9. Section 10: expanded to include calibration criteria and requirement to analyze an ICV. 10. Section 11: added detail for use of the autotitrator procedure. 11. Sections 11.3 and 11.4: specified manual titration and added pH meter check requirements. 12. Section 14: method modifications added. 13. Section 16: updated SM2320B reference.	04Nov2015
S-IN-I-003-rev.12	1. Converted to the Corporate 27-section format. 2. Cover page: updated phone number, method reference and document control format. 3. Section 1.1: updated method reference. 4. Section 4.1: added soil as an applicable matrix. 5. Section 5.1: added default RL for soils. 6. Table 7.1: added soil information and revised storage temperature format. 7. Section 9.1: added balance. 8. Section 10.1: updated reagent information. 9. Section 12: added warning not to filter, dilute or alter the samples. 10. Section 12.3: added instructions for MB and LCS analysis and added corrective action for failed CCV. 11. Section 12.4: added instructions for MB and LCS analysis and added corrective action for failed CCV. 12. Section 12.5: added corrective action for failed CCV. 13. Section 25: updated SM reference and added years to TNI reference.	20Jun2017

ENV-SOP-IND1-0006-rev.01	1. Removed cover page, table of contents and headers for use in Master Control. 2. Section 1.1: added reference to solid samples. 3. Section 9.1: added stir plate with stir bars. 4. Section 9.2: added filter paper and plastic beads. 5. Section 12.3: added section for preparation of solids. 6. Sections 12.4, 12.5, and 12.6: added solid sample filtrate as a sample type to the analytical procedures. Revised acceptance range for ongoing CCV pH. 7. Table 13.1: revised corrective action for method blank and LCS. 8. Section 14: added descriptors to equations for clarification and added equation for solids. 9. Section 19: added modification for analysis of solids.	18Feb2019

APPENDIX D-3

PACE PITTSBURGH SOPS

Document Information

Document Number: ENV-SOP-GBUR-0068 **Revision:** 00

Document Title: Analysis of Samples for Alpha Emitting Actinides and Pu-241

Department(s): Rad Chem

Previous Document Number: S-PGH-R-008-rev.13

Date Information

Effective Date: 08 Feb 2018

Next Review Date: 08 Feb 2020 **Last Review Date:**

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

STANDARD OPERATING PROCEDURE

Analysis of Samples for Alpha Emitting Actinides and Plutonium-241

Methods: ASTM Method D-3972-90 and HASL 300 Method U-02

SOP NUMBER:	S-PGH-R-008-rev.13
REVIEW:	R. Kinney
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-R-008-12
REVIEW DATE:	Upon Procedural Change

APPROVALS

Department Manager/Supervisor — 02/08/18 Date

Senior Quality Manager — 02/08/18 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

TABLE OF CONTENTS

1. Purpose

1.1 This SOP describes the procedure to be used for the determination of micro-quantities of Americium, Curium, Thorium, Plutonium (including Pu-241), Neptunium and Uranium in various sample matrices. It also addresses routinely difficult matrices such as filters, solids in quantities over two grams, and aqueous samples where precipitation as described in the procedure may not be successful.

1.2 Samples not meeting the criteria outlined in this procedure should be brought to the attention of the Department Manager/Supervisor or designee for further direction.

1.3 This procedure is applicable for determining compliance for isotopic uranium in drinking water and is substantially compliant with ASTM Method D-3972-90 and HASL 300 Method U-02. Deviations from these methods are addressed in Section 19 of this procedure.

1.4 This procedure is designed for the determination of the following radio-nuclides:

Isotope	Half-life	Alpha Energy MeV (Abnd.)
Americium 241	*458 yrs*	*5.49 (86%) 5.44 (13%)*
Americium 243	*7370 yrs*	*5.28 (88%) 5.23 (11%)*
Curium 242	*162.79 days*	*6.069 (25%) 6.112 (74%)*
Curium 244	*18 yrs*	*5.80 (76%) 5.76 (23%)*
Plutonium 238	*87.8 yrs*	*5.50 (72%) 5.46 (28%)*
Plutonium 239	*24131 yrs*	*5.16 (73%) 5.14 (15%)*
Plutonium 240	*6569 yrs*	*5.17 (74%) 5.12 (26%)*
Plutonium 241	*14.35 yrs*	*Beta 20.81Kev (5.23 Ave)*
Plutonium 242	*375850 yrs*	*4.90 (78%) 4.86 (22%)*
Neptunium 237	*2140000 yrs*	*4.79 (47%) 4.77 (25%)*
Thorium 228	*1.9132 yrs*	*5.42 (73%) 5.34 (27%)*
Thorium 230	*77000 yrs*	*4.69 (76%) 4.62 (23%)*
Thorium 232	*14050000000 yrs*	*4.01 (77%) 3.95 (23%)*
Thorium 229	*7340 yrs*	*4.85 (56%) 4.90 (10%)*
Thorium 227	*18.718 days*	*6.03 (24%), 5.98 (23%), 5.76 (20%)*
Uranium 232	*72 yrs*	*5.32 (69%) 5.26 (31%)*
Uranium 238	*4468000000 yrs*	*4.19 (77%) 4.15 (23%)*
Uranium 235	*703800000 yrs*	*4.39 (55%) 4.36 (11%)*
Uranium 236	*23415000 yrs*	*4.49 (74%) 4.45 (26%)*
Uranium 234	*244500 yrs*	*4.78 (72%) 4.72 (27%)*
Uranium 233	*159200 yrs*	*4.82 (84%) 4.78 (13%)*

2. Scope and Application

2.1 This procedure covers the measurement of various isotopic alpha emitters in various matrices including drinking water. Since all plutonium isotopes behave the same, this procedure also addresses the isolation of beta emitting Pu-241. With the exception of drinking water sources, most other matrices, especially soils, contain elements, which may complex some actinides, making it necessary to aggressively treat such samples.

2.2 This method is a laboratory promulgated method based on multiple accredited methods and the behavior of individual alpha emitters.

2.3 Sample results are decay corrected to the client supplied collection date and time for all analytes reported using this SOP.

2.4 Alpha count sources generated as the product of this SOP are analyzed as documented in the current revision of Pace SOP PGH-R-020, “Alpha Spectroscopy Instrument Operations.”

2.5 Plutonium-241 count sources generated as the product of this SOP are analyzed as documented in the current revision of Pace SOP PGH-R-022, “Liquid Scintillation Counter Operations.”

2.6 Beta-emitting tracer sources produced from application of this SOP are analyzed for yield determination as documented in the current revision of Pace SOP PGH-R-002, “Gas Flow Proportional Counter Operation.”

3. Summary of Method

3.1 The nuclides listed in Section 1 are first separated from the interfering substances by iron hydroxide precipitation, and appropriately dissolved in either a hydrochloric acid or nitric acid solution. Uranium and Plutonium separation can be accomplished using an anion exchange column. Subsequent separation and purification of Americium and Curium are accomplished using Tru-Resin™ columns. For Thorium and Neptunium, separation can be accomplished using anion exchange columns. Additionally, Americium/Curium spectral resolution can be improved by using TEVA-Resin™ columns.

3.2 Following separation, the individual isotopes are micro-precipitated onto a filter and the corresponding alpha activity is determined using an alpha spectrometer.

3.3 Counting efficiency is determined by micro-precipitating a solution composed of three different energy range alpha standards (such as Cm-244, Pu-239, and Th-230) and counting the sources in each detector of an alpha spectrometry system or using a commercially prepared source with at least 3 different energy range nuclides.

4. Interferences

4.1 Any nuclide with an alpha emission similar in energy to the isotopes in question that cannot be separated from the target nuclide will interfere with this analysis.

4.1.1 It is not always necessary to re-prep samples where both sufficient tracer counts and an interfering nuclide are present.

4.1.2 A clean-up may be performed on the micro-precipitated source to remove the interfering nuclides.

4.1.3 Analysts should consult with the Department Manager/Supervisor or the specified designee on how to proceed.

4.2 Samples that contain isotopes employed as working tracers will lead to an overestimate of yield and low bias in measured results. If the sample activity is known, or can be determined, and the tracer activity corrected to reflect the true concentration of the tracer nuclide present in the sample, accurate results can be obtained.

4.3 Daughters of Th-229 will interfere with Cm-244 analysis. Thorium and americium should be run separately in order to exclude such interferences.

4.3.1 If sample volume limits running these analyses separately, Method 4 (Purification of Americium Using Teva-Resin™) must be performed, subsequent to Method 3 (Purification of Americium Using Tru-Resin™), to remove any thorium decay daughters from the americium/curium fraction.

4.4 Unless isolated separately, Neptunium-237 will interfere with the Pu-242 yield calculation, therefore Pu-236 should be used as a tracer when it is desirable to extract and count plutonium with neptunium on the same counting source.

4.5 Plutonium-236 decays to U-232, which in turn decays to Th-228, therefore it is important to know when the last U-232 separation was performed on the Pu-236 working tracer.

4.5.1 Analysts should be mindful of the potential for a bias in the uranium tracer recovery depending on the length of time since the separation of U-232 from the working tracer.

4.5.2 Plutonium and thorium can be run sequentially if Th-228 is not desired or thorium decay daughters were previously separated from the Pu-236 working tracer.

4.6 Excess fluoride during sample digestions may produce insoluble actinide complexes leading to low yields. Addition of saturated boric acid solution must be performed at the completion of sample digestion to avoid this.

4.7 Silica in solution may cause problems with uranium and thorium separations and analyte retention on columns.

4.8 Excess carbonate in solution will prevent the iron hydroxide precipitation of the uranium isotopes. To prevent this, it is extremely important to thoroughly boil water samples during the initial precipitation steps of uranium analysis.

4.9 The analysis volume for samples known to contain elevated concentrations of uranium should be controlled so as to limit the quantity of uranium carried through to the final source preparation. Excessive mass

contained in the final micro-precipitated count source may negatively affect peak resolution (FWHM) for which there are control limits required by this SOP.

5. Safety

5.1 Procedures must be carried out in a manner that protects the health and safety of all personnel. Since this analysis is for a radioactive constituent, the sample must be treated as radioactive.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.3 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye-protection, gloves, and a lab coat must be worn.

5.4 Exposure to radioactivity and chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous and/or non-radioactive, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 In order to minimize the potential for cross contamination of high and low levels of radioactive samples, good housekeeping and good laboratory practices are essential and must be strictly adhered to.

5.6 Organic samples of unknown content must be handled with extreme caution and under the direct instruction of the Department Manager or Manager-specified designee. Direct treatment of organic matrices with strong oxidizing chemicals such as nitric acid and/or hydrogen peroxide is strictly prohibited.

5.7 Hydrofluoric acid is particularly hazardous because a serious skin exposure may cause no immediate sensation of pain. The acid penetrates the skin and spreads internally, causing tissue damage deep under the skin. The resulting burn is painful, difficult to treat, and easily infected. Gloves must be checked for pinhole leaks before use. They must be rinsed before they are removed and must be discarded after use. HF burn gel shall be put on suspected HF burns after flushing (except the eyes) until medical help can be obtained. Medical attention shall be sought even if suspicions arise after working hours. Contact your group leader immediately for further information if a HF burn is suspected.

5.8 In addition, HF vapors are also hazardous. Exposure can cause permanent damage. Breathing HF vapors even for a short time and at a low temperature can be injurious to the respiratory system and even fatal. All such direct contact must be avoided.

5.9 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety

information can be obtained from the MSDS files maintained in the laboratory.

6. Definitions

6.1 Batch: For all analysis, an analytical batch contains 20 or fewer samples of a similar matrix, prepared at the same time, by the same analyst, using the same reagents.

6.2 SRM: Standard Reference Material.

6.3 Throughout this procedure, approximate weights and measures will be designated by the use of whole numbers when referring to masses exceeding 1g or volumes in excess of 1mL. Measurements of masses and volumes so designated can be made with top loading balances, graduated cylinders, etc. For approximate measures below 1g or 1mL, the word "approximately" must be used prior to the described mass or volume.

6.4 Throughout this procedure, exact or critical masses and volumes will be designated by the use of one or more decimal places. Measurements of weights and volumes so designated should be made with accurate analytical instruments such as analytical balances, calibrated pipettes, etc.

6.5 When aliquotting samples on a balance, the observed mass on the balance must be recorded in preparation logbooks to the lowest weight indicated on the balance. Sample aliquot masses must not be targeted. Once sample is removed from the sample container and transferred to a beaker, it must not be removed from the beaker.

6.6 The method utilized for obtaining the sample aliquot, whether on a balance, in a graduated cylinder, or by pipette, must be clearly annotated in the preparation logbook.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Aqueous Samples

8.1.1 Containers used for sample collection must never be re-used. Either plastic or glass containers may be used for sample collection.

8.1.1.1 Aqueous samples must be preserved at the time of collection by adding enough concentrated (16N) HNO_3 to the sample to make the sample pH <2. Typically, 2mL of 16N HNO_3 per liter of sample is sufficient to obtain the desired pH. Samples must be preserved within five days of collection. If samples are collected without preservation, they must be received by the laboratory and preserved within five days of collection. Following preservation with acid, samples must be held in the original container for a minimum of 24 hours before analysis or transfer of sample. For samples preserved at the time of receipt, the pH must be re-checked by laboratory personnel prior to removing sample for analysis. The pH re-check date and time, the initials of the analyst verifying the pH, as well as any adjustments or notes regarding the preservation must be recorded in the pH Verification Logbook.

8.1.1.2 For dissolved analysis, samples must be filtered through a 0.45μm membrane filter and then preserved to a pH <2.

8.1.1.3 For total analysis, the sample is not filtered, but is preserved to a pH<2.

8.1.2 Refrigeration is not required for aqueous or solid samples, but is recommended for all biological samples.

8.1.4 The maximum hold time for samples analyzed by this procedure is 180 days between sample collection and sample analysis.

9. Equipment and Supplies

9.1 Multi-channel Analyzer:

9.2 Alpha Spectrometer: Refer to SOP PGH-R-020, current revision "Alpha Spectroscopy Instrument Operation" for instructions on alpha spectroscopy system operation.

9.3 Electric hot plate or griddle.

9.4 Ion exchange columns, 2mL, disposable from Eichrom or equivalent.

9.5 TRU and TEVA cartridges from Eichrom.

9.6 Vacuum box apparatus and applicable parts, disposable yellow and white tips, 10-50mL syringe barrels, etc from Eichrom or equivalent.

9.7 Polypropylene filters, 25mm, 0.1μm pore size from Environmental Express, or equivalent.

9.8 PTFE FEP Beakers, 100mL size and other assorted sizes, or equivalent.

9.9 Multi-port vacuum filtering apparatus for 25mm filters (referred to as the filter rig).

9.10 Miscellaneous glassware: beakers, watch glass covers, and stir rods.

9.11 Membrane Filters, 5.5cm diameter, 0.45μm pore size.

9.12 Analytical Balance: Sensitivity to 0.1mg, capacity 0 - 160g.

9.13 Top loader balance, sensitivity to 0.1g, capacity 0-2000g.

9.14 Vacuum filtration apparatus for 5.5cm diameter membrane filters.

9.15 General-purpose centrifuge and disposable centrifuge tubes, 50mL made of high-density polyethylene or equivalent.

9.16 Vortex mixer.

9.17 Liquid scintillation vials, glass.

9.18 Muffle oven capable of 105ºC to 550ºC, with or without ramping capabilities.

9.19 Software supplied with the instrument to control instrument operation. Refer to SOP PGH-R-020, current revision "Alpha Spectroscopy Instrument Operation" for applicable software details.

9.20 Computer capable of running the Alpha spectrometer Counter System software, monitor, mouse, keyboard, and printer. Refer to SOP PGH-R-020, current revision "Alpha Spectroscopy Instrument Operation" for computer hardware specifications.

10. Reagents and Standards

10.1 Reagents must be prepared from reagent grade chemicals, unless specified otherwise. Distilled or deionized (DI) water. ASTM Type II as produced using the specifications documented in SOP PGH-C-027, current revision. Consult the Safety Data Sheets for the properties of these reagents, and how to work with them.

10.2 Anion exchange resin, Bio-Rad AG 1x8 (100 - 200 mesh, Cl^- form) or equivalent. Slurry the resin in a squirt bottle with ASTM Type II DI water.

10.3 Ammonium Hydroxide, 15N, concentrated, sp. gr. 0.90, 56.6%.

10.4 Ammonium Thiocyanate, 6M: Dissolve 476g ammonium thiocyanate in 300mL of ASTM Type II DI water and dilute to 1.0L with ASTM Type II DI water.

10.4.1 CAUTION! The reaction is extremely exothermic and the bottle may become very slippery.

10.5 Ammonium Thiocyanate, 3M/ 0.1N Formic acid: Dilute 250mL 6M ammonium thiocyanate and 50mL 1.0N formic acid to 500mL with ASTM Type II DI water. Prepare fresh daily.

10.6 Ammonium Thiocyanate, 1M/ 0.1N Formic acid: Dilute 100mL 6M ammonium thiocyanate and 60mL 1.0N formic acid to 600mL with ASTM Type II DI water. Prepare fresh daily.

10.7 Ascorbic Acid, 1.0M: Dissolve 17.6g ascorbic acid into 50mL ASTM Type II DI water and dilute to 100mL with ASTM Type II DI water. Prepare weekly.

10.8 Boric Acid, 5% Saturated Solution: Add 50g granulated boric acid to 500mL ASTM Type II DI water and dilute to 1L with ASTM Type II DI water. The boric acid should not completely dissolve.

10.9 Distilled or deionized DI water. Resistance value between 0.5 and 2.0 Mmhos (2.0 to 0.5µohms/cm specific conductivity) at 25˚C.

10.10 Deionized Water adjusted to a pH of 10.0 by the addition of 6-8 drops of ammonium hydroxide to each 500mL of DI.

10.10.1 The pH should be checked prior to each addition of ammonium hydroxide, since it is not always necessary to add the full 6-8 drops each time pH 10 DI is made up.

10.11 Ethanol, 80%. 800mL of reagent grade alcohol mixed with 200mL of ASTM Type II DI water.

10.12 Formic acid, concentrated, 88%.

10.13 Formic acid, 1.0N: Dilute 42.5mL concentrated formic acid to 1.0L with ASTM Type II DI water.

10.14 Hydrochloric acid, 12N, concentrated, sp. gr. 1.19, 37%.

10.15 Hydrochloric acid, 9N / 0.10% Hydrogen Peroxide: For every 100mL of 9N HCl, add 0.1mL of 30% H_2O_2. Shake well and allow to sit for 5 minutes prior to use. Prepare daily.

10.16 Hydrochloric acid, 9N: Dilute 750mL concentrated 12N HCl to 1L with ASTM Type II DI water.

10.17 Hydrochloric acid, 6N: Dilute 500mL concentrated 12N HCl to 1L with ASTM Type II DI water.

10.18 Hydrochloric acid, 4N: Dilute 332mL concentrated 12N HCl to 1L with ASTM Type II DI water.

10.19 Hydrochloric acid, 0.1N: Dilute 8.3mL concentrated 12N HCl to 1L with ASTM Type II DI water.

10.20 Hydrochloric acid, 6N / 0.52N Hydrofluoric acid Solution: Dilute 500mL of concentrated 12N HCl and 18mL of concentrated HF to 1L with ASTM Type II DI water.

10.21 Hydrochloric acid, 9N / 0.05M Ammonium Iodide Solution: For every 100mL of 9N HCl, add 0.724g of NH_4I solid. Shake well and let stand for 5 minutes prior to use. Prepare daily.

10.22 Hydrazine Dihydrochloride, 25% Solution: 25g hydrazine dihydrochloride dissolved in 75mL of ASTM Type II DI water.

10.23 Hydrogen Peroxide (30%) H_2O_2.

10.24 Hydrofluoric acid, 29N, concentrated, sp. gr. 1.18, 49%. Must be stored in a plastic container.

10.25 0.1% Hydrofluoric acid: Dilute 1.0mL concentrated HF to 1L with DI.

10.26 Iron Carrier: 10.0mg Fe/ml: Dissolve 72.4 g $[Fe(NO_3)_3]\bullet 9\ H_2O$ in 500mL of ASTM Type II DI water and dilute to 1L with ASTM Type II DI water.

10.27 Neodymium carrier (0.5mg/mL): Dilute 5.0mL of 10mg/mL of neodymium carrier to 100mL of ASTM Type II DI water.

10.28 Nitric acid, 16N, concentrated, sp. gr. 1.42, 70%.

10.29 Nitric acid, 2N: Dilute 125mL of conc. 16N HNO_3 to 1L with DI water.

10.30 Nitric acid, 8N: Dilute 500mL of conc. 16N HNO_3 to 1L with DI water.

10.31 Nitric acid, 2N / 0.5M $Al(NO_3)_3$: Dissolve 188g aluminum nitrate nonahydrate in 500mL of ASTM Type II DI water. Add 125mL conc. 16N HNO_3 to the solution and then dilute to 1L with ASTM Type II DI water.

10.32 Nitromethane, ACS reagent.

10.33 Potassium Thiocyanate Solution, 0.1N: purchased ready made from Fisher Scientific, or equivalent.

10.34 Tru-Resin™: Eichrom Inc., Mix 100g (s-grade) of Tru-Resin with 428mL ASTM Type II DI water and 2mL of conc. 16N HNO_3.

10.35 TEVA-Resin™: Eichrom Inc., Mix 100g (s-grade) of TEVA-Resin with 428mL of ASTM Type II DI water and 2mL conc. 16N HNO_3.

10.36 Titanium (III) Chloride: 10% wt. Solution.

10.37 Standards

10.37.1 Tracer: A solution containing Am-243, Np-239 (prepared from Am-243), Pu-242, Pu-236, Th-229, Th-234 (prepared from U-238), or U-232 prepared from a NIST-traceable and certified solution, or equivalent. Tracer spike aliquots shall have DPM values consistent with the activity of the samples. Check the certificate for the expiration date.

10.37.2 Laboratory Control Sample (LCS)

10.37.2.1 Liquid: A solution of Am-241, Cm-244, Pu-239, Pu-241, Np-237, Th-230, or U-238 prepared from a NIST-traceable and certified source, or equivalent. Check the calibration certificate for the expiration date.

10.37.2.2 Solid: A soil containing Am-241, Cm-244, Pu-239, Pu-241, Np-237, Th-230, or U-238 prepared from a NIST-traceable and certified source, or equivalent. Check the certificate for the expiration date.

Note: Equivalent is defined as being traceable to any international source that provides a certificate of calibration. As the project requires, a solution may be used where the isotopic activity has been confirmed by multiple laboratory analyses.

11. Calibration

11.1 Plated sources can be purchased from a NIST supplier, but they must have the same size effective area and they must be positionable so the effective area is the same distance from the detector as those sources prepared for sample counting.

11.2 If plated sources cannot be purchased, sources can be prepared using NIST traceable standards as follows.

11.3 Sources for alpha spectroscopy system calibration must be prepared in a fashion that will ensure >99% recovery of each calibration source analyte.

11.4 Concentrated standards or SRMs that limit the volume of the standard to less than 0.5mL per radioisotope must be used in order to ensure that the acid concentration is kept as dilute as practical. Quantitative precipitation of many actinides from acid solutions with concentrations greater than 0.5N is impossible and will lead to erroneous results.

11.5 Transfer an appropriate volume or mass of analytical standard to a labeled, disposable centrifuge tube. Record the standard numbers utilized and mass or volume information in the appropriate standard dilution logbook. Dilute the combination of standards to 20mL with 0.1N HCl.

11.6 Add the following to the solution in the centrifuge tube:

11.6.1 0.1mL of neodymnium carrier solution (0.5mg/mL)

11.6.2 Four drops of the iron carrier solution.

11.6.3 Seven drops of the 1M ascorbic acid solution

11.6.3.1 This reduces the iron to the +2 state.

11.6.3.2 Proper reduction of iron will result in a clear, colorless solution.

11.7 Cap each tube and swirl the solution to mix the contents. Place tubes in a warm water bath to ensure proper equilibration between the carrier and the radioisotopes.

11.8 After five minutes, add 3mL concentrated HF acid to each source and swirl the source to mix the contents. Let the sources sit in the warm water bath for 15 minutes, then remove them, and allow them to cool for 15 minutes.

11.9 Prepare a filter apparatus by placing a filter funnel into an HDPE vacuum flask. Turn on the vacuum and rinse the apparatus with several mLs of ASTM Type II DI water.

11.10 Carefully wash and rinse a filter funnel that is dedicated to, and set aside for, the preparation of calibration sources.

11.11 Place a polypropylene filter onto the filtering apparatus and ensure it is centered.

11.12 Place the clean filter funnel on the rig and secure it, being careful not to rip the filter in the process.

11.13 Rinse the inside surface of each funnel with the 80% ethanol solution then rinse the inside surface of each funnel with approximately 10mL of ASTM Type II DI water.

11.14 Transfer the calibration solution to the filter funnel and allow it to pass through the filter. After all of the calibration solution has passed through the filter, rinse the centrifuge tube with approximately 5mL of the 80% ethanol solution and transfer it to the filter funnel as a rinse.

11.15 Rinse the inside of the funnel with an additional 2-3mL of the 80% ethanol solution.

11.16 Label the metal backside of a one inch counting disk with the appropriate standard number as determined from the standard preparation logbook, and remove the paper backing from the pre-taped side of the disk.

11.17 Remove the filter funnel and carefully remove the calibration filter from the filtration rig and affix it to the disk.

11.18 Allow the disk to air dry for a minimum of 15 minutes.

11.19 When the calibration source has dried, place it in a labeled petri dish and submit it to the count room for counting.

11.20 Perform calibration of alpha spectrometry detectors as specified in the current version of Pace SOP PGH-R-020, “Alpha Spectroscopy Instrument Operations”. Count sources long enough to obtain a minimum of 10000 net counts in each of the three nuclides regions of interest.

11.21 Transfer the contents of the vacuum flask to a 600mL PTFE beaker.

11.21.1 Rinse the flask three times with 50mL of ASTM Type II DI water and add the rinses to the beaker.

11.22 Evaporate the solution to dryness on a hotplate on a low to medium heat setting.

11.23 Carefully add 10mL of concentrated nitric acid and 1mL of 30% hydrogen peroxide solution to the beaker and evaporate the solution to dryness.

11.24 Carefully add 10mL of concentrated nitric acid and 1mL of 5% boric acid solution to the beaker and evaporate the solution to dryness.

11.25 Dissolve the residue into 20mL of 8N nitric acid solution by heating the solution.

11.26 Allow the solution to cool, then transfer it to a 100mL volumetric flask.

11.26.1 Rinse the beaker three times with 10mL of ASTM Type II DI water and add the rinses to the volumetric flask.

11.26.2 Dilute the solution to the mark with ASTM Type II DI water.

11.26.3 Transfer the diluted calibration effluent to a labeled HDPE bottle.

11.27 Analyze 10mL of each calibration effluent sample for gross alpha content using the most recent revision of SOP PGH-R-001.

11.27.1 Calculate the total alpha content for the entire source effluent.

11.27.2 Calculate the total alpha activity of each calibration source.

11.27.3 Compare the total effluent activity to the theoretical activity to ensure that the effluent contains less than 1% of the total activity. Calibration sources must contain >99% of each analyte in order to be accepted for calibration purposes.

11.27.4 Consult with the Department Manager/Supervisor or specified designee if the sources are not acceptable.

11.28 The Plutonium-241 calibration is performed separately on a liquid scintillation counter. Add 1000 to 2000 dpm of Pu-241 by mass to ten, labeled, glass scintillation vials. Add 1.0mL of concentrated HCl to each vial and heat the sources to dryness on a hotplate.

11.29 Add 2.0mL of 0.1N HCl to each vial to dissolve the residue. Then add 15mL of Ultima Gold AB liquid scintillation cocktail to each vial. Cap each vial and shake it vigorously to mix the contents.

11.30 Establish variations in quench by carefully opening the vials and adding nitro methane to each vial in increasing increments. Nitro methane is not added to one of the vials and not to the background vial. For example, add 10 µL to one vial, 20 µL to another, 40 µL, 70 µL, 100 µL and so on, documenting the amount of nitro methane added to each vial for future reference.

11.31 Count calibration sources according to the Pace SOP, PGH-R-022, “Liquid Scintillation Counter Operations”. Count the samples long enough to obtain 10,000 net counts in the Pu-241 window. Count times will vary from source to source based on the quench factor. Adjust the amount of nitro

methane in each vial and recount the set as necessary to achieve the most representative range of values for the quench curve.

11.32 Calculate the Pu-241 efficiency based on the quench values using Microsoft Excel or equivalent curve plotting software.

11.33 Calibrations must be verified initially prior to counting samples and annually thereafter by counting a separate source in the detector and processing the source as a sample. The resulting activity of the source must be within 10% of the known target activity of the source for the calibration to be deemed acceptable. Additionally, all criteria with regards to FWHM and spectral resolution must be satisfied. Verifications which do not meet these criteria require a new calibration to be performed. In some instances this may involve replacing the actual detector prior to attempting a re-calibration. A new calibration is required whenever a detector is replaced or when calibration verification does not meet the defined acceptance criteria. Calibrations related to the analysis of Drinking Waters must be verified initially using a source that is un-related to the initial calibration source. Subsequent annual calibration verifications may be performed using the initial calibration source or a source that is un-related to the initial calibration source.

12. Procedure

Unless specified otherwise, the documented analysis process must be followed, as written, including the order of analytical process and the addition of chemicals.

12.1 Waters and Liquids, Including Drinking Water

12.1.1 Shake each sample and weigh 300g of aqueous sample into an appropriately sized beaker. Record the observed measured mass of sample to the lowest decimal on the balance. Do not remove sample from the beaker once it has been added. The actual quantity of sample used may be less than 300g if matrix interferences are expected or there is limited sample quantity available to the laboratory. If less than 300g of sample is used, dilute the sample with ASTM Type II DI water to the 300mL mark on the beaker. Fortify the pH of diluted samples by adding 2mL of HNO_3.

12.1.2 Prepare appropriate batch Quality Control samples including a Method Blank, Laboratory Control Sample (LCS), and LCS Duplicate (LCSD) by weighing an appropriate quantity of ASTM type II DI water to an appropriate size beaker. To each QC sample add 5mL of concentrated 16N HNO_3.

12.1.3 Add the applicable spikes to the appropriate QC samples in the amounts specified in Section 14 of this SOP. Add a pre-selected amount of the applicable working tracers to each of the samples and QC samples.

12.1.4 Add 1mL of iron carrier to each sample.

12.1.5 If there is a significant amount of residue present in the sample and total analysis is requested,

12.1.5.1 Filter the sample through a 0.45µm Metricel™ filter.

12.1.5.1.1 Transfer filtered sample to a labeled glass beaker

12.1.5.1.2 Transfer the Metricel™ filter and the residue to a labeled PTFE beaker.

12.1.5.2 To digest the filter and solids, add 10mL conc. 16N HNO_3, 10mL conc. 12N HCl, and 10mL conc. HF to the PTFE beaker. Cover the PTFE beaker with a cover and reflux on a hotplate for one hour.

12.1.5.3 Remove the cover and continue to heat the sample to dryness.

12.1.5.3.1 Repeat Step 12.1.5.2 as necessary based on the amount of residue remaining.

12.1.5.4 Dissolve the residue in 10mL conc. 12N HCl and 1mL saturated boric acid. Place the sample back on the hot plate and heat it to dryness again.

12.1.5.5 Dissolve the digested filter in 10mL of conc. 16N HNO_3. Place the sample back on the hotplate and heat to dryness.

12.1.5.6 Dissolve the digested filter in 10mL conc. 16N HNO_3. Use 8N HNO_3 to transfer the digested filter into the corresponding glass beaker (12.1.5.1.1) that contains the filtered aqueous sample fraction.

12.1.6 Place a watch glass on the glass beaker to cover the sample and heat it to boiling on a hotplate for a minimum of one hour.

12.1.7 Carefully add several mLs of conc. 15N NH_4OH to the sample while stirring until the pH of the sample is adjusted to 10 and a visible precipitate forms within the sample.

12.1.8 Heat the sample to boiling for another thirty minutes or longer, until an iron hydroxide precipitate breaks up into small particles.

12.1.9 Remove the sample from the hot plate and allow it to cool and the precipitate to settle.

12.1.10 Decant the excess supernate from the sample and discard it in the appropriate waste stream. Transfer the precipitate to a labeled disposable centrifuge tube with pH 10 ASTM Type II DI water.

12.1.11 Centrifuge the sample, and discard the supernate in the appropriate waste stream.

12.1.12 Rinse the iron precipitate with at least double its volume in pH 10 ASTM Type II DI water.

12.1.12.1 Vortex and centrifuge the sample. Discard the rinse in the appropriate waste stream. This rinse will eliminate excess ammonium hydroxide.

12.1.13 Proceed to the appropriate separation method beginning in Section 12.5. For Uranium in drinking water analysis, perform the uranium-specific method detailed in section 12.5.

12.2 Filter Samples

12.2.1 If the filter is cellulose:

12.2.1.1 Place a representative portion depending on the client requirements or radioactivity levels of the sample (usually one half or one quarter) of the filter into a clean ceramic crucible and pipette a selected amount of the working tracers onto it.

12.2.1.2 Cover the sample with aluminum foil and heat sample in a muffle furnace using the RAMP feature to ash the filter.

12.2.1.2.1 Use the temperature ramping guidelines in the current revision of the sample preparation SOP.

12.2.1.2.2 NOTE: Mark the PACE sample ID on each crucible with a high temperature wax pencil.

12.2.2 If the filter is glass fiber or otherwise non-organic:

12.2.2.1 Place a suitable portion of the filter into a PTFE beaker and pipette a selected amount of the working tracers onto the sample.

12.2.3 Proceed to step 12.3.3 for the sample digestion.

12.3 Soil and Vegetation Samples

12.3.1 Weigh a suitable amount of the dried sample into a ceramic crucible and pipette a selected amount of the working tracers onto the sample. Prepare a crucible designated as the LCS and LCSD if applicable and spike with the appropriate spike solutions. Prepare a crucible designated as the MB, and add 0.5mL iron carrier to the samples and all QC samples.

12.3.2 Cover the crucibles with a ceramic lid and place the crucible into a cold muffle furnace. Set the final temperature at 550ºC. Once this temperature has been reached, maintain for at least 4 hours or longer depending on the amount of material in the crucible. (For samples which are obviously highly organic, use the muffle oven's RAMP feature to prevent flashover as the sample organic components burn off.)

12.3.2.1 At the end of 4 hours, turn off the oven, allow the samples to cool to room temperature, and remove the samples from the furnace.

12.3.3 Remove the crucibles from the oven and re-label the crucibles. Add 10mL of conc. HNO_3 and 10mL of conc. HCl to the sample and heat it to dislodge the solids.

12.3.4 If the soil/solid sample does not require uranium or thorium then proceed to 12.4. Otherwise transfer the sample to a clean, labeled PTFE beaker.

12.3.4.1 Use a PTFE scraper to remove any residue that is stuck to the bottom of the crucible and rinse it into the PTFE beaker with 9N HCl.

12.3.5 Add 10mL of conc. HF to each sample in the PTFE beaker and then cover with a PTFE watch glass.

12.3.6 Reflux on an electric griddle or hotplate set at 250ºC for a minimum of thirty minutes. After 30 minutes, remove the watch glass cover and allow the sample to evaporate to dryness.

12.3.7 Add 10mLconc. HCl, 10mL conc. HNO_3, and 10mL conc. HF to the sample. Return the sample to the griddle, and allow it to evaporate dryness. This process may be repeated as often as necessary to ensure complete dissolution of the sample. In some matrices, high temperature oxides have been formed which severely limit analyte recovery. These highly insoluble oxides must be treated with repeated and prolonged contact with mineral acid. Acids must cover the samples for multiple days at low heat in order to properly dissolve the sample.

12.3.8 Add 10mL conc. HNO_3 and 10mL conc. HCl to the sample. Return the sample to the griddle and allow it to evaporate to dryness.

12.3.9 Add 10mL 12N HCl or 16N HNO_3 depending on the acid used for the load solution in order to minimize complexants. (For example, if the load solution for the column work will be 15mL 8N HNO_3, add 10mL 16N HNO_3 to the sample for the final cookdown to remove as much chloride as possible.) Add 1mL saturated boric acid to the sample and return it to the griddle and allow it to evaporate to dryness.

12.3.10 Dissolve the sample in the appropriate load solution depending on the column method to be utilized, for example 8N HNO_3 for uranium and thorium isolation using nitric conditioned anion columns, or 9N HCl/H_2O_2 for americium and plutonium isolation using chloride conditioned anion columns.

12.3.11 Heat to aid in dissolution of the sample solids. Scrape the bottom of the beaker to dislodge any solids. Centrifuge the sample as necessary prior to loading the sample onto columns.

12.3.12 Proceed to the appropriate separation method beginning in section 12.5.

12.4 Soil leach for samples not requiring Uranium or Thorium

12.4.1 Transfer the muffled and traced sample from the crucible to a labeled 100mL glass beaker. A larger beaker may be used if necessary.

12.4.2 Add 15mL HNO_3 and 5mL of HCl to each sample and cover with a watch glass. More acid may be necessary for larger aliquots but the ration of 3:1 should remain the same.

12.4.3 Reflux on a hotplate or griddle for a minimum of thirty minutes at medium to low heat. Samples must be kept from overheating, boiling or bumping.

12.4.4 Remove the samples from the hotplate and allow them to cool. Slurry the samples in the beaker and transfer the leachate and solids to a clean, labeled centrifuge tube with the aid of ASTM Type II DI water.

12.4.5 Centrifuge the samples for 15 minutes at maximum speed.

12.4.6 Decant the leachate to a 250mL labeled glass beaker. Place this beaker on a hotplate at medium and evaporate to dryness.

12.4.7 To the solids in the centrifuge tube repeat the steps from 12.4.2 to 12.4.6 using the same labeled glass beaker until the solids appear light gray or tan.

12.4.8 After evaporating to dryness, solids must be converted to the appropriate acid type by treatment with a quantity of the appropriate concentrated acid. If the chemistry load solution is to be a nitrate column, add 10mL of concentrated nitric acid and evaporate to dryness. Likewise, if the chemical load solution is chloride-based, add 10mL of concentrated HCl and evaporate to dryness. This step is not necessary for the isotopic plutonium/neptunium analysis.

12.4.9 Proceed to the appropriate separation method beginning in Section 12.5.

12.5 Method 1: Separation of Actinides on Anion Resin Using Hydrochloric Acid Solution

12.5.1 This method uses an anion exchange resin and the parameters dissolved in a hydrochloric acid solution to separate and purify any of the following groups of actinides.

- Americium, Plutonium (Neptunium), and Uranium
- Thorium, Plutonium (Neptunium), and Uranium
- Plutonium, Neptunium, and Uranium
- Uranium in drinking water samples.

12.5.1.1 This is the default method for waters and soils (less than 2 grams) where little or no interferences are expected to be present.

12.5.1.2 It is not easy to separate americium/curium from thorium using this method, so if sequential analysis requires both analyses be performed on a single aliquot, start with Method 2 to isolate the thorium fraction first from all of the other nuclides.

12.5.2 Dissolve the sample precipitate in 15mL of 9N HCl / 0.10% H_2O_2. The hydrogen peroxide need only be used if plutonium will be isolated.

12.5.3 Prepare a 2mL resin column using Bio-Rad AG 1x8.

12.5.3.1 Slurry the resin with ASTM Type II DI water to give a resin bed of about 3cm. The final resin volume must be consistent for all columns.

12.5.3.2 Once the ASTM Type II DI water has drained, condition the column with 10mL of 9N HCl.

12.5.4 If heated, allow the sample to cool, then transfer it to the prepared resin column.

12.5.5 Collect the effluent from the column in a clean labeled centrifuge tube if either americium/curium or thorium analysis is desired.

12.5.5.1 Rinse the sample beaker or centrifuge tube with an additional 10mL 9N HCl / 0.10% H2O2 and collect.

12.5.5.2 Rinse the column with 20mL of 9N HCl and collect.

12.5.5.3 Transfer the contents of the centrifuge tube to a clean labeled glass beaker.

12.5.5.4 If the contents are to be analyzed for americium/curium, proceed to Method 3: Americium/Curium Purification on TRU-Resin™ for americium/curium analysis.

12.5.6 If it is desirable or necessary to isolate isotopic Plutonium from Neptunium, elute the plutonium from the column into a clean, labeled glass beaker with 20mL 9N HCl / 0.05N NH_4I.

12.5.6.1 If analysis for plutonium is not required, do not perform this step and proceed to step 12.5.7.

12.5.6.2 Add 10mL conc. HNO3 and 3-4 drops of the iron carrier to the plutonium fraction.

12.5.6.3 Allow enough time for the nitric acid and the hydrochloric acid to react.

12.5.6.4 With a disposable pipette, and in a drop wise fashion, slowly add approximately 1mL of 30% H_2O_2 to the solution.

12.5.6.5 Place the beaker on a hotplate and allow the plutonium fraction to evaporate to dryness.

12.5.6.6 Add 5mL concentrated HCl to each beaker and evaporate the contents to dryness on a hotplate.

12.5.6.7 Dissolve the residue in the beaker with 10mL 9N HCl.

12.5.6.8 Transfer the plutonium fraction to a labeled centrifuge tube with ASTM Type II DI water and dilute to 20mL with ASTM Type II DI water.

12.5.6.9 Proceed to Step 12.9.2, Micro-Precipitation of Plutonium.

12.5.7 Rinse the column with 15mL of 6N HCl / 0.52N HF, which will elute any neptunium from the sample (Use 20 mL if step 12.5.6 was not utilized and Plutonium is being eluted with Neptunium.

12.5.7.1 Proceed to Step 12.9.5 for the Micro-Precipitation of Neptunium. (Step 12.9.2 if analyzing for Plutonium and Neptunium simultaneously.)

12.5.7.2 If analysis for neptunium is not required, discard the effluent.

12.5.8 Rinse the column with 10mL of 9N HCl and discard the effluent.

12.5.9 Elute the uranium fraction from the column into a clean, labeled centrifuge tube with 20mL of 0.1N HCl.

12.5.9.1 Proceed to Step 12.9.3 for the Micro-Precipitation of Uranium.

12.6 **Method 2: Separation of Actinides on Anion Resin using Nitric Acid Solution**

12.6.1 This method uses an anion exchange resin and the parameters dissolved in a nitric acid solution to separate and purify the following group of actinides:

- Americium, Plutonium and Uranium from Thorium

12.6.1.1 This method is best used for solids (any amount), waters, or filters (organic based, cellulose), and when it is desirable to reuse the resin column after isolating Thorium.

12.6.2 Dissolve the sample into 15mL of 8N HNO_3

12.6.2.1 Heat the solution if necessary to aid in the dissolution of the precipitate.

12.6.3 Prepare a 2mL resin column with Bio-Rad AG 1x8.

12.6.3.1 Slurry the resin with ASTM Type II DI water to give a resin bed of about 3cm.

12.6.3.2 When the ASTM Type II DI water has drained, condition the column with 20mL 8N HNO_3.

12.6.4 Cool the sample and transfer it to the prepared resin column.

12.6.4.1 Collect the effluent from the column in a clean glass beaker if uranium/plutonium analysis is required. This fraction will also contain any Americium/Curium or Neptunium if present in the sample.

12.6.4.2 Rinse the column with an additional 15mL 8N HNO_3 and collect. The rinse will contain any residual americium, plutonium, and uranium from the sample.

12.6.4.3 Repeat step 12.6.4.2. Collect this rinse.

12.6.4.4 Place the americium, plutonium, uranium fraction on a hotplate and allow it to evaporate to dryness.

12.6.4.5 Continue with the separation of analytes in the solution in step 12.6.4.4 by proceeding to Step 12.5.2 after adding 15mL conc. HCl, and evaporating the samples to dryness.

12.6.5 Elute the thorium from the column with 25mL of 9N HCl into a labeled centrifuge tube.

12.6.5.1 Transfer the solution containing the thorium from the centrifuge tube to a clean, labeled plastic cup and add 0.8mL of 10mg/mL iron carrier.

12.6.5.2 Dilute the samples to approximately 220mL with ASTM Type II DI water.

12.6.5.3 Precipitate thorium with iron as a hydroxide by adding 22-25mL of concentrated ammonium hydroxide to each sample dilution. Stir the solution vigorously with a stir rod for several seconds until a distinct iron hydroxide precipitate forms.

12.6.5.4 Allow the samples to settle for about 15 minutes, and stir vigorously once more to further break up the iron hydroxide precipitate.

12.6.5.5 Remove the stir rod and allow the samples to completely settle for a minimum of one hour.

12.6.5.6 Decant the excess supernate and transfer the iron hydroxide precipitate to the original labeled centrifuge tubes from Step 12.6.5.1.

12.6.5.7 Centrifuge the samples and discard the supernate. Dissolve the precipitate in 3mL 9N HCl. Dilute the samples to 25mL with ASTM Type II DI water.

12.6.5.8 Proceed to Step 12.9.4 for the Micro-Precipitation of Thorium.

12.6.5.9 If the column is to be reused for the uranium purification, rinse the column with 25mL of ASTM Type II DI water.

12.6.6 Perform all of steps listed in Method 1 to purify the americium, plutonium, and uranium as required.

12.7 **Method 3: Purification of Americium/Curium Using Tru-Resin™**

12.7.1 This method may be used as the initial separation step for liquids or waters only if americium/curium is requested. It must be used subsequent to Method 1 in all other instances to purify americium/curium and separate them from thorium.

12.7.2 Add 3-4 drops of the iron carrier to the americium fraction collected in Step 12.5.5.4. Place the sample on a hotplate and evaporate the sample to dryness.

12.7.3 Add 5mL of concentrated nitric acid to each sample and evaporate to dryness to remove residual chlorides.

12.7.4 Dissolve the sample residue into 10mL of 2N HNO_3 /0.5M $Al(NO_3)_3$. Additional 2N HNO_3/0.5M $Al(NO_3)_3$ may be used to dissolve the sample fraction, but the total load volume must not exceed 15mL.

12.7.4.1 Heat the sample gently as necessary to aid in the dissolution.

12.7.5 Add one drop of 0.5M potassium thiocyanate to the sample and swirl it, then add 6-8 drops of 1.0M ascorbic acid to the sample and swirl it.

12.7.5.1 The color of the sample should go from clear to red and then back to clear again, unless there is no significant iron present in the sample.

12.7.6 The sample should be centrifuged prior to loading it on the column if there are any solids present.

12.7.7 Prepare a resin column with 5 drops of pre-resin filter followed by 3.5mL (2 grams) of Tru-Resin™.

12.7.7.1 Allow any excess water to drain.

12.7.7.2 Condition the columns by passing 5mL of 2N HNO_3 through them and discarding the effluent.

12.7.8 Load the sample onto the column.

12.7.8.1 A change in resin color should be observed, usually pink, but it may be multi-colored.

12.7.8.2 Discard the effluent.

12.7.9 Rinse the column with three 5mL aliquots of 2N HNO_3 allowing each to pass through the column. Discard the effluents.

12.7.10 Place a clean, labeled centrifuge tube under the columns and elute the americium/curium from the resin with 2mL of 9N HCl.

12.7.11 Complete the elution of the americium/curium from the column by adding 10mL 4N HCl. Combine the effluent from the column

in the centrifuge tube. If interferences are expected to cause spectral resolution issues, proceed directly to step 12.8.3.

12.7.12 Proceed to Step 12.9.1 for the Micro-Precipitation of Americium.

12.8 **Method 4: Purification of Americium/Curium Using TEVA-Resin**

12.8.1 After Method 3 has been preformed, the following steps are available to further purify the americium/curium.

12.8.2 Transfer the americium/curium eluate from step 12.7.11 to a small glass beaker. Place the sample on a hotplate and allow it to evaporate to dryness

12.8.2.1 Do not allow the samples to bake.

12.8.3 Dissolve the residue in the beaker in 10mL conc. HCl and place it back on the hotplate allowing it to evaporate to dryness.

12.8.3.1 Do not allow the sample residue to bake.

12.8.4 Add 1mL conc. formic acid to each sample and allow them to evaporate to dryness.

12.8.5 Dissolve the sample in 15mL 3M ammonium thiocyanate/ 0.1N formic acid.

12.8.5.1 Heat the sample as necessary to aid in the dissolution.

12.8.5.2 The sample should take on a light pink color.

12.8.6 Prepare a 2cm column with 3.5mL prepared (2 grams) TEVA resin™.

12.8.6.1 Allow any excess water to drain through.

12.8.6.2 Condition the column with 5mL of the 3M ammonium thiocyanate/ 0.1N formic acid.

12.8.7 Ensure that the sample has cooled and load it onto the conditioned column.

12.8.7.1 Rinse the sample beaker with 2mL 1M ammonium thiocyanate/ 0.1N formic acid.

12.8.7.2 Pour the rinse onto the column when the sample has completely passed through.

12.8.8 Rinse the column first with 3mL and then with 5mL of the 1M ammonium thiocyanate/ 0.1N formic acid.

12.8.8.1 Discard all rinses to waste. (Note: Ammonium thiocyanate should be neutralized with dilute nitric acid in an open container prior to disposal to avoid violent reactions.)

12.8.9 Elute the americium/curium from the column with 15mL of 2N HCl into a clean, labeled centrifuge tube.

12.8.10 Proceed with Step 12.9.1 for Micro-Precipitation of Americium.

12.9 Micro-precipitation of the Actinides

12.9.1 Americium/Curium

12.9.1.1 Add 0.1mL of the 0.5 mg/mL neodymnium carrier to the sample. Swirl the sample to mix the contents.

12.9.1.2 Add 3mL conc. HF to the sample. Cap the centrifuge tube and shake the sample vigorously to mix the contents.

12.9.1.3 Allow the sample to sit for thirty minutes, then proceed with Step 12.9.6 for filtration.

12.9.2 Plutonium

12.9.2.1 Add 0.1mL 0.5mg/mL neodymnium carrier to the sample and swirl to mix.

12.9.2.2 Add 12 drops of 25% dihydrazine dihydrachloride solution to each sample.

12.9.2.3 Swirl the solution to mix the contents, then allow the sample to sit for 5 minutes.

12.9.2.4 Add 3mL of conc. HF to the sample. Cap the sample and shake it vigorously to mix the contents.

12.9.2.5 Allow the sample to sit for thirty minutes.

12.9.2.6 Proceed to Step 12.9.6 for filtration.

12.9.3 Uranium

12.9.3.1 Add 0.1mL 0.5mg/mL neodymnium carrier to the sample and swirl to mix.

12.9.3.2 Add enough of the titanium chloride solution to the sample to maintain a light purple color when swirled (approximately 1-2mL).

12.9.3.3 Swirl the solution to mix the contents, then allow the sample to sit for a few minutes.

12.9.3.4 Add 3.0mL conc. HF to the sample. Cap the sample and shake it vigorously to mix the contents.

12.9.3.5 Allow the sample to sit for thirty minutes.

12.9.3.6 Proceed with Step 12.9.6 for filtration.

12.9.4 Thorium

12.9.4.1 Add 0.1mL 0.5mg/mL neodymnium carrier to each sample. Swirl the contents to mix.

12.9.4.2 Add 3.0mL conc. HF to the sample. Cap the sample and shake it vigorously to mix the contents.

12.9.4.3 Allow the sample to sit for thirty minutes.

12.9.4.4 Proceed with Step 12.9.6 for filtration.

12.9.5 Neptunium

12.9.5.1 Add 0.1mL 0.5 mg/mL neodymnium carrier to each sample. Swirl the contents to mix.

12.9.5.2 Add 3.0mL conc. HF to the sample. Cap the sample and shake it vigorously to mix the contents.

12.9.5.3 Allow the sample to sit for thirty minutes.

12.9.5.4 Proceed with Step 12.9.6 for filtration.

12.9.6 Filtration

12.9.6.1 Prepare the filtration unit by turning on the vacuum and rinsing each apparatus with severalmLs of ASTM Type II DI water.

12.9.6.2 Carefully wash and rinse each of the filter funnels and set them aside.

12.9.6.3 Place a polypropylene filter onto each unit and ensure that it is centered.

12.9.6.4 (Carefully) Place the funnels on the filtration unit.

12.9.6.4.1 Do not rip the filters.

12.9.6.4.2 Rinse the sides of the funnels with 80% reagent grade alcohol.

12.9.6.5 When the sample has completely passed through the filter, rinse the sides of the funnel with a few mLs of the 0.1% HF solution.

12.9.6.6 Rinse the funnel and filter with a few mLs of 80% reagent grade alcohol.

12.9.6.7 When the rinses have completely passed through the filter, remove the filter funnels, turn off vacuum, and carefully remove the filter paper with tweezers.

12.9.6.8 Place the filter paper onto a labeled pre-taped metal disc for counting.

12.9.6.8.1 Allow the filter to completely dry prior to counting by placing it in a labeled petri dish, and storing it in the count room until ready to count.

12.9.6.9 Count the samples in an alpha spectrometry detector as instructed in the current revision of the instrument SOP, PGH-R-020.

12.9.6.10 Obtain instrument printouts and perform calculations as detailed in Attachment 1 of this SOP.

12.9.6.11 If plutonium-241 analysis is desired, the Pu counting source must be removed from the taped disk after alpha spectroscopy counting using a minimal amount of acetone.

12.9.6.12 Place the filter in a glass liquid scintillation vial. Cover the vial with aluminum foil and muffle it in an oven at 550°C for a minimum of 2 hours or until the filter has completely ashed away and there is no black residue left in the vial.

12.9.6.13 Remove the vial from the oven and discard the foil. Add 6 drops of saturated boric acid and 1mL of concentrated HCl to each sample and heat to dryness.

12.9.6.14 Add 2.0mL 0.1N HCl to each sample to dissolve the residue and 15mL of Ultima Gold AB liquid scintillation cocktail. Cap the vial and shake it vigorously.

12.9.6.14.1 The samples should be free of any color.

12.9.6.15 Clean the outside of each vial with acetone followed by ASTM Type II DI water to remove any finger prints or residue.

12.9.6.16 Dark-adapt the samples for one hour prior to counting in a calibrated, liquid scintillation counter in accordance with the liquid scintillation instrument operating SOP, PGH-R-022, current revision.

13. Calculations

13.1 Refer to Attachment I of this SOP for all actinide analysis associated calculations.

13.2 Any verified result for drinking water that exceeds the maximum contaminant level (MCL) established for Uranium must be reported to the appropriate personnel and agencies according to the specific requirements of the state where the water was sampled. The directions for reporting and results that exceed the MCL limits are documented in the State Drinking Water Emergency Reporting Requirements Binder and Pace SOP PGH-C-025, current revision.

13.2.1 Uranium MCL >= 20 pCi/L total uranium (U-238 + U-235 + U-234)

14. Quality Control

14.1 General guidelines for drinking water samples with results that exceed the Maximum Contaminant Level include the following: (All steps are to be conducted as soon as the exceedence has been identified.)

14.1.1 Verify the result(s) to ensure that there were no transcription or calculation errors and that all QC results are within the acceptable limits. Correct any problems and determine the new result. If there were no errors or the result still exceeds the MCL, continue with the reporting process.

14.1.2 Immediately notify the Department Manager/Supervisor, and QA Department that a reportable result has been identified. Use telephone notifications to inform the contact people if the variance is identified after hours along with an e-mail follow up to document the event.

14.1.3 Refer to the State Drinking Water Emergency Reporting Requirements Binder for the state specific information regarding the proper course of action to take. Time is of the essence during this process with some of the state reporting requirements as short as 1 hour from the verification of an exceedence

14.2 Each analyst who performs this test must satisfactorily complete a Demonstration of Capability Study as documented in Section 3.4 of the most recent revision of the Quality Assurance Manual.

14.2.1 The DOC study results are evaluated against the LCS acceptance limits.

14.3 Daily instrument Quality Control checks for the alpha spectrometer must be completed following the instructions detailed in the current revision of Pace SOP PGH-R-020, “Alpha Spectroscopy Instrument Operations.”

14.4 Daily instrument Quality Control checks for the liquid scintillation counter must be completed following the instructions detailed in the current revision of Pace SOP PGH-R-022, “Liquid Scintillation Instrument Operations.”

14.5 Daily instrument Quality Control checks for the gas flow proportional counters must be completed following the instructions detailed in the current revision of Pace SOP PGH-R-002, “Gas Flow Proportional Instrument Operations.”

14.6 See Appendix II for performance indicator evaluation calculations and criteria. Numerical performance indicators may be used to assess QC for non-drinking water samples when the default assessment indicates a QC failure. The numerical performance indicator must be within +/- 3 for all other matrices. The z-score for precision assessment may be used for drinking waters with the approval of the Department Manager/Supervisor using the +/- 2 specification.

14.7 Sample Tracer Recovery/Tracer Peak Energy

14.7.1 Sample tracer is added to each sample and used to calculate sample recovery. Tracer recovery is required to be within 30%-110% for samples analyzed under jurisdiction of the DOD QSM. Pace’s default acceptance criteria for tracer recovery requires recovery between 30%-110%; however, recoveries may be acceptable between 10% and as high as 130% with the documented permission of the Department Manager/Supervisor or specified designee.

14.7.2 Samples with tracer recoveries outside of this range should be re-prepped with direction from the Department Manager or Manager-specified designee after determining possible causes.

14.7.3 Sample tracer counts should be sufficient to minimize the expanded uncertainty of the count and any potential for tailing of the tracer counts into other regions of interest. A minimum of 400 tracer counts is recommended, however, in some instances, the sample matrices may prohibit achieving a minimum 400 tracer counts, and the sample data must be evaluated prior to extending or recounting samples solely to achieve a minimum 400 tracer counts.

14.7.4 Excluding samples analyzed for isotopic thorium content using Th-229 as a tracer, samples analyzed under jurisdiction of the DOD QSM, the tracer energy must be within 40 keV of the known tracer isotope peak energy.

14.7.5 For samples associated with the DOD QSM, if the tracer energy is not within 40 keV of the known peak energy, this may indicate an issue with the detector used for analysis. The sample may be reanalyzed using an alternate detector. If re-analysis results indicate an acceptable tracer energy peak location, results may be reported. If, following re-preparation and re-analysis, the tracer peak is not within 40 keV of the known peak energy, results may be reported with appropriate “J” flagging.

14.7.6 If the tracer is a non-Th-229 alpha emitter, its peak full width half maximum (FWHM) value must be evaluated and generally should be less than 100 keV. When the FWHM is greater than 100 keV the sample data must be inspected using professional judgment to determine if the detector was functioning properly and if the procedure was adequate. Data that has FWHM up to 125 keV may be reported with qualification, except for samples analyzed under the requirements of the DOD QSM. For DOD-associated samples, if the tracer FWHM exceeds 100 keV, the affected sample must either be re-prepared and re-analyzed or the alpha count source may be “re-purified” in accordance with the process outlined in this SOP. If count source re-purification is attempted but fails the FWHM criteria, the sample must be re-prepared and re-analyzed. If upon re-preparation and re-analysis the sample exhibits a tracer peak energy outside of established control criteria, analysis results may be reported with the appropriate “J” flag.

14.7.7 Unlike other radioactive tracers used for yield monitoring, the alpha peak energies associated with Th-229 are of lower abundance and greater energy distribution over the region of interest associated with Th-229. For this reason, there is a greater uncertainty in calculating peak centroid energies and FWHM values when using spectroscopy systems that perform alpha spectral analysis of. When it is observed that the Th-229 centroid energy is calculated to be greater than 40 keV from the average Th-229 peak energy or when the Th-229 peak resolution is determined to be greater than 100 keV, analytical spectra must be reviewed and approved by the Department Manager or a

Department Manager specified designee. For approval, analytical spectra must document clear de-markation between the Th-229 tracer and adjoining analyte regions of interest.

14.8 Method Blank (MB)

14.8.1 One MB must be prepared for each analytical batch. The purpose of the MB is to monitor for cross contamination during the analytical process. When available, the MB should be prepared from a similar matrix as samples contained in the analytical batch. If appropriate blank matrix material is not available, ASTM Type II DI water (Reagent Blank) must be carried through the procedure. A reagent blank may be used for sample correction purposes following approval of affected clients.

14.8.2 The MB result must be less than the MDC. If the method blank result is greater than MDC, individual sample results may still be reportable.

14.8.2.1 PASI's default criteria allows reporting of sample results less than the CRDL (contract required detection limit) or greater than 10 times the blank result. Relative sizes of the sample and blank aliquots must be factored when making this determination (raw counts).

14.8.2.2 For samples analyzed under the DoD QSM, the Method Blank result must be less than ½ the detection limit. Corrective action is necessary for any MB result greater than ½ the detection limit.

14.9 Sample Duplicate (DUP)

14.9.1 One Duplicate Sample (DUP) must be randomly assigned within each batch. The purpose of the sample DUP is to measure precision of the analytical process. Laboratory duplicates are not intended to assess precision related to the sample collection process. Sample collection precision can only be assessed through collection of duplicate samples at the time of sample collection. The sample DUP is a duplicate volume of sample processed identically as other samples in the analytical batch.

14.9.2 For batches with drinking water samples originating from the state of Arizona, Duplicate Samples (DUP) must be randomly assigned within each batch at a frequency of no less than 10%. A batch of ten samples or fewer must contain at least one duplicate sample. A batch of greater than 10 samples up to 20 samples must contain a minimum of two duplicate samples if the batch contains samples originating from Arizona.

14.9.3 Calculation

$$\%RPD = \frac{\left|\left(R_S - R_D\right)\right|}{\left(\left(R_S + R_D\right)/2\right)}$$ Where:

R_S = sample activity concentration
R_D = duplicate activity concentration

14.9.4 Duplicate sample performance is acceptable when the %RPD is <25%.

14.10 Sample Matrix Spikes (MS)

14.10.1 Because this analytical method requires the use of radiotracers for yield determination, PASI's default QC policy is that a sample matrix spike (MS) is not required for alpha spectrometry analyses except for drinking water analysis.

14.10.2 A matrix spike is prepared by spiking a known amount of spike solution (Am-241, Cm-244, Pu-239, Th-232, U-238, Np-237, etc.) into a portion of one sample in the batch, and it must be processed identically as for other samples. The purpose of the MS is to assess the effect of sample components on the analytical process. The volume of sample used for the MS must be equivalent to the volume used for sample analysis. The spike amount should be approximately 10 times the detection limit and not less than 20% of the anticipated sample concentration.

14.10.3 Matrix Spike Recovery Calculation

$$\%REC = \frac{(x - x_0)}{c} x100$$ Where:

x = measured concentration of the spiked sample
x_0 = measured concentration of the unspiked sample
c = spike concentration added

14.10.4 MS performance is acceptable when agreement of the measured value and the expected value is within ±25% of the true value.

14.11 Sample Matrix Spike Duplicates (MSD)

14.11.1 A sample Matrix Spike Duplicate (MSD) is not required for this analysis. When required by the customer/contract, a MSD must be prepared for each analytical batch. The MSD must be prepared as a duplicate of the MS.

14.11.2 For all matrices the MSD must pass the criteria established for the MS. Additionally, the MS and MSD must pass the criteria established for duplicate precision.

14.12 Laboratory Control Sample (LCS)

14.12.1 One LCS must be prepared for each analytical batch and is a reference material that contains a known concentration of spike (Am-241, Cm-244, Pu-239, Th-232, U-238, Np-237, etc.) in a matrix that is similar to the samples within the batch. If this material is not available, a well-characterized material (WCM) may be used. If neither of these is available, DI may be spiked with a spike solution greater than 2 times the detection limit.

14.12.2 LCS Recovery calculations

$$\%REC = \frac{x}{c} x100$$ Where:

x = Analytical result of the LCS
c = Known concentration of the LCS

14.12.3 LCS performance is acceptable when the %REC is within ±25% of the known value.

14.13 Laboratory Control Sample Duplicate (LCSD)

14.13.1 A LCSD must be analyzed to measure batch precision whenever adequate sample volume is not available for sample DUP analysis. The LCSD must be prepared in an identical fashion as the LCS and processed identically as for other samples.

14.13.2 The LCSD must pass the criteria established for the LCS.

14.13.3 Additionally, the LCS and LCSD must pass the criteria established for duplicate precision.

14.14 Summary of QC related Activities:

Method Blank	One per Batch
Reagent Blank	One per Batch (as required by client)
Duplicate Sample	One per Batch (frequency of 1 per 10 samples for batches containing DW originating from AZ)
Matrix Spike	One per Batch (for drinking water analysis or as required by client)
Matrix Spike Duplicate	One per Batch (frequency of 1 per 10 samples for batches containing DW originating from AZ or as required by client)
Laboratory Control Sample	One per Batch
Laboratory Control Sample Dup	One per Batch for samples in the absence of Duplicate sample.

14.15 Corrective Actions for Out-Of-Control Data

14.15.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.15.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.15.3 Matrix Spike Recovery (MS) – MS recoveries that fail high and outside of control criteria with a sample result that is less than the reporting limit may be reported with narration. Additionally, MS recoveries that fail low and outside of control criteria for

Drinking Water samples with a sample result that is greater than the MCL must be reported with comment as potentially biased low due to matrix interference. Otherwise, MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and noted in the final report. Matrix effect must be determined by re-analysis of the MS/Sample pair or demonstration of acceptable precision between a MS/MSD pair.

14.15.4 The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.15.5 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.15.6 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.15.7 Laboratory Control Sample Duplicate (LCSD) – If an LCSD does not meet the recovery acceptance criteria, the entire analytical batch must be reanalyzed.

The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their the reporting limit, and duplicate precision meets the acceptance criteria.

14.15.8 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.16 Contingencies for handling Out-of-Control or Unacceptable Data

14.16.1 Method Blank (Reagent Blank): If the sample is exhausted, evaluate the usefulness of the data in the final report.

14.16.2 Duplicates: If the sample is exhausted, evaluate the usefulness of the data in the final report.

14.16.3 Matrix Spike Recovery: If a Matrix Spike is analyzed and the spike recoveries are not comparable, and the sample is exhausted, evaluate the data usefulness in the final report.

14.16.4 Matrix Spike Duplicate: If a Matrix Spike Duplicate is analyzed and the spike recovery is not comparable to the Matrix Spike and the sample is exhausted, evaluate the data usefulness in the final report.

14.16.5 Tracer recovery: If the tracer recovery is less than 30% but greater than 10% with more than 400 tracer counts, the sample may be reported with supervisor permission. Tracer recovery above 110% but below 130% may be reported but must be narrated. Samples with tracer recovery below 10% or above 130% must be re-analyzed. If the sample is exhausted, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.2 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.3 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

15.4 Laboratory Control Samples are analyzed with each batch, the results are charted to monitor control limits and trending.

16. Pollution Prevention and Waste Management

16.1 Place radioactive waste into the appropriate receptacles.

16.2 Discard acidified samples and unusable standards into the proper waste drains.

16.3 Dispose of waste materials in accordance to type: (Non-hazardous, hazardous, non-radioactive, radioactive or mixed).

17. References

17.1 Bishop, C. T., et.al. “Radiometric Method for the Determination of Uranium in Water,” EPA 600/7-79-093, EMSL-LV, April 1979.

17.2 Edwards, K. W. “Isotopic Analysis of Uranium in Natural Waters by Alpha Spectrometry,” Radiochemical Analysis of Water, Geological Survey Water – Supply Paper 1696-F, U.S. Government Printing Office, Washington, D.C., 1968.

17.3 Krieger, H. L. and Whittaker, E. L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, “Uranium-Radiochemical Method,” Method 908.0, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, August, 1980.

17.4 ASTM E181-93, Standard Test Methods for Detector Calibration and Analysis of Radionuclides, ASTM Standards, Vol. 12.02.

17.5 ASTM D-3972-90, Test Method for Isotopic Uranium in Water by Radiochemistry, ASTM Standards, Vol. 12.04.

17.6 Table of Radioactive Isotopes, Brown and Firestone, Shirley editor, John Wiley & Sons, 1986.

17.7 Currie, L., Limits for Quantitative Detection and Quantitative Determination, Analytical Chemistry, Vol. 40. No. 3, Pg 586-593, 1968.

17.8 Currie, L., Lower Limit of Detection: Definition and Elaboration of a Proposed Position for Radiological Effluent and Environmental Measurements, NUREG/CR - 4007, USNRC, 1984.

17.9 "American National Standard Calibration and Usage of Alpha/Beta Proportional Counters", ANSI N42.25-1997.

17.10 "Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)", July 2004, Final.

17.11 Eichrom Industries, Various Actinide Procedures. Darien, Illinois, 1995

17.12 EML Procedures Manual, HASL-300 28th Edition.

17.13 Pace SOP PGH-R-001, current revision (Analysis of Samples for Gross Alpha and Gross Beta content).

17.14 Pace SOP PGH-R-002, current revision (Gas Flow Proportional Counter Operation).

17.15 Pace SOP PGH-R-020, current revision (Alpha Spectroscopy Instrument Operations).

17.16 Pace SOP PGH-R-022, current revision (Liquid Scintillation Counter Operations).

17.17 Pace SOP PGH-R-024, current revision (Radiochem Sample Preparation).

17.18 Pace SOP PGH-C-027, current revision (Deionized Water Quality and Suitability).

17.19 Pace SOP PGH-C-025, current revision (Reporting SDWA MCL Violations).

17.20 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.21 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.22 Pace Analytical Services, LLC. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.23 Department of Defense (DOD), Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories; DOD QSM version 5.1, DOE Quality Systems for Analytical Services Version 3.1, 2017.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Attachment No 1: Concentration Calculation & Counting Uncertainty

18.2 Attachment No 2: Evaluation of QC using Numerical Indicators.

18.3 Figure No 1: Analysis Flowchart for Sequential Analysis of Am, Pu, U, and Th

18.4 Figure No 2: Analysis Flowchart for Sequential Analysis for Am, Pu, U (Regular Water or Solids)

18.5 Figure No 3: Analysis Flowchart for Sequential Analysis of Am and Pu in Solids >1 Gram

18.6 Figure No 4: Analysis Flowchart for Sequential Analysis of U and Th in solid or water

19. Method Modifications

19.1 This method for uranium in water is substantially compliant with ASTM Method D-3972-90 and HASL 300 Method U-02 for uranium with the following exceptions:

19.2 ASTM D3972-90 Modifications:

19.2.1 Ammonium iodide or HNO_3/H_2O_2 rinses have been substituted for the HI rinse to strip plutonium from the column prior to eluting uranium.

19.3 HASL U-02 Modifications:

19.3.1 U-02 foresees initial pre-concentration by simple evaporation. This can often lead to analyte loss due to poorly soluble residues. The method has been modified to employ a ferric hydroxide precipitation which both avoids formation of insoluble residues while providing additional decontamination.

19.3.2 Method HASL 300 U-02 specifies the use of AG 1X4 anion exchange resin. PASI utilizes AG 1X8 anion exchange resin due to increased loading capacity as well as enhanced selectivity in the separation of uranium from competing/interfering elements.

19.3.3 Method HASL 300 U-02 indicates the use of 7N HCL solution in the loading of uranium onto the anion exchange column with 1 N HCL as the eventual eluant for uranium. PASI utilizes a 9N HCL for loading and 0.1N HCL for elution to enhance analyte recovery.

19.3.4 Additionally, PASI utilizes intermediate stripping reagents to selectively remove plutonium (9N HCl / 0.05N NH_4I) and neptunium (6N HCl / 0.52N HF), if present in the samples.

19.3.5 Additional rinses have been added to HASL 300 U-02 to provide efficient decontamination from alpha emitting interferences.

19.3.6 Quality Control requirements have been modified to conform to PACE Analytical Services, LLC. QAP requirements and procedures.

19.4 This method for plutonium, americium and curium isotopes in all matrices and uranium in non-drinking water matrices is a PACE Analytical Services, LLC. proprietary method and is based in parts on EPA or other promulgated methods.

20. Revisions

Document No.	Reason for Change	Date
PGH-R-008-6	1. Updated cover sheet to include Periodic Review. Updated Cover Page, Headers and Footers for this revision. Added periodic review signature lines to the cover page. 2. Updated Table of Contents section to include Attachments	31Dec2012

Document No.	Reason for Change	Date
	and Flowcharts. Made TOC updateable and linked to all the primary sections. 3. Updated Flow charts for the current thorium procedure after column separation. 4. Updated flowcharts with "Count to meet MDC and obtain 400 tracer counts", removing any suggested time requirement. 5. Section 12.7.6.6 – added to include addition of HCl to match flowchart directions. 6. Corrected section 12.8.7 to direct to the correct section for Pu analysis. 7. Section 14.4.3– expanded suggested minimum tracer counts requirements. 8. Section 15 – Removed annual MDL study requirement. Not performed for radiochemical methods. 9. Section 17 – Added TNI reference 10. Removed all references allowing approval of a "senior analyst" and replaced with "approval of Department Manager or Manager-specified designee."	
PGH-R-008-7	1. Updated cover page for this revision and to update the copy right footnote. Also updated to include the Methods Referenced 2. Section 1.3 corrected location of Method Deviations section. 3. Section 6: Updated to specify not targeting weights, recording observed measurements, and not removing sample from beakers once transferred from bottle. 4. Section 10: DI reference to ASTM Type II, and SOP reference. 5. Section 12: Updated to specify spiking and tracing preceding all chemical additions beyond initial preservation. 6. Section 17: Updated to include ASTM D 3972-90 and PASI-PGH QAM. 7. Section 19: Updated deviations from HASL 300 U-02 method.	07Nov2013
PGH-R-008-8	1. Annual SOP review and update. 2. Section 2 – Added references to applicable instrument operation SOPs. Included these references where instrumentation is discussed in other areas of the document. 3. Section 8.1.1 – Included pH verification requirements and recording. 4. Section 8.1.4 – Added maximum hold time requirement. 5. Section 9 – Included references to Pace SOP for instrument operations and listed instrumentation. 6. Section 12.1 – Clarified aqueous sample analysis amounts and instructions for diluting samples. 7. Section 12.6 – Urine samples measured with graduated cylinders not weighed. 8. Section 14.5 – Changed to be consistent with other SOPs for discussion of numerical indicator application. 9. Section 14 – Included duplicate requirement for Arizona drinking water samples in applicable sections.	13Jul2014

Document No.	Reason for Change	Date
	10. Section 15 – added CDOC requirements 11. Section 17 – Added applicable instrument SOP references. 12. Reformatted document.	
PGH-R-008-9	1. Removed from section 5.1: Analysts must be trained as radiation workers and personal dosimeter worn. 2. Section 14 modified to add tracer peak quality control requirements for USDOD-related sample analysis. 3. Section 17 modified to add reference to the US DOD/DOE QSM version 5.0.	20Feb15
PGH-R-008-10	1. Annual review and update. 2. Updated section references throughout document. 3. Updated section 12.4.7 to discuss the process for treating highly oxidized solids to improve analyte recovery.	27Jul2015
PGH-R-008-11	1. Periodic review and update. 2. Section 2.3 – All analytes are decay corrected to the supplied collection date and time. 3. Section 3.2 – Removed reference to a Rapid Extraction Method, not performed. 4. Sections 12.6, 12.11, 12.12, 12.13, and 12.14 – Removed the instructions for Urine analysis, and all instructions referring to specialized methods which are not being performed. 5. Section 10 – Removed reagents associated with the removed methods/sections. 6. Section 12.10.3 and 12.10.4 removed since they are not used. 7. Methods 1 and 2 – Removed the “additional” volumes on each step, since various sized columns are not utilized.	15Mar2017
PGH-R-008-12	1. Periodic review and update. 2. Section 4.9- Inserted comment regarding MAPEP soil series interferences and enhanced dissolution process outlined in section 12.11 3. Section 9- Included additional apparatus for performing the enhanced dissolution procedure. 4. Sections 10- Included additional reagents needed for performing enhanced dissolution. 5. Section 12.1 – Removed precipitate rinse using pH 10 DI water. 6. Section 12.4.2.2 – Added due to section 12.11. 7. Section 12.6.6- Changed wording to reflect when it is necessary to perform this step. 8. Section 12.7.4.5, 12.7.5- Adjusted to reflect volumes used for these steps. 9. Section 12.11- Added to provide instruction for performing enhanced dissolution by fusion method for Uranium/plutonium analysis of MAPEP solid samples. 10. Section 17 – Included references for fusion method.	26Sep2017
S-PGH-R-008-rev.13	1. Section 8.1.1.1 samples must be held minimum of 24 hours. 2. Section 2.1 updated to remove biota as a matrix. 3. Sections 8.1.2 and 8.1.3 updated to remove urine as a matrix. 4. Section 11.33 updated to broaden instructions for	08Feb2018

Document No.	Reason for Change	Date
	calibration verifications. 5. Section 12.3 deleted to remove reference to biota samples which are not analyzed by the lab. All subsequent sections moved up in the SOP. 6. Line references updated to adjust for removal of section 12.3. 7. Numerous sections updated to remove reference to urine and biota. 8. Section 12.5.6 and 12.5.7, updated to current practice with explanation. 9. Section 13.2 and 14.1 added to discuss uranium MCL violation determination and actions. 10. Section 14.8.2 updated to include DoD QSM method blank requirements. 11. Section 14.14.3 modified to enhance assessment of failing MS/MSDs.	

Attachment I - Calculations

The **radioactivity concentration** of a sample is calculated according to the following equations:

Eq. 1 $$A = \frac{(S_S / T_s)}{Denom}$$

Eq. 2 $$E_T = R * E$$

Eq. 3 $$E_i = \frac{S_E}{T_E * C_E * F_E * D_E}$$

Eq. 4 *E = average of individual isotope efficiencies*

Eq. 5 $$D = e^{-\lambda t}$$

Eq. 6 $$\lambda = \frac{\ln 2}{T_{1/2}}$$

Eq. 7 $$Denom = E_T * V * 2.22 * D * F$$

Eq. 8 $$R = \frac{(S_T / T_S)}{(E * C)}$$

Where:

A = The radioactivity concentration for the radioisotope being measured in units of pCi per Liter, gram, filter, or sample. ***"Activity."***

S_S = Represents the background corrected net counts for the radioisotope being measured. ***"Peak Net Cts."***

B = Represents the Bkg Cts acquired in the applicable region of interest (ROI) referenced to the sample count time. "***Bkg Cts (ref to Sample ct time)".***

T_S = Represents the count time for the sample. ***"Sample time (min)."***

T_B = Represents the count time for the background. ***"Bkg Time (min)."***

E_T = Represents the total system efficiency for the counted sample. This represents the detector efficiency corrected for chemical recovery. ***"Total Eff."***

V = Represents the sample volume (in liters), mass (in grams), filter portion analyzed (fractional), or sample portion analyzed (fractional). ***"Aliquot."***

2.22 = Represents the factor to convert from disintegrations per minute (dpm) to picocuries (pCi). ***"Act. Conv. From dpm to pCi."***

D = Represents the fraction of analyte remaining after decay time T. ***"Fract. Remain."***

F = Represents the summed branching ratio for all alpha particles emitted in the region of interest. In most cases this is 100% (+/- 1%). If the branching ratio varies significantly (greater than associated uncertainty) from 100%, this correction should be applied. ***"abnd."***

R = Represents the analytical chemical recovery for the tracer analyte. ***"Chemical Yield."***

S_T = Represents the background corrected net tracer peak counts in the applicable region of interest (ROI). Located in the **"Peak Net Cts"** column for the tracer nuclide row.

B_T = Represents the background counts for the tracer analyte acquired in the tracer region of interest (ROI) referenced to the sample count time. Located in the **"Bkg Cts (ref to Sample Ct time)"** column for the tracer nuclide row.

E = Represents the efficiency for the detector used for sample counting. The efficiency is a fixed number for each detector representing the fractional percent of radioactive events that are measured by the counting system. ***"Det. Eff. (cpm/dpm)."***

C = Represents the dpm of tracer (decay corrected to the time of sample counting) added to the sample. ***"Spike dpm."***

$T_{1/2}$ = Represents the half-life of the radionuclide being measured. ***"T1/2 (y)."***

t = Represents the elapsed time between the reference and count dates in the same units as $T_{1/2}$.

The sample specific **counting uncertainty** is calculated as follows.

Eq. 9 $$\textit{Counting Uncertainty} = \frac{1.96 * \sqrt{\left((S_S/T_S)/(T_S)\right) + \left((B/Ts)/(T_B)\right)}}{\text{Denom}}$$

As summed background and analyte count rates approach zero, assumptions underlying the uncertainty calculation are violated and it will return an unrealistic value of zero (0) uncertainty when zero summed counts are observed. The following equation provides a more accurate estimate of count uncertainty at zero and near-zero count rates.

Eq. 10 $$\text{ZeroUnc} = \frac{1.96 * \sqrt{zaf / T_S / T_S + zaf / T_B / T_B}}{Denom}$$

Where:

zaf = zero activity factor

and T_S, T_B, and Denom were previously defined

Note 1: Depending on sample type and contract requirements the zero activity factor may be either 3.0 or 2.71. PASI's default is 2.71 consistent with the current version of ANSI N42.23. Bioassay samples must be calculated using 3.0 to be consistent with ANSI N13.30.

Note 2: The Zero Count Uncertainty is compared to the count uncertainty above. The larger of the two is used as the counting uncertainty in subsequent total error calculations.

The error term is further evaluated to provide an estimate of total error hereafter referred to as the *Combined Standard Uncertainty* (CSU a.k.a. TPU).

Eq. 11 $$\text{CSU (pCi/unit)} = \sqrt{(\text{CountingUncertainty})^2 + (UE1 * A)^2 + (UE2 * A)^2 + (UE3 * A)^2 + (UE4)^2}$$

UE1, UE2, UE3, and UE4 represent partial derivatives estimating the relative uncertainty at the ***95% confidence interval*** for various factors in the activity calculation as follows:

UE1 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with preparation (e.g., sample aliquot or transfers and splits prior to addition and equilibration of tracer).

UE2 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with analysis (e.g., peak integration, peak overlap, tracer contaminants).

UE3 represents combined factors estimating relative uncertainty (fractional) associated with yield correction (e.g., count uncertainty for tracer peak, SRM known value, tracer volume or mass aliquot, tracer equilibration efficiency).

UE4 represents the factor estimating additional uncertainty (activity) associated with an individual sample -- to be used in exceptional circumstances with approval of the Department Manager or Manager-specified designee and with appropriate documentation and narration only.

The Minimum Detectable Concentration (MDC), Decision Level (DL) activity and Critical Level are calculated per guidance of ANSI N42.23 and N13.30 as:

Eq. 12
$$MDC = \frac{4.65 * \sqrt{(B/Ts) * T_S} + ZeroActFact}{Ts * Denom}$$

The Critical Level (LC), is calculated per guidance of ANSI N42.23 as:

Eq. 13
$$LC = \frac{1.65 * \sqrt{(B/Ts) * (1/T_S + 1/T_B)}}{Denom}$$

Attachment II - (Numerical Performance Indicators)

1. **Method Blank (MB)**

1.1 The numerical performance indicator for the method blank is calculated by:

$$Z_{Blank} = \frac{x}{u(x)}$$

Where:
x = Measured blank activity
u(x) = Combined standard uncertainty (1 sigma) in the blank measurement

1.2 MB performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. MB performance indicator values should be recorded on a control chart.

2. **Laboratory Control Sample (LCS)**

2.1 The numerical performance indicator for a laboratory control sample is calculated by:

$$Z_{LCS} = \frac{x - c}{\sqrt{u^2(x) + u^2(c)}}$$

Where:

x = Analytical result of the LCS
c = Known concentration of the LCS
$u^2(x)$ = Combined standard uncertainty (1 sigma) of the result squared.
$u^2(c)$ = Combined standard uncertainty (1 sigma) of the LCS value squared.

2.2 LCS performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. Performance indicator values should be recorded on a control chart.

3. **Duplicates (DUP)**

3.1 These criteria are applicable for the evaluation of the Duplicate, Matrix Spike Duplicate and Laboratory Control Sample Duplicates.

3.2 The numerical performance indicator for laboratory duplicates is calculated by:

$$Z_{Dup} = \frac{x_1 - x_2}{\sqrt{u^2(x_1) + u^2(x_2)}}$$

Where:
x_1, x_2 = Two measured activity concentrations
$u^2(x_1)$, $u^2(x_2)$ = The combined standard uncertainty (1 sigma) of each measurement squared.

3.3 Duplicate sample performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. DUP performance indicator values should be recorded on a control chart for each QC sample type (Dup, MSD, LCSD)

4. **Matrix Spike/Matrix Spike Duplicate (MS/MSD)**

4.1 The numerical performance indicator for a matrix spike sample is calculated by:

$$Z_{MS} = \frac{x - x_0 - c}{\sqrt{u^2(x) + u^2(x_0) + u^2(c)}}$$

Where:
x = measured concentration of the spiked sample
x_0 = measured concentration of the unspiked sample
c = spike concentration added
$u^2(x)$, $u^2(x_0)$, $u^2(c)$ = the squares of the respective combined standard uncertainties (1 sigma) of these values.

4.2 MS performance for all matrices is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. MS performance indicator values should be recorded on a control chart.

Figure 1. Analysis Flowchart for Sequential Analysis of Am, Pu, U, and Th (Method 2)

BOX 1___Precondition a small anion column with 20mL 8N HNO_3 – discard
___Dissolve sample in 15mL 8N HNO_3 - heat to aid in dissolution as necessary – samples must be clear – centrifuge if suspended solids are present
___Load sample onto conditioned columns – collect in clean c-tubes labeled **ALL**
___Rinse sample c-tube with 15mL 8N HNO_3 and add to columns – collect for **ALL**
___Rinse column with 15mL 8N HNO_3 – collect for **ALL**
___Pour contents of **ALL** c-tubes into clean glass beakers and heat to dryness. **Proceed to Box 3.**
___Place new c-tubes under columns labeled **TH** – elute and collect thorium by adding 25mL 9N HCl to columns. **Proceed to Box 2.**
___Save columns for re-use

BOX 2___Transfer **TH** fraction to new labeled 250mL disposable cup.
___Add 0.80ml of iron carrier and dilute to the 220mL mark with DI water
___Precipitate the thorium as a hydroxide by adding 22mL of NH4OH and stirring with a disposable pipette.
___Stir the samples vigorously after 15 minutes.
___Allow the precipitate to settle for 30 minutes, decant the supernate, and transfer the rest to the original c-tube with pH 10 DI water.
___Centrifuge and discard the supernate.
___Dissolve **TH** residue in 3mL 9N HCl
___Dilute the dissolved **TH** with DI water to a final volume of 25mL
___Microprecip **TH** with Neodymnium and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 3___Add 15mL conc HCl to beakers labeled **ALL** and heat to dryness
___Dissolve contents of beakers labeled **ALL** in 15mL 9N HCl / 0.1% H_2O_2 – heat to aid in dissolution
___Load samples onto columns previously used – collect in c-tubes labeled **AM**
___Rinse **ALL** beakers with 10mL 9N HCl / 0.1% H_2O_2 and pour on columns – collect for **AM**
___Rinse columns with 20mL 9N HCl – collect for **AM. Proceed to Box 4**
___Place new c-tubes under columns labeled **PU –** elute and collect plutonium by adding 20mL 9N HCl / 0.05N NH_4I. **Proceed to Box 5**
___Rinse columns with 15mL 6N HCl / 0.52N HF – discard to waste
___Rinse columns with 10mL 9N HCl – discard
___Elute uranium into c-tubes labeled **U** by adding 20mL 0.1N HCl
___Microprecip **U** with neodymnium, titanous chloride to persistent purple color, and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 4___Transfer contents of c-tubes labeled **AM** to new glass beakers, add 3 drops Fe carrier and heat to dryness
___Add 5mL conc HNO_3 and heat to dryness
___Prepare Tru resin columns with pre-filter resin on bottom
___Condition columns with 5mL 2N HNO_3 - discard
___Dissolve contents of beaker in 10ml 2N HNO_3 / 0.5N $AlNO_3$
___Add 1 drop KSCN indicator and 6-8 drops of fresh 1N ascorbic acid – samples should be clear
___Pour sample onto columns – discard
___Rinse sample beaker with 5mL 2N HNO_3 – add to column - discard
___Rinse with 5mL 2N HNO_3 - discard
___Rinse with 5mL 2N HNO_3 - discard
___Elute AM into c-tubes with 2mL 9N HCL followed by 10mL 4N HCl
___Transfer to beakers and heat to dryness
___Add 1.0mL formic acid – heat to dryness
___Condition TEVA columns with 5mL fresh 3N Ammonium Thiocyanate / 0.1N Formic acid
___Dissolve samples in 15mL 3N AThio/ 0.1N formic
___Load sample onto columns – discard
___Rinse columns with 2mL 1N AThio/ 0.1N formic – discard
___Rinse with 3mL 1N AThio/ 0.1N formic – discard
___Rinse with 5ml 1N AThio/ 0.1N formic – discard
___Elute **AM** into new c-tubes with 15mL 2N HCl
___Microprecip **AM** with neodymnium and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 5___Transfer **PU** fraction to new glass beakers
___Add 10mL conc HNO_3 and 3 drops iron carrier
___Heat until reactions subside
___Add H_2O_2 dropwise to destroy NH_4I – about 15 drops
___Heat to dryness
___Add 5mL conc HCl
___Heat to dryness
___Dissolve **PU** residue in 10mL 9N HCl
___Transfer to new c-tubes with DI water to a final volume of 20mL
___Microprecip **PU** with neodymnium, 10-12 drops 25% dihydrazine dihydrochloride, and HF
___Count to meet MDC and obtain 400 tracer counts.

Figure 2: Analysis Flowchart for Sequential Analysis for Am, Pu, U (Water or Solids) Method 1

Box 1___Prepare samples in accordance with the applicable section based on the matrix (12.1 for aqueous samples, 12.4 for solid samples). Solids must undergo complete digestion with HF.
___Condition prepared anion columns with 10mL 9N HCl.
___**Proceed to Box 2.**

BOX 4___Transfer **PU** fraction to new glass beakers
___Add 10mL conc HNO_3 and 3 drops iron carrier
___Heat until reactions subside
___Add H_2O_2 dropwise to destroy NH_4I – about 15 drops
___Heat to dryness
___Add 5mL conc HCl
___Heat to dryness
___Dissolve **PU** residue in 10mL 9N HCl
___Transfer to new c-tubes with DI water to a final volume of 20mL
___Microprecip **PU** with neodymnium, 10-12 drops 25% dihydrazine dihydrochloride, and HF
___Count for to meet MDC and obtain 400 tracer counts.

BOX 2___Dissove sample residue/precipitate in 15mL 9N HCl / 0.1% H_2O_2 – heat to aid in dissolution
___Centrifuge samples if necessary
___Load samples onto columns collect in c-tubes labeled **AM**
___Rinse sample c-tube with 10mL 9N HCl / 0.1% H_2O_2 and pour on columns – collect for **AM**
___Rinse columns with 20mL 9N HCl – collect for **AM.**
Proceed to Box 3
___Place new c-tubes under columns labeled **PU –** elute and collect plutonium by adding 20mL 9N HCl / 0.05N NH_4I. **Proceed to Box 4**
___Rinse columns with 15mL 6N HCl / 0.52N HF – discard to waste
___Rinse columns with 10mL 9N HCl – discard
___Elute uranium into c-tubes labeled **U** by adding 20mL 0.1N HCl
___Microprecip **U** with neodymnium, titanous chloride to persistent purple color, and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 3___Transfer contents of c-tubes labeled **AM** to new glass beakers, add 3 drops Fe carrier and heat to dryness
___Add 5mL conc HNO_3 and heat to dryness
___Prepare Tru resin columns with pre-filter resin on bottom
___Condition columns with 5mL 2N HNO_3 - discard
___Dissolve contents of beaker in 10ml 2N HNO_3 / 0.5N $AlNO_3$
___Add 1 drop KSCN indicator and 6-8 drops of fresh 1N ascorbic acid – samples should be clear
___Pour sample onto columns – discard
___Rinse sample beaker with 5mL 2N HNO_3 – add to column - discard
___Rinse with 5mL 2N HNO_3 - discard
___Rinse with 5mL 2N HNO_3 - discard
___Elute AM into c-tubes with 2mL 9N HCL followed by 10mL 4N HCl
___Microprecip **AM** with neodymnium and HF
___Count to meet MDC and obtain 400 tracer counts.

Figure 3: Analysis Flowchart for Sequential Analysis of Am and Pu in Solids >1g

Box 1___1. Aliquot 3-4 grams of dry pulverized solid into clean labeled ceramic crucible.
___2. Add 1.0mL of iron carrier. Add tracers to all samples, and spike solution to LCS and MS.
___3. Cover sample with crucible lid and place in oven at 550C overnight (minimum of 4 hours).
___4. Remove samples from oven, re-label, and carefully loosen solid with a disposable pipette.
___5. Transfer loosened solid to a labeled glass beaker with a minimal amount of 8N HNO_3.
___8. Add 5mL 16N HNO_3 and 5mL 12N HCl to the crucible and place on hotplate at medium heat to loosen/remove the remaining solid.
___9. Transfer this solution to the appropriate glass beaker with 9N HCl. Repeat the above step as necessary to remove solid from the crucible.
___10. __ __Add 15mL 16N HNO_3 and 15mL 12N HCl to each sample beaker.
___11. __ __Cover sample with a watch glass and leach for 30 minutes on hotplate at medium heat.
___12. __ __Cool sample and transfer to a centrifuge tube using DI water. Centrifuge the sample.
___13. __ __Transfer the supernate to a clean labeled glass beaker and heat to dryness.
___14. __ __Transfer the solid back to the original beaker with 9N HCl.
___15. Repeat steps 10-14 two additional times adding the supernate from each centrifuge cycle to the beaker in step 13. The solid should be lighter in color indicating complete leaching of iron metal from the sample.
___16. Heat the supernate to dryness.
___17. Add 10mL 12N HCl to each sample beaker and heat to dryness. **Proceed to Box 2.**

BOX 4___Transfer **PU** fraction to new glass beakers
___Add 10mL conc HNO_3 and 3 drops iron carrier
___Heat until reactions subside
___Add H_2O_2 dropwise to destroy NH_4I – about 15 drops
___Heat to dryness
___Add 5mL conc HCl
___Heat to dryness
___Dissolve **PU** residue in 10mL 9N HCl
___Transfer to new c-tubes with DI water to a final volume of 20mL
___Microprecip **PU** with neodymnium, 10-12 drops 25% dihydrazine dihydrochloride, and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 2___Precondition small anion column with 10mL 9N HCl.
___Dissolve contents of beakers in 15mL 9N HCl / 0.1% H_2O_2 – heat to aid in dissolution – centrifuge sample
___Load samples onto columns – collect in c-tubes labeled **AM**
___Rinse beakers/c-tubes with 10mL 9N HCl / 0.1% H_2O_2 and pour on columns – collect for **AM**
___Rinse columns with 20mL 9N HCl – collect for **AM.**
Proceed to Box 3
___Place new c-tubes under columns labeled **PU –** elute and collect plutonium by adding 20mL 9N HCl / 0.05N NH_4I.
Proceed to Box 4
___Rinse columns with 15mL 6N HCl / 0.52N HF – discard to waste
___Rinse columns with 10mL 9N HCl – discard
___Elute uranium into c-tubes labeled **U** by adding 20mL 0.1N HCl
___Microprecip **U** with neodymnium, titanous chloride to persistent purple color, and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 3___Transfer contents of c-tubes labeled **AM** to new glass beakers, add 3 drops Fe carrier and heat to dryness
___Add 5mL conc HNO_3 and heat to dryness
___Prepare Tru resin columns with pre-filter resin on bottom
___Condition columns with 5mL 2N HNO_3 - discard
___Dissolve contents of beaker in 10ml 2N HNO_3 / 0.5N $AlNO_3$
___Add 1 drop KSCN indicator and 6-8 drops of fresh 1N ascorbic acid – samples should be clear
___Pour sample onto columns – discard
___Rinse sample beaker with 5mL 2N HNO_3 – add to column - discard
___Rinse with 5mL 2N HNO_3 - discard
___Rinse with 5mL 2N HNO_3 - discard
___Elute AM into c-tubes with 2mL 9N HCL followed by 10mL 4N HCl
___Transfer to beakers and heat to dryness
___Add 10mL HCl and heat to dryness
___Add 1.0mL formic acid – heat to dryness
___Condition TEVA columns with 5mL fresh 3N Ammonium Thiocyanate / 0.1N Formic acid
___Dissolve samples in 15mL 3N AThio/ 0.1N formic
___Load sample onto columns – discard
___Rinse columns with 2mL 1N AThio/ 0.1N formic – discard
___Rinse with 3mL 1N AThio/ 0.1N formic – discard
___Rinse with 5ml 1N AThio/ 0.1N formic – discard
___Elute **AM** into new c-tubes with 15mL 2N HCl
___Microprecip **AM** with neodymnium and HF
___Count to meet MDC and obtain 400 tracer counts.

Figure No 4: Analysis Flowchart for Sequential Analysis of U and Th in solid or water utilizing Anion Resin.

BOX 1___Precondition a small anion column with 20mL 8N HNO_3 – discard
___Dissolve sample in 15mL 8N HNO_3 - heat to aid in dissolution as necessary – samples must be clear – centrifuge if suspended solids are present. An extra 5mL of 8N HNO_3 may be used if transferring solids to a centrifuge tube.
___Load sample onto conditioned columns – collect in clean c-tubes labeled **U**
___Rinse sample c-tube with 15mL 8N HNO_3 and add to columns – collect for **U**
___Rinse column with 15mL 8N HNO_3 – collect for **U**
___Pour contents of **U** c-tubes into clean glass beakers and heat to dryness. **Proceed to Box 3.**
___Place new c-tubes under columns labeled **TH** – elute and collect thorium by adding 25mL 9N HCl to columns. **Proceed to Box 2.**
___Save columns for re-use

BOX 2___Transfer **TH** fraction to new labeled 250mL disposable cup.
___Add 0.80ml of iron carrier and dilute to the 220mL mark with DI water
___Precipitate the thorium as a hydroxide by adding 22mL of NH4OH and stirring with a disposable pipette.
___Stir the sample vigorously after 15 minutes.
___Allow the precipitate to settle for 30 minutes, decant the supernate, and transfer the rest to the original c-tube with pH 10 DI water.
___Centrifuge and discard the supernate.
___Dissolve **TH** residue in 3mL 9N HCl
___Dilute the dissolved **TH** with DI water to a final volume of 25mL
___Microprecip **TH** with Neodymnium and HF
___Count to meet MDC and obtain 400 tracer counts.

BOX 3___Add 5mL conc HCl to beakers labeled **U** and heat to dryness
___Dissolve contents of beakers labeled **U** in 15mL 9N HCl– heat to aid in dissolution
___Load samples onto columns previously used
___Rinse **U** beakers with 10mL 9N HCl and pour on columns
___Rinse columns with 20mL 9N HCl
___Rinse columns with 20mL 6N HCl / 0.52N HF – discard to waste
___Rinse columns with 10mL 9N HCl – discard
___Elute uranium into c-tubes labeled **U** by adding 20mL 0.1N HCl
___Microprecip **U** with neodymnium, titanous chloride to persistent purple color, and HF
___Count to meet MDC and obtain 400 tracer counts.

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Notes

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STANDARD OPERATING PROCEDURE

Analysis of Water Samples for Radium-226

Methods: EPA 903.1, SM7500-Ra C

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APPROVALS

Maureen K. DeRubeis
Senior Quality Manager — 02/08/18 Date

Department Manager/Supervisor — 02/08/18 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
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Table of Contents

1. Purpose

1.1 This SOP documents the analytical procedure to be used for analysis drinking water and other aqueous samples for radium-226.

2. Scope and Application

2.1 This procedure covers the measurement of radium-226 in drinking water samples and should be employed after the gross alpha or gross radium alpha screening technique had indicated possible non-compliance with the alpha radioactivity limits set forth in the Safe Drinking Water Act, PL 93-523. 40 FR 34324.

2.2 Additionally, this SOP is applicable to the analysis of other aqueous sample types without modification.

2.3 This procedure is specific for radium-226, and is based on the emanation of radon-222, a daughter product of radium-226. Radium-226 concentration is determined by scintillation counting of radon-222, polonium-218, and polonium-214 (daughters of radon-222).

2.4 The detection limit for this procedure assures measuring radium-226 concentrations lower than 1.0pCi/L and potentially as low as 0.1pCi/L.

2.5 Without qualification, this procedure, as written, is compliant with Method 903.1 of "*Prescribed Procedures for Measurement of Radioactivity in Drinking Water*, EPA-600/4-80-032". Deviations from the promulgated methods are discussed in Section 18 of this SOP.

2.6 Pace Analytical applies isotope decay correction only in instances where the total impact in the analysis result is 2% or greater. Assuming a maximum hold time of 180 days, a 2% isotope decay would occur only for radioisotopes with a half-life of 17.14 years or less. The parameters reported in this SOP are not affected by this policy. Decay correction has not been applied to the parameters measured by this SOP.

3. Summary of Method

3.1 The radium-226 in the drinking water sample is concentrated and separated by co-precipitation on barium sulfate. The precipitate is dissolved in EDTA reagent and placed in a sealed bubbler. Radon-222 is flushed from the sample using inert helium or nitrogen gas. The bubbler is stored for ingrowth of radon-222. After ingrowth, the gas is purged into a scintillation cell. When the short-lived radon-222 daughters are in equilibrium with the parent, the scintillation cell is counted for alpha activity.

3.2 The absolute measurement of radium-226 is ensured by calibrating the scintillation cell system with a standard solution of radium-226.

4. Interferences

4.1 There are no radioactive interferences in this method.

4.2 To prevent possible cross contamination during the emanation of multiple samples through the same apparatus, apply vacuum intermittently to the apparatus and attached drying tube. This will allow the drying tube and apparatus to be flushed with room air.

4.3 To prevent contamination of bubblers, samples with visible suspended material must be centrifuged prior to transfer to the bubbler for ingrowth.

5. Safety

5.1 Procedures must be carried out in a manner that protects the health and safety of all personnel. Since this analysis is for a radioactive constituent, the sample must be treated as radioactive.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves will be cleaned immediately.

5.3 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye-protection, gloves, and lab coat must be worn.

5.4 Exposure to radioactivity and chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous and/or non-radioactive, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 In order to minimize the potential for cross contamination of high and low levels of radioactive samples, good housekeeping and good laboratory practices are essential and must be strictly adhered to.

5.6 Organic samples of unknown content must be handled with extreme caution and under the direct instruction of a Department Manager/Supervisor or Department Manager/Supervisor's specified designee. Direct treatment of organic matrices with strong oxidizing chemicals such as nitric acid and/or hydrogen peroxide is strictly prohibited.

5.7 Hydrofluoric acid is particularly hazardous because a serious skin exposure may cause no immediate sensation of pain. The acid penetrates the skin and spreads internally, causing tissue damage deep under the skin. The resulting burn is painful, difficult to treat, and easily infected. Gloves must be checked for pinhole leaks before use. They must be rinsed before they are removed and must be discarded after use. HF burn gel shall be put on suspected HF burns after flushing (except the eyes) until medical help can be obtained. Medical attention shall be sought even if suspicions arise after working hours. Contact your group leader immediately for further information if a HF burn is suspected.

5.8 In addition, HF vapors are also hazardous. Exposure can cause permanent damage. Breathing HF vapors even for a short time and at a low temperature can be injurious to the respiratory system and even fatal. All such direct contact must be avoided.

5.9 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory.

5.10 Refer to the Pace Analytical Services, LLC. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.11 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.12 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 See the glossary section of the most recent revision of the Pace Analytical Services LLC. Quality Assurance Manual for commonly used laboratory terms.

6.2 Batch: For all matrices, an analytical batch contains 20 or fewer samples of a similar matrix, prepared at the same time, by the same analyst, using the same reagents.

6.3 Throughout this procedure, approximate weights and measures will be designated by the use of whole numbers when referring to masses exceeding 1g or volumes in excess of 1mL. Measurements of weights and volumes so designated can be made with top loading balances, graduated cylinders, etc. For approximate measures below 1g or 1mL, the word "approximately" must be used prior to the described mass or volume.

6.4 Throughout this procedure, exact or critical masses and volumes will be designated by the use of one or more decimal places. Measurements of masses and volumes so designated should be made with accurate analytical instruments such as analytical balances, calibrated pipettes, etc.

6.5 Observed masses must be recorded in logbooks to the lowest weight indicated on the balance. Sample aliquot masses cannot be targeted. Once sample is aliquotted, it cannot be removed from the beaker.

6.6 The method employed to measure the sample, whether it be by balance, pipette, or graduated cylinder, must be clearly documented in the preparation logbook.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Plastic or glass containers may be used for sample collection.

8.1.1 Containers used for sample collection must never be re-used.

8.2 Aqueous samples must be preserved at the time of collection by adding enough concentrated (16N) HNO_3 to the sample to make the sample pH <2. Typically, 2mL of 16N HNO_3 per liter of sample is sufficient to obtain the desired pH. Samples must be preserved within five days of collection. If samples are collected without preservation, they must be received by the laboratory and preserved within five days of collection. Following preservation with acid, samples must be held in the original container for a minimum of 24 hours before analysis or transfer of sample. Samples preserved upon receipt at the laboratory, must be re-checked by laboratory personnel a minimum of 24 hours after preservation. The pH re-check date and time, the initials of the analyst verifying the pH, as well as any adjustments or notes regarding the preservation must be recorded in the pH Verification Logbook.

8.2.1 For dissolved analysis, samples must be filtered through a 0.45μm membrane filter and preserved to a pH <2.

8.2.2 For total analysis, the sample is not filtered, but is preserved.

8.3 Refrigeration is not required for aqueous samples.

The maximum hold time for samples analyzed by this SOP is 180 days from collection to analysis.

9. Equipment and Supplies

9.1 Scintillation Cell system.

9.2 Radon emanation apparatus consisting of 1) radon bubbler, 2) scintillation cell and 3) a drying tube.

9.3 Electric hot plate.

9.4 Centrifuge and disposable 50mL centrifuge tubes.

9.5 Membrane filters, 0.45μm, 47mm, Metricel® or equivalent.

9.6 Glassware, various sizes.

9.7 Analytical balance.

9.8 Vacuum manifold.

9.9 Vortex mixer

9.10 Hot water bath.

10. Reagents and Standards

10.1 Reagents should be prepared from reagent grade chemicals, unless otherwise specified below. NOTE: Consult the Safety Data Sheets for the properties of these reagents, and how to work with them.

10.2 Distilled or deionized (DI) water. ASTM Type II as produced using the specifications documented in SOP PGH-C-027, current revision.

10.3 Acetic acid, 17.4N: glacial CH_3COOH (conc.), sp. Gr. 1.05, 99.8%.

10.4 Ammonium hydroxide, 15N: NH_4OH (conc.), sp. gr. 0.90, 56.6%.

10.5 Ammonium sulfate, 200mg/mL: Dissolve 20 g $(NH_4)_2SO_4$ in water and dilute to 100 mL.

10.6 Anti-foaming agent, Anti-foam B, or equivalent.

10.7 Ascarite, drying reagent: 8-20 mesh.

10.8 Barium carrier, 16 mg/mL, standardized. Dissolve 28.46 g $BaCl_2 \bullet 2H_2O$ in water, add 5.0 mL 16N HNO_3, and dilute to 1.0L with ASTM Type II DI Water.

10.9 Citric acid, 1M: Dissolve 192 g of $C_6H_8O_7 \bullet H_2O$ in water and dilute to 1.0L with ASTM Type II DI water.

10.10 EDTA reagent, basic, (0.25M): Dissolve 20 g NaOH in 750mL water and slowly add 93g disodium ethylenedinitriloacetate dihydrate, $(Na_2C_{10}H_{14}O_8N_2 \bullet 2H_2O)$ while stirring. After the salt is in solution, dilute to 1L with ASTM Type II DI Water. The heat generated from the solid sodium hydroxide added to DI water should be sufficient so as to support complete dissolution of EDTA. If the EDTA does not readily dissolve, gradually heat the reagent until dissolved.

10.11 Helium Gas, ultra high purity.

10.12 Nitrogen gas, ultra high purity.

10.13 Lead carrier, 150mg/mL: Dissolve 239.7 g $Pb(NO_3)_2$ in ASTM Type II DI water, add 5.0mL 16N HNO_3 and dilute to 1.0L with ASTM Type II DI water.

10.14 Methyl Orange Indicator, 0.1%: Dissolve 0.1g methyl orange indicator in 100mL ASTM Type II DI water.

10.15 Nitric acid, 16N: HNO_3 (conc.), Sp. Gr. 1.42, 70.4%.

10.16 Magnesium perchlorate, $Mg(ClO_4)_2$: reagent grade.

10.17 Radioactivity standard solutions: radium-226 may be utilized for batch control spike samples or instrument calibrations and barium-133 may be used for radio-tracer yield determinations. All radioactive standards must be NIST traceable.

10.18 Sodium hydroxide, 10N: Dissolve 400 g NaOH in 500 mL deionized water, cool, and dilute to 1.0L with ASTM Type II DI Water.

10.19 Sulfuric acid, 18N: 50% V/V, ACS grade. Yttrium carrier, 18 mg/mL: Add 22.85g Y_2O_3 to an Erlenmeyer flask Add 50mL of ASTM Type II DI water. Carefully add 40mL of concentrated nitric acid. Heat the mixture to boiling while stirring on a magnetic stirring hotplate. The solution must heat to boiling. Additional water and nitric acid may be added as necessary to aid in dissolution. Measure the additions of Type II DI water and concentrated nitric acid and record the reagent volumes added into the reagent preparation logbook. Scrape the bottom of the Erlenmeyer flask with a Teflon® scraper if the yttrium oxide is caked onto the glass to enhance dissolution. Once the yttrium oxide has completely dissolved, add a quantity of concentrated nitric acid so that the total volume of

concentrated nitric acid added is 100 mL. Do not add more than 100mL of nitric acid total. Upon complete dissolution, remove the beaker from the hotplate and cool completely. Dilute to 1L with ASTM Type II DI water.

11. Calibration

11.1 Cell/Detector calibrations are performed uniformly, independent of sample analysis matrix type. The calibration values determined by application of this process are applied universally for all matrices for which the analytical process is defined in this SOP.

11.2 Cell/Detector calibrations must be performed on an annual basis.

11.3 Transfer between 500 to 1500 dpm of radium-226 (25mL volume) standard into a bubbler that has been designated for calibration purposes only.

11.4 Note: The specified calibration source activities have been optimized to allow manageable count times for individual sources.

11.5 Attach the bubbler to the radon assembly.

11.6 With the scintillation cell disconnected, bubble helium (or nitrogen) gas through the solution for 20 minutes to remove all Rn-222.

11.7 Close both stopcocks on the bubbler to establish zero time for ingrowth of Rn-222. Record the date and the time of the calibration source flushing on the appropriate bench sheet. Store the bubbler to allow ingrowth of Rn-222.

11.8 Following adequate ingrowth time for the calibration source, proceed with steps 12.12 through 12.18, Radon Emanation Technique.

11.8.1 EPA Method 903.1, “Radium-226 in Drinking Water Radon Emanation Technique” requires a minimum of 18 hours of ingrowth for the calibration. Pace has adopted a minimum ingrowth period of four days for calibrations and samples.

11.9 The calibration constant includes the de-emanation efficiency of the system, the counting efficiency of the cell, and the alpha activity contributed by Po-218 and Po-214, which will be in equilibrium with Rn-222 when the sample is counted approximately 4 hours (minimum of 3 hours) after the de-emanation. Calibration sources must be counted until a minimum of 10,000 counts has been obtained.

11.10 Proceed to Section 13 to determine the cell calibration constant.

11.11 Following the cell counting, flush the cell by alternating vacuum and room air to remove Rn-222 from the cell. Store the cell for a minimum of 24 hours prior to use for samples. This delay allows adequate decay of Rn-222 daughters. Lucas cells must be counted for a minimum of ten minutes to determine the cell background prior to use for sample analysis.

11.12 The bubbler used for Ra-226 calibration should not be used for sample analysis. It should be set aside and retained for future calibrations. The

cell/detector combination must be calibrated annually. Additionally, calibrations must be performed if either the cell or the detector undergo any major maintenance. New cells and cells returned from a repair facility must be given a new ID.

11.13 For cells previously successfully calibrated, the new cell constant should be within 10% of the previously acceptable cell constant (CAL A) counted in the same detector. Typical cell constants will be around 2.2 to 2.5, and may vary for the same cell among each individual detector. For a new calibration attempt (CAL B), any deviation outside of the 10% rule may indicate a problem during calibration (CAL B) and the calibration should be re-performed using a different calibration source (bubbler). If the new calibration value (CAL C) is within 5% of the most recent calibration value (CAL B), the newest calibration value (CAL C) should be used as the cell/detector calibration value. If the new calibration value (CAL C) is greater than 5% of the most recent calibration value (CAL B) but within 10% of the previously-implemented calibration value (CAL A), this indicates that the process in performing CAL B was compromised. In this case, the newest calibration value (CAL C) should be used as the cell/detector calibration value. Cells for which calibration values do not comply with the listed requirements must be removed from future service until appropriate corrective action has been applied and documented. At a minimum, prior to repeating the calibration process, check the cell for damage, especially around the stopcock, base of the stem, and the window, which could cause gas loss during calibration.

11.14 Cell constants will vary slightly based on the imperfect mechanism of applying the zinc sulfide interior coating, as well as minor differences in cell volume. Cells which cannot be calibrated should be sent out for repair which will include resealing the stopcock stem, re-applying the zinc sulfide coatings, and cleaning and replacing the glass surface.

12. Procedure

Unless specified otherwise, the documented analysis process must be followed, as written, including the order of analytical process and the addition of chemicals

12.1 Weigh approximately 500g of aqueous sample into an appropriately sized glass beaker. Record the observed mass of the sample added to the beaker (do not remove any sample from the beaker). The actual amount of sample used may vary based on sample availability and expected or possible matrix interferences, but the routine amount is approximately 500 grams. When using < 500g, samples should be diluted with ASTM Type II DI water to the 500 ml mark on the beaker, and acidified with nitric acid.

12.2 Prepare a Method Blank (MB), Laboratory Control Sample (LCS), and Laboratory Control Sample Duplicate (LCSD), by weighing about 500g of ASTM Type II DI water into a labeled beaker, and record the actual mass observed in the logbook. Add 2.0 ml of concentrated nitric acid to the MB, LCS, and LCSD. Add the appropriate amount of Ra-226 spike

solution to the LCS and LCSD based on the requirements listed in Section 14.6.3 of this SOP.

12.3 If a Matrix Spike (MS) is prepared (MS is required when analyzing drinking water samples or when specified by the client), add the appropriate amount of spike solution to the MS sample based on the requirements of Section 14.9.2 of this SOP.

12.4 To all samples including the QC samples, add 5mL 1N citric acid solution and a few drops methyl orange indicator. The solution should be red. If the solution is not red, check the solution pH with pH indicator strips capable of determining pH 0-14. The sample pH must be <2.0. Otherwise, refer to Section 8.2 regarding sample preservation requirements.

12.5 Add 1mL lead carrier (150 mg/mL), 1mL yttrium carrier (18 mg/mL) and 2.0mL barium carrier (16 mg/mL). Add a suitable amount of barium-133 tracer based on the guidance in section 14.11 if yield determination is to be made by radio-tracer counting. Stir well. Heat to incipient boiling and maintain at this temperature for 30 minutes.

12.6 Add a few drops methyl orange indicator again as it is destroyed upon prolonged heating. Add 15N NH_4OH until a definite yellow color is obtained, then add a few drops excess. Precipitate lead and barium sulfates by adding 18N H_2SO_4 until the red color reappears, then add 0.25mL excess. Add 5mL $(NH_4)_2SO_4$ (200 mg/mL) and stir vigorously until a precipitate forms. Allow the solution to heat for a minimum of 30 minutes, and then remove the samples from the hot plate to cool.

12.7 Allow the sample precipitate to settle overnight or for a minimum of 2 hours until completely clear; then siphon most of the supernatant liquid and discard, saving the precipitate.

12.8 Transfer the precipitate with the aid of 0.1N H_2SO_4 to a 50mL disposable centrifuge tube; centrifuge, and discard the supernatant liquid.

12.8.1 For wastewater samples or samples containing suspended solids, add 20mL of 16N HNO_3 to each centrifuge tube and heat in a hot water bath for 30 minutes. This step will aid in the removal of interfering element components.

12.8.2 Centrifuge and discard acid solution into an appropriate waste stream. Rinse the precipitate in 20mL 16N HNO_3. Shake to mix, centrifuge, and discard acid rinses into an appropriate waste stream.

12.8.3 Rinse the precipitate two times with 10mL aliquots of 0.1N H_2SO_4. Add the acid to the precipitate in the centrifuge tube, cap and vortex to rinse. Centrifuge and discard the supernate into the appropriate waste stream.

12.9 Add 25mL 0.25M EDTA solution to the sulfate precipitate. Vortex the samples and heat in a water bath to enhance dissolving of the precipitate.

If the precipitate does not readily dissolve, add 10N NaOH solution dropwise. Do not add more than 7 drops total of the 10N NaOH.

12.9.1 If there is still undissolved material, centrifuge the sample and transfer the solution to a clean disposable centrifuge tube. Submit the supernate solution for gamma spectroscopy counting for Ba-133 determination. If the resulting yield is within acceptable limits, continue with the analysis. If it is not within the expected limits, combine the supernate and the solid material and reheat.

12.10 Ensure that the sample solution volume is 25mL (+/- 1 mL) using the graduated markings on the centrifuge tube as a guide. If the sample volume is less than 25 mL, dilute the sample to 25 mL(+/- 1 mL) with 0.25M EDTA solution using the graduated markings on the centrifuge tube as a guide.

12.10.1 Optionally: Proceed to Section 12.21 to determine the radiotracer yield prior to transferring the solution to the bubbler. If this option is used, extreme care must be exercised when transferring the solution from the centrifuge tube to the bubbler in order to ensure that it is performed quantitatively.

12.11 Centrifuge and transfer the supernate to a labeled radon bubbler. Discard the centrifuge tube into an appropriate waste stream.

12.12 Connect the bubbler to the helium (nitrogen) source then open both the upper and the lower stopcocks of the radon bubbler and de-emanate the solution by slowly passing helium (nitrogen) gas through the bubbler for about 20 minutes.

12.12.1 Add 2 drops of antifoaming agent to the bubbler if excessive foaming occurs while passing the helium (nitrogen) through the solution.

12.13 Close the two stopcocks and record the time. Store the solution to allow for ingrowth of Rn-222.

12.13.1 A minimum of 4 days of ingrowth is required.

12.14 At the end of the storage period, fill the upper approximate half of an absorption tube with magnesium perchlorate and the lower approximate half with ascarite. Magnesium perchlorate may clump over time preventing easy transfer to the absorption tube; if necessary, grind a portion of the reagent using a mortar and pestle prior to adding to the tube. Attach the drying tube to the vacuum monitoring manifold with a rubber o-ring and clamp. Ensure the end with the white magnesium perchlorate is at the top, and the ascarite end is at the bottom.

12.14.1 Note:For minimizing corrections that would be required in subsequent calculations, the voids above the bubbler must be kept very small. Capillary tubing should be used whenever possible, and the drying tube volume with the ascarite and magnesium chlorite must be kept to a minimum. A typical system consists of a drying tube 10 cm x 1.0 cm (I.D.), with each

of the drying agents occupying 4 cm and being separated by small glass wool plugs. The column can be reused several times before the chemicals need to be replaced as long as the ascarite appears dry and not hardened.

12.15 Attach the sample bubbler to the drying tube so the liquid containing portion of the bubbler is directly below the drying tube, and attach the helium (nitrogen) supply hose to the bubbler inlet (the thin capillary tube side).

12.16 Evacuate the desired Lucas cell using a vacuum pump and close the stopcock. Ensure a background count has been performed for the cell and detector combination prior to each use. Using the appropriate clip, firmly attach the Lucas cell to the top of the vacuum monitoring manifold connected to the correct bubbler.

12.17 Open the stopcock on the scintillation cell and check the vacuum gauge to ensure that vacuum is maintained. The gauge should indicate a vacuum of approximately -20 to -25 psi relative to atmospheric. Gradually open the outlet stopcock on the bubbler. When the stopcock is fully open and no further significant bubbling takes place, the pressure gauge should still indicate a vacuum, but less vacuum relative to atmospheric, approximately -15 to -20 psi

12.18 Adjust the helium (nitrogen) gas pressure so that the gas flows at slightly above atmospheric pressure.

12.19 Gradually open the inlet stopcock on the bubbler using the bubbling as a guide. Continue bubbling with the helium (nitrogen) gas until the vacuum gauge indicates neutral (atmospheric) pressure. The de-emanation process should take approximately 15-20 minutes to complete. Toward the end of the de-emanation, when the vacuum is no longer effective, it will be necessary to gradually increase the helium (nitrogen) gas pressure. When the system is at atmospheric pressure, close the inlet and outlet stopcocks of the cell and bubbler, shut off the gas, and disconnect the tubing from the bubbler inlet. Record this time as the beginning of the Rn-222 decay and ingrowth of Rn-222 daughters.

12.20 Store the scintillation cell for approximately 4 hours (minimum of 3 hours) to ensure equilibrium between radon and radon daughters. Proceed to Section 12.22 to “count” the Lucas cells.

12.21 If not already determined in Step 12.10, transfer the sample bubbler contents to a labeled 50mL centrifuge tube.

12.21.1 If gamma counting is to be performed to determine yield by Ba-133 counting, dilute the tube contents to a final volume of 30mL with ASTM Type II DI water, cap the tubes, shake vigorously, and submit them to the analyst responsible for gamma counting.

12.21.2 Barium yield by gravimetric assessment (used if Ba-133 is unavailable or not suitable to sample matrix).

12.21.2.1 If yield assessment is to be made by gravimetric measurement of barium sulfate, proceed as follows:

12.21.2.2 Add 1mL of ammonium sulfate solution (200 mg/mL) and stir thoroughly. Add 2mL conc. acetic acid until barium sulfate precipitates. Digest in a hot water bath for 10 minutes. Cool, centrifuge, and discard the supernate.

12.21.2.3 Slurry the precipitate with 10ml of ASTM Type II DI water, centrifuge and discard the supernate.

12.21.2.4 Slurry the precipitate with 7mL of ASTM Type II DI water and transfer to a tared, 2-inch stainless steel planchet. Dry the precipitate under a heat lamp, cool and re-weigh for yield determination. Refer to Section 13 of this SOP for barium recovery calculation.

12.22 Lucas Cell Counting

12.22.1 Perform the required daily source check prior to counting cells for daily background. Daily source check counting and routine maintenance for the Ludlum Counters is specified in the associated instrument operations SOP, PGH-R-065, current revision.

12.22.2 Remove the top cover from the photomultiplier tube (PMT) unit or counter, and remove the rubber protector from the base of the Lucas cell. Center the Lucas cell on the glass platform on the top of the base of the counter and carefully replace the top cover.

12.22.3 Press the top cover down firmly to ensure the counting rod makes contact with the counter base. There should be an audible click when the counting rod is properly engaged. Tighten the screws on both sides of the top cover to ensure the counting rod remains engaged through sample counting.

12.22.4 Set the count time on the front of the Model 2000 Scaler unit to the count time necessary to meet the desired reporting limit. Count times should not be less than 10 minutes, and should not routinely exceed 20 minutes.

12.9.4.1 Count times longer than 20 minutes should only be used for drinking water samples where it is necessary to achieve the Ra-226 reporting limit of 1.0 pCi/L.

12.22.5 Press the COUNT button on the front of the scaler unit. Record this time as the count start time in the appropriate section of the analysis logbook.

12.9.4.2 A red light above the COUNT button will light to indicate the unit is active. Observe counts on the LED display to ensure the counting rod is correctly engaged on the counter.

12.9.4.3 Do not remove the top cover while the unit is counting as this may damage the photomultiplier tube.

12.22.6 Once the red light has turned off, record the counts from the LED display into the appropriate section of the analysis logbook.

12.22.7 Unscrew the screws on the sides of the top cover of the counter and carefully lift the top cover off of the counter ensuring the cell is not knocked over. Return the rubber protector to the base of the Lucas cell, and set the Lucas cell aside for evacuation.

12.22.8 Repeat steps 12.22.2 through 12.22.7 until all Lucas cells have been counted.

12.22.9 Following counting and after data have been processed, flush the Lucas cell by alternating vacuum and helium (nitrogen) gas to remove Rn-222 from the cell. Store the cells with vacuum applied for a minimum of 3 hours prior to using for another sample. A new background must be counted on the cell prior to use.

13 Calculations

13.1 Refer to Attachment I of this SOP for Ra-226 associated calculations.

13.1 Any verified result for drinking water that exceeds the maximum contaminant level (MCL) established for Radium-226 must be reported to the appropriate personnel and agencies according to the specific requirements of the state where the water was sampled. The directions for reporting any results that exceed the MCL limits are documented in the State Drinking Water Emergency Reporting Requirements Binder and in Pace SOP PGH-C-025, current revision.

13.2.1 The Ra-226 MCL for drinking water is defined as >5.0 pCi/L Ra-226 individually or when summed with Ra-228.

14 Quality Control

14.1 General guidelines for drinking water samples with results that exceed the Maximum Contaminant Level are specified in Pace SOP PGH-C-025, current revision, and include the following: (All steps are to be conducted as soon as the exceedence has been identified.)

14.1.1 Verify the result(s) to ensure that there were no transcription or calculation errors and that all QC results are within the acceptable limits. Correct any problems and determine the new result. If there were no errors or the result still exceeds the MCL continue with the reporting process.

14.1.2 Immediately notify the Department Manager/Supervisor, and QA department that a reportable result has been identified. Use telephone notifications to inform the contact people if the variance is identified after hours along with an e-mail follow up to document the event.

14.1.3 Refer to the State Drinking Water Emergency Reporting Requirements Binder for the state specific information regarding the proper course of action to take. Time is of the essence during this process with some of the state reporting requirements as short as 1 hour from the verification of an exceedence.

14.2 Each analyst who performs this test must satisfactorily complete a Demonstration of Capability Study as documented in Section 3.4 of the most recent revision of the Quality Assurance Manual.

14.2.1 The DOC study results are evaluated against the LCS acceptance limits.

14.2.2 IDOC and DOCs for drinking water methods must be performed at a spiking level between the sensitivity level and MCL.

14.2.3 Continuing DOCs must be performed annually by each analyst who may be expected to perform the analysis during the course of the year. A Continuing DOC may be compiled from 4 successive LCS analyses from multiple batches, and are evaluated against the LCS acceptance limits.

14.3 Daily instrument Quality Control checks must be completed following the instructions detailed in the SOP for alpha scintillation counters, current revision.

14.4 See Appendix II for performance indicator evaluation calculations and criteria. Numerical performance indicators may be used to assess QC for non-drinking water samples when the default assessment indicates a QC failure. The numerical performance indicator must be within +/- 3 for all other matrices. The z-score for precision assessment may be used for drinking waters with the approval of the Department Manager/Supervisor using the +/- 2 specification.

14.5 Method Blank (MB)

14.5.1 One MB must be prepared for each analytical batch. The purpose of the MB is to monitor for cross contamination during the analytical process. When available, the MB should be prepared from a similar matrix as samples contained in the analytical batch. If appropriate blank matrix material is not available, ASTM Type II DI water (Reagent Blank) must be carried through the procedure. A reagent blank may be used for sample correction purposes following approval of a Department Manager/Supervisor or a specified designee and affected clients.

14.5.2 The results of the method blank must be <RL. The reporting limit for Ra-226 is 1.0 pCi/L.

14.5.2.1 If the method blank is out of control, individual sample results may still be reportable if results are less than the CRDL (contract required detection limit) or > 10 times the blank result. Relative sizes of the sample and blank

aliquots must be factored when making this determination (raw counts).

14.6 Laboratory Control Sample (LCS)

14.6.1 One LCS must be prepared for each analytical batch.

14.6.2 A typical detection limit is 1.0 pCi/L for Ra-226.

14.6.3 The Ra-226 spike activity must be > 2 times the detection limit.

14.6.4 A standard reference material (SRM) containing a known concentration of radium-226 radioactivity in the same matrix as the batch is analyzed with the batch.

14.6.4.1 If this material is not available, a well-characterized material (WCM) may be used.

14.6.4.2 If neither of these are available, ASTM Type II DI water may be spiked with the appropriate radium-226 standard.

14.6.5 Percent Recovery Calculation

$$\%REC = \frac{(LCSConc)}{TrueValue} * 100$$

Where:

LCSConc = Analytical result of the LCS
TrueValue= Known concentration of the LCS

14.6.6 LCS %REC acceptance limits are 73 - 135%.

14.7 Laboratory Control Sample Duplicate (LCSD)

14.7.1 A LCSD is not required for radium-226 analysis; however analysis of an LCSD must be utilized to measure batch precision whenever adequate sample volume is not available for sample DUP analysis. The LCSD must be prepared in an identical fashion as the LCS and processed identically as for other samples.

14.7.2 The LCSD must pass the acceptance criteria for the LCS and the criteria established for duplicate precision (RPD 32% or less).

14.7.3 If the LCS and LCSD both pass %REC criteria, but fail RPD criteria, the batch results may be qualified and reported at the discretion of the analyst with guidance from the Department Manager/Supervisor.

14.8 One Duplicate Sample (DUP) must be randomly assigned within each batch. The purpose of the sample DUP is to measure precision of the analytical process. Laboratory duplicates are not intended to assess precision related to the sample collection process. Sample collection precision can only be assessed through collection of duplicate samples at

the time of sample collection. The sample DUP is a duplicate volume of sample processed identically as other samples in the analytical batch.

14.8.1 Relative Percent Difference Calculation

$$RPD = \frac{|(R1 - R2)|}{(R1 + R2)/2} * 100$$

Where:

R1 = Result Sample 1
R2 = Result Sample 2

14.8.2 Duplicate sample RPD acceptance limits are <32% for radium-226.

14.8.3 Sample duplicate criteria cannot be applied if results are below their associated MDC.

14.8.4 Drinking water samples from the state of Arizona must be batched at a frequency of 1 duplicate for every 10 samples or fewer.

14.9 Sample Matrix Spikes (MS)

14.9.1 Because this analytical method requires the use of carriers or radiotracers for yield determination, PASI's default QC policy is that a sample matrix spike (MS) is not required for radium-226 analysis with the exception of drinking water analysis.

14.9.2 Typical detection limits for Ra-226 are 1 pCi/L. The spike amount must be > 10 times the detection limit.

14.9.3 The MS is prepared by spiking a portion of radium-226 radioactivity solution into a portion of one sample in the batch and processing identically as for other samples.

14.9.4 The purpose of the MS is to assess the affect of sample components on the analytical process. The volume of sample used for the MS must be equivalent to the volume used for sample analysis.

14.9.5 Percent Recovery Calculation

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue} * 100$$

NOTE: The SampleConc is zero (0) for the LCS and Surrogate Calculations

14.9.6 MS acceptance limits are 71 - 136% for radium-226.

14.10 Sample Matrix Spike Duplicates (MSD)

14.10.1 A sample Matrix Spike Duplicate (MSD) is not required for this analysis. When required by the customer/contract, a MSD must

be prepared for each analytical batch. The MSD must be prepared as a duplicate of the MS.

14.10.2 The MSD must pass the acceptance criteria established for the MS recovery and the criteria established for duplicate precision.

14.10.3 An MS/MSD sample analysis may be performed instead of a sample duplicate analysis. If MS/MSD are prepared instead of a sample duplicate, and the batch includes drinking water samples from the state of Arizona, the duplicate analysis criteria for frequency in Section 14.8.4 of this SOP must be met.

14.11 PASI's default criteria for carrier and/or tracer yield are 30-110% of the expected value.

14.11.1 Barium-133 is routinely used as the tracer for Ra-226 analysis. Since Ba-133 has no potential for interference during sample counting, the amount utilized as a tracer has been optimized to ensure a minimum of 400 tracer counts is achieved in five minutes during yield analysis utilizing a sodium iodide gamma detector. This amount is approximately 6500 dpm Ba-133.

14.11.2 The amount added to each sample is consistent and added with a verified pipette, but may be changed with each new Ba-133 standard. Typical Ba-133 standards are prepared at a level between 12000 and 16000 dpm/ml depending on the concentration of the Ba-133 source purchased from a NIST traceable vendor.

14.12 Summary of QC related Activities:

Method Blank	One per Batch
Reagent Blank	One per Batch (as required by client)
Duplicate Sample	One per Batch or a frequency of 10% for batches containing samples from Arizona
Matrix Spike	One per Batch (for drinking waters or as required by client)
Matrix Spike Duplicate	One per Batch or a frequency of 10% for batches containing samples from Arizona (as required by client)
Laboratory Control Sample	One per Batch
Laboratory Control Sample Dup	One per Batch in the absence of Duplicate sample

14.13 Corrective Actions for Out-Of-Control Data

14.13.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.13.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.13.3 Matrix Spike Recovery (MS) – MS recoveries that fail high and outside of control criteria with a sample result that is less than the reporting limit may be reported with narration. Additionally, MS recoveries that fail low and outside of control criteria for Drinking Water samples with a sample result that is greater than the MCL must be reported with comment as potentially biased high due to matrix interference. Otherwise, MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and noted in the final report. Matrix effect must be determined by re-analysis of the MS/Sample pair or demonstration of acceptable precision between a MS/MSD pair.

14.13.3.1 The analyst must evaluate the MS results to attempt to determine the cause of the failure. All decisions made must be documented.

14.13.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.13.5 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.13.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.13.6 Laboratory Control Sample Duplicate (LCSD) – If an LCSD does not meet the recovery acceptance criteria, the entire analytical batch must be reanalyzed.

14.13.6.1 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their the reporting limit, and duplicate precision meets the acceptance criteria.

14.13.7 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report. Chemical/Tracer recoveries: If the chemical and/or tracer recovery is outside of the acceptance criteria, the sample must be reanalyzed. If a matrix interference is suspected to be the cause, sample reanalysis should be performed with a lower volume to minimize interferences.

14.13.7.1 Acceptance criteria for gravimetric carriers are 30-110% and for radioactive tracers the criteria are 10-110%. Yields as high as 130% may be reported with the approval of the Department Manager/Supervisor.

15 Method Performance

15.1 Laboratory control samples are analyzed with each batch, the results are charted to monitor control limits and trending. Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.2 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.3 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16 Pollution Prevention and Waste Management

16.1 Place radioactive waste into appropriate receptacles.

16.2 Discard acidified samples and unusable standards into proper waste drains.

16.3 Dispose of waste materials in accordance to type: Non-hazardous, hazardous, non-radioactive, radioactive or mixed.

17 References

17.1 ASTM E181-93, Standard Test Methods for Detector Calibration and Analysis of Radionuclides, ASTM Standards, Vol. 12.02.

17.2 Blanchard, R.L. Uranium Decay Series Disequilibrium in Age Determination of Marine Calcium Carbonates. Doctoral Thesis, Washington University, St. Louis, MO. (June 1963).

17.3 Currie, L., Limits for Quantitative Detection and Quantitative Determination, Analytical Chemistry, Vol. 40. No. 3, Pg 586-593, 1968.

17.4 Currie, L., Lower Limit of Detection: Definition and Elaboration of a Proposed Position for Radiological Effluent and Environmental Measurements, NUREG/CR - 4007, USNRC, 1984.

17.5 Ferri, E., P. J. Magno, and L. R. Setter. Radionuclide Analysis of Large Numbers of Food and Water Samples. U.S. Department of Health, Education, and Welfare, Public Health Services Publication No. 999-RH-17 (1965).

17.6 Krieger, H. L. and Whittaker, E. L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, "Radium-226 – Radon Emanation Technique," Method 903.1, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, August, 1980.

17.7 Krieger, H. L. and Whittaker, E. L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, "Radium-228 in Drinking Water," Method 904.0, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, August, 1980.

17.8 Eaton, A. D., et. al., editors, Standard Methods for the Examination of Water and Wastewater, 19th Edition, "Radium – Sequential Precipitation Method," Method 7500-Ra C., American Public Health Association, Baltimore, MD, 1995.

17.9 Eaton, A. D., et. al., editors, Standard Methods for the Examination of Water and Wastewater, 20th Edition, "Radium – Sequential Precipitation Method," Method 7500-Ra C., American Public Health Association, Baltimore, MD, 1998.

17.10 "Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)", Final Version, July 2004.

17.11 Rushing, D. E. The Analysis of Effluents and Environmental Samples from Uranium Mills and of Biological Samples for Uranium, Radium, and Polonium. SM/41-44, Symposium on Radiological Health and Safety, Vienna, Austria (August 1963).

17.12 Steiner, E. H. "Planning and Analysis of Results of Collaborative Tests." Statistical Manual of the AOAC, Association of Official Analytical Chemists, Washington, D. C. 1975.

17.13 Table of Radioactive Isotopes, Brown and Firestone, Shirley editor, John Wiley & Sons, 1986.

17.14 Youden, W. J. "Statistical Techniques for Collaborative Tests." Statistical Manual of the AOAC Association of Official Analytical Chemists, Washington, D. C. 1975.

17.15 "American National Standard Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories", ANSI N42.23-1996.

17.16 Department of Defense Quality System Manual for Environmental Laboratories (DoD QSM), current version.

17.17 "Manual for the Certification of Laboratories Analyzing Drinking Water" Fifth Edition, January 2005, EPA 815-R-05-004.

17.18 National Primary Interim Drinking Water Regulations (NIPDWR), Part 141.15.

17.19 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.20 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.21 Pace Analytical Services, LLC. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.22 Pace SOP PGH-R-003, current revision (Analysis of Water Samples for Ra-228).

17.23 Pace SOP PGH-R-065, current revision (Alpha Scintillation Counter Operations).

17.24 Pace SOP PGH-C-025, current revision (MCL Violation Reporting).

17.25 Pace SOP PGH-C-027, current revision (Deionized Water Quality and Suitability).

17.26 SOP PGH-C-032, Support Equipment, current version.

17.27 SOP PGH-Q-038, Laboratory Equipment, current version.

17.28 SOP PGH-Q-040, Internal and External Audits, current version

17.29 SOP PGH-Q-039, Corrective and Preventative Action, current version.

17.30 SOP S-ALL-Q-020, Training, current version.

17.31 SOP S-ALL-Q-028, Lab Track, current version.

18 Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Attachment I: Calculations

18.2 Attachment II: Numerical Performance Indicators

19 Method Modifications

19.1 The strict co-precipitation technique specified in EPA 903.1, “Radium-226 in Drinking Water” generates a sulfate precipitate that is not easily dissolved when following the detailed methodology. The precipitation technique detailed in this SOP generates a soluble precipitate that is easily dissolved in EDTA solution. This minimizes the potential for reporting erroneous carrier yields and limits the spread of insoluble contamination in the bubbler system.

19.2 The barium/radium sulfate co-precipitation technique utilized in this SOP has been enhanced to allow for quality improvements in analysis and production efficiency. Excluding the addition of strontium carrier, the co-precipitation technique utilized in steps 12.1 through 12.7 of this SOP mirrors the precipitation technique employed in Pace SOP PGH-R-003, current revision, Analysis of Water Samples for Ra-228. Excluding the modifications specifically cited in this SOP, modifications between Pace SOP PGH-R-003, current revision, and EPA 904.0, “Radium-228 in Drinking Water” are documented in Section 19 of Pace SOP PGH-R-003, current revision.

19.3 The addition of barium carrier (16 mg/mL) and yttrium carrier (18 mg/mL) at step 12.5 of this SOP are added in reverse order that is cited in Pace SOP PGH-R-003, current revision, and EPA 904.0, “Radium-228 in Drinking Water.”

19.4 EPA Method 903.1 specifies the dissolution of the barium/radium co-precipitate generated in this procedure using 20 mL of 0.25 M EDTA solution. For some samples, it is necessary to use additional EDTA

solution to dissolve the barium sulfate precipitate. EPA method 904.0 for Ra-228 analysis requires an initial addition of 25 mL of EDTA solution to dissolve the barium/radium co-precipitate. In order to maintain consistency on a sample-level basis, Pace uses 25 mL of EDTA for precipitate dissolution. Adhering to the strict solution volume prior to sample analysis ensures consistency between sample analysis volumes and calibration solution volumes, thereby ensuring consistent exchange of radon and nitrogen gas when emanating radon gas from the sample bubblers.

19.5 When using bubblers of the exact dimension specifications described in EPA 903.1, there is a high probability of loss of sample solution contained in the bubblers when emanating radon from the bubbler. This can lead to contamination of the manifold system, including the Lucas cell used for analysis. Pace utilizes a bubbler design of larger dimensions so as to limit the negative impact of sample overflow. Pace ensures the appropriate ratio of radon to nitrogen gas exchange by using equivalent bubbler solution volumes between samples and calibration sources.

19.6 The preparation of the yttrium carrier solution documented in step 10.20 of this SOP does not explicitly follow the specifications of EPA Method 904.0. Additional concentrated nitric acid and ASTM Type II DI water are added at the onset of yttrium oxide dissolution so as to enhance the dissolution. The final ratio of yttrium to nitric acid solution for the yttrium carrier prepared within this SOP matches the ratios specified in EPA 904.0.

19.7 Counting the samples (and calibration cells) after only 3 hours from de-emanation instead of 4 hours as specified in EPA 903.1 allows for increased productivity and results in an error of < 0.47% for high activity sample and is negligible for low activity samples.

19.8 Concentration of radium by co-precipitation with barium is quantitative, however, collection of the precipitate is highly variable and is relative to individual analyst technique. Since there is inherent room for losses, any assumption that 100% of the sample makes it from initial precipitation, dissolution, and into the bubbler for analysis, biases the sample results low. Although the use of a tracer (Ba-133) is not specified in EPA 903.1, Pace's barium recovery measurement technique was determined by accrediting authorities to improve method precision and accuracy and was thereby allowed.

19.9 The use of anti-foaming agent in the bubbler to prevent samples from foaming and resulting in sample loss is not specified in EPA 903.1. The use and addition does not adversely impact the Ra-226 results.

19.10 Due to a world-wide shortage of helium gas, nitrogen gas is used as an alternate gas for the specified emanation process.

19.11 EPA Method 903.1 specifies to use 1,000 mL of sample for analysis. Pace analyzes approximately 500 mL of sample for analysis. All samples are measured by mass as specified within this SOP. Pace further

restricts the analysis volume for samples known to contain matrix components that would limit analyte recovery. Pace restricts the analysis volume so as to limit the quantity of waste generated and to enhance productivity. The required detection limit of 1 pCi/L is achieved using a 500 gram analysis quantity.

19.12 For the preparation of 0.25M EDTA, EPA Method 903.1 specifies to add sodium hydroxide to DI water then heat prior to adding the solid EDTA for dissolution. The heat generated from the dissolution of sodium hydroxide in water is sufficient to dissolve the EDTA and so, hot-plate heating is not performed.

20 Revisions

Document Number	Reason for Change	Date
PGH-R-007-11	1. Table of contents added. 2. Modified Section 11.6.1 to require minimum ingrowth time for calibration cells. 3. Modified Section 12.10 to require minimum ingrowth time for samples. 4. Clarified step 12.17 to document when gravimetric recovery for barium yield is allowed. 5. Section 15 modified to “Method Performance.” “Pollution Prevention and Waste Management” Section moved to Section 16. 6. “References” Section moved to Section 17. 7. “Tables, Diagrams, Flowcharts, Appendices, etc.” Section moved to Section 18. 8. “Deviations from Promulgated Methods” changed to Method Modifications Section moved to Section 19. 9. Revised Equation 7 to document the recovery calculation for Ba yield assessment. 10. Section 14: Added 14.7.2.1 to discuss yield criteria. Also modified Section to discuss non-conformance tracking with LabTracks and evaluating usefulness of data and qualifying or narrating to allow for when clients do not want a final report. 11. Section 17: Added references, ANSI N42, 23, TNI Standard, and DoD QSM. 12. Defined variables into Calculations Section for Ba recovery calculation. 13. Definition of UE4 in the Calculations Uncertainty Section was changed to require approval of the Department Supervisor for UE4. 14. Inserted Calculation number 15, the critical level calculation.	4/19/2012
PGH-R-007-12	1. Updated Table of Contents to include Attachments I and II. 2. Section 3.1, 10.12 – added nitrogen gas as optional to helium, and also included in parenthesis wherever helium is	26June2013

Document Number	Reason for Change	Date
	mentioned. 3. Section 6.5 and 12.1 – Included comment about recording observed masses and not targeting sample aliquots. 4. Section 10.2 – Added Type II DI SOP reference. 5. Section 11– defined calibration constant acceptance criteria and optimal cell constant range, process for recalibrating, assigning Ids, and repair. 6. Section 12.2 – added comment about how to proceed if methyl orange pH indicator is not red in sample. 7. Section 12 – clarified where each piece is attached when performing the radon emanation into the Lucas cell. 8. Section 12.20 – added instructions on counting cells and reference instrument operation SOP. 9. Section 13.2 and 14.1 – added to provide instruction for recognizing and reporting DW MCL exceedances. Pace SOP PGH-C-025 referenced. 10. Section 14.4 – added comment regarding using numerical indicators to assess QC and applicability. 11. Section 14.8.4 and 14.10.3 – added to include duplicate sample analysis requirement of 10% for Arizona, and 5% for all else. 12. Entire document – changed all references of DI water to ASTM Type II DI water to conform to method verbiage.	
PGH-R-007-13	1. Annual SOP review. 2. Section 4.2 and 4.3 – Added comments regarding preventing sources of cross contamination during emanation and in bubblers due to solids, 3. Section 6.6 – Added comment regarding documenting the use of pipette, graduated cylinders, or balances for sample measuring. 4. Section 8.2 – Inserted requirements for pH verification and documentation. 5. Section 11 – Clarified calibration acceptance criteria. 6. Section 12.1 to 12.3 – Inserted instructions for diluting samples, preparing QC samples, and ensuring QC are spiked prior to the addition of all other chemicals. 7. Section 14 – Added DOC and CDOC requirements. 8. Section 14 – Added MSD frequency for AZ DW samples. 9. Section 14.13.2 – Updated to discuss failed LCS/LCSD RPD actions and qualification. 10. Section 17 – Added DW Manual reference and NIPDWR reference. 11. Section 19.2 – Updated to point to the concurrent steps in the Ra-228 SOP PGH-R-003, instead of the EPA 904.0 method. 12. Section 19 – Added use of anti-foam agent and nitrogen gas into deviation from methods. 13. Edited for spelling and grammatical errors. 14. Reformatted document.	13Jul2014

Document Number	Reason for Change	Date
PGH-R-007-14	1. Removed from section 5.1: Analysts must be trained as radiation workers and personal dosimeter worn. 2. Section 12.17 - Clarified the observed changes in vacuum indicated on the gauge during sample emanation. 3. Section 14.11 – Added typical Ba-133 tracer concentrations and the determination of the tracer levels.	20Feb2015
PGH-R-007-15	1. Section 10.20-Updated the preparation of yttrium carrier (18 mg/mL) in order to match the analytical process and to more closely match the method process. 2. Sections 12.9 and 12.10-Modified the volume of 0.25M EDTA solution used in the process to match the volume used for process calibration. This standardization of the volume of EDTA used, ensures consistency between samples and the calibration process. 3. Updated section 19, Method Modifications to address changes to this SOP revision. Added a modification specifying differences between the bubbler used and the bubbler specifications in the method, EPA 903.1.	15July2015
PGH-R-007-16	1. Section 12.20 corrected to specify the correct reference section for Lucas Cell Counting. 2. Section 19 updated to include the analysis volume difference between this SOP and the method, EPA 903.1.	14Dec2015
PGH-R-007-17	1. Updated Inc. to LLC. 2. Updated PGH-R-064 to PGH-R-065. 3. Updated section 19.2 to add: excluding the addition of strontium carrier. 4. Added section 19.3 to add: The addition of barium carrier (16 mg/mL) and yttrium carrier (18 mg/mL) at step 12.5 of this SOP are added in reverse order that is cited in Pace SOP PGH-R-003, current revision, and EPA 904.0, “Radium-228 in Drinking Water.”	21Dec2016
S-PGH-R-007-rev.18	1. Section 8.2 samples must be held minimum of 24 hours. 2. Modified section 10.10 to remove the requirement to heat EDTA solution during preparation. Heating is not necessary to prepare the solution. 3. Modified section 10.19 to document purchase and use of pre-diluted 18 N sulfuric acid from the manufacturer. 4. Modified section 12.14 to specify filling of absorption tube with half ascarite and half magnesium perchlorate to enhance removal of moisture known to be present in the samples. 5. Modified section 12.21 to remove the requirement to rinse bubblers into the tracer-recovery phase. 6. Modified sections 12.17 and 12.19 to remove the requirement to close the bubbler stopcock when bubbling ceases. The emanation system, including the bubbler is designed to prevent leakage. Closing the bubbler stopcock creates system structure pressure that could create loss of analyte. 7. Section 12.22.9 modified to specify use of inert helium or	08Feb2018

Document Number	Reason for Change	Date
	nitrogen gas for cell flushing, rather than room air. 8. Sections 14.13.3 and 14.13.4 modified to clarify the corrective actions for failed sample matrix spikes and/or sample matrix spike duplicates.	

Attachment I
Calculations

The **radium-226 concentration** of a sample is calculated according to the following equations:

Eq. 1 $$Act = \frac{(S_A - B_A)}{(Denom)}$$

Eq. 2 $$Denom = E * V * 2.22 * I_S * D_1 * D_2 * R$$

Eq. 3 $$E = \frac{(S_C - B_C)}{(A_C * I_C * D_{1C} * D_{2C})}$$

Eq. 4 $$I_S = 1 - e^{-\lambda t1}$$

Eq. 5 $$D_1 = e^{-\lambda t2}$$

Eq. 6 $$D_2 = (1-e^{-\lambda t3})/(\lambda t_3)$$

Eq. 7 $$R = \frac{M_B}{T_B} \text{ OR } R = \frac{M_{Ba133}}{T_{Ba133}}$$

Eq. 8 $$I_C = 1 - e^{-\lambda t4}$$

Eq. 9 $$D_{1C} = e^{-\lambda t5}$$

Eq. 10 $$D_{2C} = e^{-\lambda t6}$$

Where:

Act	=	Radium-226 sample concentration in pCi/unit (L, g, F, etc.)
S_A	=	gross count rate for the sample (in cpm)
B_A	=	cell background (in cpm)
S_C	=	gross count rate for the calibration source (in cpm)
B_C	=	calibration source cell background (in cpm)
A_C	=	activity of the calibration source in dpm
2.22	=	conversion factor from dpm to pCi
E	=	cell efficiency in cpm/dpm of radon-222
V	=	sample volume, mass, or fraction (in L, g, or %filter, etc)
R	=	fractional recovery of barium sulfate or Ba-133 tracer
M_B	=	mass of barium sulfate recovered (in mg)
M_{Ba133}	=	Measured sample Ba-133 Net Cts from the sodium iodide counter yield measurement
T_B	=	standardized barium carrier conc. (in mg barium sulfate per mL of barium carrier used)
T_{Ba133}	=	Measured Net Cts of the reference source for the specific sodium iodide detector used for the sample recovery determination
I_S	=	Radon-222 ingrowth factor for the sample

D_1	=	Radon-222 decay between second de-emanantion and counting for the sample
D_2	=	Radon-222 decay during counting for the sample
I_C	=	Radon-222 ingrowth factor for the calibration source
D_{1C}	=	Radon-222 decay between second de-emanantion and counting for the calibration sample
D_{2C}	=	Radon-222 decay during counting for the calibration source
λ	=	Decay constant of radon-222, (0.000125883 min^{-1})
t_1	=	the elapsed time in minutes between the first and second de-emanations for the sample
t_2	=	the elapsed time in minutes between the second de-emanation and sample counting for the sample
t_3	=	the sample counting time in minutes
t_4	=	the elapsed time in minutes between the first and second de-emanations for the calibration source in hours
t_5	=	the elapsed time in minutes between the second de-emanation and calibration source counting in hours
t_6	=	the calibration source counting time in minutes
Measured	=	either barium sulfate mass recovered in mg or Ba-133 measured by gamma spec
Expected	=	standardized barium sulfate target (in mg) or Ba-133 reference value (in pCi/L)

The sample specific **counting uncertainty** is calculated as follows.

$$\text{Eq. 11}\quad \textit{Counting Uncertainty} = \frac{1.96 * \sqrt{((S_A/t_3)) + ((B_A/t_7)}}{\text{Denom}}$$

Where:

t_7 = background count time in minutes

As summed background and analyte count rates approach zero, assumptions underlying the uncertainty calculation are violated and it will return an unrealistic value of zero (0) uncertainty when zero summed counts are observed. The following equation provides a more accurate estimate of count uncertainty at zero and near-zero count rates.

$$\text{Eq. 12}\quad \text{ZeroUnc} = \text{ZeroActFact}/\text{SmplTime}$$

Note 1: Depending on sample type and contract requirements the zero activity factor may be either 3.0 or 2.71. PASI's default is 2.71 consistent with the current version of ANSI N42.23. Bioassay samples must be calculated using 3.0 to be consistent with ANSI N13.30

Note 2: The Zero Count Uncertainty is compared to the count uncertainty above. The larger of the two is used as the counting uncertainty in subsequent total error calculations.

The error term is further evaluated to provide an estimate of total error hereafter referred to as the *Combined Standard Uncertainty* (CSU a.k.a. TPU).

Eq.13

$$\text{CSU (pCi/unit)} = \sqrt{(\text{CountingUncertainty})^2 + (UE1 * Act)^2 + (UE2 * Act)^2 + (UE3 * Act)^2 + (UE4 * Act)^2}$$

UE1, UE2, UE3, and UE4 represent partial derivatives estimating the relative uncertainty at the ***95% confidence interval*** for various factors in the activity calculation as follows:

UE1 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with preparation (e.g., sample aliquot or transfers and splits prior to addition and equilibration of tracer).

UE2 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with analysis (e.g., peak integration, peak overlap, tracer contaminants).

UE3 represents combined factors estimating relative uncertainty (fractional) associated with yield correction (e.g., count uncertainty for tracer peak, SRM known value, tracer volume or mass aliquot, tracer equilibration efficiency).

UE4 represents the factor estimating additional uncertainty (activity) associated with an individual sample -- to be used in exceptional circumstances with approval of The Department Supervisor and appropriate documentation and narration only.

The Minimum Detectable Concentration (MDC) is calculated per guidance of ANSI N42.23 and N13.30 as:

Eq. 14 $$\text{MDC} = \frac{4.65 * \sqrt{(B_A) * t_3} + ZeroActFact}{t_3 * \text{Denom}}$$

Where B_A, t_3, *ZeroActFact*, and Denom have previously been identified.

The critical level (Lc) is calculated per guidance of ANSI N42.23 as:

Eq. 15 $$Lc = \frac{1.65 * \sqrt{(B) * (1/Ts + 1/Tb)}}{Denom}$$

Where:

B, T_s, T_b, *ZeroActFact*, and Denom are as previously defined.

Attachment II
(Numerical Performance Indicators)

1. **Method Blank (MB)**

1.1 The numerical performance indicator for the method blank is calculated by:

$$Z_{Blank} = \frac{x}{u(x)}$$

Where:
x = measured blank activity
u(x) = standard uncertainty (1 sigma) in the blank measurement

1.2 MB performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. MB performance indicator values should be recorded on a control chart.

2. **Laboratory Control Sample (LCS)**

2.1 The numerical performance indicator for a laboratory control sample is calculated by:

$$Z_{LCS} = \frac{x - c}{\sqrt{u^2(x) + u^2(c)}}$$

Where:

x = Analytical result of the LCS
c = Known concentration of the LCS
$u^2(x)$ = combined standard uncertainty (1 sigma) of the result squared.
$u^2(c)$ = combined standard uncertainty (1 sigma) of the LCS value squared.

2.2 LCS performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. Performance indicator values should be recorded on a control chart.

3. Duplicates (DUP)

3.1 These criteria are applicable for the evaluation of the Duplicate, Matrix Spike Duplicate and Laboratory Control Sample Duplicates.

3.2 The numerical performance indicator for laboratory duplicates is calculated by:

$$Z_{Dup} = \frac{x_1 - x_2}{\sqrt{u^2(x_1) + u^2(x_2)}}$$

Where:
x_1, x_2 = two measured activity concentrations

$u^2(x_1)$, $u^2(x_2)$ = the combined standard uncertainty (1 sigma) of each measurement squared.

3.3 Duplicate sample performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. DUP performance indicator values should be recorded on a control chart for each QC sample type (Dup, MSD, LCSD)

4. **Matrix Spike/Matrix Spike Duplicate (MS/MSD)**

4.1 The numerical performance indicator for a matrix spike sample is calculated by:

$$Z_{MS} = \frac{x - x_0 - c}{\sqrt{u^2(x) + u^2(x_0) + u^2(c)}}$$

Where:
x = measured concentration of the spiked sample
x_0 = measured concentration of the unspiked sample
c = spike concentration added
$u^2(x)$, $u^2(x_0)$, $u^2(c)$ = the squares of the respective combined standard uncertainties (1 sigma) of these values.

4.2 MS performance for all matrices is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. MS performance indicator values should be recorded on a control chart.

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STANDARD OPERATING PROCEDURE

Analysis of Water Samples for Ra-228

Methods: EPA 904.0 and 9320/SM7500-RaD (Ra-228)

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Maureen K. DeKubeis
Senior Quality Manager — 02/08/18 Date

Department Manager/Supervisor — 02/08/18 Date

PERIODIC REVIEW
SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

TABLE OF CONTENTS

SECTION **PAGE**

1. Purpose

1.1 This SOP documents the analytical procedure to be used for the analysis of drinking water and other aqueous samples for Ra-228 content. This SOP is based on EPA 904.0, 9320, and SM7500-RaD.

2. Scope and Application

2.1 This procedure is applicable for the analysis of radium-228 in drinking water, wastewater, and other aqueous matrices. Without qualification, this procedure, as written, is compliant with Method 904.0 of "*Prescribed Procedures for Measurement of Radioactivity in Drinking Water,* EPA-600/4-80-032", Method 9320 of "*Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW846), Volume 1C, Third Edition", and Standard Method 7500-Ra D of "*Standard Methods for the Examination of Water and Wastewater*".

2.2 Radium-228 in an aqueous sample is determined by the isolation and direct measurement of Ac-228, the beta-emitting daughter of Ra-228, utilizing a gas flow proportional counter.

2.3 The efficiency of the Gas flow proportional counting (GFPC) system used for radioactivity measurement fluctuates relative to the energy of radioactivity emissions. Actinium-228 has a half life of 6.3 hours, so it is not practical to perform system calibrations directly with Ac-228, therefore, a beta isotope of similar energy is utilized for calibration purposes. This SOP requires that Sr-89 be utilized for calibration purposes.

2.4 Pace Analytical services, LLC. (PASI) applies isotope decay correction only in instances where the total impact in the analysis result is 2% or greater. Assuming a maximum hold time of 180 days, a 2% isotope decay would occur only for radioisotopes with a half-life of 17.14 years or less. The parameters reported using this SOP are affected by this policy and results for Ra-228 are decay corrected for the time from the collection date and time supplied by the client to the start of instrument analysis.

3. Summary of Method

3.1 Radium in aqueous samples is pre-concentrated by co-precipitation with barium and lead as a sulfate. Barium and radium are isolated from lead by repeated precipitation as a sulfate from EDTA solution. The final purified barium/radium sulfate precipitate is dissolved in EDTA solution and stored to allow ingrowth of Ac-228, the beta-emitting daughter of Ra-228.

3.2 Following the ingrowth of Ac-228, potentially interfering radioisotopes of lead that may be present are removed by precipitation as lead sulfide. Actinium-228 in the sample is separated by co-precipitation with yttrium as hydroxide, then converted to yttrium oxalate and mounted for beta counting by GFPC. Radium recovery is determined by gravimetric measurement of barium sulfate precipitate recovered during analysis, or by use of Ba-133 as a radiotracer. Actinium recovery is determined by gravimetric measurement of yttrium oxalate precipitate recovered during analysis.

4. Interferences

4.1 The presence of high levels of Sr-90 in a water sample will produce a positive bias to the Ra-228 activity measured.

4.2 Elemental barium contained in the water sample will result in a falsely high gravimetrically measured barium yield and will result in an underestimation of Ra-

228 content. This interference will not affect the yttrium or Ba-133 results. Ba-133 radiotracer is utilized to eliminate possible chemical recovery biases which would occur if stable barium was present in the sample and yield determination was performed gravimetrically.

4.3 In some samples, unidentified sample interferences can cause Ba-133 to carryover to the final source planchet, elevating the sample beta count rate, and biasing the sample result high. Additional instructions for determining if Ba-133 carryover has occurred are outlined in Section 12.5 of this SOP.

4.4 Samples containing excessive sodium and calcium will cause excess sulfate precipitate to form during the initial sulfate precipitation steps. Excessive sulfate precipitates can cause low chemical yields, because the additional precipitate may not completely dissolve in EDTA during the initial ingrowthing steps. Additional steps in Section 12.7 are designed to minimize the interference of sodium and calcium sulfate precipitates.

5. Safety

5.1 Procedures must be carried out in a manner that protects the health and safety of all personnel.

5.2 At a minimum, eye protection, a laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves will be cleaned immediately.

5.3 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye-protection, gloves, and lab coat must be worn.

5.4 Exposure to radioactivity and chemicals must be maintained as low as reasonably achievable. Samples known to be hazardous and/or radioactive, must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 In order to minimize the potential for cross contamination of high and low levels of radioactive samples, good housekeeping and good laboratory practices are essential and must be strictly adhered to.

5.6 Organic samples of unknown content must be handled with extreme caution and under the direct instruction of a department manager or manager-specified designee. Direct treatment of organic matrices with strong oxidizing chemicals such as nitric acid and/or hydrogen peroxide is strictly prohibited.

5.7 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the SDS files maintained in the laboratory and in the PASI-PGH Chemical Hygiene Plan.

6. Definitions

6.1 See the Glossary Section of the most recent version of the Pace Analytical Services, LLC. Quality Assurance Manual for commonly used laboratory terms.

6.2 Batch: For all matrices, an analytical batch contains 20 or fewer samples of a similar matrix, prepared at the same time, by the same analyst, using the same reagents.

6.3 Throughout this procedure, approximate weights and measures will be designated by the use of whole numbers when referring to masses exceeding 1gor volumes in excess of1mL. Measurements of masses and volumes so designated can be made with top loading balances, graduated cylinders, etc. For approximate measures below 1gor1mL, the word "approximately" must be used prior to the described mass or volume.

6.4 Throughout this procedure, exact or critical mass and volumes will be designated by the use of one or more decimal places. Measurements of mass and volumes so designated should be made with accurate analytical instruments such as analytical balances, calibrated pipettes, etc.

6.5 Any reference to a “hot water bath” indicates a container filled with water, which has been heated to a temperature just below the boiling point of the water.

6.6 When aliquotting samples on a balance, the observed mass on the balance must be recorded in preparation logbooks to the lowest mass indicated on the balance. Sample aliquot masses must not be targeted. Once sample is removed from the sample container and transferred to a beaker, it must not be removed from the beaker.

6.7 The method utilized for obtaining the sample aliquot, whether on a balance, in a graduated cylinder, or by pipette, must be clearly annotated in the preparation logbook.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Aqueous samples

8.1.1 Containers used for sample collection must never be re-used. Either plastic or glass containers may be used for sample collection.

8.1.2 Aqueous samples must be preserved at the time of collection by adding enough concentrated (16N) HNO_3 to the sample to make the sample pH <2. Typically, two mL of 16N HNO_3 per liter of sample is sufficient to obtain the desired pH. Samples must be preserved within five days of collection. If samples are collected without preservation, they must be received by the laboratory and preserved within five days of collection. Following preservation with acid, samples must be held in the original container for a minimum of 24 hours, and the pH must be rechecked by laboratory personnel prior to removing sample for analysis. The pH recheck date and time, the initials of the analyst verifying the pH, as well as any adjustments or notes regarding the preservation must be recorded in the pH Verification Logbook.

8.1.2.1 For dissolved analysis, samples must be filtered through a 0.45μm membrane filter and preserved to a pH <2.

8.1.2.2 For total analysis, the sample is not filtered, but is preserved.

8.1.3 Refrigeration is not required for aqueous samples.

8.1.4 The maximum hold time for samples analyzed by this procedure is 180 days between sample collection and sample analysis.

9. Equipment and Supplies

9.1 Gas Flow Proportional Counting System. (Low background beta <3 cpm). Refer to SOP PGH-R-002, current revision “Gas Flow Proportional Counter Operation” for instructions on GFPC system operation.

9.2 Software supplied with the instrument to control instrument operation. Refer to SOP PGH-R-002, current revision “Gas Flow Proportional Counter Operation” for applicable software details.

9.3 Computer capable of running the Gas Flow Proportional Counter System software, monitor, mouse, keyboard, and printer. Refer to SOP PGH-R-002, current revision “Gas Flow Proportional Counter Operation” for computer hardware specifications.

9.4 Electric hot plate.

9.5 Centrifuge, capable of greater than 2500 rpm.

9.6 Centrifuge tubes, 50 mL high density polyethylene, or equivalent.

9.7 Filter paper, Fisherbrand Q2, 11.0cm diameter, or equivalent.

9.8 Membrane filter, 0.45μm, 47mm, Metricel®, or equivalent.

9.9 Drying lamp.

9.10 Glassware, various sizes.

9.11 Stirring Rods, glass.

9.12 Stainless steel counting planchets. 2 inch diameter, 1/8 inch deep.

9.13 Analytical balance (capable of measuring to 0.0001g).

9.14 Top Loading balance (capable of measuring to 0.01g).

9.15 Vortex mixer.

10. Reagents and Standards

10.1 Reagents should be prepared from reagent grade chemicals, unless otherwise specified below. Reagent water must be at least ASTM Type II quality or better. NOTE: Consult the Safety Data Sheets for the properties of these reagents, and how to work with them.

10.2 Distilled or deionized (DI)water. ASTM Type II generated as specified in Pace SOP PGH-C-027, current revision.

10.3 Acetic acid, 17.4N: glacial CH_3COOH (conc.), sp. Gr. 1.05, 99.8%.

10.4 Ammonium hydroxide, 15N: NH_4OH (conc.), sp. Gr. 0.90, 56.6%.

10.5 Ammonium oxalate, 5%: Dissolve 50.0g $(NH_4)_2C_2O_4 \cdot H_2O$ in boiling ASTM Type II DI water, cool, and dilute to 1.0 L with ASTM Type II DI water.

10.6 Ammonium sulfate, 200mg/mL: Dissolve 200g $(NH_4)_2SO_4$ in water and dilute to 1.0L with ASTM Type II DI water.

10.7 Ammonium sulfide, 2%: Dilute 2.0mL $(NH_4)_2S$, (20-24%), to 20mL with ASTM Type II DI water.

10.8 Barium carrier, 16mg/mL, standardized. Dissolve 28.46 g $BaCl_2 \cdot 2H_2O$ in water, add 5.0mL 16N HNO_3, and dilute to 1.0L with ASTM Type II DI water.

10.9 Barium-133 standard solution, NIST traceable for use as a radiotracer for yield monitoring.

10.10 Citric acid, 1M: Dissolve 192.0g $C_6H_8O_7 \cdot H_2O$ in water and dilute to 1.0L with ASTM Type II DI water.

10.11 EDTA reagent, basic, (0.25M): Dissolve 20 g NaOH in 750mL water and slowly add 93g disodium ethylenedinitriloacetate dihydrate, $(Na_2C_{10}H_{14}O_8N_2 \bullet 2H_2O)$ while stirring. After the salt is in solution, dilute to 1L with ASTM Type II DI Water. The heat generated from the solid sodium hydroxide added to DI water should be sufficient so as to support complete dissolution of EDTA. If the EDTA does not readily dissolve, gradually heat the reagent until dissolved.

10.12 Lead carrier, 150mg/mL: Dissolve 239.7 g $Pb(NO_3)_2$ in ASTM Type II DI water, add 5.0mL 16N HNO_3 and dilute to 1.0 L with ASTM Type II DI water.

10.13 Lead carrier, 1.5 mg/mL: Dilute 10mL lead carrier (150 mg/mL) to 1.0L with ASTM Type II DI water.

10.14 Methyl Orange Indicator, 0.1%: Dissolve 1.0g methyl orange indicator in 1.0L ASTM Type II DI water.

10.15 Nitric acid, 16N: HNO_3 (conc.), sp. gr. 1.42, 70.4%.

10.16 Nitric acid, 6N: Add 375mL of 16N HNO_3 to 500mL of deionized water, cool and dilute to 1Liter with ASTM Type II DI water.

10.17 Nitric acid, 1N: Dilute 62.5mL 16N HNO_3 to 1Liter with deionized water.

10.18 Radium-228 standard solution, NIST traceable for use as a Laboratory Control Sample spiking material.

10.19 Sodium carbonate, 2N: dissolve 124 g $Na_2CO_3 \cdot H_2O$ (or 106 g Na_2CO_3) in ASTM Type II DI water and dilute to 1Liter with ASTM Type II DI water.

10.20 Sodium hydroxide, 18M: Dissolve 720g NaOH in ASTM Type II DI water and dilute to 1.0L with ASTM Type II DI water.

10.21 Sodium hydroxide, 10M: Dissolve 400g NaOH in ASTM Type II DI water and dilute to 1.0L with ASTM Type II DI water.

10.22 Strontium carrier, 10mg/mL: Dissolve 24.16 g $Sr(NO_3)_2$ in ASTM Type II DI water and dilute to 1.0L with ASTM Type II DI water.

10.23 Strontium-89 standard solution, NIST traceable for use in instrument calibration.

10.24 Sulfuric acid, 18N: Cautiously mix 1 volume 36N H_2SO_4 (conc.) with 1 volume of ASTM Type II DI water in a tub of ice or cool water. As water evaporates replace with ASTM Type II DI water to desired final volume.

10.25 Sulfuric acid, 0.1N: Dilute 5.56 mL of 18N sulfuric acid to 1.0L using ASTM Type II DI water.

10.26 Yttrium carrier, 18 mg/mL: Add 22.85 g Y_2O_3 to an Erlenmeyer flask Add 50mL of ASTM Type II DI water. Carefully add 40mL of concentrated nitric acid. Heat the mixture to boiling while stirring on a magnetic stirring hotplate. The solution must heat to boiling. Additional water and nitric acid may be added as necessary to aid in dissolution. Scrape the bottom of the Erlenmeyer flask with a Teflon scraper if the yttrium oxide is caked onto the glass. Do not add more than 100mL of nitric acid total. Upon complete dissolution, remove the beaker from the hotplate and cool completely. Dilute to 1Liter with ASTM Type II DI water.

10.27 Yttrium carrier, 9 mg/mL: Dilute 500mL yttrium carrier (18 mg/mL) to 1.0L with ASTM Type II DI water. Standardize this carrier in accordance with the steps outlined in section 11.

10.28 Strontium-yttrium mixed carrier, 0.9 mg/mL Sr^{+2} – 0.9 mg/mL Y^{+3}:

10.28.1 Solution A: Dilute 100mL yttrium carrier (18 mg/mL) to 1.0L with ASTM Type II DI water.

10.28.2 Solution B: Dissolve 4.348 g $Sr(NO_3)_2$ in ASTM Type II DI water and dilute to 1.0L with ASTM Type II DI water.

10.28.3 Combine Solutions A and B and label.

11. Calibration

Beta radioactivity emissions are inhibited by the medium through which they must travel. For this reason, when counting radioactivity emissions by gas flow proportional counting, system efficiency decreases as sample residue thickness increases. Over the applicable mass range for this method, this “self-attenuation” effect may be insignificant with certain

gas flow counting systems. If it can be demonstrated that counting efficiency fluctuates by less than 2% over the applicable mass range, for a particular instrument, then calibrations need not take mass-attenuation into account. Otherwise, an appropriate system calibration that corrects for this "self-absorption" characteristic must be performed. Detector calibrations are performed universally independent of sample analysis matrix type. The calibration values determined by application of this process are applied universally for all matrices for which the analytical process is defined in this SOP.

11.1 Beta self-absorption calibration using Sr-89:

11.1.1 The applicable counting mass range for this method is between approximately 10 mg and approximately 30 mg. If it has been demonstrated that the instrument efficiency varies less than 2% over this mass range for the analyte of interest (Sr-89), then correction for self-attenuation is not required for this method. If self-attenuation is not applicable, then instrument calibration should be performed using a minimum of four calibration sources prepared at the optimum sample analysis mass (approximately 20 mg).

11.1.2 For a mass attenuation calibration using Sr-89, to labeled, disposable centrifuge tubes, add varying amounts of strontium carrier solution (10 mg/mL) which will generates a final theoretical strontium carbonate mass range that covers the practical mass range. This expected residue mass range is based on the routine gravimetric target mass for analysis andPASI's minimum and maximum allowable gravimetric recovery limits for this test. An example calibration source setup may be as follows:

Cal. Source Number	Volume of Sr carrier (10 mg/mL)
1	0.5 mL
2	1.0 mL
3	1.5 mL
4	2.0 mL
5	2.5 mL

11.1.3 For a calibration where the average of four efficiencies will be used, add 2.0mL of standardized strontium carrier to each of four labeled centrifuge tubes.

11.1.4 Add between 500 and 1500 dpm (by mass) of a NIST traceable Sr-89 standard to each calibration tube and record the standard mass on the bench sheet. Equivalent amounts of Sr-89 solution should be used for each source. Dilute each calibration solution to approximately 20 mL with ASTM Type II DI water.

Note: The specified calibration source activities have been optimized to allow manageable count times for individual sources. Maximum calibration source activities have been set to minimize the potential impact of any cross contamination within the detector system.

11.1.5 Add 5 mL of conc. NH_4OH solution to each calibration tube.

11.1.6 Add 5 mL of 2N Na_2CO_3 solution to each tube, then heat them in a hot water bath for 15 minutes. Remove each calibration tube from the hot water bath and allow it to cool.

11.1.7 Centrifuge each calibration source for 10 minutes and discard the supernate.

11.1.8 Wash the carbonate precipitate with 20mL of ASTM Type II DI water. Centrifuge and discard the supernate.

11.1.9 Slurry the carbonate precipitate with a few mL of ASTM Type II DI water and quantitatively transfer it to a tared, 2-inch stainless steel planchet.

11.1.10 Dry the calibration sources under a heat lamp.

11.1.11 Re-weigh each source to determine the mass of strontium carbonate recovered.

11.1.12 Count calibration sources in a low-background gas flow proportional counting system as detailed in the instrument SOP, PGH-R-002, "Gas Flow Proportional Counter Operation" current revision. Count each calibration source in each detector requiring calibration long enough to acquire 10,000 net beta counts. Perform efficiency calculations as detailed in Attachment 1 of this SOP.

11.2 Calibration curve acceptance criteria

Calibration curves generated by the process detailed in this SOP must meet the following minimum criteria to be used for sample analysis.

11.2.1 Instrument mass-attenuation calibration must include a minimum of five calibration points for each detector being calibrated. Non-mass-attenuation calibrations must include a minimum of four calibration points with final source mass near the optimum method mass of 20 mg.

11.2.2 If the RSD between all calibration efficiency points is less than 5%, the average efficiency of the calibration points should be calculated and used in all sample calculations.

11.2.3 If the RSD of the efficiencies of the calibration points is greater than 5%, plot the system efficiency (as cpm/dpm) versus source mass (in mg) for each calibration source. Utilize a least squares curve-fitting, exponential or polynomial whichever yields the best fit against the measured data.

11.2.4 Following regression analysis, measured pCi values for each calibration source must be calculated using the calibration curve. Each measured source should be within 10% of known. If the value is not within 10%, assess the point using a z-score. If the z-score for the point is greater than 2.56, the point must be removed from use for calculation purposes. Calibration points may not be removed from the calibration curve without approval of the Department Manager/Supervisor.

11.2.5 Following the removal of individual points, the efficiency must be recalculated using the data for the remaining calibration sources and the calculation process must be repeated until the criteria established in this SOP have been met. A narrative discussing technical justification for modifications or exclusions of any calibration point must be created and kept with the calibration data.

11.3 Calibration Frequency

11.3.1 Calibrations or calibration re-verification for tests associated with drinking water analyses must be performed on an annual basis.

11.3.2 As allowed by specifications within the Manual for the Certification of Laboratories Analyzing Drinking Water, calibration sources may be retained for calibration re-verification purposes. Since Sr-89 is the isotope used for determining efficiency for Ra-228 calculations, and the

half-life is less than 2 months, it is not practical to save Sr-89 calibration sources and reuse them to verify a calibration. New sources must be prepared for verification or calibrations and analyzed annually.

11.3.3 New sources used for verification purposes must be prepared at a similar mass and activity as those used in the initial calibration. Depending on the type of initial calibration used, a minimum of three sources of varying mass must be used to verify a mass attenuation curve, or a minimum of two sources of similar mass must be used to verify an average efficiency.

11.3.4 For the mass attenuation verification, the calculated activity of each of the three verification sources must be within 10% of their target source activity. Any detector not meeting this criteria requires a full calibration as outlined beginning in Section 11.1.2 of this SOP.

11.3.5 For an average efficiency verification, the calculated average efficiency of the two verification sources must be within 10% of the average efficiency determined in the initial calibration. Any detector not meeting these criteria requires a full calibration as outlined beginning in Section 11.1.3 of this SOP.

11.4 Yttrium carrier standardization

11.4.1 Yttrium carrier standardization must be performed prior to analyzing samples in which the yttrium carrier was used.

11.4.2 Add 1.0mL of yttrium carrier (9mg/mL) to each of 5 labeled centrifuge tubes.

11.4.3 Add 20mL 0.25M EDTA solution to each centrifuge tube.

11.4.4 Add 5mL 18M NaOH, stir well, and digest in a hot water bath until yttrium hydroxide coagulates. Centrifuge samples and discard the supernatant.

11.4.5 Dissolve the samples in 2.0 mL of 6N HNO_3, add 5.0 mL of ASTM Type II DI water, and re-precipitate yttrium as a hydroxide by adding 3.0 mL of 10N NaOH.

11.4.6 Heat the samples in a hot water bath for 12 minutes. Centrifuge the samples and discard the supernate.

11.4.7 Dissolve the precipitate in 1.0 mL of 1.0 N HNO_3. Cap the samples and vortex to mix. If cloudy, add 1.0 N HNO_3 dropwise until the solution is clear, up to 6 drops.

11.4.8 Heat the samples in a hot water bath for 3 minutes.

11.4.9 Remove the samples and add 3 mL ASTM Type II DI water and 2.0 mL of 5% ammonium oxalate solution to precipitate yttrium oxalate.

11.4.10 Cap and vortex the samples and return them to the hot water bath for an additional 3 minutes.

11.4.11 Remove the samples form the hot water bath, centrifuge, and discard the supernate.

11.4.12 Add 10.0mL of ASTM Type II DI water to each sample, and 6 drops each of the 1.0 N HNO_3 and 5% ammonium oxalate solution.

11.4.13 Cap and vortex the samples to break up the precipitate.

11.4.14 Return the samples to the hot water bath for 3 minutes. Remove and centrifuge the samples, discard the supernate.

11.4.15 Slurry the precipitate in 6.6 mL of ASTM Type II DI water and quantitatively transfer the contents to a tared planchet placed under a heatlamp. Evaporate the samples to dryness and allow them to cool completely before reweighing.

11.4.16 Enter the tare and gross masses into the yttrium standardization calculation spreadsheet. Calculate the average mass of the five standards and the corresponding percent RSD and standard deviation among them.

11.4.17 The five standard masses must agree within 5% RSD and within ± 3 standard deviations to use the average mass.

11.4.18 Enter the average concentration into the Ra-228 activity calculations spreadsheet as the yttrium target mass for chemical recovery purposes.

11.5 Barium Carrier standardization

11.5.1 Pace employs Ba-133 tracer as the default yield monitor in this procedure. The following steps are included in this SOP in the event the Ba-133 yield assessment cannot be made. Barium carrier standardization is only necessary to perform when required.

11.5.2 Pipette 2.0mL barium carrier to each of 5 labeled centrifuge tubes.

11.5.3 Add 20mL 0.25M EDTA solution and 5mL 18N NaOH to each centrifuge tube.

11.5.4 Add 4mL 16N HNO_3 and swirl to mix.

11.5.5 Add 2.0mL ammonium sulfate (200 mg/mL) .

11.5.6 Add 3mL acetic acid. Cap the samples and vortex to mix.

11.5.7 Heat in a hot water bath for 15 minutes until the precipitate settles.

11.5.8 Centrifuge and discard the supernatant. Rinse the precipitate with 15mL of ASTM Type II DI water. Vortex vigorously.

11.5.9 Centrifuge and discard the supernatant.

11.5.10 Slurry the precipitate in 7mL of ASTM Type II DI water and transfer quantitatively to a tared 2 inch stainless steel planchet. Heat to dryness under an infrared lamp.

11.5.11 Calculate the average of the five standards masses and the corresponding percent RSD and standard deviation among them. The five standard masses must agree within 5% RSD and within ± 3 standard deviations to use the average mass.

11.5.12 Enter the average concentration into the Ra-228 activity calculations spreadsheet as the barium target mass for chemical recovery purposes.

12. Procedure

Unless specified otherwise, the documented analysis process must be followed, as written, including the order of analytical process and the addition of chemicals.

12.1.1 Weigh 800g of aqueous sample into an appropriately sized beaker. Record the observed measured mass of sample to the lowest decimal on the balance. Do not remove sample from the beaker once it has been

added. The actual quantity of sample used may be less than 800 grams if matrix interferences are expected or there is limited sample quantity available to the laboratory. If less than 800g of sample is used, dilute the sample with ASTM Type II DI water to the 800mL mark on the beaker. Fortify the pH of diluted samples by adding 2mL of HNO_3. The cause for utilizing reduced sample volume must be recorded in the analytical logbook. Some sample dilution comments could include; 1. Limited sample was available for analysis, 2. Sample matrix interferences expected, 3. Elevated historical or anticipated sample activity.

12.2 Prepare a Method Blank (MB), Laboratory Control Sample (LCS), and Laboratory Control Sample Duplicate (LCSD) by weighing 800g of ASTM Type II DI water into an appropriately sized beaker. Add 2.0mL of concentrated nitric acid to the MB, LCS, and LCSD. Add the appropriate amount of Ra-228 spike solution to the LCS and LCSD based on the requirements listed in section 14.6.3.

12.3 If a Matrix Spike (MS) is prepared, add the appropriate amount of Ra-228 spike solution to the MS sample based on the requirements listed in section 14.9.2.

12.4 To all samples and QC, add 5mL of 1M citric acid ($C_6H_8O_7 \cdot H_2O$) and a few drops methyl orange indicator and stir. The solution should be red.

12.4.1 If the solution does not turn red, verify the pH of the original sample. If the pH is correct (acidic <2.0), proceed with the analysis. If the pH is not correct, go to Section 8.1.2.

12.5 Add 1mL lead carrier (150 mg/mL), 2mL strontium carrier (10 mg/mL), 2.0mL barium carrier (16 mg/mL), and 1mL yttrium carrier (18 mg/mL). PASI's default procedure for yield determination is made using Ba-133 radiotracer. Add an appropriate quantity of Ba-133 to each sample according to the guidelines in section 12.33.1 of this SOP. Stir well. Heat to incipient boiling and maintain at this temperature for 30 minutes.

12.5.1 Note: The default yield determination method is the use of Ba-133 tracer with tracer recovery determined by sodium iodide counting. For some samples, the Ba-133 tracer carries over to the sample planchet used for measurement of Ac-228 by GFPC counting. The sample components or interferences that are the cause of this phenomenon have not been identified. Discoloration of the final source prepared for Ac-228 counting may be an indication that interference exists, especially for samples yielding a dark oxalate precipitate for the count source.

12.5.2 The presence of Ba-133 on the Ac-228 (Y) oxalate planchet can be confirmed by direct qualitative counting on a gamma spectrometer or recounting the sample planchet on a GFPC detector the following day. Contributions to the beta count rate which are caused by Ba-133 carryover will be consistent from one day to the next due to the relatively long half life of Ba-133 versus the short half life of the Ac-228.

12.5.3 Unless samples have historically indicated the pattern of interference indicated in 12.5.1, all samples should be analyzed using the Ba-133 tracing approach. For all cases, the quantity of barium carrier added is the same.

12.5.4 Samples exhibiting Ba-133 carryover may be re-ingrowthed and reanalyzed providing the Ba-133 tracer yield is significant enough to be able to meet the required MDL upon reanalysis (greater than 50%). Otherwise, the sample should be reprepped using a lower aliquot, and

possibly using stable barium carrier in lieu of Ba-133 tracer to determine chemical yield.

12.6 If necessary, add a few drops methyl orange indicator again as it is destroyed upon prolonged heating. Add 15N NH_4OH until a definite yellow color is obtained, then add a few additional drops. Precipitate lead and barium sulfates by adding 18N H_2SO_4 until the red color reappears, then add 0.25mL in excess. Add 5mL of $(NH_4)_2SO_4$ (200 mg/mL) and stir the sample vigorously until a precipitate forms. Allow the solution to heat for a minimum of 30 minutes and remove the samples to cool.

12.7 Allow the sample precipitate to settle overnight or for a minimum of 2 hours, and siphon off most of the supernatant liquid and discard, saving the precipitate.

12.7.1 The layer of precipitate should be relatively thin on the bottom of the beaker. If a significant amount of precipitate forms, it may be an indication of the presence of excessive sodium or calcium in the sample.

12.7.2 Sodium sulfate and calcium sulfate are soluble in cold water. Calcium sulfate, in particular, has an inverse solubility relationship with temperature, so the colder the water, the more calcium sulfate dissolves.

12.7.3 To remove most of the extra sodium and calcium sulfate precipitate, add ASTM Type II DI water to the beaker up to 800 mL mark on the beaker, stir the sample vigorously, remove the stir rod, and place the sample beaker in an ice water bath or refrigerator for a minimum of thirty minutes or until the precipitate settles completely.

12.7.4 Siphon off the supernatant liquid and discard, saving the precipitate.

12.7.5 Repeat steps 12.7.3 and 12.7.4 two additional times, and proceed to step 12.8 to transfer the reduced precipitate to a centrifuge tube.

12.8 Transfer the precipitate with the aid of 0.1 N sulfuric acid to a 50mL disposable centrifuge tube; centrifuge, and discard the supernatant liquid.

12.8.1 Sample centrifuging compacts the precipitate to the point where it should be possible to completely invert the tube during decanting to remove all of the supernatant chemical solution. When decanting, carefully tilt the tubes until it can be determined that the precipitate is compacted fully then invert the tube to fully decant. Adhere to this requirement for all subsequent decantations from centrifuge tubes.

12.9 Add 25mL EDTA solution to the sulfate precipitate. Vortex vigorously, and heat in a water bath to enhance dissolving of the precipitate. If the precipitate does not readily dissolve, add 10M NaOH solution dropwise. Do not add more than 7 drops of 10M NaOH.

12.9.1 If there is any undissolved material remaining, centrifuge the sample and transfer the solution to a clean disposable centrifuge tube. Submit the supernate solution for NaI detector counting for Ba-133 determination. If the resulting yield is within acceptable limits continue with the analysis. If it is not within the expected limits, combine the supernate and the solid material and reheat.

12.9.2 White precipitate is indicative of sulfate precipitates, and every effort must be made to dissolve as much as possible. Precipitates of any other color are more indicative of solids which may have been present in the sample prior to preparation and can be centrifuged from the sample and discarded in the appropriate waste receptacle.

12.10 To the dissolved sample in EDTA solution, add 1mL strontium-yttrium mixed carrier and stir thoroughly. Add a few drops of 10M NaOH if any precipitate forms.

12.11 Add 1mL $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add 2 mL of acetic acid (glacial), with stirring, until the white precipitate of barium (radium) sulfate has formed. Digest in a hot water bath until the precipitate settles and the solution clears. Centrifuge the sample and discard the supernatant.

12.12 Add 20mL EDTA solution to the sample, vortex vigorously, and heat it until the precipitate dissolves. If needed, add 10M NaOH dropwise to enhance dissolution. Do not add more than 7 drops.

12.13 Repeat steps 12.11 and 12.12 one additional time. **At the conclusion of step 12.12 note the time of the last barium sulfate precipitation. (This is the beginning of the Ac-228 ingrowth).**

12.14 Add 20mL of EDTA solution.

12.15 Add 1.0mL yttrium carrier (9 mg/mL standardized) and 1mL lead carrier (1.5 mg/mL). Vortex the sample and heat in a hot water bath for 10 minutes to ensure equilibrium between the yttrium carrier and the actinium in the solution and to dissolve any precipitate.

12.15.1 If the precipitate does not readily dissolve, add 10M NaOH solution drop wise. Do not add more than 7 drops. Cap the centrifuge tube and vortex to mix then store a minimum of 36 hours to allow complete ingrowth of Ac-228. It is important to note that no precipitate is present at this point.

12.16 Following ingrowth, add 0.3mL $(NH_4)_2S$ and stir well. Add 0.5 mL of 10M NaOH. Cap the tube and vortex until lead sulfide flocks. Wait a minimum of **10 minutes** then centrifuge and decant supernatant into a clean, labeled tube.

12.17 Add 1mL lead carrier (1.5 mg/mL). Add 0.1mL $(NH_4)_2S$ and four drops of 10M NaOH to repeat the precipitation of lead sulfide as before (step 12.1.13). Cap the tube and vortex until lead sulfide flocks. Wait a minimum of **10 minutes** then centrifuge and decant supernatant into a clean tube.

12.18 Filter the supernatant through a 11.0 cm diameter Fisherbrand type Q2 or equivalent filter paper into a clean labeled tube.

12.19 NOTE: It is important to proceed without delay to the final separation and count of the Actinium 228 activity to minimize decay. Optimally, the following steps will take approximately 3 hours to complete.

12.20 Add 5mL 18M NaOH, stir well, and digest in a hot water bath for **12 minutes** until yttrium hydroxide coagulates. Centrifuge samples and decant supernatant into a clean, labeled centrifuge tube. Save the supernatant for Ba-133 yield determination, step 12.33. **(Record the time that the 18M NaOH is added [time of separation]; this is the end of the actinium-228 ingrowth time and beginning of Ac-228 decay time)**.

12.21 To remove residual Ba-133 tracer which can cause erroneously high sample results, add 5 mL of ASTM Type II DI water to each sample, vortex, and centrifuge. Discard the supernate.

12.22 Carefully dissolve the precipitate in 0.5 mL 6N HNO_3. Cap and vortex the samples to ensure dissolution. Add 5mL ASTM Type II DI water. Reprecipitate yttrium hydroxide by adding 3mL 10M NaOH. Heat and stir in a hot water bath

for **12 minutes** until precipitate coagulates. Centrifuge sample and discard supernatant.

12.23 To remove residual hydroxide and Ba-133 tracer, add 5 mL of ASTM Type II DI water to each sample, vortex and centrifuge. Discard the supernate.

12.24 Dissolve the precipitate in 0.25 mL of 1N HNO_3. Cap the tubes and vortex. The samples should be cloudy.

12.25 Remove the caps from the tubes and add 1N HNO_3 dropwise to each sample until the samples are almost clear. Do not add excess, as this will result in fractionation of the Ac-228 from the yttrium carrier, biasing results low. Include a note in the preparation logbook for any samples that do not turn clear.

12.26 Cap the samples, vortex and return them to the hot water bath for **3 minutes**.

12.27 Add 3.5mL of DI and add 2mL 5% ammonium oxalate. Cap and vortex the samples.

12.27.1 The samples should appear “milky” at this step.

12.28 Heat the samples in a hot water bath for **3 minutes**. (Prolonged heating may result in significant dissolution of yttrium oxalate back into solution and reduced yield recovery.) Centrifuge the samples and discard supernate.

12.29 Add 10mL ASTM Type II DI water to the precipitate. Add 6 drops of 1N HNO_3 and 6 drops of 5% ammonium oxalate.

12.30 Vortex vigorously and heat in a hot water bath for **3 minutes**. (Prolonged heating may result in significant dissolution of yttrium oxalate back into solution and reduced yield recovery.) Centrifuge sample and discard supernatant.

12.31 Slurry the oxalate precipitate with 6.6mL of ASTM Type II DI water and transfer quantitatively to a tared, 2-inch stainless steel planchet. Dry under an infrared lamp, cool, and reweigh to determine yttrium recovery.

12.32 To determine Ra-228 (Ac-228) content, count samples in a low-background gas flow proportional counting system as detailed in the instrument SOP, PGH-R-002, “Gas Flow Proportional Counter Operation” current revision. The specific Gas Flow Proportional detectors utilized must have been calibrated following instructions in Section 11 of this SOP.

12.32.1 Following beta counting, perform calculations as detailed in Attachment 1 of this SOP. Note: Due to the short half-life of Ac-228 (6.02 hours), it is imperative to count sources as soon as possible following yttrium hydroxide precipitation as performed in Step 12.20 of this SOP.

12.32.2 The maximum practical count time for achieving the RL of 1.0pCi/L is 600 minutes. Samples which do not meet the RL within 600 minutes may require re-ingrowth or reprep depending on the possible reasons the samples could not meet the RL.

12.33 Barium-133 Yield Assessment

12.33.1 Barium-133 is diluted from a NIST traceable solution. Approximately 2500-3000 dpm is added to each sample. The amount added is based on minimizing the required count time for yield determination while ensuring the tracer does not carryover and contribute extraneous counts during the final sample count by GFPC counting.

12.33.1.1 Dilute the barium solution from step 12.20 to 30mL with ASTM Type II DI water. Cap the tube and shake it to mix the sample thoroughly.

12.33.1.2 Prepare a Ba-133 reference solution by adding a known quantity of barium-133 tracer to a 50mL centrifuge tube. Add 20mL of 0.25M EDTA solution and 5mL 18M NaOH. Dilute to 30mL with ASTM Type II DI water. Cap and shake to mix. (The proportion of the quantity added to the samples in 12.5 and the quantity added to the reference solution must be known in order for the yields to be determined.)

12.33.1.3 Count the reference solution and samples for Ba-133 gamma activity on a sodium iodide detector. Perform Ba-133 yield calculations as detailed in Attachment 1 of this SOP.

12.34 Barium yield by gravimetric assessment (used if Ba-133 is unavailable or for samples suspected to have interference from the use of Ba-133 tracer as indicated in Section 12.5 of this SOP.)

12.34.1 Perform Steps 11.5.4 through 11.5.10 on the solution saved from step 12.20.

12.34.2 Calculate the mass recovered on the planchet and calculate chemical recovery based on the target barium sulfate mass obtained during the barium carrier standardization.

13. Calculations

13.1 Refer to Attachment I of this SOP for Ra-228 associated calculations.

13.2 Any verified result for drinking water that exceeds the maximum contaminant level (MCL) established for (the sum of) Radium 228 and Radium 226 must be reported to the appropriate personnel and agencies according to the specific requirements of the state where the water was sampled. The directions for reporting any results that exceed the MCL limits are documented in the State Drinking Water Emergency Reporting Requirements Binder and Pace SOP PGH-C-025, current revision.

13.2.1 The MCL for radium in drinking water is Ra-226 + Ra-228 ≥5pCi/L OR either Ra-226 OR Ra-228 ≥ 5 pCi/L.

14. Quality Control

14.1 General guidelines for drinking water samples with results that exceed the Maximum Contaminant Level include the following: (All steps are to be conducted as soon as the exceedence has been identified.)

14.1.1 Verify the result(s) to ensure that there were no transcription or calculation errors and that all QC results are within the acceptable limits. Correct any problems and determine the new result. If there were no errors or the result still exceeds the MCL continue with the reporting process.

14.1.2 Immediately notify the Department Manager/Supervisor or specified designee, Department Manager/Supervisor and Quality department that a reportable result has been identified. Use telephone notifications to inform the contact people if the variance is identified after hours along with an e-mail follow up to document the event.

14.1.3 Refer to the State Drinking Water Emergency Reporting Requirements Binder for the state specific information regarding the proper course of action to take. Time is of the essence during this process with some of the state reporting requirements as short as 1 hour from the verification of an exceedence.

14.2 Each analyst who performs this test must satisfactorily complete a Demonstration of Capability Study as documented in Section 3.4 of the most recent revision of the Quality Assurance Manual.

14.2.1 The DOC study results are evaluated against the LCS acceptance limits.

14.2.2 IDOC and DOCs for drinking water methods must be done at a spiking level between the sensitivity level and MCL.

14.3 Daily instrument Quality Control checks for gas flow proportional counter must be completed following the instructions detailed in the SOP for Gas Flow Proportional Counter Operation, PGH-R-002 (current revision).

14.4 See Appendix II for performance indicator evaluation calculations and criteria. Numerical performance indicators may be used to assess QC for non-drinking water samples when the default assessment indicates a QC failure. The numerical performance indicator must be within +/- 3 for all other matrices. The z-score for precision assessment may be used for drinking waters with the approval of the Department Manager/Supervisor using the +/- 2 specification.

14.5 Method Blank (MB)

14.5.1 One MB must be prepared for each analytical batch. The purpose of the MB is to monitor for cross contamination during the analytical process. When available, the MB should be prepared from a similar matrix as samples contained in the analytical batch. If appropriate blank matrix material is not available, ASTM Type II DI water (Reagent Blank) must be carried through the procedure. A reagent blank may be used for sample correction purposes following approval of the Department Manager and affected clients.

14.5.2 The results of the method blank must be less than the reporting limit.

14.5.2.1 If the Method Blank is out of control, individual sample results may still be reportable if results are less than the CRDL (contract required detection limit) or greater than 10 times the blank result. Relative quantities of the sample and blank must be factored when making this determination (raw counts).

14.6 Laboratory Control Sample (LCS)

14.6.1 One LCS must be prepared for each analytical batch.

14.6.2 Typical detection limits are 1 pCi/L for Ra-228.

14.6.3 The Ra-228 spike activity must be between 2 and 10 times the detection limit.

14.6.4 A reference material containing a known concentration of radium-228 radioactivity in the same matrix as the batch is analyzed with the batch.

14.6.4.1 If this material is not available, a well-characterized material (WCM) may be used.

14.6.4.2 If neither of these are available, ASTM Type II DI water may be spiked with the appropriate radium-228 standard.

14.6.5 Calculations of LCS activity include source decay correction to account for decay between the LCS spike solution certificate reference date/time and the LCS sample analysis date/time.

14.6.6 Percent Recovery Calculation

$$\%REC = \frac{(LCSConc)}{TrueValue(decaycorrected)} * 100$$

Where:

LCSConc = Analytical result of the LCS
TrueValue = Known concentration of the LCS

14.6.7 LCS %REC acceptance limits are 60-135%.

14.7 Laboratory Control Sample Duplicate (LCSD)

14.7.1 An LCSD is not required for radium-228 analysis; however analysis of an LCSD must be utilized to measure batch precision whenever adequate sample quantity is not available for sample DUP analysis. The LCSD must be prepared in an identical fashion as the LCS and processed identically as for other samples.

14.7.2 The LCSD must pass the acceptance criteria for the LCS and the criteria established for duplicate precision (RPD 36% or less).

14.7.3 If the LCS and LCSD both pass %REC criteria however fail RPD criteria the batch results may be qualified and reported at the discretion of the analyst with guidance from the department manager.

14.8 Sample Duplicate (DUP)

14.8.1 One Duplicate Sample (DUP) must be randomly assigned within each batch. The purpose of the sample DUP is to measure precision of the analytical process. Laboratory duplicates are not intended to assess precision related to the sample collection process. Sample collection precision can only be assessed through collection of duplicate samples at the time of sample collection. The sample DUP is a duplicate quantity of sample processed identically as other samples in the analytical batch.

14.8.2 For batches with drinking water samples originating from the state of Arizona, Duplicate Samples (DUP) must be randomly assigned within each batch at a frequency of no less than 10%. A batch of 10 samples or fewer must contain at least one duplicate sample. A batch of greater than 10 samples up to 20 samples must contain a minimum of two duplicate samples if the batch contains samples originating from Arizona.

14.8.3 Relative Percent Difference Calculation (RPD)

$$RPD = \frac{|(R1 - R2)|}{(R1 + R2)/2} * 100$$

Where

R1 = Result Sample 1
R2 = Result Sample 2

14.8.4 Duplicate sample RPD acceptance limits are <36% for radium-228.

14.8.5 Sample duplicate criteria cannot be applied if results are below their associated MDC.

14.8.6 Due to the limits for acceptable LCS/LCSD recovery, it is possible to have an acceptable LCS and LCSD, and still not meet the duplicate samples RPD acceptance limit. In this case, if the individual LCS and LCSD recovery criteria are met, the sample data may be reported with narration.

14.9 Sample Matrix Spikes (MS)

14.9.1 Because this analytical method requires the use of carriers or radiotracers for yield determination, PASI's default QC policy is that a sample matrix spike (MS) is not required for radium-228 analysis with the exception of drinking water analysis.

14.9.2 Typical detection limits for Ra-228 are 1 pCi/L. The spike amount must be greater than 10 times the detection limit.

14.9.3 The MS is prepared by spiking a portion of radium-228 radioactivity solution into a portion of one sample in the batch and processing identically as for other samples.

14.9.4 The purpose of the MS is to assess the affect of sample components on the analytical process. The quantity of sample used for the MS must be equivalent to the quantity of sample used for sample analysis.

14.9.5 Calculations of MS activity include source decay correction to account for decay between the spike solution source certificate reference date/time and the MS sample collection date/time.

14.9.6 Percent Recovery Calculation

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue(decaycorrected)} * 100$$

NOTE: The SampleConc is zero (0) for the LCS

14.9.7 MS acceptance limits are 60-127% for radium-228.

14.10 Sample Matrix Spike Duplicates (MSD)

14.10.1 A sample Matrix Spike Duplicate (MSD) is not required for this analysis. When required by the customer/contract, a MSD must be prepared for each analytical batch. The MSD must be prepared as a duplicate of the MS.

14.10.2 The MSD must pass the acceptance criteria established for the MS recovery and the criteria established for duplicate precision.

14.11 PASI's default criteria for carrier and/or tracer yield are 30-110% of the expected value.

14.12 Summary of QC related Activities:

Method Blank	One per Batch
Reagent Blank	One per Batch (as required by client)

Duplicate Sample	One per Batch or a frequency of 10% for batches containing DW samples from Arizona.
Matrix Spike	One per Batch (for drinking waters or as required by client)
Matrix Spike Duplicate	One per Batch (or a frequency of 10% for batches containing DW samples from Arizona.or as required by client)
Laboratory Control Sample	One per Batch
Laboratory Control Sample Dup	One per Batch (in absence of Duplicate sample)

14.13 Corrective Actions for Out-Of-Control Data

14.13.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis and evaluate the usefulness of the data in the final report.

14.13.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.13.3 Matrix Spike Recovery (MS) – MS recoveries that fail high and outside of control criteria with a sample result that is less than the reporting limit may be reported with narration. Additionally, MS recoveries that fail low and outside of control criteria for Drinking Water samples with a sample result that is greater than the MCL must be reported with comment as potentially biased high due to matrix interference. Otherwise, MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and noted in the final report. Matrix effect must be determined by re-analysis of the MS/Sample pair or demonstration of acceptable precision between a MS/MSD pair.

14.13.4 The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.13.5 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.13.6 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.13.7 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.13.8 Laboratory Control Sample Duplicate (LCSD) – If an LCSD does not meet the recovery acceptance criteria, the entire analytical batch must be reanalyzed.

14.13.9 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their reporting limit, and duplicate precision meets the acceptance criteria.

14.13.10 If there is no available sample volume remaining for re-analysis and evaluate the usefulness of the data in the final report. Carrier Recovery: If analysis of samples other than drinking water matrices results in a carrier recovery outside of the default acceptance range, results may be reported with appropriate qualification and approval of the client. If analytical results are reported, they are noted in the case narrative. For all other analyses (including Drinking Water analysis), samples that result in a carrier recovery outside of the default acceptance range must be reanalyzed. If reanalysis results in a carrier recovery outside of the default acceptance range, the results are reported and qualified.

14.13.10.1 Default acceptance limits are 30-110% for gravimetric carriers. Results as high as 130% may be reported with permission of the Department Manager/Supervisor or manager-specified designee.

14.13.11 Tracer Recovery: If analysis of samples other than drinking water matrices results in a tracer recovery outside of the default acceptance range, results may be reported with appropriate qualification and approval of the client. If analytical results are reported, the results are noted in the case narrative. For all other analyses (including Drinking Water analysis), samples that result in a tracer recovery outside of the default acceptance range must be re-analyzed. If re-analysis results in a tracer recovery outside of the default acceptance range, the results are reported, and noted in the case narrative. For Ra-228 analysis using Ba-133 tracer, the uncertainty calculations for yield measurement include a maximum allowable 1 sig. uncertainty of 5% which correlates to 400 net tracer counts. If tracer yield measurement results in the acquisition of less than 400 net tracer counts, the result must be appropriately qualified.

14.13.11.1 Default acceptance limits are 10-110% for radioactive tracers. Results as high as 130% may be reported with permission of the department manager or manager-specified designee.

14.14 Contingencies for handling Out-of-Control or Unacceptable Data

14.14.1 Method Blank (Reagent Blank): If the sample is exhausted, evaluate the usefulness of the data and appropriately qualified and/or narrated.

14.14.2 Duplicates: If the sample is exhausted evaluate the usefulness of the data and appropriately qualified and/or narrated.

14.14.3 Matrix Spike Recovery: If a Matrix Spike Duplicate is analyzed and the spike recoveries are not comparable, and the sample is exhausted, evaluate the usefulness of the data and appropriately qualified and/or narrated.

14.14.4 Matrix Spike Duplicate: If a Matrix Spike Duplicate is analyzed and the spike recovery is not comparable to the Matrix Spike and the sample is

exhausted, evaluate the usefulness of the data and appropriately qualified and/or narrated.

14.14.5 Carrier Recovery: If the sample is exhausted evaluate the usefulness of the data and appropriately qualified and/or narrated.

14.14.6 Tracer Recovery: If the sample is exhausted, evaluate the usefulness of the data and appropriately qualified and/or narrated.

15. Method Performance

15.1 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.2 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.3 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

15.4 Laboratory control samples are analyzed with each batch, the results are charted to monitor control limits and trending.

16. Pollution Prevention and Waste Management

16.1 Place radioactive waste into appropriate receptacles.

16.2 Discard acidified samples and unusable standards into proper waste drains.

16.3 Dispose of waste materials in accordance to type: Non-hazardous, hazardous, non-radioactive, radioactive or mixed.

17. References

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17.2 Eaton, A. D., et. al., editors, Standard Methods for the Examination of Water and Wastewater, 20th Edition, "Radium – Sequential Precipitation Method," Method 7500-Ra D., American Public Health Association, Baltimore, MD, 1998.

17.3 U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW846), Volume 1C, Third Edition, "Radium-228," Method 9320, U. S. Government Printing Office, Washington, D.C., September 1986.

17.4 ASTM E181-93, Standard Test Methods for Detector Calibration and Analysis of Radionuclides, ASTM Standards, Vol. 12.02.

17.5 Table of Radioactive Isotopes, Brown and Firestone, Shirley editor, John Wiley & Sons, 1986.

17.6 Currie, L., Limits for Quantitative Detection and Quantitative Determination, Analytical Chemistry, Vol. 40. No. 3, Pg 586-593, 1968.

17.7 Currie, L., Lower Limit of Detection: Definition and Elaboration of a Proposed Position for Radiological Effluent and Environmental Measurements, NUREG/CR - 4007, USNRC, 1984.

17.8 “American National Standard Calibration and Usage of Alpha/Beta Proportional Counters”, ANSI N42.25-1997.

17.9 "Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)", July 2004, Final.

17.10 "American National Standard Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories", ANSI N42.23-1996.

17.11 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.12 Department of Defense Quality System Manual (DoD QSM) version 4.2 (or most recent version).

17.13 "Manual for the Certification of Laboratories Analyzing Drinking Water" Fifth Edition, January 2005, EPA 815-R-05-004.

17.14 National Primary Interim Drinking Water Regulations (NIPDWR), Part 141.15.

17.15 Pace Pittsburgh SOP, PGH-R-002, current revision, Gas Flow Proportional Instruments Operation.

17.16 Pace SOP PGH-C-025, current revision (MCL Violation Reporting).

17.17 Pace SOP PGH-C-027, current revision (Deionized Water Quality and Suitability).

17.18 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.19 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.20 Pace Analytical Services, LLC. - Pittsburgh Laboratory Quality Assurance Manual, current version.

17.21 SOP PGH-C-032, Support Equipment, current version.

17.22 SOP PGH-Q-038, Laboratory Equipment, current version.

17.23 SOP PGH-Q-040, Internal and External Audits, current version

17.24 SOP PGH-Q-039, Corrective and Preventative Action, current version.

17.25 SOP S-ALL-Q-020, Training, current version,

17.26 SOP S-ALL-Q-028, Lab Track, current version

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Attachment I: Calculations

18.2 Attachment II: Numerical Performance Indicators

19. Method Modifications.

19.1 For routine analysis of aqueous samples, PASI's default process for measuring the quantity of sample to be analyzed is to measure the mass of sample transferred and the mass of sample used is documented in the appropriate logbook. Subsequent calculations for analysis of aqueous samples assume the density of aqueous samples to be 1.0 g/mL. For these samples, analysis results are reported in volume units without density correction.

19.2 EPA method 904.0 specifies the use of 10mL of lead carrier with a concentration of 15 mg/mL, while this procedure uses 1 mL of lead carrier with a concentration of 150 mg/mL. The amount of lead added is equivalent. PASI uses a more

concentrated solution to reduce the chemical reagent footprint within the laboratory.

19.3 EPA method 904.0 specifies the use of 5 mL of Ammonium sulfate, 200mg/mL per liter of sample. This SOP requires the consistent addition of 5 mL of ammonium sulfate, 200mg/mL to samples independent of sample volume.

19.4 For Section 12.8 of this SOP, samples are siphoned and centrifuged to isolate the barium precipitate, whereas, the EPA method 904.0 specifies filtering the sample to collect the precipitate. Sample losses due to this difference are accounted for with the barium yield determination and do not adversely affect sample results.

19.5 In Section 12.21 and 12.23 of this SOP, a rinse of the yttrium hydroxide precipitate using ASTM Type II DI water has been added to enhance removal of residual Ba-133 tracer which could contribute to the beta count rate during sample analysis. Ba-133 tracer is not utilized in EPA method 904.0. Sample losses due to the rinses are accounted for with the yttrium oxalate yield determination and do not adversely affect sample results.

19.6 EPA method 904.0, section 8.13, specifies the addition of 10N NaOH dropwise with vigorous stirring until lead sulfide precipitates, then add 10 drops excess. Pace has quantified the addition of 10N NaOH to 0.5 mL in section 12.16 of this SOP.

19.7 EPA method 904.0, section 8.14, specifies washing the filter with a few mL of DI water. Pace does not rinse the filter. Sample losses due to this difference are accounted for with the barium and yttrium yield determination and do not adversely affect sample results.

19.8 EPA method 904.0 specifies the addition of 2mL of 6N HNO_3 for the second yttrium hydroxide precipitation and 1mL of 1N HNO_3 for the initial yttrium oxalate precipitation. The correlating steps in this procedure have reduced the volumes to 0.5mL of 6N HNO_3 and 0.25mL of 1N HNO_3. The reduction in acid is necessary, due to the ASTM Type II DI water rinses of Sections 12.21 and 12.23. Excessive acidity causes actinium and yttrium to fractionate, creating a chemical disconnect between the analyte (actinium-228) and the carrier (yttrium), contributing to a low bias for analytical results.

19.9 EPA Method 904.0 specifies to use 1,000 mL of sample for analysis. Pace analyzes approximately 800 mL of sample for analysis. All samples are measured by mass as specified within this SOP. Pace further restricts the analysis volume for samples known to contain matrix components that would limit analyte recovery. Pace restricts the analysis volume so as to limit the quantity of waste generated and to enhance productivity. The required detection limit of 1 pCi/L is achieved using a 800 gram analysis quantity.

19.10 EPA Method 904.0 calculations for activity do not show decay correction from the collection of samples to the analysis date of samples. Pace decay corrects Ra-228 results for all samples to the client specified collection date and time. This calculation is defined in Eq 5. of this SOP.

19.11 For the preparation of 0.25M EDTA, EPA Method 904.0 specifies to add sodium hydroxide to DI water then heat prior to adding the solid EDTA for dissolution. The heat generated from the dissolution of sodium hydroxide in water is sufficient to dissolve the EDTA and so, hot-plate heating is not performed.

20. Revisions

Document Number	Reason for Change	Date
PGH-R-003-13	1. Added note at step 12.5.1 to describe process for full decantation of sample in centrifuge tubes. 2. Revised section 12.12 to wait 10 minutes rather than five for lead flocking to occur. 3. Added steps 12.18 and 12.20 to perform a 5mL DI water rinse to remove Ba-133 tracer interference from samples. 4. Revised step 12.19 to use 0.5 mL 6N HNO3 instead of 2.0 mL to prevent fractionation of yttrium due to high acid content 5. Revised step 12.21 to use 0.25 mL of 1N HNO3 and to add dropwise to just slightly cloudy, to prevent fractionation of yttrium due to high acid content. 6. Revised step 12.22 and 12.23 to place samples in the hot water bath for 3 minutes following the addition of 1N HNO3 in following with the EPA written method. 7. Revised step 12.25 and 12.27 to limit the time the yttrium oxalate precipitate is in the hot water bath to 3 minutes to prevent yield losses. 8. Added 14.8.5 to include the ability to report samples results when a LCS/LCSD RPD failure occurs. 9. Modified section 14.5.1 to require approval of the Department Manager for approval to blank correct sample results. 10. Revised section 14 to address default criteria for gravimetric carriers and radioactive tracers. 11. Change wording in section 14 to address non-conformance with LabTracks and also to evaluate data and appropriately qualify or discuss in narrative for reports that do not include a case narrative.	25Apr2012
PGH-R-003-14	1. Updated Cover page, headers/footers for this revision 2. Added Arizona Drinking water batching requirements for Duplicate to Section 14.8.2.	11July2012
PGH-R-003-15	1. Updated Cover Sheet, Headers and Footers. 2. Section 4: Added noted interferences and the step in this SOP where they are addressed. 3. Section 6: Added reference to glossary section of QAM for definitions of terms and added section regarding recording observed measurements, prohibiting weight targeting, and not removing sample from beakers once added. 4. Section 10: Added ASTM Type II DI water preparation and reference, changed all DI water to ASTM Type II DI water throughout document. 5. Section 11: Added calibration frequency requirements, documentation required for removal of calibration points. 6. Section 12: Added comment regarding performing steps and chemical additions in order specified. 7. Section 12.2: Inserted steps to ensure the Ra-228 spike is added to LCS/LCSD samples after the initial sample acidification and prior to any other chemical additions.	23Sep2013

Document Number	Reason for Change	Date
	8. Section 12.3: Inserted to ensure Ra-228 spike additions to the MS are specified to occur prior to all chemical additions. 9. Section 12.5: Added information regarding determining if Ba-133 carryover has occurred and how to proceed. 10. Section 12.7: Added instructions on reducing excess sulfate precipitates due to calcium and sodium interferences. 11. Section 12.9.2: Clarified types of precipitates expected and which need to be dissolved. 12. Section 14: Added criteria for appropriate use of Numerical Performance Indicators. 13. Section 17: Updated references. 14. Section 19: Added comments regarding Pace's default sample measurement technique, density assumptions, and how to use the quantity measurement in the spreadsheet. 15. Attachment II: Updated combined standard uncertainties are assessed at 1 sigma.	
PGH-R-003-16	1. Annual SOP review and update. 2. Section 2.1 – Included reference to standard methods. 3. Section 2.4 – Moved the decay correction application discussion from Section 3 to be consistent with other Pace SOPs. 4. Section 8.1.2 – Added pH verification requirement and recording. 5. Section 8.4 – Added hold time requirement. 6. Section 9 – Added reference for instrument SOP and GFPC instrument components. 7. Section 9.7 and 9.9 – Changed filter paper to current brand and type being utilized by laboratory, added sample planchet dimensions. 8. Section 10 – Included preparation of Na_2CO_3 solution since it is used in calibration process. 9. Section 11.3 – Inserted to specify amount of strontium carrier added to calibration sources when preparing average efficiency calibration (not mass attenuation). 10. Section 11.3.3-11.3.5 – Added source preparation requirements for verification sources and calibration verification acceptance criteria. 11. Section 11.4.1 and 11.5.1 – Inserted comment for when carrier standardization is required. 12. Section 12.1 – Inserted instructions for diluting samples. 13. Section 12.5 – Changed order of chemical addition to match EPA method 904.0, inserted strontium carrier – inadvertently omitted in prior revision. 14. Section 12.9 – changed EDTA amount from 20 mL to 25 mL to match EPA method 904.0. 15. Section 12.33.1 – Included amount of Ba-133 added to samples and comment regarding concentration. 16. Included reference to actual GFPC Pace SOP, PGH-R-	13Jul2014

Document Number	Reason for Change	Date
	002, current rev where instrumentation discussed throughout document. 17. Section 14.12 – Included AZ DW QC requirements for duplicate and MSD. 18. Section 15.3 – Included CDOC requirements. 19. Section 17 – Added GFPC Instrument SOP, PGH-R-002, current revision. 20. Section 19 – Added notable deviations from methods including concentration of lead carrier, siphoning versus filtration, use of Ba-133 and ASTM Type II DI rinses, decreased acid volumes for 6N and 1N HNO_3 additions. 21. Reformatted document.	
PGH-R-003-17	1. Updated Section 4.3 to reference the correct SOP location which addresses Ba-133 carryover and bias. 2. Updated Section 4.4 to reference the correct SOP location which specifies the treatment option for samples generating excess calcium sulfate and sodium sulfate during the initial sample pre-concentration. 3. Section 19 updated to include the analysis volume difference between this SOP and the method, EPA 904.0.	17Dec2015
PGH-R-003-18	1. Section 2.4 – Clarified how decay correction is applied to samples. 2. Section 12.1.1 – Updated to include notating reasons for not using routine samples aliquots. 3. Section 14.6.5 and 14.9.5 – Included to specify how the spike true value for the LCS and MS are decay corrected. 4. Section 19.3 and 19.6 – Updated to include deviations in the amount of 10N NaOH and 200 mg/mL ammonium sulfate added to each sample. 5. Section 19.7 – Deviation for rinsing with filter DI water. 6. Section 19.10 – Added deviation for applying decay correction to sample collection date and time to sample results.	21Dec2016
S-PGH-R-003-rev.19	1. Updated section 8.1.2 samples must be held minimum of 24 hours. 2. Modified section 10.11 to remove the requirement to heat EDTA solution during preparation. Heating is not necessary to prepare the solution. 3. Sections 14.13.3 and 14.13.4 modified to clarify the corrective actions for failed sample matrix spikes and/or sample matrix spike duplicates. 4. Added notation at Section 19.11 to specify non-heating of EDTA solution during preparation as a modification.	08Feb2018

Attachment I – (Calculations)

The **radium-228 concentration** of a sample is calculated according to the following equations:

Eq. 1 $$A = \frac{(S - B)}{(Denom)}$$

Eq. 2 $$Denom = E * V * 2.22 * D * I * C * X * R_A * R_B$$

Eq. 3 $$D = e^{-\lambda t1}$$

Eq. 4 $$C = \frac{(1 - e^{-\lambda t3})}{\lambda t3}$$

Eq. 5 $$X = e^{-\lambda 2t4}$$

Eq. 6 $$I = 1 - e^{-\lambda t2}$$

Eq. 7 $$\lambda = \frac{\ln 2}{T_{1/2}}$$

Eq. 8 $$\lambda 2 = \frac{\ln 2}{T_{1/2Ra}}$$

Eq. 9 $$R_A = \frac{M_Y}{T_Y}$$

Eq. 10 $$R_B = \frac{M_B}{T_B} \text{ OR } R_B = \frac{M_{Ba133}}{T_{Ba133}}$$

Where:

A	=	Ra-228 concentration in pCi/L.
S	=	Sample gross beta count rate (in cpm).
B	=	Background beta count rate (in cpm).
2.22	=	Conversion factor from dpm to pCi.
E	=	Detector efficiency (As determined in Section 11 of this SOP)
V	=	Sample volume (in liters).
D	=	Ac-228 decay factor between initial precipitation and start of count.
I	**=**	**Fractional ingrowth of Ac-228 into the purified radium sample**
C	=	Ac-228 decay factor from beginning of count to midpoint of count.

X	=	Ra-228 decay factor from sample collection date and time to count start date and time.
t1	=	Decay time in hours between final yttrium hydroxide precipitation and midpoint of count time.
t2	=	Ingrowth time in hours between first yttrium hydroxide precipitation and second yttrium hydroxide precipitation.
t3	=	Count time in hours.
t4	=	Decay time in days between the sample collection date and the sample count date.
$T_{1/2}$	=	Half-life of Ac-228 in hours (6.02 hours).
$T_{1/2Ra}$	=	Half-life of Ra-228 in years (5.75 years)
R_A	=	Fractional recovery of yttrium.
R_B	=	Fractional recovery of barium.
M_Y	=	Mass of yttrium oxalate recovered (in mg).
M_B	=	Mass of barium sulfate recovered (in mg).
M_{Ba133}	=	Measured sample Ba-133 Net Cts from the sodium iodide counter yield measurement
T_Y	=	Standardized yttrium carrier conc. (in mg yttrium oxalate per mL of yttrium carrier used)
T_B	=	Standardized barium carrier conc. (in mg barium sulfate per mL of barium carrier used)
T_{Ba133}	=	Measured Net Cts of the reference source for the specific sodium iodide detector used for the sample recovery determination.

The sample specific **counting uncertainty** C.U. is calculated as follows.

Eq. 11 $$C.U. = \frac{1.96 * \sqrt{((S/T_S)+((B/T_B)}}{Denom}$$

Where:

T_S	**=**	***Count time for the sample (in minutes)***
T_B	=	Count time for the background count (in minutes)

S, B, and Denom as previously defined.

As summed background and analyte count rates approach zero, assumptions underlying the uncertainty calculation are violated and it will return an unrealistic value of zero (0) uncertainty when zero summed counts are observed. The following equation provides a more accurate estimate of count uncertainty at zero and near-zero count rates.

Eq. 12 $$ZeroUnc=ZeroActFact/SmplTime$$

Note 1: Depending on sample type and contract requirements the zero activity factor may be either 3.0 or 2.71. PASI's default ZeroActFact is 2.71 consistent with the current version of ANSI N42.23. Bioassay samples must be calculated using 3.0 to be consistent with ANSI N13.30

Note 2: The Zero Count Uncertainty is compared to the count uncertainty above. The larger of the two is used as the counting uncertainty in subsequent total error calculations.

The error term is further evaluated to provide an estimate of total error hereafter referred to as the *Combined Standard Uncertainty* (CSU a.k.a. TPU). The CSU is calculated as follows:

Eq. 13 $$\text{CSU (pCi/U)} = \sqrt{(\text{C.U.})^2 + (UE1 * A)^2 + (UE2 * A)^2 + (UE3 * A)^2 + (UE4 * A)^2}$$

Where:

UE1, UE2, UE3, and UE4 represent partial derivatives estimating the relative uncertainty at the ***95% confidence interval*** for various factors in the activity calculation as follows:

UE1 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with preparation (e.g., sample aliquot or transfers and splits prior to addition and equilibration of tracer).

UE2 represents combined factors estimating routine maximum relative uncertainty (fractional) associated with analysis (e.g., peak integration, peak overlap, tracer contaminants).

UE3 represents combined factors estimating relative uncertainty (fractional) associated with yield correction (e.g., count uncertainty for tracer peak, SRM known value, tracer volume or mass aliquot, tracer equilibration efficiency).

UE4 represents the factor estimating additional uncertainty (activity) associated with an individual sample -- to be used in exceptional circumstances with approval of the Department Manager and appropriate documentation and narration only.

The Minimum Detectable Concentration (MDC) is calculated per guidance of ANSI N42.23 and N13.30 as:

Eq. 14 $$\text{MDC} = \frac{4.65 * \sqrt{B * T_S} + ZeroActFact}{T_S * \text{Denom}}$$

Where:

B, T_S, ZeroActFact, and Denom are as previously defined.

The critical level (Lc) is calculated per guidance of ANSI N42.23 as:

Eq. 15 $$Lc = \frac{1.65 * \sqrt{(\text{B}) * (1/Ts + 1/Tb)}}{Denom}$$

Where:

B, T_s, T_b, *ZeroActFact*, and Denom are as previously defined.

Attachment II - (Numerical Performance Indicators)

1. **Method Blank (MB)**

1.1 The numerical performance indicator for the method blank is calculated by:

$$Z_{Blank} = \frac{x}{u(x)}$$

Where:
x = measured blank activity
u(x) = combined standard uncertainty (1 sigma) in the blank measurement

1.2 MB performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. MB performance indicator values should be recorded on a control chart.

2. **Laboratory Control Sample (LCS)**

2.1 The numerical performance indicator for a laboratory control sample is calculated by:

$$Z_{LCS} = \frac{x - c}{\sqrt{u^2(x) + u^2(c)}}$$

Where:

x = Analytical result of the LCS
c = Known concentration of the LCS
$u^2(x)$ = Combined standard uncertainty (1 sigma) of the result squared.
$u^2(c)$ = Combined standard uncertainty (1 sigma) of the LCS value squared.

2.2 LCS performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. Performance indicator values should be recorded on a control chart.

3. Duplicates (DUP)

3.1 These criteria are applicable for the evaluation of the Duplicate, Matrix Spike Duplicate and Laboratory Control Sample Duplicates.

3.2 The numerical performance indicator for laboratory duplicates is calculated by:

$$Z_{Dup} = \frac{x_1 - x_2}{\sqrt{u^2(x_1) + u^2(x_2)}}$$

Where:
x_1, x_2 = two measured activity concentrations
$u^2(x_1)$, $u^2(x_2)$ = the combined standard uncertainty (1 sigma) of each measurement squared.

3.3 Duplicate sample performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. DUP performance indicator values should be recorded on a control chart for each QC sample type (Dup, MSD, LCSD)

4. **Matrix Spike/Matrix Spike Duplicate (MS/MSD)**

4.1 The numerical performance indicator for a matrix spike sample is calculated by:

$$Z_{MS} = \frac{x - x_0 - c}{\sqrt{u^2(x) + u^2(x_0) + u^2(c)}}$$

Where:
x = Measured concentration of the spiked sample
x_0 = Measured concentration of the unspiked sample
c = Spike concentration added
$u^2(x)$, $u^2(x_0)$, $u^2(c)$ = the squares of the respective combined standard uncertainties (1 sigma) of these values.

MS performance for all matrices is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. MS performance indicator values should be recorded on a control chart.

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QM Approval

Name/Signature	Title	Date	Meaning/Reason
Nasreen Derubeis (009976)	Quality Manager II	20 Dec 2018, 05:43:40 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Penelope Westrick (005649)	Manager - Client Services	20 Dec 2018, 02:06:23 PM	Approved

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to outline the procedures involved with the receipt, login, storage, and disposal of samples received by Pace Analytical Services, LLC, (PASL) Pittsburgh.

2. Summary of Method

2.1. Samples are delivered to the laboratory via several delivery mechanisms. Samples received are checked for adherence to the Sample Acceptance Policy with any discrepancies noted. Discrepancies are communicated to the client for their acknowledgement and decision making.

2.2. The Laboratory Information Management System (LIMS, Epic Pro) assigns all samples with a unique sample number and manages the analyses assigned to each sample.

2.3. Samples are labeled with the appropriate information and staged in refrigerated sample storage coolers if temperature preservation is required or on open shelves for samples not requiring sub-ambient temperature preservation. Samples will remain under these conditions until prepared and/or analyzed.

2.4. Samples and associated sub-samples (digestates, extracts, etc.), with the exception of air cans, are maintained for a minimum of 45 days from receipt of samples unless otherwise requested by the client or other regulatory agency.

2.5. Samples are disposed of in accordance with local laboratory regulatory requirements, waste handling procedures and any USDA regulated soil requirements.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP apply to all personnel involved in the receipt, login, storage, and disposal of samples.

3.2. The Sample Acceptance Policy (Attachment I) contains the guidelines for acceptable sample conditions. Any deviation from these guidelines requires detailed documentation within the final test report (as required by 2009 TNI Standard V1M2 Section 5.8.7.2(b)(ii), usually as a footnote, or on the chain-of-custody (COC), Non-Conformance Form (NCF) or Sample Condition Upon Receipt (SCUR) form. Additionally, clients may be notified by email, phone, or other methods..

3.3. **Parameters**: Not applicable to this SOP.

4. Applicable Matrices

4.1. Not applicable to this SOP.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Samples may be prone to cross-contamination from others within the same delivery group (SDG) or from other client projects. The sample receiving personnel must make every effort to minimize cross-contamination.

6.2. Preservation checks are one of the most likely situations where cross-contamination may occur. Materials used in the process must be specific to each sample and may not used for multiple samples.

6.3. Samples are stored under specific conditions and in specific locations, typically by container type. However, consideration must be given to samples that are uniquely different from others. Samples that

are anticipated to be severely contaminated should be segregated from others in anticipation that the high levels of contaminants may cross-contaminate others in close proximity.

6.3.1. If a sample is identified to be potentially environmentally hazardous by either the client or by sample receiving, the sample(s) are segregated by containing them within a cooler that is clearly marked on the outside with the work order number and the suspected or known contaminant.

6.3.2. When samples arrive at the lab bearing the designation "UN 2910", they are assumed to contain some level of radioactivity until otherwise determined by the lab by the use of a frisker or by gamma spec analysis. Any sample(s) that are determined to be radioactive are stored on shelving away from other samples that have not yet been analyzed. If a sample is determined to have a very high level of radioactivity, it is stored in a designated area. All such samples with known radioactivity levels are clearly marked with a sticker that shows the universal radioactivity symbol.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Acceptable sample preservation, containers, required volumes for tests completed locally, and hold times are listed in Attachment VI of this SOP. They may also be located in the PASL Quality Assurance Manual, the laboratory's method SOPs or in the applicable test method. Samples are stored separately from all standards and reagents and any known highly contaminated samples.

7.2. **NOTE**: To avoid contamination, no food or drink products can be located near the areas where samples are unpacked, labeled, or staged.

7.3. Rad Aqueous Samples: Pace-Pittsburgh provides sample containers with the proper preservatives for each test at no additional cost to the clients who submit samples to the laboratory. Clients who subcontract work to Pace-Pittsburgh will be informed of this option when they arrange for sample analysis. For EPA region 4 work, Pace Pittsburgh provides all the sample containers with proper preservatives; therefore a field blank for sample containers is not required.

7.4. Sample Storage: See Section 12.3 for general storage guidelines.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services LLC. Quality Manual, Glossary Section.

8.2. **Chain of Custody (COC):** a form used to record the field identification of samples collected, analyses requested, date and time of collection, sample preservation used, and traceability of samples from time of collection until delivery to the laboratory. This is a legal document.

8.3. **Laboratory Information Management System (LIMS):** a computer system used to manage the flow and traceability of environmental samples and associated data within the laboratory.

8.4. **Matrix:** the bulk characteristics of a sample. See Table 8.1 below.

8.5. **Non-**Conformance Form (NCF): a form used to record the condition of samples received in the laboratory. This form is used with the 08-09-2018 version of the COC.

8.6. **Safety Data Sheet (SDS):** contains information on chemicals used in the laboratory.

8.7. **Sample Custody:** a sample is considered to be in someone's custody if:

8.7.1. It is in one's physical possession;

8.7.2. It is in someone's view, after being in someone's physical possession;

8.7.3. It is kept in a secured area, restricted to authorized personnel only.

8.8. **SCUR: - Sample Condition Upon Receipt:** a form used to record the condition of samples received in the laboratory. This form is used with client specific COC forms, and the forms that were in place prior to 08-09-2018.

8.9. **Sample Receipt Form (SRF):** form generated by LIMS system after a project is logged in. Contains sample and project information.

8.10. **UN Number:** identification numbers preceded by the letters UN are associated with proper shipping names considered appropriate for international and domestic transportation. These shipping names along with the identification numbers are located in the Federal Register (49CFR172.101).

Table 8.1

NELAC/TNI defined matrix	Corresponding EPIC Pro matrices
Air and Emissions: Whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbant tube, impinger solution, filter, or other device.	Air (AR)
Aqueous: any aqueous sample excluded from the definition of Drinking Water or Saline/Estuarine. Includes surface water, ground water effluents, and TCLP or other extracts.	Water (WT)
Biological tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin. Would include tissue and plant samples.	Tissue (TS) or Tissue Dry (TD)
Chemical Waste: a product or by-product of an industrial process that results in a matrix not previously defined. Includes any non-solid material not classified as waters.	Oil (OL) or Other (OT)
Drinking Water: any aqueous sample that has been designated a potable or potentially potable water source.	Drinking Water (DW)
Non-aqueous liquid: any organic liquid with < 15% settleable solids.	Other (OT)
Saline/Estuarine: any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake.	Water (WT)- not assigned as a separate matrix.
Solids: includes soils, sediments, sludges and other matrices with > 15% settleable solids.	Solid (SL)
(No corresponding matrix to wipes; wipes would be included in with solids). Includes wipe samples or swabs taken to check for surface contamination	Wipe (WP) or Swab (SW)

9. Equipment and Supplies (Including Computer Hardware and Software)

Table 9.1

Equipment/Supplies	Description/ Comments
Sample Labels	
Thermometers	Infrared, digital, NIST traceable
Sample storage cooling units	Capable of holding required storage temperatures
Chain-of-Custody forms	Pace controlled document or client provided form
Sample Condition Upon Receipt (SCUR) Form	Pace controlled document
Non-Conformance Form (NCF)	Pace controlled document
pH Paper	Range 0-14

Equipment/Supplies	Description/ Comments
Label Printer	
LIMS computer system	EPIC Pro
Disposable pipettes	
Sample containers	Pre-cleaned and certified from an approved vendor

10. Reagents and Standards

10.1. All reagents used in this procedure must be labeled with:

10.1.1. Laboratory reagent identification number;

10.1.2. Unless otherwise noted, the name and concentration of the reagent;

10.1.3. Date the reagent was received, opened and, as needed, prepared;

10.1.4. Person preparing reagent;

10.1.5. Expiration date.

10.2. **Reagents: Table 10.1**

Reagent	Formula	Concentration
Sulfuric Acid	H_2SO_4	1:1
Nitric Acid	HNO_3	1:1
Hydrochloric Acid	HCl	1:1
Sodium Hydroxide	NaOH	50% or Pellets
Sodium Thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	Pill
Zinc Acetate Solution (for sulfide)	ZnOAc	1:1
Methanol	MeOH	Purge and Trap Grade
Ascorbic Acid (for cyanide)		
Sodium Bisulfate		
a,a,a-Trifluorotoluene	$C_6H_5CF_3$	2.5mg/L

10.3. For acids, bases and other reagents obtained from other laboratory departments, this information is located in the department reagent preparation log. In the event that these reagents are managed within the Sample Receiving group, the department must maintain its own reagent preparation log.

10.4. Some Pace labs use pre-preserved sample containers. In this case, documentation must be maintained for bottleware and preservation traceability.

11. Calibration and Standardization

11.1. Thermometers, IR-guns, and other equipment used for measuring temperatures must be calibrated according to SOP ENV-SOP-GBUR-0041, Support Equipment, or its equivalent revision or replacement.

11.2. Any maintenance to the equipment including calibration and battery changes must be recorded in the appropriate logbook.

12. Procedure

12.1. **Sample Receipt**

12.1.1. The laboratory receives client samples via three major methods: mail/commercial delivery service, PASL courier/field services and hand delivery.

12.1.2. **Courier COC Procedure**: PASL- Pittsburgh uses courier services that pick up client samples on either a regular schedule or on an as-needed basis as communicated by Project Managers or by the client.

12.1.2.1. When the client is present during courier pick-up, the client signs the chain-of-custody (COC) relinquishing custody to the courier. The courier signs the COC as accepting the samples and provides the client with a copy of the COC. When the courier returns to the lab with the client samples, the courier signs the COC as relinquishing the samples to the lab.

12.1.2.2. If the client is not present during courier pick-up, the courier signs the COC as accepting the samples and leaves a copy of the COC for the client. If a client also has a sample log in use, the courier must sign and date the log when the samples are picked up. When the courier returns to the lab with the client samples, the courier signs the COC as relinquishing the samples to the lab. The date/time of delivery to the lab by the courier is the official date/time received by the lab (analogous to the official date/time of receipt by an outside commercial carrier or courier).

12.1.2.3. To ensure the sample security, the PASL courier locks the vehicle at each client pick-up location, and any time the courier is not inside or in direct sight of the vehicle. IMPORTANT: PASL courier/field services personnel must open the sample coolers and verify there is adequate ice in the coolers before transporting or shipping to the laboratory. An exception to this policy would be for coolers already custody-sealed by the client. These coolers are not to be opened except by the receiving lab personnel.

12.1.2.3.1. If no custody seals are present, the courier checks the cooler to see if there is sufficient ice to keep the samples cool until they are returned to the lab. If there is not sufficient ice present, the courier will add ice and indicate by adding a comment to the COC listing the amount of ice that was added at the time of receipt from the client.

12.1.2.3.2. If the client does not have the samples packed into a cooler, the courier will pack the samples into a cooler and add ice if thermal preservation is required. The courier will note that ice was added at the time of receipt from the client, the amount of ice, and the date and time it was added.

12.1.2.4. The lab must provide pertinent information to the person or persons responsible for taking and transporting samples. This information includes sampling procedures (where applicable), and information on storage and transport of samples, including any information on factors that may influence the test results.

12.1.3. **Lab COC Procedures**: The chain of custody (COC) (see example Attachment I) is signed immediately upon receipt of the samples from the client. If the client drops off the samples or they are picked up by the Pace courier, a copy of the signed COC is given to the client at that time. If samples are received via commercial carrier or mail delivery, the COC should be signed immediately when the cooler or package is opened and ultimately placed in the project file. The delivery date and time is considered the date/time received.

12.1.4. **Samples Dropped Off**: Sample receiving personnel must review the COC for any evidence of rush turnaround requests and analyses with short hold times. Projects that fall under these conditions must be given immediate attention. The project manager responsible for that client must be alerted in the event that they have not already alerted the laboratory to the project as it may be possible that the client did not pre-schedule the project. Once the samples are received and logged into the LIMS, the sample technician and project manager will coordinate the notification and delivery of samples to the laboratory.

12.1.4.1. Internal Chain-of-Custody: If the lab uses an internal chain-of-custody (ICOC) procedure, the Project Manager must determine, prior to log-in, which projects require ICOC processing.

12.1.5. **Sample Acceptance Policy:** Copies of this policy must be provided, in the form of a letter, fax, or e-mail to each client or sampler, as necessary. Samples are considered acceptable if they meet the following criteria listed in the Sample Acceptance Policy (See Attachment IIA):

12.1.5.1. There is proper, full, and complete documentation (e.g., chain-of-custody) including:

12.1.5.1.1. Unique client sample identification. Sample containers are labeled using unique client sample identifications (traceable to the chain-of-custody or other documentation) on durable, waterproof labels or equivalent;

12.1.5.1.2. Location of sampling (site), time and date of sample collection;(COC and containers)

12.1.5.1.3. Sampler's name and signature;

12.1.5.1.4. Preservative used (if any);

12.1.5.1.5. Sample type (matrix);

12.1.5.1.6. Requested analyses;

12.1.5.1.7. Any special analysis requirements.

12.1.5.2. Appropriate sample containers have been used;

12.1.5.3. Holding times have not been exceeded upon receipt (holding times are available in Attachment VI and laboratory SOPs). If they have been exceeded, client permission to proceed and documentation in the final report are required;

12.1.5.4. Adequate sample volume has been received for all tests requested (if not, client permission to proceed is required). For data packages requiring quality control samples to be analyzed on client specific samples, the client must submit adequate sample volume to complete the QC samples as well;

12.1.5.5. When there is insufficient sample to complete the QC samples and the client does not wish to send more sample, or more sample cannot be obtained because of sample volume available or holding time issues, the lack of appropriate volume or mass is noted as a sample acceptance policy deviation on the final report. Batch Quality Control samples will be used in place of project-specific Quality Control samples;

12.1.5.6. Samples that require sub-ambient thermal preservation are considered acceptable if they are within ± 2.0 °C of the required temperature (for samples needing to be at 4.0 °C, the acceptable range is just above freezing to 6.0 °C, as defined by NELAC/TNI). Biological tissue samples are considered acceptable if they are received $\leq$ 0°C. The sample cooler (ice chest) temperature is recorded directly on the COC. Samples received outside of this criterion must have a notation on the COC, Non-Conformance Form (NCF) or Sample Condition Upon Receipt (SCUR) form, and qualified in the final report indicating that the temperature was outside of criteria;

12.1.5.6.1. Samples that are delivered to the lab on the same day they are collected may not meet the requirements of section 12.1.5.6. In these cases, the samples shall be considered acceptable if the samples were received on ice. If samples arrive at temperatures that are outside these requirements, the client will be notified and analysis will NOT proceed unless otherwise directed by the client, or if a holdtime is

close to expiration. Data will be appropriately qualified on the final report:

12.1.5.6.2. If sample analysis is begun within fifteen minutes of collection, thermal preservation is not required.

12.1.5.6.3. Thermal preservation is not required in the field if the laboratory receives and refrigerates the sample within fifteen minutes of collection.

12.1.5.7. Data associated with any deviations from the above sample acceptance policy requirements will be appropriately qualified on the final report.

12.1.6. **Measuring temperature when temperature blank present:** Open the cooler and verify the temperature of the samples by taking the temperature of the cooler as described in section 12.1.7. Do not use the temperature blank.

12.1.7. **Measuring temperature when NO temperature blank present**: Open the cooler and verify the temperature of the samples by, measuring the temperature of representative sample bottles using the infrared (IR) thermometer gun. A representative sample will reflect an "average" condition of the containers in the cooler and, depending on the manner in which they are packed, may not necessarily be in direct contact with the cooling material. The temperature should be measured from 2 to 3 representative containers and averaged. If the containers in a cooler are from more than one client site location, the temperature must be measured for 2 to 3 representative containers from each site or group of samples collected at the same location.

12.1.7.1. **Temperature blanks are not acceptable for samples originating from West Virginia.**

12.1.7.2. **The temperature for samples originating from West Virginia must be verified on every container received. Measure the temperature of every container and note any non-compliance on the COC, NCF or SCUR document. The client must be notified and the non-compliance noted in the analytical section of the final report.**

12.1.7.3. NOTE: When an IR gun is used, the temperature should be measured on an opaque surface such as the bottle label. Measurements taken through a transparent surface (clear or amber glass) may not be reliable and should incorporate a specific temperature correction factor for that surface reading.

12.1.8. Record the uncorrected and corrected cooler temperatures temperature on the COC (example in Attachment I) and/or SCUR (example in Attachment II). In addition, record the type of "ice" used for packing the cooler (e.g., wet ice, "blue ice", gel packs, etc.) on the SCUR.

12.1.9. If samples within a project are spread over multiple coolers and one or more of the coolers are outside of the temperature criteria, then the contents of the cooler must be itemized and the samples and sample containers must be listed on a Cooler Temperature Breakdown form (Attachment IIIA) or NCF or SCUR. Sample containers affected by an out of control temperature must be included as a qualifier in the final report. This itemization must be retained in the project file for future reference.

12.1.10. Unpack the cooler and chain of custody (COC). Organize the samples, grouped by client sample ID, according to the order on the COC. Review COC against samples to make sure the bottles received match the analysis requested. All anomalies must be recorded on the COC, NCF or SCUR form and must be transferred to data qualifiers for the final report.

12.1.10.1. If a cooler will not be unpacked the same day that it is received, at a minimum the temperature of the samples as well as chemical preservation of the sample(s) (if required) must be checked and recorded on the NCF or SCUR. Also, the

presence/absence of ice, packaging material, custody seals, and method of delivery (e.g., Client, Courier, etc.) must be recorded on the COC, NCF or SCUR and must be transferred to data qualifiers on the final report.

12.1.10.2. Discard any ice or water that remains in the cooler and the packing material used to secure the samples. Water or ice should be discarded down a drain that connects to the local sewer. Packing materials should be placed in the garbage. If a sample container has broken, the contents remaining in the cooler MUST be discarded in a manner consistent with the hazardous waste handling standard operating procedure.

12.2. **Screening Rad Aqueous Samples**

12.2.1. Measure the emission rate of aqueous samples being tested for radiochemistry at the time of receipt when samples are unpacked from the cooler.

12.2.2. Using a MicroRem Doserate Meter, set the meter dial to X 0.1.

12.2.3. Pass the meter over or in front of the capped sample containers on any side.

12.2.4. If the meter needle reaches the limit, turn the dial to X1 and rescan the samples.

12.2.5. Document that the samples were scanned on the COC or SCUR. If any sample measures to be greater than 0.5 mrem/hr, place the sample on the shelf dedicated for the samples greater than 0.5 mrem/hr and notify the laboratory RSO or designee. Document on the NCF or SCUR.

12.3. **pH and Residual Chlorine Verification Instructions**

12.3.1. **Preservation must be checked for all sample containers to confirm that each container was correctly chemically preserved or correctly not chemically preserved.**

12.3.2. The pH of all sample bottles must be measured during sample receipt and check in. (see exceptions below in section 12.3.4).

12.3.3. The lot number of the pH paper used must be recorded on the NCF or SCUR in the box marked pH paper lot #.

12.3.4. Open each bottle (except as noted below in section 12.3.4). Do not dip the pH paper into the sample bottle or lid. Use a new disposable pipette, a stirring bar or another inert utensil to withdraw a small portion of the sample. Dispense the aliquot on a sample specific narrow-range pH strip by holding the pH strip over a waste container and allowing the sample to be dispensed on the paper. The sample is not to be allowed to re-enter the sample container after it comes in contact with the pH paper. Verify that the pH meets the requirements for that container type.

12.3.5. NOTE: Do not check the pH of samples for coliform, volatiles, TOC, WI-DRO (Wisconsin), oil and grease, phenolics, or hexane extractables (Method 1664A). These analyses will be checked by the analyst at the bench prior to or following analysis, and should not be opened by sample management personnel.

Table 12.3 – General pH Preservation Requirements by Preservative

Sample Preservatives	Sample pH Requirement
Hydrochloric Acid (HCl)	must be <2
Nitric Acid ($HN0_3$)	must be <2
Sulfuric Acid (H_2SO_4)	must be <2
Sodium Hydroxide (NaOH)	must be >12
Zinc Acetate & Sodium Hydroxide (NaOH)	must be >9
Unpreserved Sample	Unpreserved

12.3.6. If the pH is not within the required range, indicate the anomaly on the NCF, SCUR and/or on the COC and include the anomaly in a data qualifier on the final report. If there is any indication of a problem with a sample's preservation, the client must be contacted for instructions on how to proceed, and the laboratory must keep a record of this as per 2009 TNI standard V1M2 Section 5.8.3. In some cases the client may indicate to proceed despite the deviation, but the results must always be clearly qualified in the final report.

12.3.7. If an unpreserved sample appears to be preserved, the client must be contacted before proceeding with any analyses. The client can resample or instruct the lab to proceed with analysis. The lab must not adjust the pH of the sample. If the lab proceeds with analysis, this deviation must be documented and results qualified appropriately.

12.3.8. If a sample container does not meet the pH preservation required, the pH of the sample must be recorded on the NCF, COC or SCUR, and the anomaly must be reported as a data qualifier in the final report. Contact the Project Manager so that they can contact the client to verify if preservation should be completed at the lab. Additional preservative is added so that the preservative content is <1% of the sample container volume. The sample is mixed and the pH is measured again. The new pH reading is also recorded on the NCF, COC or SCUR along with the amount, type and lot number of the preservative added. In addition, the sample container is marked with the preservative added, volume added, date, time and initials of the technician.

12.3.9. Water samples received for radiochemistry testing by EPA 900 series methods must be preserved within 5 days of collection and held for 24 hours prior to analysis if not preserved in the field during sample collection.

12.3.10. **pH Preservation Adjustments:** Document on the NCF or SCUR if the pH preservation requirements are or are not met. Document that all containers have been checked, and that all containers are in compliance with EPA recommendation. If a sample container does not meet the pH preservation requirement, the pH of the sample must be recorded on the NCF or SCUR. Additional preservative is added so that the preservative content is < 1% of the sample container volume. For example:

A. For a 100mL container, a maximum of 1mL of preservative may be added;

B. For a 250mL container, a maximum of 2.5mL of preservative may be added;

C. For a 500mL container, a maximum of 5mL of preservative may be added;

D. For a 1L container, a maximum of 10mL of preservative may be added

12.3.10.1. The appropriate preservative is added to the sample container, the sample is mixed and the pH is taken again. The new pH reading is also recorded on the COC, NCF or SCUR along with the amount, type and lot number of the preservative added. In addition, the sample container is marked with the preservative added, volume added, date, time and initials of the technician.

12.3.10.2. For Metals analyses specifically, the lab must wait 24 hours after pH adjustment to pH < 2 before sample preparation can begin.

12.3.11. **Total Residual Chlorine Verification** – Total residual chlorine must be verified at the time of receipt or at the bench as required by the method or individual state regulatory agency for certain analyses (see Table 12.3). Sample receipt personnel must only check the sample bottles listed as YES in the check at receipt column.

12.3.11.1. Open the appropriate sample container. Utilizing a new disposable pipette, withdraw a 10 ml (approximate) portion of the sample and transfer it to a small clean container. Dispense an aliquot of DPD reagent into the aliquot of sample. The presence of residual chlorine is indicated by the presence of any pink color. The use of chlorine test strips is prohibited.

12.3.11.2. If any chlorine is detected, regardless of the amount, note the information on the NCF or SCUR, in the final report, and on the container.

12.3.11.3. Notify the laboratory department performing the scheduled test that the container needs to be dechlorinated as soon as practical.

Table 12.3A Analyses Requiring Residual Chlorine Verification

Analyses	Check at Receipt
Ammonia (NH3)	NO
Nitrate (NO3)	NO
Biochemical Oxygen Demand (BOD)	NO
Cyanides	NO
TKN	NO
Dioxin 1613B	NO
DRO by 8015	NO
EDB/DBCP by 8011	NO
PBDE 1614	NO
PCB's 1668A	NO
Volatile Organics (624) (8260) (GRO)	NO
Extractable organics (608) (625) (8081) (8082) (8270)	YES

12.3.12. Note any discrepancies pertaining to samples as defined by the sample acceptance policy detailed above on the COC, NCF or SCUR, and as a qualifier in the final report. Any discrepancies involving temperature, preservation, hold time, collection dates and times, sample volume, sample containers, and unclear requested analyses, must be reported to Project Management as soon as possible.

12.3.13. **Checking for Sulfide in Cyanide analyses:** Testing for sulfide by using the lead acetate paper is done in by the Wet Chemistry department.. Darkening of the paper indicates the presence of sulfide. Refer to laboratory's cyanide SOP ENV-SOP-GBUR-0137.

12.3.14. For short hold samples, the laboratory is notified and the samples are staged per section 12.1.4.

Table 12.3B – Analyses with Hold Times Less Than 72 Hours

Short Hold Time	Analyses	Details
15 minutes	Field Parameters	pH, Dissolved Oxygen, Residual Chlorine, ferrous iron
6 Hours/2 Hours	Total / Fecal Coliform (MPN, MF)	Must be received at lab within 6 hours of sampling. Analysis must begin within 2 hours of receipt.
24 Hours	Hexavalent Chromium	Aqueous Samples Only Field filtered within 15 minutes of collection
30 Hours	Total Coliform (Presence / Absence)	
48 Hours	Color	
48 Hours	MBAS	

Short Hold Time	Analyses	Details
48 Hours	Nitrate (unpreserved)	If Preserved, reported as NO_3+NO_2
48 Hours	Nitrite (unpreserved)	If Preserved, reported as NO_3+NO_2
48 Hours	Ortho –phosphate	Field filtered within 15 minutes of collection
48 Hours	Settable Solids	
48 Hours	Turbidity	
48 Hours	VOA - Soils by Unpreserved EPA5035	Jars, Encores®, Sleeves
48 Hours	Gross Alpha (NJ 48hr method)-waters	EPA NJAC 7:18-6
72 Hours	3030C Metals	
96 Hours	Radon	This parameter is included because travel time to the laboratory shortens the time for analysis to 72 hours.

12.4. **Sample Login**

12.4.1. All samples received by the laboratory must be logged into the LIMS. Rush projects and/or projects with short holds should be logged in first. After these projects have been addressed, projects should be addressed on a first in, first out basis. See table 12.4 for short hold tests.

12.4.2. Samples must be logged into the LIMS so the samples can be uniquely identified (Lab sample identification numbers). These lab sample ID numbers are used to track the prep and analysis activities of the samples, as well as identify the sub-samples, digestates, extracts, and other sample byproducts. This laboratory code maintains an unequivocal link with the unique client field sample ID code assigned to each sample.

12.4.3. Samples are logged into LIMS by using the associated profile and client information provided on the COC or by the Project Manager. Detailed information on the login process in EPIC-PRO can be found in Module 03: Epic Pro - Login Guide.

12.4.4. All samples are logged in with the client ID, collection date and time, received date and time and analysis requested. If a client does not provide a collection date the field is left blank. The project manager will contact the client to confirm a collection date as soon as possible. If the client provides a date but no time, the receiving personnel should enter 00:01 as the most conservative collection time.

12.4.5. For parameters with hold times measured in hours, identification of samples that were collected outside of the receiving laboratory's time zone must be qualified in LIMS and recorded on the NCF or SCUR. This information is used to ensure that hold times are met and that time zone information is taken into consideration.

12.4.6. Each sample is assigned one or more line items of a profile to assign tests to the sample within the LIMS system.

12.4.7. Generate sample labels and Sample Receipt Form (SRF) (see Attachment III).

12.4.8. Review the NCF or SCUR for errors and omissions, and initial the top right box of the SCUR or the bottom right box of the NCF

12.4.8.1. Create the SRF by selecting Systems, Submit Job. Enter the job type LLSRF Login Labels and SRF. Type the requested workorder ID into the Value box for Workorder. Select F10 or the save icon at the top of the screen to send the pdf to the Horizon system for archival. This will also print the sample labels and folder labels at the same time.

12.4.9. Attach the sample labels to the appropriate sample bottles.

12.4.10. Attach the bar code label to the chain of custody..

12.4.11. When labeling the samples, check to see that the IDs, date and time on the labels match the sample bottles. If there is a discrepancy, contact the person logging in the project or the appropriate project manager.

12.4.12. Initial the top right box of the SCUR or the bottom right box of the NCF to indicate the person placing the labels on the bottles.

12.4.13. Scan the chain of custody and NCF or SCUR to the network drive.

12.4.14. The Project Manager must review and verify the following information by comparing the COC to SRF. Some of this information may not be provided by the client and those fields should be left blank:

- Report Recipient,
- Invoice Recipient,
- Additional Report Recipient,
- PO#,
- Project Name,
- Project Number,
- Requested Due Date,
- Sample ID,
- Matrix,
- Collection Date & Time,
- Received Date & Time,
- Analysis: Double check compound lists,
- Price,
- Region Codes,
- Work Region % Split (for Pace internal subcontracted work),
- Has subcontracted work been shipped.
- Containers and preservation

12.4.15. If any samples require analyses performed outside of the laboratory, prepare the samples for subcontracting according to the procedures listed in the SOP describing the subcontracting of analytical services, ENV-SOP-GBUR-0002, Subcontracting Samples and SOP ENV-SOP-GBUR-0050, Evaluation and Qualification of Vendors.

12.5. **Sample Storage**

12.5.1. While awaiting login on the day received, samples may remain in the shipping cooler as received prior to login. Once unpacked, samples will be logged into the LIMS in a timely manner and returned to appropriate storage conditions as soon as possible. For the exceptional case where samples are not logged in the day they were received, they must be stored under appropriate temperature-controlled conditions until login takes place. In all cases, the same temperatures must be taken as soon after receipt as possible and the samples stored so as to maintain the required storage conditions while awaiting log-in.

12.5.2. Once logged into the LIMS and labeled, samples are placed in the appropriate storage areas. Specific temperature requirements are outlined in the analytical methods, but general guidelines are outlined below:

12.5.3. Biological tissue samples are staged by receiving date or project number on shelves in a freezer for all types of analyses.

12.5.4. Summa® canisters and Tedlar® bags are stored on designated shelving at ambient temperature.

12.5.5. Volatiles: Aqueous samples are stored by receiving date or by project number in a segregated volatiles cooler. Associated trip blanks are stored with the samples.

12.5.6. Volatiles: Soil and other solid samples received preserved in methanol are stored by receiving date or by project number in a segregated volatile cooler. Associated trip blanks are stored with the samples.

12.5.7. Volatiles: Soil and other solid samples received preserved with a stir bar, or deionized water and a stir bar, are stored by receiving date or by project number in a segregated volatiles freezer. Associated trip blanks are stored with samples.

12.5.8. Volatiles: Soil and other solid samples received in 4oz containers or similar bottleware must be preserved within 48 hours. In order to preserve these samples, it is necessary to collect a 5g aliquot of the sample and transfer it to a 40mL vial. One of the following preservation options must be utilized:

12.5.8.1. The 5g aliquot is preserved with a stir bar, 10 mL of deionized (DI) water and a stir bar, or 10 mL of sodium bisulfate and a stir bar and stored in a freezer until analysis, or;

12.5.8.2. Within 48 hours of collection in the field, the 5g aliquot must be immediately extracted with 5mL of methanol and stored in a segregated volatiles cooler until analysis, or;

12.5.8.3. Within 48 hours of collection in the field, the 5g aliquot can be preserved with 10mL of deionized water and a stir bar, stored in a segregated volatile cooler and analyzed within 48 hours of collection.

12.5.9. Volatiles: Soil and other solid samples received in Encore samplers should be managed within 48 hours of collection by freezing the Encore or extruding it into a 4 or 8oz jar.

12.5.9.1. If extruding the sample into a 40mL vial containing a stir bar or a stir bar and 10mL of deionized water, then the sample is stored in the segregated volatile freezer until analysis.

12.5.9.2. If extruding the sample into methanol, then the sample is extracted within 48 hours of collection and the sample is stored in a segregated volatile cooler until analysis.

12.5.10. NOTE: If samples are not received within 48 hours of collection or are not received with enough time to process the samples correctly within 48 hours of collection, this must be noted in a way that will be visible on the final report (e.g., footnote in LIMS).

12.5.11. General Chemistry/Semi-volatiles: Waters and other liquid samples are staged by receiving date or by project number on the shelves in the appropriate sample storage cooler.

12.5.12. General Chemistry/Semi-volatiles: Soils and other solid samples are staged by receiving date or by project number on the shelves in the appropriate sample storage cooler.

12.5.13. Metals Solids and Liquids: These samples are staged by receiving date or by project number on designated shelving in the laboratory or appropriate designated area. These samples may be stored at ambient temperature unless Mercury or Hexavalent Chromium analysis is needed. If Mercury or Hexavalent Chromium analysis will be performed, the samples are staged by receiving date or by project number in the appropriate sample storage cooler.

12.5.14. Internal Chain-of-Custody (if required by the client): When an analyst removes samples from a storage unit, the ICOC form must be completed in the applicable ICOC logbook. The following items must be documented: lab sample ID, analyst initials, date and time samples are removed, and sample container type. The project number is optional and only necessary when it is needed to uniquely identify a specific sample container. Once the analyst is finished with the sample, the sample must be returned to the applicable storage unit. The analyst must again document the necessary information in the ICOC logbook (date and time samples are returned to the storage unit and the analyst's initials). If the sample was entirely consumed, then document with the appropriate comment code.

12.5.15. Internal Chain-of-Custody (if required by the client): Similar steps must be taken for sample by-products such as extracts, digestates, and leachates. Once a sample is prepared for analysis, sample custody of the sample by-product must be transferred to the appropriate analytical group sample storage unit. Analytical staff must document in their ICOC logbook when removing and returning the sample by-products from and to the analytical sample storage location. If the sample by-product is entirely consumed during analysis, then document with the appropriate comment code.

12.6. **Sample Retention and Disposal**

12.6.1. Unused portions of samples are retained by the laboratory based on the program or customer requirements for retention and storage. The minimum sample retention time is 45 days from sample receipt. Samples requiring thermal preservation may be stored at ambient temperature when the hold time has expired; the report has been delivered, and/or allowed by the customer, program or contract. Samples requiring storage beyond the minimum sample retention time due to special requests or contractual obligations may be stored at ambient temperature unless the laboratory has sufficient capacity and their presence does not compromise the integrity of other samples.

12.6.2. If samples must be returned to customers, the lab must take special care to ensure that the samples are not damaged during any handling, testing, storing, or transporting processes.

12.6.3. Disposal of Unconsumed Samples: Refer to the laboratory standard operating procedure for waste handling and disposal (ENV-SOP-GBUR-0006).

13. Quality Control

13.1. For any sample received at the laboratory that does not meet the sample acceptance, hold time or preservation criteria, the client must be contacted by project management and advised of the situation.

13.2. If the client instructs the laboratory to proceed with the analysis, all appropriate personnel/departments must be informed and the client approval must be documented on the NCF, SCUR or COC or saved to an electronic file in e-reports. Data will be appropriately qualified in the final report.

13.3. The client may also instruct the laboratory to preserve the samples at the laboratory prior to proceeding with analysis. This must be documented on the COC, NCF or the SCUR or saved to an electronic file in e-reports, and must be qualified in the final laboratory report.

13.4. All supporting documentation related to sample custody must be retained by the laboratory. This includes; memoranda, fax transmissions, all paperwork received with the COC and copies of email transmissions. Documenting Discrepancies during receipt of samples: The following are examples of client discrepancies that must be qualified in the final report.

13.4.1. Lost samples/insufficient sample volume,

13.4.2. Broken or missing bottles,

13.4.3. Missing COC,

13.4.4. Mislabeled bottles,

13.4.5. Preservation error,

13.4.6. Missing sample related details (date, time, sample type).

13.5. PASL sample management discrepancies will be documented on the SCUR form, NCF form, COC or within the project files and noted on the final report. Discrepancies attributable to errors and omissions on the part of the laboratory will be addressed and resolved through the lab's corrective action process.

14 Data Analysis and Calculations

14.1 Not applicable to this SOP.

15 Data Assessment and Acceptance Criteria for Quality Control Measures

15.1 Not applicable to this SOP.

16 Corrective Actions for Out-of-Control Data

16.1 Not applicable to this SOP.

17 Contingencies for Handling Out-of-Control or Unacceptable Data

17.1 Not applicable to this SOP.

18 Method Performance

18.1 All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

19 Method Modifications

19.1 Not applicable to this SOP.

20 Instrument/Equipment Maintenance

20.1 Not applicable to this SOP.

21 Troubleshooting

21.1 Not applicable to this SOP.

22 Safety

22.1 Hazards and Precautions: Use extreme caution in handling samples and wastes as they may be hazardous. Each reagent and chemical used in this method should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats, safety glasses, and ventilation hoods. Safety Data Sheets (SDS) are on file and available to all personnel.

22.2 All personnel involved in sample management are responsible for complying with OSHA and DOT regulations. These regulations pertain to the safe handling and/or shipping of the chemicals specified in this procedure. Refer to the Sample Receiving Supervisor for any questions or concerns related to the safe handling and shipment of hazardous materials.

22.3 Other laboratory safety requirements are contained in the Chemical Hygiene Plan/Safety Manual. Immediate questions can also be addressed with the local Safety Officer.

23 Waste Management

23.1 Refer to the laboratory standard operating procedure for waste handling and disposal (ENV-SOP-GBUR-0006).

24 Pollution Prevention

24.1 Refer to Pace Safety Manual, COR-POL-0021.

25 References

25.1 Department of Defense (DoD) Quality Systems Manual - current approved version.

25.2 SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA, current revision.

25.3 American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1995, Standard Methods for the Examination of Water and Wastewater, A.E. Greenberg, L.W. Clesceri, A.D. Eaton and M.A.H. Franson, eds., 19th ed., American Public Health Association, Washington D.C.

25.4 U.S. Environmental Protection Agency, 1983, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

25.5 U.S. Environmental Protection Agency, 1988, Methods for Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.

25.6 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (current approved revision).

25.7 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current approved version.

25.8 Pace Analytical Services, LLC. - Pittsburgh Laboratory Quality Assurance Manual, current version.

25.9 SOP ENV-SOP-GBUR-0041, Support Equipment, current version.

14.1 SOP ENV-SOP-GBUR-0047, Laboratory Equipment, current version.

14.2 SOP ENV-SOP-GBUR-0049, Internal and External Audits, current version.

14.3 SOP ENV-SOP-GBUR-0048, Corrective and Preventative Action, current version.

14.4 SOP ENV-SOP-GBUR-0059, Training, current version.

14.5 SOP ENV-SOP-CORQ-0007, Lab Track, current version.

15 Tables, Diagrams, Flowcharts, and Validation Data

15.1 Attachment I – Example Chain of Custody Form.

15.2 Attachment II – Example Sample Condition Upon Request (SCUR) Form and Sample Receiving Non-Conformance Form (NCF)

15.3 Attachment IIA - Sample Acceptance Policy

15.4 Attachment III – Example Sample Receipt Form (SRF)

15.5 Attachment IIIA - Example Cooler Temperature Breakdown

15.6 Attachment IV - Epic Container Code Key

15.7 Attachment V - Sample Receipt Form - Epic Container Codes

15.8 Attachment VI Tests, Sample Containers and Required Volumes

14 Revisions

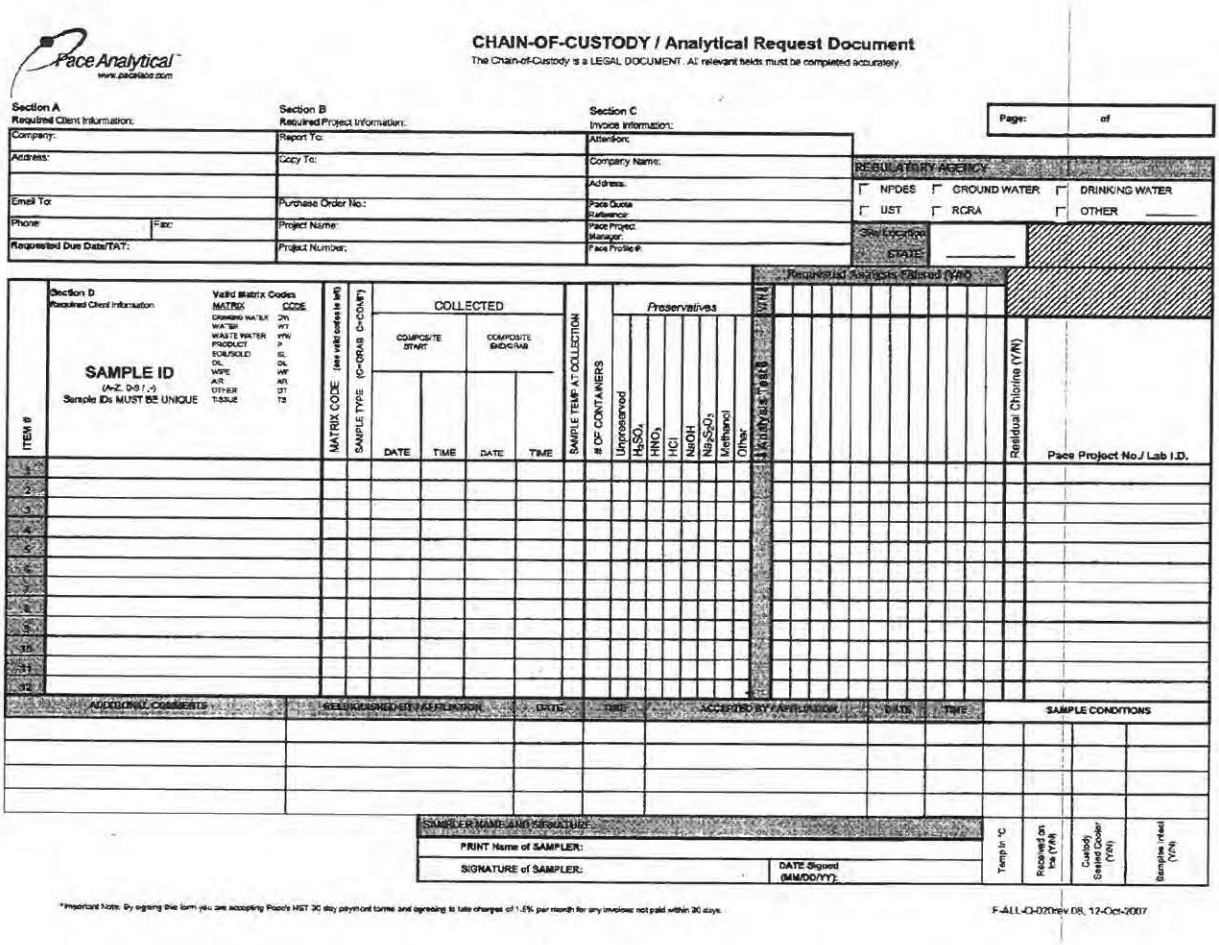
Document Number	Reason for Change	Date
PGH-C-001-4	1. Updated SOP to the new corporate template. Changes to the template are indicated above.	02Apr2013
PGH-C-001-5	1. Added to section 3.2: Any deviation from these guidelines requires detailed documentation within the final test report (as required by 2009 TNI Standard V1M2, Section 5.8.7.2(b) (ii). Additionally, clients may be notified by email, phone, or other methods. 2. Added throughout the SOP that samples received outside the sample acceptance policy are qualified in the final report. 3. Edited for grammar and spelling. 4. Added SOP references.	15Jul2014
PGH-C-001-6	1. Section 12.4 & 12.5 added if required by the client. 2. Updated section 12.6.1 to add sample retention time.	25Nov2015

Document Number	Reason for Change	Date
PGH-C-001-7	1. Section 12.3.3 NOTE: add phenolics. 2. Remove section 12.1.12 and 12.2 Total Residual Chlorine Verification Instructions and Table. 3. Renumber 12.2 thru 12.6. 4. Revised sections 12.4.8 - 12.4.14 to match the current terminology within LIMS, remove printing references. 5. Add 12.4.10. 6. Add 12.4.13. 7. Inserted revised SCUR Attachment II. Updated SCUR to add documentation of Rad aqueous scanning. 8. Add 7.3 Radiochemistry aqueous field blank. 9. Example Cooler Temperature Breakdown Form, C036-1 2June2016 added. 10. The SOP was renumbered through some sections. 11. Updated SOP references.	26Jun2016
PGH-C-001-8	1. Section 7.1 inserted required volumes for tests completed locally. 2. Section 7.3 revised wishes to prefers. 3. Table 9.1 – added Range 0-14. 4. Table 10.2 added ZnOAc. 5. Section 12.1.6 added If the containers in a cooler are from more than one client site location, the temperature must be measured for 2 to 3 representative containers from each site. 6. Add 12.3.1 Preservation must be checked on all sample. containers (see exceptions below). 7. Renumbered 12.3.2 through 12.3.9. 8. Table 12.2 – add Unpreserved samples to be checked. 9. 12.4.14 add Containers and Preservatives. 10. Added: Attachment VIII, Tests, Sample Containers and Required Volumes. 11. Updated the SCUR.	06Dec2016
PGH-C-001-9	1. Add sections 12.1.6.1 and 12.1.6.2 for specific temperature measurement requirements. 2. Renumber and add section 12.3.9 Total Residual Chlorine Verification. 3. Add Table 12.3 Analyses Requiring Residual Chlorine Verification. 4. Added an updated Attachment II.	27Dec2016
PGH-C-001-10	1. Updated and clarified the language in Section 12.3. 2. Corrected section 12.3.2: The pH of <u>all sample</u> bottles must be measured during sample receipt and check in. (see exceptions below in section 12.3.4).	18April2017

Document Number	Reason for Change	Date
PGH-C-001-11	1. Updated to SOT-All-C-001-rev.06. 2. Section 2.5 added USDA regulated soil reference. 3. Section 3.2 added reference to sample acceptance policy, removed TNI reference 4. Section 7.3, updated header to Rad Aqueous samples. Specified for EPA region 4 work, Pace Pittsburgh provides all the sample containers with proper preservatives, therefore a field blank for sample containers is not required. 5. Updated table 8.1 6. Section 12.1.2 added title Courier COC Procedure. 7. Section 12.1.2.3 added: An exception to this policy would be for coolers already custody-sealed by the client. These coolers are not to be opened except by the receiving lab personnel. 8. Added title Lab COC Procedures to section 12.1.3. 9. Added title Samples Dropped off to section 12.14. 10. Removed Table 12.1 and added to section 12.3.13. 11. Corrected section numbers in section 12.1.5.6.1-12.1.5.6.3. 12. Added header title to sections 12.1.6 and 12.1.7. 13. Added to section 12.1.8, recorded uncorrected and corrected temperature. 14. Updated section 12.1.9, use Above Cooler temperature breakdown form or SCUR. 15. Added section 12.3.9, pH Preservation Adjustments. 16. Added section 12.3.13, checking for sulfide in cyanide analyses, done in the Wet Chem department. 17. Added Attachment IIA, Sample Acceptance Policy. 18. Added the updated SCUR form.	19Sep2017
PGH-C-001-12	1. Updated section 12.1.6, do not use the temp blank to take the temperature of the cooler. Referred this section to section 12.1.7 2. Updated section 12.1.7 to use the IR gun to take the temperature of the cooler. Updated the sub sections numbering. 3. Removed references to using jacketed thermometer. Lab always uses IR gun.	10Oct2017
S-PGH-C-001-rev.13	Clarified section 12.3.9: Document on the SCUR if the pH preservation requirements are or are not met. Document that all containers have been checked, and that all containers are in compliance with EPA recommendation. If a sample container does not meet the pH preservation requirement, the pH of the sample must be recorded on the SCUR.	22Dec2017
S-PGH-C-001-rev.14	1. Section 12.3.3 updated to include documentation of the pH paper lot number on the SCUR. 2. SCUR updated to include space to document the pH lot number.	01Mar2018

Document Number	Reason for Change	Date
ENV-SOP-GBUR-0001 Rev.01	1. Updated all references to the SCUR document to include a reference to the Pace Non-Conformance Form (NCF). 2. Added definition for Non-Conformance Form and descriptions of when the SCUR and NCR are used. 3. 7.3 correct punctuation after preservatives. 4. Added NCF to Equipment and Supplies Table 9.1 5. 12.4.8 and 12.4.12, added "the bottom right box of the NCF" 6. 12.4.15 added Subcontracting Samples SOP reference.	20Dec2018

Attachment I – Example Chain-of-Custody Form



Pace Analytical
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CHAIN-OF-CUSTODY / Analytical Request Document
The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately.

Page: of

Section A Required Client Information:
Company:
Address:
Email To:
Phone: Fax:
Requested Due Date/TAT:

Section B Required Project Information:
Report To:
Copy To:
Purchase Order No.:
Project Name:
Project Number:

Section C Invoice Information:
Attention:
Company Name:
Address:
Pace Quote Reference:
Pace Project Manager:
Pace Profile #:

REGULATORY AGENCY:
☐ NPDES ☐ GROUND WATER ☐ DRINKING WATER
☐ UST ☐ RCRA ☐ OTHER
Site Location: STATE:

Section D Required Client Information

Valid Matrix Codes

MATRIX	CODE
Drinking WATER	DW
WATER	WT
WASTE WATER	WW
PRODUCT	P
SOIL/SOLID	SL
OIL	OL
WIPE	WP
AIR	AR
OTHER	OT
TISSUE	TS

SAMPLE ID
(A-Z, 0-9 / ,-)
Sample IDs MUST BE UNIQUE

ITEM #	MATRIX CODE (see valid codes to left)	SAMPLE TYPE (G=GRAB C=COMP)	COLLECTED: COMPOSITE START DATE	COLLECTED: COMPOSITE START TIME	COLLECTED: COMPOSITE END/GRAB DATE	COLLECTED: COMPOSITE END/GRAB TIME	SAMPLE TEMP AT COLLECTION	# OF CONTAINERS	Preservatives: Unpreserved	H_2SO_4	HNO_3	HCl	NaOH	$Na_2S_2O_3$	Methanol	Other	Analyses Test	Requested Analyses Filtered (Y/N)	Residual Chlorine (Y/N)	Pace Project No./ Lab I.D.
1																				
2																				
3																				
4																				
5																				
6																				
7																				
8																				
9																				
10																				
11																				
12																				

ADDITIONAL COMMENTS	RELINQUISHED BY / AFFILIATION	DATE	TIME	ACCEPTED BY / AFFILIATION	DATE	TIME	SAMPLE CONDITIONS			

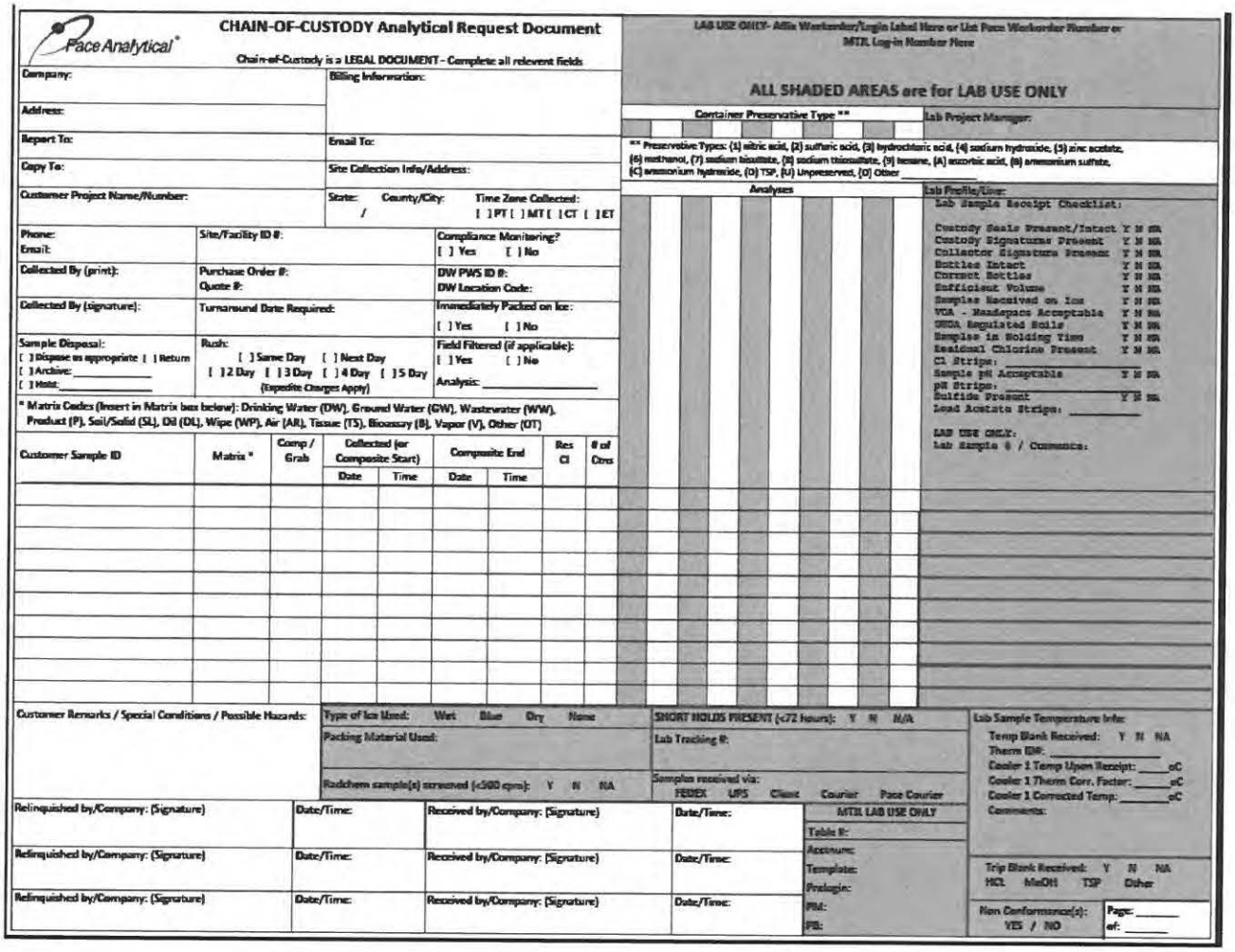
SAMPLER NAME AND SIGNATURE
PRINT Name of SAMPLER:
SIGNATURE of SAMPLER: DATE Signed (MM/DD/YY):

Temp in °C | Received on Ice (Y/N) | Custody Sealed Cooler (Y/N) | Samples Intact (Y/N)

*Important Note: By signing this form you are accepting Pace's NET 30 day payment terms and agreeing to late charges of 1.5% per month for any invoices not paid within 30 days.

F-ALL-Q-020rev.08, 12-Oct-2007

Attachment I – Example Pace Analytical Services LLC Chain of Custody 08-09-2018



Pace Analytical®

CHAIN-OF-CUSTODY Analytical Request Document

Chain-of-Custody is a LEGAL DOCUMENT - Complete all relevant fields

LAB USE ONLY- Affix Workorder/Login Label Here or List Pace Workorder Number or MTJL Log-in Number Here

ALL SHADED AREAS are for LAB USE ONLY

Company: | Billing Information: | Container Preservative Type ** | Lab Project Manager:

Address:

Report To: | Email To:

Copy To: | Site Collection Info/Address:

** Preservative Types: (1) nitric acid, (2) sulfuric acid, (3) hydrochloric acid, (4) sodium hydroxide, (5) zinc acetate, (6) methanol, (7) sodium bisulfate, (8) sodium thiosulfate, (9) hexane, (A) ascorbic acid, (B) ammonium sulfate, (C) ammonium hydroxide, (D) TSP, (U) Unpreserved, (O) Other _____

Customer Project Name/Number: | State: / County/City: | Time Zone Collected: [ ] PT [ ] MT [ ] CT [ ] ET

Analyses

Phone: / Email: | Site/Facility ID #: | Compliance Monitoring? [ ] Yes [ ] No

Collected By (print): | Purchase Order #: / Quote #: | DW PWS ID #: / DW Location Code:

Collected By (signature): | Turnaround Date Required: | Immediately Packed on Ice: [ ] Yes [ ] No

Sample Disposal: [ ] Dispose as appropriate [ ] Return [ ] Archive: _____ [ ] Hold: _____

Rush: [ ] Same Day [ ] Next Day [ ] 2 Day [ ] 3 Day [ ] 4 Day [ ] 5 Day (Expedite Charges Apply)

Field Filtered (if applicable): [ ] Yes [ ] No Analysis: _____

Lab Profile/Line:

Lab Sample Receipt Checklist:

Custody Seals Present/Intact Y N NA
Custody Signatures Present Y N NA
Collector Signature Present Y N NA
Bottles Intact Y N NA
Correct Bottles Y N NA
Sufficient Volume Y N NA
Samples Received on Ice Y N NA
VOA - Headspace Acceptable Y N NA
USDA Regulated Soils Y N NA
Samples in Holding Time Y N NA
Residual Chlorine Present Y N NA
Cl Strips: _____
Sample pH Acceptable Y N NA
pH Strips: _____
Sulfide Present Y N NA
Lead Acetate Strips: _____

LAB USE ONLY:
Lab Sample # / Comments:

* Matrix Codes (Insert in Matrix box below): Drinking Water (DW), Ground Water (GW), Wastewater (WW), Product (P), Soil/Solid (SL), Oil (OL), Wipe (WP), Air (AR), Tissue (TS), Bioassay (B), Vapor (V), Other (OT)

Customer Sample ID	Matrix *	Comp / Grab	Collected (or Composite Start) Date	Collected (or Composite Start) Time	Composite End Date	Composite End Time	Res Cl	# of Ctnrs

Customer Remarks / Special Conditions / Possible Hazards: | Type of Ice Used: Wet Blue Dry None | Packing Material Used: | Radchem sample(s) screened (<500 cpm): Y N NA | SHORT HOLDS PRESENT (<72 hours): Y N N/A | Lab Tracking #: | Samples received via: FEDEX UPS Client Courier Pace Courier

Lab Sample Temperature Info:
Temp Blank Received: Y N NA
Therm ID#: _____
Cooler 1 Temp Upon Receipt: ____oC
Cooler 1 Therm Corr. Factor: ____oC
Cooler 1 Corrected Temp: ____oC
Comments:

Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:
Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:
Relinquished by/Company: (Signature)	Date/Time:	Received by/Company: (Signature)	Date/Time:

MTJL LAB USE ONLY
Table #:
Acctnum:
Template:
Prelogin:
PM:
PB:

Trip Blank Received: Y N NA
HCL MeOH TSP Other

Non Conformance(s): YES / NO

Page: _____ of: _____

Attachment II – Example Sample Condition Upon Request Form

Pittsburgh Lab Sample Condition Upon Receipt

Pace Analytical **Client Name:** _____ **Project #** _____

Courier: ☐ Fed Ex ☐ UPS ☐ USPS ☐ Client ☐ Commercial ☐ Pace Other _____ **Label** _____

Tracking #: _____ **LIMS Login**

Custody Seal on Cooler/Box Present: ☐ yes ☐ no Seals intact: ☐ yes ☐ no

Thermometer Used _____ **Type of Ice:** Wet Blue None

Cooler Temperature **Observed Temp** _____ °C Correction Factor: _____ °C Final Temp: _____ °C

Temp should be above freezing to 6°C

Comments:	Yes	No	N/A	pH paper Lot#	Date and Initials of person examining contents:
Chain of Custody Present:				1.	
Chain of Custody Filled Out:				2.	
Chain of Custody Relinquished:				3.	
Sampler Name & Signature on COC:				4.	
Sample Labels match COC:				5.	
-Includes date/time/ID Matrix:					
Samples Arrived within Hold Time:				6.	
Short Hold Time Analysis (<72hr remaining):				7.	
Rush Turn Around Time Requested:				8.	
Sufficient Volume:				9.	
Correct Containers Used:				10.	
-Pace Containers Used:					
Containers Intact:				11.	
Orthophosphate field filtered				12.	
Hex Cr Aqueous Compliance/NPDES sample field filtered				13.	
Organic Samples checked for dechlorination:				14.	
Filtered volume received for Dissolved tests				15.	
All containers have been checked for preservation.				16.	
All containers needing preservation are found to be in compliance with EPA recommendation.					
exceptions: VOA, coliform, TOC, O&G, Phenolics				Initial when completed	Date/time of preservation
				Lot # of added preservative	
Headspace in VOA Vials (>6mm):				17.	
Trip Blank Present:				18.	
Trip Blank Custody Seals Present					
Rad Aqueous Samples Screened > 0.5 mrem/hr				Initial when completed:	Date:

Client Notification/ Resolution:

Person Contacted: _____ Date/Time: _____ Contacted By: _____

Comments/ Resolution: _____

☐ **A check in this box indicates that additional information has been stored in ereports.**

Note: Whenever there is a discrepancy affecting North Carolina compliance samples, a copy of this form will be sent to the North Carolina DEHNR Certification Office (i.e. out of hold, incorrect preservative, out of temp, incorrect containers)

***PM review** is documented electronically in LIMS. When the Project Manager closes the SRF Review schedule in LIMS. The review is in the Status section of the Workorder Edit Screen.

J:\QAQC\Master\Document Management\Sample Mgt\Sample Condition Upon Receipt Pittsburgh (C056-7 16Feb2018)

Attachment II – Example Sample Receiving Non-Conformance Form (NCF)

Pace Analytical

Sample Receiving Non-Conformance Form (NCF)

Date:	Evaluated by:	Affix Workorder/Login Label Here or List Pace Workorder Number or MTJL Log-in Number Here
Client:		

1. If Chain-of-Custody (COC) is not received: contact client and if necessary, fill out a COC and indicate that it was filled out by lab personnel. Note issues on this NCF.

2. If COC is incomplete, check applicable issues below and add details where appropriate:

☐ Collection date/time missing or incorrect	☐ Analyses or analytes: missing or clarification needed	☐ Samples listed on COC do not match samples received (missing, additional, etc.)
☐ Sample IDs on COC do not match sample labels	☐ Required trip blanks were not received	☐ Required signatures are missing

Comments/Details/Other issues not listed above:

3. Sample integrity issues: check applicable issues below and add details where appropriate:

☐ Samples: Past holding time	☐ Samples: Condition needs to be brought to lab personnel's attention (details below)	☐ Preservation: Improper
☐ Samples: Not field filtered	☐ Containers: Broken or compromised	☐ Temperature: not within acceptance criteria (typically 0-6C)
☐ Samples: Insufficient volume received	☐ Containers: Incorrect	☐ Temperature: Samples arrived frozen
☐ Samples: Cooler damaged or compromised	☐ Custody Seals: Missing or compromised on samples, trip blanks or coolers	☐ Vials received with improper headspace
☐ Samples: contain chlorine or sulfides	☐ Packing Material: Insufficient/improper	☐ Other:

Comments/Details:

4. If Samples not preserved properly and Sample Receiving adjusts pH, add details below:

Sample ID:	Date/Time:	Amount/type pres added:
Preserved by:	Initial and Final pH:	Lot # of pres added:
Sample ID:	Date/Time:	Amount/type pres added:
Preserved by:	Initial and Final pH:	Lot # of pres added:
Sample ID:	Date/Time:	Amount/type pres added:
Preserved by:	Initial and Final pH:	Lot # of pres added:

5. Client Contact: If client is contacted for any issue listed above, fill in details below:

Client:	Contacted per:	
PM Initials:	Date/Time:	

Client Comments/Instructions:

F-ALL-C-011-rev.00, 05Jul2018

Attachment IIA – Sample Acceptance Policy (from F-ALL-C-006)

In accordance with regulatory guidelines, Pace Analytical facilities comply with the following sample acceptance policy for all samples received.

If the samples do not meet the sample receipt acceptance criteria outlined below, the Pace facility is required to document all non-compliances, contact the client, and either reject the samples or fully document any decisions to proceed with analyses of samples that do not meet these criteria. Any results reported from samples not meeting these criteria are appropriately qualified on the final report.

Sample Acceptance Policy requirements:

1. Sample containers must have unique client identification designations, and dates and times of collection, that are clearly marked with indelible ink on durable, water-resistant labels. The client identifications must match those on the chain-of-custody (COC);
2. There must be clear documentation on the COC, or related documents such as the Sample Condition Upon Receipt (SCUR) form, that lists the unique sample identification, sampling site location (including state; some regulations may require city, county, etc.), date and time of sample collection, and name and signature of the sample collector;
3. There must be clear documentation on the COC, or related documents, that lists the requested analyses, the preservatives used, sample matrix, and any special remarks concerning the samples (i.e., data deliverables, samples are for evidentiary purposes, field filtration, etc.);
4. Samples must be in appropriate sample containers. If the sample containers show signs of damage (i.e., broken or leaking) or if the samples show signs of contamination, the samples will not be processed without prior client approval;
5. Samples must be correctly preserved upon receipt, unless the method requested allows for laboratory preservation. If the samples are received with inadequate preservation, and the samples cannot be preserved by the lab appropriately, the samples will not be processed without prior client approval;
6. Samples must be received within required holding time. Any samples with hold times that are exceeded will not be processed without prior client approval;
7. Samples must be received with sufficient sample volume or weight to proceed with the analytical testing. If insufficient sample volume or weight is received, analysis will not proceed without client approval;
8. All samples that require thermal preservation are considered acceptable if they are received at a temperature within 2°C of the required temperature, or within the method-specified range. For samples with a required temperature of 4°C, samples with a temperature ranging from just above freezing to 6°C are acceptable. Samples that are delivered to the lab on the same day they are collected are considered acceptable if the samples are received on ice. Any samples that are not received at the required temperature will not be processed without prior client approval.
9. For all compliance **drinking water** samples, analyses will be rejected at the time of receipt if they are not received in a secure manner, are received in inappropriate containers, are received outside the required temperature range, are received outside the recognized holding time, are received with inadequate identification on sample containers or COC, or are improperly preserved (with the exception of VOA samples- tested for pH at time of analysis and TOC- tested for pH in the field).
10. Some specific clients may require custody seals. **For these clients**, samples or coolers that are not received with the proper custody seals will not be processed without prior client approval.

Attachment III – Example Sample Receipt Form

Sample Receipt Form

Pace Analytical Services, Inc.
Indiana

Pace Analytical
www.pacelabs.com

Sample Acknowledgement Recipients:

Email:

Bill to:

Final Report Recipients:

Line Item Descriptions:
(4) Water Short VOC

Client P O No:
Phone: 1(317)875-5894
Project Manager: Phaedra Zucksworth
Client Project ID:

Lab Project No: 5018684
Project Deliverables Type: Standard Report
Project Report Due Date: 09/25/08
Profile: 907

Lab Smp ID: 5018684001 **Client Smp ID: RW-3:G090908** Collected Date: 09/09/08 11:25
Proj Smp No: 1 Matrix: Water Smp Type: PS Line Item: 4 Received Date: 09/11/08 10:19
Location: OH BUSTR

Auxillary Data:

Consultant Project Number:	NA	ENFOS Project (AAAAA-0000):	
Site ID/Facility Number:		Phase:	01
Gem Portfolio:	CENTRAL	SubPhase/Task:	03
State of Sample Collection:	OH	Cost Element:	05
Consultant Name:	URS	RCOP:	no
Rush Charges:	0		

PARAMETER	METHOD	UNIT PRICE	WR	SPL	%
8260 WUST - 8260 MSV UST	EPA 8260	$27.00			

COMPOUND	PQL	UNITS
Benzene	5	ug/L
Ethylbenzene	5	ug/L
Methyl-tert-butyl ether	4	ug/L
Toluene	5	ug/L
Xylene (Total)	10	ug/L

Sub Total - Sample 208364 $27.00

Lab Smp ID: 5018684002 **Client Smp ID: RW-4:G090908** Collected Date: 09/09/08 11:00
Proj Smp No: 2 Matrix: Water Smp Type: PS Line Item: 4 Received Date: 09/11/08 10:19
Location: OH BUSTR

PARAMETER	METHOD	UNIT PRICE	WR	SPL	%
8260 WUST - 8260 MSV UST	EPA 8260	$27.00			

COMPOUND	PQL	UNITS
Benzene	5	ug/L
Ethylbenzene	5	ug/L
Methyl-tert-butyl ether	4	ug/L
Toluene	5	ug/L
Xylene (Total)	10	ug/L

Thursday, September 11, 2008 11:43:27 AM Page 1 of 11

Attachment IIIA - Example Cooler Temperature Breakdown Form

Pace Pittsburgh Laboratory

Temperature Cooler Breakdown

	Glass Jar 1L	Glass Jar 500mL	Glass Jar 250 mL	Glass Jar 120mL	Soil Kit	Chem 1-liter	Chem 500 ml	Chem 250	Organics	Nutrient 250	Nutrient 500	Phenolics	TOC	TOX	Total metals 250	Dissolved Metals 250	O&G	VOA	Cyanide	Sulfide	Bacteria	Wipes/swipe/smear/filter	Radchem	Cubitainer	Ziploc	Other

Cooler ID	Temp	Ice present Y/N

Comments

Initials _____

J:\QAQC\Master\Document Management\Sample Mgt\Cooler Temp Breakdown checksheet (C036-1 2June2016)

Attachment IV
EPIC Container Code Key

First Char	type
A	Amber
B	Borosilicate (clear)
C	Cassettes
D	VOA-water
E	Extract
F	Filter
G	Gallon
I	Wipe/Swab
J	Jar
K	Kit
M	Media
N	None
P	Polyurethane foam
R	Terra core
S	nondescript
T	nondescript
U	Summa
V	VOA-soil
W	wide mouth jar
X	XAD trap
Z	Ziploc

Second Char	material
G	Glass
P	Plastic
T	Tube
C	Cubitainer
N	General
S	Septa

Third Char	size
1	1 liter
2	500 nml
3	250 ml
5	120 ml
9	40 ml
F	4 oz

Fourth Char	preservative	
H	HCl	Hydrochloric acid
S	H2SO4	Sulfuric acid
T	NaThiosulfate	Sodium Thiosulfate
U	Unpreserved	Unpreserved
A	Ascorbic Acid	Ascorbic Acid
Z	Zn Acetate	Zinc Acetate
B	NaBisulfite	Sodium Bisulfite
0	NaOH	Sodium Hydrozide
N	HNO3	Nitric acid
M	MeOH	Methanol
X	Hexane	Hexane
W	Preweighed	Preweighed
C	Mea2	Methylene chloride
P	TSP	Trisodium phosphate

Wildcards	
AF	Air Filter
BTBE	Brass Tube
C	Air cassettes
DIG	Lab Digestate Container
EXT	Lab Extract Container
EZH	25g Encore
EZI	5g Encore
F	Large Air Filter
GCUB	1 Gallon Cubitainer
GJ	1Gallon Jug
GN	General Unpreserved
GNHC	General preserved with HCL
GNN	General preserved with Nitric Acid
I	Wipe/Swab
KE	Endotoxin kit
KL	Legionella kit
M	Plate media
NONE	No Container Needed
PUF	Polyurethane Foam
R	Terra core
STBE	Shelby Tube
T	Tedlar Bag
TCLP	Kit for Standard TCLP analysis
U	Summa Can
VSG	Headspace septa vial & HCl
VSGU	20mL scintillation vial
WK	WhirlPak Bag
XAD	XAD Trap
ZPLC	Ziploc Bag

Attachment IV
Common EPIC Container Codes

Contianer Code	Description
AF	Air Filter
AGIN	1L amber glass HCl
AG1S	1L amber glass H2SO4
AGIT	1L amber glass Na Thiosulfate
AG1U	1L amber glass unpreserved
AG2N	500mL amber glass HNO3
AG2S	500mL amber glass H2504
AG2U	500mL amber glass unpreserved
AG3S	250mL amber glass H2504
AG3U	250mL amber glass unpreserved
BG1H	1L clear glass HCl
BG1S	1L clear glass H2504
BG1T	1L clear glass Na Thiosulfate
BG1U	1L clear glass unpreserved
BP1A	1L plastic NAOH, Asc Acid
BP1N	1L plastic HNO3
BP1S	1L plastic H2504
BP1U	1L plastic unpreserved
BP1Z	1L plastic NaOH, Zn Ac
BP2A	500mL plastic Na0H,Asc Acid
BP2N	500mL plastic HNO3
BP2O	500mL plasitc NaOH
BP2S	500mL plastic H2SO4
BP2U	500mL plastic unpreserved
BP2Z	500mL plastic NaOH, Zn Ac
BP3A	250mL plastic Na0H, Asc Acid
BP3C	250m1 plastic NAOH
BP3N	250mL plastic HNO3
BP3S	250mL plastic H2804
BP3U	250mL plastic unpreserved
BP3Z	250mL plastic NaOH, Zn Ac
BTBE	Brass Tube
C	Air cassettes
DG9B	40mL amber VOA vial Na Bisulfate
DG9H	40mL amber VOA vial NCI
DG9M	40mL clear VOA vial Me0H
DG9P	40mL amber VOA vial TSP
DG9S	40mL amber VOA vial H2504
DG9T	40mL amber VOA vial Na Thio
DG9U	40mL amber VOA vial
DIG	Lab Digestate Container
EXT	Lab Extract Container
EZH	25g Encore
EZI	5g Encore

Contianer Code	Description
F	Large Air Filter
GCUB	1 Gallon Cubitainer
GJ	1Gallon Jug
GN	General Unpreserved
GNHC	General preserved with HCL
GNN	General preserved with Nitric Acid
I	Wipe/Swab
JGFM	4oz amber wide jar Me0H
JGFS	4oz amber wide jar H2SO4
JGFU	4oz amber wide jar
KE	Endotoxin kit
KL	Legionella kit
M	Plate media
NONE	No Container Needed
PUF	Polyurethane Foam
R	Terra core
SPST	120mL Coliform Na Thiosulfate
STBE	Shelby Tube
T	Tedlar Bag
TCLP	Kit for Standard TCLP analysis
U	Summa Can
VG9H	40mL clear VOA vial HCl
VG9T	40mL clear VOA vial Na Thiosulfate
VG9U	40mL clear VOA vial
VG9W	40mL glass VOA vial preweighted (EPA 5035)
VSG	Headspace septa vial & HCl
VSGU	20mL scintillation vial
WGFC	4oz wide jar and wipe with MeCl
WGFU	4oz wide jar unpreserved
WGFX	4oz wide jar and wipe Hexane
WGKU	8oz wide jar unpreserved
WK	WhirlPak Bag
WPDU	16oz clear wide mouth jar
XAD	XAD Trap
ZPLC	Ziploc Bag

Attachment V
Sample Receipt Form - EPIC Container Codes

Example of multiple containers for the same analysis on the same sample. 1/3, 2/3 and 3/3 indicate 3 samples each uniquely identified. This also appears on the labels applied to the samples.

Sample Receipt Form

Pace Analytical Services, Inc.
Pittsburgh

Containers

Lab ID	Container ID	Type	Location	Preservative	Utilization
3017[redacted]001	3017[redacted]001 AG1U1/1	AG1U		NA	8082 W
	3017[redacted]001 BP3N1/1	BP3N		NA	6010 WD,7470 WD
	3017[redacted]001 VG9H1/3	VG9H		NA	8260 W
	3017[redacted]001 VG9H2/3	VG9H		NA	SI-34MSV
	3017[redacted]001 VG9H3/3	VG9H		NA	
3017[redacted]002	3017[redacted]002 AG1U1/1	AG1U		NA	8082 W
	3017[redacted]002 BP3N1/1	BP3N		NA	6010 WD,7470 WD
	3017[redacted]002 VG9H1/3	VG9H		NA	8260 W
	3017[redacted]002 VG9H2/3	VG9H		NA	SI-34MSV
	3017[redacted]002 VG9H3/3	VG9H		NA	
3017[redacted]003	3017[redacted]003 AG1U1/1	AG1U		NA	8082 W
	3017[redacted]003 BP3N1/1	BP3N		NA	6010 WD,7470 WD
	3017[redacted]003 VG9H1/3	VG9H		NA	8260 W,SI-34MSV
	3017[redacted]003 VG9H2/3	VG9H		NA	
	3017[redacted]003 VG9H3/3	VG9H		NA	
3017[redacted]004	3017[redacted]004 VG9H1/3	VG9H		NA	8260 W,SI-34MSV
	3017[redacted]004 VG9H2/3	VG9H		NA	
	3017[redacted]004 VG9H3/3	VG9H		NA	
3017[redacted]005	3017[redacted]005 AG1U1/1	AG1U		NA	
	3017[redacted]005 BP3N1/1	BP3N		NA	7470 WD
	3017[redacted]005 VG9H1/3	VG9H		NA	8260 W,SI-34MSV
	3017[redacted]005 VG9H2/3	VG9H		NA	
	3017[redacted]005 VG9H3/3	VG9H		NA	6010 WD,8082 W
3017[redacted]006	3017[redacted]006 AG1U1/1	AG1U		NA	8082 W
	3017[redacted]006 BP3N1/1	BP3N		NA	6010 WD,7470 WD
	3017[redacted]006 VG9H1/3	VG9H		NA	8260 W
	3017[redacted]006 VG9H2/3	VG9H		NA	SI-34MSV
	3017[redacted]006 VG9H3/3	VG9H		NA	
3017[redacted]007	3017[redacted]007 AG1U1/1	AG1U		NA	8082 W
	3017[redacted]007 BP3N1/1	BP3N		NA	6010 WD,7470 WD
	3017[redacted]007 VG9H1/3	VG9H		NA	8260 W
	3017[redacted]007 VG9H2/3	VG9H		NA	SI-34MSV
	3017[redacted]007 VG9H3/3	VG9H		NA	
3017[redacted]008	3017[redacted]008 AG1U1/1	AG1U		NA	8082 W
	3017[redacted]008 BP3N1/1	BP3N		NA	6010 WD,7470 WD
	3017[redacted]008 VG9H1/3	VG9H		NA	8260 W
	3017[redacted]008 VG9H2/3	VG9H		NA	SI-34MSV
	3017[redacted]008 VG9H3/3	VG9H		NA	
3017[redacted]009	3017[redacted]009 AG1U1/1	AG1U		NA	8082 W
	3017[redacted]009 BP3N1/1	BP3N		NA	6010 WD,7470 WD
	3017[redacted]009 VG9H1/3	VG9H		NA	8260 W
	3017[redacted]009 VG9H2/3	VG9H		NA	SI-34MSV
	3017[redacted]009 VG9H3/3	VG9H		NA	
3017[redacted]010	3017[redacted]010 AG1U1/1	AG1U		NA	8082 W
	3017[redacted]010 BP3N1/1	BP3N		NA	6010 WD,7470 WD
	3017[redacted]010 VG9H1/3	VG9H		NA	8260 W
	3017[redacted]010 VG9H2/3	VG9H		NA	SI-34MSV
	3017[redacted]010 VG9H3/3	VG9H		NA	
3017[redacted]011	3017[redacted]011 AG1U1/1	AG1U		NA	8082 W
	3017[redacted]011 BP3N1/1	BP3N		NA	6010 WD,7470 WD
	3017[redacted]011 VG9H1/3	VG9H		NA	8260 W
	3017[redacted]011 VG9H2/3	VG9H		NA	SI-34MSV
	3017[redacted]011 VG9H3/3	VG9H		NA	
3017[redacted]012	3017[redacted]012 AG1U1/1	AG1U		NA	8082 W
	3017[redacted]012 BP3N1/1	BP3N		NA	6010 WD,7470 WD
	3017[redacted]012 VG9H1/3	VG9H		NA	8260 W,SI-34MSV
	3017[redacted]2 VG9H2/3	VG9H		NA	

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Attachment VI
Tests, Sample Containers and Required Volumes

Parameter	Method	Matrix	Container	Preservative	Volume Needed (mL or g)	Max Hold Time
Acidity	SM2310B	Water	Plastic/Glass	≤ 6°C	100 mL	14 Days
Actinides	HASL-300	Water		pH<2 HNO_3	300 mL	180 Days
Actinides	HASL-300	Solid		None	500 g	180 Days
Alkalinity	SM2320B/310.2	Water	Plastic/Glass	≤ 6°C	100 mL	14 Days
Total Alpha Radium (see note 3)	9315/903.0	Water	Plastic/Glass	pH<2 HNO_3	600 mL	180 days
Total Alpha Radium (see note 3)	9315	Solid	Plastic/Glass	None	500 g	180 days
Anions (Br, Cl, F, NO_2, NO_3, o-Phos, SO_4, bromate, chlorite, chlorate)	300.0/300.1/SM4110B	Water	Plastic/Glass	≤ 6°C; EDA if bromate or chlorite run	50 mL per ion being tested	All analytes 28 days except: NO_2, NO_3, o-Phos (48 Hours); chlorite (immediately for 300.0; 14 Days for 300.1). NO_2/NO_3 combo 28 days.
Bacteria, Total Plate Count	SM9221D	Water	Plastic/WK	≤ 6°C; $Na_2S_2O_3$	100 mL	24 Hours
Base/Neutrals and Acids	8270	Solid	8oz Glass	≤ 6°C	15 g	14/40 Days
Base/Neutrals and Acids	625/8270	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	1000 mL 3X volume for QC	7/40 Days
BOD/cBOD	SM5210B	Water	Plastic/Glass	≤ 6°C	1000 mL	48 hours
Cation Exchange	9081	Solid	8oz Glass	None		unknown
Chloride	SM4500Cl-C,E	Water	Plastic/Glass	None	50 mL	28 Days
Chlorine, Residual	SM4500Cl-D,E,G/330.5/Hach 8167	Water	Plastic/Glass	None	50 mL	15 minutes
COD	SM5220C, D/410.4/Hach 8000	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	10 mL	28 Days
Coliform, Fecal	SM9222D	Water	100mL Plastic	≤ 6°C $Na_2S_2O_3$	100 mL	6 Hours
Coliform, Fecal	SM9222D	Solid	100mL Plastic	≤ 6°C$Na_2S_2O_3$	100 mL	6 Hours
Coliform, Total and Escherichla (E. coli)	SM9223B	Water	100mL Plastic	≤ 10°C; $Na_2S_2O_3$	100 mL	48 Hours after collection; results from samples analyzed 30-48 Hours after collection must be qualified as analyzed >30 hours
Color	SM2120B,E	Water	Covered Plastic/Acid Washed Amber Glass	≤ 6°C	100 mL	24 Hours

Parameter	Method	Matrix	Container	Preservative	Volume Needed (mL or g)	Max Hold Time
Cyanide, Reactive	SW846 chap.7	Water	Plastic/Glass	None	100 mL	28 Days
Cyanide, Reactive	SW846 chap.7	Solid	Plastic/Glass	None	30 g	28 Days
Cyanide, Total and Amenable	SM4500CN-A,B,C,D,E,G,I,N/9010/9012/335.4	Water	Plastic/Glass	pH≥12 NaOH; ≤ 6°C; ascorbic acid if Cl present	100 mL	14 Days (24 Hours if sulfide present- applies to SM4500CN only)
Diesel Range Organics- TPH DRO	8015	Solid	8oz Glass Jar	≤ 6°C	15 g	14/40 Days
Diesel Range Organics- TPH DRO	8015	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	1000 mL 3X volume for QC	7/40 Days
EDB/DBCP (8011) EDB/DBCP/1,2,3-TCP (504.1)	504.1/8011	Water	40mL vials	≤ 6°C; $Na_2S_2O_3$ if Cl present	40 mL X 3 plus Trip Blank	14 Days
Ferrous Iron	SN3500Fe-D	Water	Glass	None	10 mL	Immediate
Flashpoint/Ignitability	1010	Liquid	Plastic/Glass	None	50 mL	28 Days
Flashpoint/Ignitability	1010	Solid	Plastic/Glass	None	50 g	28 Days
Fluoride	SM4500Fl-C,D	Water	Plastic	None	500 mL	28 Days
Gamma Emitting Radionuclides (see note 3)	901.1	Water	Plastic/Glass	pH<2 HNO_3	2 X 1000 mL	180 days
Gamma Emitting Radionuclides	901.1	Solid	Plastic/Glass	None	500 g	180 days
Gasoline Range Organics	8015	Water	40mL vials	pH<2 HCl	40 mL X 3 plus Trip Blank	14 Days
Gasoline Range Organics	8015	Solid	5035 vial kit	See note 1	Terracore kit plus Trip Blank	14 days
Gross Alpha (NJ 48Hr Method)	NJAC 7:18-6	Water	Plastic/Glass	pH<2 HNO_3	200 mL	48 Hrs
Gross Alpha and Gross Beta (see note 3)	9310/900.0	Water	Plastic/Glass	pH<2 HNO_3	400 mL	180 Days
Gross Alpha and Gross Beta	9310	Solid	Glass	None	500 g	180 Days
Hardness, Total ($CaCO_3$)	SM2340B,C/130.1	Water	Plastic/Glass	pH<2 HNO_3	50 mL	6 Months
Hexavalent Chromium	7196/218.6/SM3500Cr-C,D	Water	Plastic/Glass	≤ 6°C	250 mL	24 Hours
Hexavalent Chromium	7196 (with 3060A)	Solid		≤ 6°C	10 g	24 Hours after extraction
Mercury	7471	Solid	8oz Glass Jar	≤ 6°C	2 g	28 days
Mercury	7470/245.1/245.2	Water	Plastic/Glass	pH<2 HNO_3	25 mL	28 Days
Metals (ICP/ICPMS)	6010/6020	Solid	8oz Glass Jar	None	2 g	6 months
Metals (ICP/ICPMS)	6010/6020/200.7/200.8	Water	Plastic/Glass	pH<2 HNO_3	50 mL	6 Months
Nitrogen, Ammonia	SM4500NH3/350.1	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	50 mL	28 Days
Nitrogen, Kjeldahl (TKN)	351.2	Solid	Plastic/Glass	≤ 6°C	10 g	28 Days
Nitrogen, Kjeldahl (TKN)	SM4500-Norg/351.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	50 mL	28 Days
Nitrogen, Nitrate	SM4500-NO3/352.1	Water	Plastic/Glass	≤ 6°C	50 mL	24 Hours preferred

Parameter	Method	Matrix	Container	Preservative	Volume Needed (mL or g)	Max Hold Time
Nitrogen, Nitrate & Nitrite combination	SM4500-NO3/353.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	50 mL	28 Days
Nitrogen, Nitrite or Nitrate separately	SM4500-NO2/353.2	Water	Plastic/Glass	≤ 6°C	10 mL	48 Hours
Oil and Grease/HEM	1664A/SM5520B/9070	Water	Glass	pH<2 HCl ; ≤ 6°C	1000 mL 3X volume for QC	28 Days
Oil and Grease/HEM	9071	Solid	Glass	≤ 6°C	75 g	28 Days
PCBs and Pesticides, Organochlorine (OC)	608	Water	1L Amber Glass	≤ 6°C; NaOH or HCl if not extracted within 72 hours	1000 mL 3X volume for QC	Pest: 7/40 Days; PCB: 1 Year/1 Year
Pesticides, Organochlorine (OC)	8081	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	1000 mL 3X volume for QC	7/40 Days
Pesticides, Organochlorine (OC)	8081	Solid	8oz Glass Jar	≤ 6°C	15 g	14/40 Days
PCBs (Aroclors)	8082	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	1000 mL 3X volume for QC	1 Year/1 Year
PCBs (Aroclors)	8082	Solid	8oz Glass Jar	≤ 6°C	15 g	1 Year/1 Year
Oxygen, Dissolved (Probe)	SM4500-O	Water	Glass	None	1000 mL	15 minutes
Paint Filter Liquid Test	9095	Water	Plastic/Glass	None	100 mL	N/A
Paint Filter Liquid Test	9095	Solid	Plastic/Glass	None	100 g	N/A
pH	SM4500H+B/9040	Water	Plastic/Glass	None	50 mL	15 minutes
pH	9045	Solid	Plastic/Glass	None	20 g	Contact local lab
Phenol, Total	420.1/420.4/9065/9066	Water	Glass	pH<2 H_2SO_4; ≤ 6°C	50 mL	28 Days
Phosphorus, Orthophosphate	SM4500P/365.1/365.3	Water	Plastic	Filter; ≤ 6°C	100 mL This requires a separate container for filtration	Filter within 15 minutes, Analyze within 48 Hours
Phosphorus, Total	SM4500P/ 365.1/365.3/365.4	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	100 mL	28 Days
Phosphorus, Total	365.4	Solid	Plastic/Glass	≤ 6°C	5 g	28 Days
Polynuclear Aromatic Hydrocarbons (PAH)	8270 SIM	Solid	8oz Glass Jar	≤ 6°C	15 g	14/40 Days
Polynuclear Aromatic Hydrocarbons (PAH)	8270 SIM	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	1000 mL 3X volume for QC	7/40 Days
Radioactive Strontium (see note 3)	905.0	Water	Plastic/Glass	pH<2 HNO_3	200 mL	180 days
Radium-226 (see note 3)	903.0/903.1	Water	Plastic/Glass	pH<2 HNO_3	600 mL	180 days
Radium-228 (see note 3)	9320/904.0	Water	Plastic/Glass	pH<2 HNO_3	800 mL	180 days

Parameter	Method	Matrix	Container	Preservative	Volume Needed (mL or g)	Max Hold Time
Radium-228 (see note 3)	9320/901.1	Solid	Plastic/Glass	None	500 g	180 days
Radon	7500-Rn-B	Water	40 ml glass	None	40 mL X 2	96 hours
Silica, Dissolved	SM4500Si-D	Water	Plastic	≤ 6°C		28 Days
Solids, Settleable	SM2540F	Water	Glass	≤ 6°C	1000 mL	48 Hours
Solids, Total	SM2540B	Water	Plastic/Glass	≤ 6°C	100 mL	7 Days
Solids, Total Dissolved	SM2540C	Water	Plastic/Glass	≤ 6°C	100 mL	7 Days
Solids, Total Suspended	SM2540D/USGS I-3765-85	Water	Plastic/Glass	≤ 6°C	100 mL	7 Days
Solids, Total Volatile	160.4/SM2540E	Water	Plastic/Glass	≤ 6°C	100 mL	7 Days
Solids, Total Volatile	160.4	Solid	Plastic/Glass	≤ 6°C	20 g	7 Days
Specific Conductance	SM2510B/9050/120.1	Water	Plastic/Glass	≤ 6°C	100 mL	28 Days
Sulfate	SM4500SO4/9036/ 9038/375.2/ASTM D516	Water	Plastic/Glass	≤ 6°C	10 mL	28 Days
Sulfide, Reactive	SW-846 Chap.7	Water	Plastic/Glass	None	100 mL	28 Days
Sulfide, Reactive	SW-846 Chap.7	Solid	Plastic/Glass	None	30 g	28 Days
Sulfide, Total	SM4500S/9030	Water	Plastic/Glass	pH>9 NaOH; ZnOAc; ≤ 6°C	250 mL	7 Days
Sulfite	SM4500SO3	Water	Plastic/Glass	None	500 mL	15 minutes
Surfactants (MBAS)	SM5540C	Water	Plastic/Glass	≤ 6°C	250 mL	48 Hours
Total Organic Carbon (TOC)	SM5310B,C,D/9060	Water	40 mL glass	pH<2 H_2SO_4 ; ≤ 6°C	40 mL X 2	28 Days
Tritium	906.0	Water	Glass	None	200 mL	180 days
Turbidity	SM2130B/180.1	Water	Plastic/Glass	≤ 6°C	50 mL	48 Hours
Total Uranium (see note 3)	ASTM D5174-97	Water	Plastic/Glass	pH<2 HNO3	50 mL	180 days
Volatiles	8260	Solid	5035 vial kit	See note 1	Terracore plus Trip Blank	14 days
Volatiles	8260	Water	40mL vials	pH<2 HCl; ≤ 6°C; $Na_2S_2O_3$ if Cl present	40 mL X 3 plus Trip Blank	14 Days
Volatiles	624	Water	40mL vials	pH<2 HCl; ≤ 6°C; $Na_2S_2O_3$ if Cl present, unpreserved for specific compounds	40 mL X 3 plus Trip Blank	14 Days (7 Days for aromatics if unpreserved)

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Document Number: ENV-SOP-GBUR-0088 **Revision:** 00

Document Title: Gamma Spectroscopy Analysis - Prep - 901.1

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All Dates and Times are listed in: Central Time Zone

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Document Number: ENV-SOP-GBUR-0088 **Revision:** 00

Title: Gamma Spectroscopy Analysis - Prep - 901.1

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Review: ENV-SOP-GBUR-0088 00 Gamma Spectroscopy Analysis - Prep - 901.1

Review

Name/Signature	Title	Date	Meaning/Reason
Raelyn Sylvester (005634)	Qa Analyst I	21 Feb 2019, 11:29:49 AM	Reviewed
Nasreen Derubeis (009976)	Quality Manager II	21 Feb 2019, 04:23:04 PM	Reviewed

STANDARD OPERATING PROCEDURE

Gamma Spectroscopy Analysis - Sample Preparation

Method: 901.1

SOP NUMBER:	S-PGH-R-040-rev.07
REVIEW:	R. Kinney
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	PGH-R-040-6

APPROVALS

Department Manager/Supervisor — 03/01/18 Date

Senior Quality Manager — 03/01/18 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date

TABLE OF CONTENTS

1. Purpose

1.1 This SOP documents the analytical process of preparing and analyzing a variety of matrices for gamma emitters using the HPGe gamma spectrometry detector.

2. Scope and Application

2.1 This method describes the use of HPGe gamma spectroscopy detector to measure the gamma photons emitted from multiple radionuclides in a single sample. This technique makes it possible to determine the concentration of specific gamma emitters in homogenous aqueous and solid samples and is considered a non-destructive test for most matrices.

2.2 In the case of man made nuclides in drinking water, limits set forth in PL 93-523, 40 FR 34324 set the limiting concentration that will produce an annual dose equivalent to 4 mrem/year. This calculation is based on the consumption of 2 liters of drinking water per day and utilizes the 168 hour data listed in NBS Handbook 69. If multiple radionuclides are present, the sum of their annual doses must not exceed 4 mrem/year.

2.3 This procedure will be applicable only to the use of the HPGe detectors, but may be adapted to include the use of NaI(Tl) detectors, which are more efficient at detecting photons, but have poorer energy resolution. Due to the energy resolution advantage and the availability of the large active volume, HPGe detectors are recommended for measuring gamma emitting radionuclides.

2.4 This method is applicable for analyzing samples with gamma photon energy ranges from 60 to 2000 keV. The National Interim Drinking Water Regulations, Section 141.25, lists the required sensitivities of measurement for more hazardous gamma emitters. For compliance, the detection limits for photon emitters must be 1/10 of any applicable limits.

2.5 As written, this SOP is compliant with the EPA Method 901.1, Gamma Emitting Radionuclides in Drinking Water.

2.6 Solid samples analyzed using this SOP are prepared according to Pace SOP PGH-R-024, current revision (Radchem Sample Prep).

3. Summary of Method

3.1 Preserved samples are transferred to a standard geometry for counting purposes. Counting efficiencies must be determined for each standard geometry using a standard (known) radionuclide activity.

3.2 Samples are counted long enough to meet the required detection limit for each assessed radionuclide. Drinking water method detection limits are specified by the NIPDWR. Non-drinking water matrix method detection limits may be assigned by the client depending on their needs.

3.3 The gamma spectrum is processed by the gamma spectroscopy analysis software, and stored in the gamma system computer. The final analytical data are printed and results are entered into the LIMS database for reporting.

4. Interferences

4.1 Sample preservation ensures sample homogeneity in water and aqueous samples, by preventing the disposition of the nuclides on the container walls. Samples must be preserved in accordance with Section 8 of this SOP.

4.2 Solid samples must be dried and ground to a consistent mesh size. Settling must be minimized during the sample geometry preparation process by tapping and shaking the container to remove air and achieve level height/volume of sample in the can or jar.

4.3 Significant interferences occur when counting the sample on a NaI (Tl) detector and the sample radionuclides emit nearly identical gamma energies. This is minimized by using HPGe detectors.

4.4 Several radionuclides emit multiple gamma photons with multiple energies each having different abundances. The gamma software must be capable of calculating the final concentration of any one nuclide from another.

5. Safety

5.1 Procedures must be carried out in a manner that protects the health and safety of all personnel. Since this analysis is for a radioactive constituent, the sample must be treated as radioactive. Analysts must be trained as radiation workers and personal dosimeter worn.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves will be cleaned immediately.

5.3 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye-protection, gloves, and lab coat must be worn.

5.4 Exposure to radioactivity and chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous and/or non-radioactive, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 In order to minimize the potential for cross contamination of high and low levels of radioactive samples, good housekeeping and good laboratory practices are essential and must be strictly adhered to.

5.6 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory.

6. Definitions

6.1 Refer to the Glossary Section of the most recent revision of the Pace Analytical Services, LLC. Quality Manual for the definitions of commonly used laboratory terms used throughout this SOP.

6.2 Batch: For gamma spectroscopy analysis, a batch consists of 20 samples of similar matrix in uniform geometry counted with a single set of QC samples. An analysis batch may be counted over several days by multiple persons, and is distinctly different from a preparation batch.

6.3 Geometry: For gamma spectroscopy analysis, geometry refers to a container with specified dimensions and physical composition utilized in sample counting to provide uniformity in reporting results from one sample to another. A calibration source is required for each type of geometry utilized in gamma spectroscopy counting.

6.4 Throughout this procedure, approximate weights and measures will be designated by the use of whole numbers when referring to masses exceeding one (1) gram or volumes in excess of one (1) milliliter. Measurements of mass and volumes so designated can be made with top loading balances, graduated cylinders, etc. For approximate measures below one gram or one milliliter, the word "approximately" must be used prior to the described weight or volume.

6.5 Throughout this procedure, exact or critical mass and volumes will be designated by the use of one or more decimal places. Measurements of masses and volumes so designated should be made with accurate analytical instruments such as analytical balances, calibrated pipettes, etc. The method utilized for obtaining the sample aliquot, whether on a balance, in a graduated cylinder, or by pipette, must be clearly annotated in the preparation logbook.

6.6 When measuring samples on a balance, the observed mass on the balance must be recorded in preparation logbooks to the lowest weight indicated on the balance. Sample aliquot masses must not be targeted. Once sample is removed from the sample container and transferred to a beaker, it must not be removed from the beaker.

6.7 Samples which are diluted to a specific geometry for analysis by gamma spectroscopy must be transferred to a new labeled container large enough to contain the entire diluted sample volume and clearly labeled as having been diluted. The label must include the dilution factor, date, analyst initials, and how the dilution was prepared, either by volume or by mass.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Aqueous Samples

8.1.1 Containers used for sample collection must never be reused. Either plastic or glass containers may be used for sample collection.

8.1.2 Aqueous samples not requiring I-131 analysis must be preserved at the time of collection by adding enough concentrated (16N) HNO_3 to the sample to make the sample pH <2. Typically, two mL 16N HNO_3 per liter of sample is sufficient to obtain the desired pH.

8.1.3 Samples must be preserved within five days of collection. If samples are collected without preservation, they must be received by the laboratory and preserved within five days of collection. Following preservation with acid, samples must be held in the original container for a minimum of 16 hours. After a minimum of 16 hours has elapsed, the sample pH must be re-checked and verified to be less than the required pH of 2. The date and time, as well as the analyst initials, and results of the pH check must be

recorded in the pH Verification Logbook, along with any comments or further adjustments. The pH must be verified to be less than 2 for a minimum of 16 hours before analysis or transfer of sample.

8.1.3.1 For dissolved analysis, samples must be filtered through a 0.45μm membrane filter and then preserved to a pH <2.

8.1.3.2 For total analysis, the sample is not filtered, but is preserved to a pH<2.

8.1.4 Samples requiring I-131 analysis must not be preserved upon collection. The addition of acid to samples may cause the complete loss of iodine in the sample due to co-precipitation of iodide with chlorides found to be present in the sample.

8.1.5 Refrigeration is not required for aqueous or solid samples, but is recommended for all biological samples, especially urine.

8.1.6 Urine: It is recommended that the sample be preserved before a sample aliquot is taken to ensure that the requested analytes do not adhere to the sample container.

8.1.6.1 This is especially true if the sample has visible solids present.

8.2 Solid Samples: No preservation or refrigeration is required. Samples must be dried at 105°C and ground to a fine mesh according to Pace SOP PGH-R-024, current revision.

8.3 Analysts should consult with the Radiochemistry Department Supervisor for direction on samples which do not meet the above criteria. If samples are received non-compliant (not within the criteria of preservation) as dictated in section 8.1, then the Project Manager and the client must be notified. Sample analysis can only proceed after the client has given permission to do so.

9. Equipment and Supplies

9.1 HPGe detectors, >50cm3, Ortec, Canberra, or equivalent.

9.2 Gamma Spectrometry Analyzer with a minimum 2048 channels for HPGe or 512 for NaI(Tl).

9.3 Associated analysis software for each detector type, computer, and printer.

9.4 Standard geometry sample counting containers: 3.0L Marinelli beakers, 500 gram plastic wide mouth jar, 8 oz salmon can, 2 oz can, centrifuge tube, etc.

9.4.1 Marinelli beakers are the only analysis containers that may be re-used for sample analyses. Following analysis of samples in Marinelli beakers, transfer the sample to the original sample container or into a new appropriately labeled container.

9.4.2 Rinse the Marinelli beaker using ASTM Type II DI water into the sink/drain designated for sample disposal. To the Marinelli beaker

and lid, add an appropriate quantity of Contrad solution and add enough ASTM Type II DI water to create an adequate volume for washing. Scrub the interior surfaces of the Marinelli beaker and lid using a soft bristle brush or sponge pad. Once washing is complete, rinse the beaker and lid using ASTM Type II DI water until soap is removed. Transfer a minimum of 2.0 liters of 2 M nitric acid to the beakers and soak for a minimum of 30 minutes to dissolve trace levels of solids from the beakers. Rinse the beakers using ASTM Type II DI water and drain into the sink/drain designated for sample disposal. Hand-dry the beakers and lids using paper towels.

9.5 Additional geometries may be prepared as needed, however, for each geometry, a calibration source must be prepared and used for instrument calibration for the specific geometry prior to sample counting. A second source different from the calibration source must be prepared in each counting geometry for the performance of LCS analysis.

9.6 Top loader balance capable of weighing 1.00g to 3000.00g.

9.7 Graduated Cylinder, 1.0 Liter, Class A.

10. Reagents and Standards

10.1 ASTM Type II (DI) water for reagent and standard preparation and sample dilution. ASTM Type II DI water generated as specified in Pace SOP PGH-C-027, current revision.

10.2 Nitric acid, 16N: HNO3 (conc.), sp. gr. 1.42, 70.4%, high purity grade.

10.3 Nitric acid, 2N: Mix 124mL of concentrated nitric acid with ASTM Type II DI water and dilute to a final volume of 1.0L with ASTM Type II DI water.

10.4 Calibration and Control sample solutions must contain a minimum of 7 radionuclides to include low, mid, and high energy gamma photon emitters within the range of 60-2000 keV. All standard solutions must be NIST certified.

10.5 Sodium Chloride, NaCl, reagent grade.

11. Calibration

11.1 Specific Details regarding instrument calibration are documented in SOP-PGH-R-023, current revision. The following are general comments regarding the calibration process:

11.2 Prepare a stock solution containing a minimum of the following nuclides: Am-241 (or Pb-210), Cd-109, Co-57, Ce-139, Cs-137, and Co-60 (both energy lines).

11.3 Prepare as many geometries as desired for future analysis and count the sample to obtain a minimum of 10000 net peaks for each nuclide present.

11.4 Upon counting, follow the steps outlined in the operations manual to adjust the amplifier “gain” and analog to digital converter “zero offset” to locate the peak in the appropriate channel. For HPGe detectors, a 0.25 keV per channel calibration is recommended.

11.5 Counting efficiencies for the various energies are determined by comparing the activity counts to the known values. An energy versus channel number calibration is performed first followed by an instrument counting efficiency versus gamma energy calibration. The calibration process is completed for each container geometry and for each detector that is to be used for sample analysis.

11.6 Efficiency calibration equations are generated within the applicable software program. The efficiency curve is acceptable if the difference between the calculated efficiency and the applied efficiency is less than 10% for all radionuclides measured in the calibration source. This is automatically calculated during the calibration process but the analyst must be aware of this requirement and work with the Department Supervisor to ensure that each data points used complies with this requirement.

12. Procedure

12.1 Aqueous Samples:

12.1.1 The preferred geometry for aqueous samples is a 2.0 liter volume in a 3 Liter Marinelli beaker. Measure sample volumes by transferring to a 1.0 liter Class A graduated cylinder. For samples with 2.0 liters available for analysis, measure two 1.0 liter volumes. Transfer sample volumes into the labeled Marinelli Beaker. Record the sample volume for analysis in the sample preparation logbook. For samples that do not have 2.0 liters available for analysis, transfer the available volume into the graduated cylinder and record the volume in the sample preparation logbook. Add ASTM Type II DI water to dilute the total volume to 2.0 liters. Transfer sample volume into the labeled Marinelli beaker. In all instances, record the sample volume on the beaker lid in addition to the sample ID. Some clients prefer analysis of aqueous samples by mass. For these clients, measure the sample volume using the Class A graduated cylinder but transfer the sample into a tared Marinelli beaker. Record the sample mass in the sample preparation logbook. Never remove sample after dilutions are performed. Fortify diluted samples with additional nitric acid to ensure a starting pH of <2.

12.1.2 Prepare a batch method blank by weighing the same amount of ASTM Type II DI water into the same size clean labeled standard geometry container.

12.1.3 Perform gamma spectroscopy instrument daily checks in accordance with the current revision of the SOP PGH-R-023, Gamma Spectroscopy Instrument Operations.

12.1.4 Count the method blank, samples, and one duplicate sample for the desired amount of time to achieve the required MDC for all analytes desired to be reported to the client.

12.1.5 Count a laboratory control sample of the same standard geometry for a duration determined to generate a minimum ratio of 5:1 of analyte concentration versus analyte Minimal Detectable

Concentration for all quality control analytes. Ordinarily for aqueous samples, sufficient sample volume is not available for sample duplicate analysis. In these cases, perform a duplicate count of the LCS for precision assessment.

12.1.6 Process the data and enter the results into LIMS. Submit the data for review.

12.2 Solid Samples:

12.2.1 Dry and homogenize the samples in accordance with the current revision of the SOP PGH-R-024, Sample Preparation.

12.2.2 Weigh an appropriate mass of sample into the largest standard geometry available for which there is enough sample. Do not tamp the cans, as the process of tamping causes striation of the varied particle sizes of the soil. The final volume of the sample must be equivalent to the volume used during calibration. Using a clean, flat press, press the soil and add additional processed soil until the can is full. Record the mass of sample and the canning/sealing date in the gamma spectroscopy preparation logbook.

12.2.3 If Ra-226 analysis is desired, seal the container completely to allow for ingrowth and capture of the Ra-226 decay daughters. Ingrowth is considered ideal after 21 days, but with both the clients' and Supervisor's permission, a shorter ingrowth period may be used.

12.2.4 Prepare a method blank using a radionuclide-free reagent grade sodium chloride (NaCl).

12.2.5 Count the method blank, samples, and one duplicate sample for the desired amount of time to achieve the required MDC for all analytes desired to be reported to the client.

12.2.6 Count a laboratory control sample of the same standard geometry for a duration determined to generate a minimum ratio of 5:1 of analyte concentration versus analyte Minimal Detectable Concentration for all quality control analytes.

12.2.7 Process the data and enter the results into LIMS. Submit the data for review.

12.3 Miscellaneous Samples

12.3.1 In instances where the sample cannot be configured into an existing geometry for which there is a calibration, it may be necessary to prepare a calibration.

12.3.2 If a new calibration cannot be prepared for the new counting geometry, the sample must be counted using the closest geometry calibration comparable to the sample counting geometry.

12.3.3 For example, if a composite filter is received for analysis, and a calibration does not exist for this material, and preparing a

calibration for this material is not practical, the best geometry to use would be a solid geometry in the same size to which the filter composite can be tightly packed.

13. Calculations

13.1 Refer to the operation manuals for each of the operating systems for all gamma spectroscopy calculations and algorithms.

14. Quality Control

14.1 Daily instrument Quality Control checks for Gamma Spectroscopy Counting Systems must be completed following the instructions detailed in Pace SOP PGH-R-023 current revision, the SOP for Gamma Spectroscopy Counter Operations.

14.2 The LCS solutions or Well characterized material (WCM) must consist of at least 3 of the same nuclides as those used for calibration, one in each of the low, medium and high energy regions. The LCS solutions or WCM must come from a source other than that used for the calibration.

14.3 See Appendix I for performance indicator evaluation calculations and criteria.

14.4 Method Blank (MB)

14.4.1 One MB must be prepared for each analytical batch. The purpose of the MB is to monitor for cross contamination during the analytical process. When available, the MB should be prepared from a similar matrix as samples contained in the analytical batch. If appropriate blank matrix material is not available, ASTM Type II DI water (Reagent Blank) must be carried through the procedure for analysis of aqueous samples. For solid sample analyses NaCl must be used for MB analysis. A reagent blank may be used for sample correction purposes following approval of the Department Manager or a Manager-specified designeerand affected clients.

14.4.2 The results of the method blank must be less than the Contract Required Detection Limit (CRDL).

14.4.2.1 If the method blank is out of control, individual sample results may still be reportable if results are less than the CRDL (contract required detection limit) or greater than 10 times the blank result. Relative sizes of the sample and blank aliquots must be factored when making this determination (raw counts).

14.4.2.2 Additionally, the Z-score for the MB (Zblank) as discussed in Attachment I should be used to determine if the MB result indicates a positive detect or if the result could be a statistical aberration.

14.5 Laboratory Control Sample (LCS)

14.5.1 One LCS must be analyzed for each analytical batch. The LCS is usually a “static” source that is prepared once but used repeatedly for batch analysis.

14.5.2 Spike solution activities of the radionuclides analyzed in the LCS must be greater than 2 times their respective detection limit.

14.5.3 A reference material containing a known concentration of at least 3 of the radionuclides analyzed in the calibration and in the same matrix as the batch is analyzed with the batch.

14.5.3.1 If this material is not available, a well-characterized material (WCM) may be used.

14.5.3.2 If neither of these is available, ASTM Type II DI water may be spiked with the appropriate standard(s).

14.5.4 Percent Recovery Calculation

$$\%REC = \frac{(LCSConc)}{TrueValue} * 100$$

Where:

LCSConc = Analytical result of the LCS
TrueValue= Known concentration of the LCS

14.5.5 LCS %REC acceptance limits are 75-125% for each measured analyte.

14.5.6 Additionally, the Z-score for the LCS (Z_{LCS}) as discussed in Attachment I should be used to determine if the analysis variables for the LCS count (count duration, etc.) were sufficient to document acceptable analysis or if the result could be a statistical aberration.

14.6 Laboratory Control Sample Duplicate (LCSD)

14.6.1 A LCSD is not required for gamma analyses; however analysis of an LCSD must be utilized to measure batch precision whenever adequate sample volume is not available for sample DUP analysis. The LCSD must be analyzed in an identical fashion as the LCS and processed identically as for other samples.

14.6.2 The LCSD must pass the acceptance criteria for the LCS and the criteria established for duplicate precision.

14.6.3 Additionally, the Z-score for the LCS (Z_{LCS}) as discussed in Attachment I should be used to determine if the analysis variables for the LCS count (count duration, etc.) were sufficient to document acceptable analysis or if the result could be a statistical aberration. Likewise, the Z_{DUP} should be calculated.

14.7 Sample Duplicate (DUP)

14.7.1 One Duplicate Sample (DUP) may be randomly assigned within each batch. Analysis batch must include either analysis of a sample duplicate or a LCSD. The purpose of the sample DUP is to measure precision of the analytical process. Laboratory duplicates are not intended to assess precision related to the sample collection process. Sample collection precision can only be assessed through collection of duplicate samples at the time of

sample collection. The sample DUP is a duplicate volume of sample processed identically as other samples in the analytical batch.

14.7.2 Relative Percent Difference Calculation

$$RPD = \frac{|(R1 - R2)|}{(R1 + R2)/2} * 100$$

Where:

R1 = Result Sample 1
R2 = Result Sample 2

14.7.3 Duplicate sample RPD acceptance limits are <25% for all gamma radionuclides reported.

14.7.4 Additionally, the Z-score for the Duplicate (Z_{DUP}) as discussed in Attachment I should be used to determine if the observed precision is acceptable. For low-level analysis results, it is highly likely that precision will not be within the percent recovery limits as recovery limits are generated using results with higher concentrations such as observed for LCSs.

14.8 Summary of QC related Activities:

Method Blank	One per Batch
Duplicate Sample	One per Batch
Matrix Spike	N/A
Matrix Spike Duplicate	N/A
Laboratory Control Sample	One per Batch
Laboratory Control Sample Dup	One per Batch for samples in absence of Duplicate sample.

14.9 Corrective Actions for Out-Of-Control Data

14.9.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.9.2 Duplicate (DUP) – DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.9.3 Matrix Spike Recovery (MS) – Sample Matrix Spikes are not performed for gamma spectroscopy since the test is a non-destructive method for which chemical separations are not employed.

14.9.4 Matrix Spike Duplicate (MSD) - See comments for the Matrix Spike Analysis documented in section 14.9.3.

14.9.5 Laboratory Control Sample (LCS) – If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed.

14.9.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit.

14.9.6 Laboratory Control Sample Duplicate (LCSD) – If an LCSD does not meet the recovery acceptance criteria, the entire analytical batch must be reanalyzed.

14.9.6.1 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than their the reporting limit, and duplicate precision meets the acceptance criteria.

14.9.7 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.10 Contingencies for Handling Out-of-Control or Unacceptable Data

14.10.1 Method Blank (Reagent Blank): If the sample is exhausted, evaluate the usefulness of the data in the final report.

14.10.2 Laboratory Control Sample: If sample is still available, recount the entire batch, otherwise evaluate the usefulness of the data in the final report.

14.10.3 Duplicates: If the sample is exhausted, evaluate the usefulness of the data in the final report.

15. Method Evaluation

15.1 Laboratory control samples are analyzed with each batch, the results are charted to monitor control limits and trending.

15.2 Each analyst must read and understand this procedure with written documentation maintained in their training file on the Learning Management System (LMS).

15.3 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained on file in each analysts training file in the LMS.

15.4 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Place radioactive waste into appropriate receptacles.

16.2 Discard acidified samples and unusable standards into proper waste drains.

16.3 Dispose waste materials in accordance to type: Non-hazardous, hazardous, non-radioactive, radioactive or mixed.

17. References

17.1 Krieger, H. L. and Whittaker, E. L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, "Gamma Emitting Radionuclides in Drinking Water," Method 901.1, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, August, 1980.

17.2 ASTM E181-93, Standard Test Methods for Detector Calibration and Analysis of Radionuclides, ASTM Standards, Vol. 12.02.

17.3 Table of Radioactive Isotopes, Brown and Firestone, Shirley editor, John Wiley & Sons, 1986.

17.4 Currie, L., Limits for Quantitative Detection and Quantitative Determination, Analytical Chemistry, Vol. 40. No. 3, Pg 586-593, 1968.

17.5 Currie, L., Lower Limit of Detection: Definition and Elaboration of a Proposed Position for Radiological Effluent and Environmental Measurements, NUREG/CR - 4007, USNRC, 1984.

17.6 "Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)", July 2004.

17.7 Nuclide Identification Algorithms and Software Verification and Validation Manual, 07-0464-02, Canberra Industries, November 1993.

17.8 Peak Search Program Algorithm Manual, 07-0064, Canberra Industries, March 1985.

17.9 Gamma-Vision 3.0 Program Manual, Ortec, 2000.

17.10 "American National Standard Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories", ANSI N42.23-1996.

17.11 Department of Defense Quality System Manual for Environmental Laboratories (DoD QSM), current version.

17.12 EML Procedures Manual, HASL-300, 27th Edition, Volume 1, 1990, Method 4.5.2.3 – Gamma.

17.13 Pace SOP PGH-R-023, current revision (Gamma Spectroscopy Instrument Operation).

17.14 Pace SOP PGH-R-024, current revision (Rad Sample Preparation).

17.15 Pace SOP PGH-C-027, current revision (Deionized Water Quality and Suitability).

17.16 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.17 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.18 Pace Analytical Services, LLC. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 Appendix I, Numerical Performance Indicators

19. Method Modifications

19.1 None

20. Revisions

Document Number	Reason for Change	Date
PGH-R-040-0	1. Table of Contents added (Updateable Version). 2. All references to Ge(Li) detectors replaced with HPGe. 3. Section 8 modified to specify non-preservation of samples requiring I-131 analysis and require specific authorization to proceed when non-compliant sample collection requirements are observed. 4. Section 9.5 updated to expand on requirement to use calibration source for detector calibration. 5. Section 10 modified to require use of ASTM Type II water and use of high-purity concentrated nitric acid. 6. Section 11 modified to include reference to the instrument operation SOP for calibration instructions. Order of calibrations energy followed by efficiency added. 7. Section 12.1.2 added instructions for performing and recording aqueous sample dilutions. 8. Method Evaluations Section added as Section 15. 9. Rotated previous Sections 15-18 as new Sections 16-19. 10. Updated references at 17.11 and 17.12 to include ANSI N42, 23 and reference to the TNI standard. 11. Renamed Section 19, “Deviations for Promulgated Methods” as “Method Modifications”	29May2012

Document Number	Reason for Change	Date
PGH-R-040-2	1. Annual review and update. 2. Added specifications for DI water as ASTM Type II DI water and included reference to SOP PGH-C-027, the SOP that documents the DI water production and testing process. 3. Updated references to require Department Manager or Manager-specified designee approval of technical modifications removing approval by a senior analyst. 4. Section 9, added procedure to be used for washing re-usable Marinelli beakers. 5. Section 12 modified to require recording of sample weights for volume analyses, dis-allowing the targeting of weights and removal of sample transferred for analysis. 6. Modified Section 14 to clarify the allowed use of empty geometry containers for solid sample MB analysis. 7. Modified Section 14 to clarify use of LCSDs for precision analysis in lieu of sample duplicates, if desired. 8. Modified Section 14.5 to allow use of “static” sources for batch LCS/LCSD analyses. 9. At 17.14 Added reference to *EML Procedures Manual*, HASL-300, 27th Edition, Volume 1, 1990, Method 4.5.2.3 – Gamma.	26Jun2013
PGH-R-040-3	1. Annual review and update 2. Section 6 – Updated for not targeting weights, recording measuring apparatus, not returning sample to containers once removed. 3. Section 8 – Updated for pH verification check and recording. 4. Added references to Pace SOP for Sample Preparation, ASTM Type II DI water preparation. 5. Reformatted document.	17Jul2014
PGH-R-040-4	1. Moved sections 8.1.4.1 & 8.1.4.2 under section 8.1.3.	03Dec2015
PGH-R-040-5	1. Section 12.2.5 modified to require use of sodium chloride for solid sample method blank analysis. 2. Section 10 modified to list sodium chloride as a chemical.	01Mar2016
PGH-R-040-6	1. Section 12.2 modified to eliminate the use of tamping to fill gamma analysis containers. 2. Section 12.2.4 added to define process for preparing solid PT samples on an “as-received” basis.	14Feb2017

Document Number	Reason for Change	Date
S-PGH-R-040-rev.07	3. Section 9.4 modified to remove reference to 1.0 Liter Marinelli Beakers. 4. Section 9.4.2 modified to document process used for acid-soaking Marinelli Beakers. 5. Section 9 modified to include Class A graduated cylinder and a top-loading balance as necessary equipment. 6. Section 10.3 modified to remove 1 N nitric acid as a reagent and add in 2 N nitric acid as a reagent. 7. Section 12.1.1 modified to document revised process for preparation of aqueous samples. 8. Sections 12.1.5 and 12.2.6 modified to remove a specific count duration for LCS samples. 9. Sections 14.9.3 and 14.9.4 modified to document that sample matrix spikes and MS duplicates are not analyzed for gamma-spectroscopy.	01Mar2018

Appendix I

(Numerical Performance Indicators)

1. **Method Blank (MB)**

1.1 The numerical performance indicator for the method blank is calculated by:

$$Z_{Blank} = \frac{x}{u(x)}$$

Where:
x = measured blank activity
u(x) = standard uncertainty in the blank measurement

1.2 MB performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. MB performance indicator values should be recorded on a control chart.

2. **Laboratory Control Sample (LCS)**

2.1 The numerical performance indicator for a laboratory control sample is calculated by:

$$Z_{LCS} = \frac{x - c}{\sqrt{u^2(x) + u^2(c)}}$$

Where:

x = Analytical result of the LCS
c = Known concentration of the LCS
$u^2(x)$ = combined standard uncertainty of the result squared.
$u^2(c)$ = combined standard uncertainty of the LCS value squared.

2.2 LCS performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to +2. Performance indicator values should be recorded on a control chart.

3. Duplicates (DUP)

3.1 These criteria are applicable for the evaluation of the Duplicate, Matrix Spike Duplicate and Laboratory Control Sample Duplicates.

3.2 The numerical performance indicator for laboratory duplicates is calculated by:

$$Z_{Dup} = \frac{x_1 - x_2}{\sqrt{u^2(x_1) + u^2(x_2)}}$$

Where:
x_1, x_2 = two measured activity concentrations
$u^2(x_1)$, $u^2(x_2)$ = the combined standard uncertainty of each measurement squared.

3.3 Duplicate sample performance is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been

established as –2 to 2. DUP performance indicator values should be recorded on a control chart for each QC sample type (Dup, MSD, LCSD)

4. **Matrix Spike/Matrix Spike Duplicate (MS/MSD)**

4.1 The numerical performance indicator for a matrix spike sample is calculated by:

$$Z_{MS} = \frac{x - x_0 - c}{\sqrt{u^2(x) + u^2(x_0) + u^2(c)}}$$

Where:
x = measured concentration of the spiked sample
x_0 = measured concentration of the unspiked sample
c = spike concentration added
$u^2(x)$, $u^2(x_0)$, $u^2(c)$ = the squares of the respective standard uncertainties of these values.

4.2 MS performance for all matrices is acceptable when the numerical performance indicator calculation yields a value between –3 and 3. Warning limits have been established as –2 to 2. MS performance indicator values should be recorded on a control chart.

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QM Approval

Name/Signature	Title	Date	Meaning/Reason
Nasreen Derubeis (009976)	Quality Manager II	22 Feb 2019, 11:52:15 AM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Nasreen Derubeis (009976)	Quality Manager II	22 Feb 2019, 11:01:17 AM	Approved
Richard Kinney (005816)	Manager - Lab Operations	22 Feb 2019, 11:40:31 AM	Approved

1. Purpose

This procedure describes the general operation and maintenance of the gamma spectroscopy instrumentation utilized by the Pace Analytical Services, LLC. For additional operational details not discussed in this SOP, the user should consult the instrument and software operations manuals referenced in Section 17. These documents are located in the gamma instrument room.

2. Scope and Application

2.1 Pace SOP ENV-SOP-GBUR-0044 current revision (Laboratory Equipment) addresses general requirements regarding the purchase, installation, operation, maintenance, and disposition of laboratory equipment.

2.2 This procedure addresses the process for analyzing sample sources generated as the product of current revision analytical SOPs: ENV-SOP-GBUR-0080 current revision (Analysis of Neutron Dosimeter Wires by Gamma Spectroscopy), ENV-SOP-GBUR-0081 current revision (Analysis of Neutron Dosimeter Capsules for Cesium-137), and ENV-SOP-GBUR-0082 current revision (Iodine-129 Analysis).

2.3 Samples for non-destructive gamma spectroscopy analysis are prepared using the current revision of Pace SOP ENV-SOP-GBUR-0079 current revision.

2.4 This procedure applies to the measurement of gamma particles emitted from a variety of sample types. Several detection systems are utilized, but all analysis, data processing, storage, and reporting can be performed using different software commands within one flexible user interface for each system type. Each system type has an independent user platform consisting of a computer and detector-specific software that controls instrument operation, spectral analysis, and calculations.

2.5 Sample specific preparation is not discussed in this SOP. The final sample geometry must conform to one of the existing calibration geometries at the time of counting. Deviations in sample geometry from the calibration geometry require a new calibration.

2.6 This procedure describes the performance of the gamma detector efficiency, energy, and FWHM calibration; monthly background determination; and daily or prior to use (PTU) continuing calibration verification checks. Also discussed are the general systems operating requirements and maintenance.

2.7 This procedure is applicable to gamma spectroscopy detectors of HPGe “p” type, HPGe “n” type, or LeGe (LEPS) type, utilizing multiple software components.

2.8 Gamma spectral analysis software can decay correct data for all nuclides based on the individual half-lives listed in the nuclide library. Decay correction for individual nuclides is applied from the client-specified collection date and time to the instrument analysis start date and time.

3. Summary of Method

3.1 The system is calibrated for efficiency, energy, and resolution full width-half max (FWHM) for all new counting geometries. Sources may be commercially available or laboratory prepared with NIST traceable materials

and equipment. Long backgrounds (minimum of 1000 minute duration) are performed within 30 days prior to all sample analyses or more frequently as necessary. Daily (or PTU) checks of the efficiency, energy, FWHM, and background are performed to ensure detector function prior to use.

3.2 Samples are counted upon completion of a daily check, utilizing the system software available, on a detector capable of detecting the nuclides of interest in the sample. Once counting is complete on Canberra system, the system software automatically processes the data, and the primary count analyst must review spectra and enter the data into LIMS for client delivery. For the Ortec system, the user must manually process data.

4. Interferences

4.1 Sample counting geometries must be of uniform consistency for accurate results. Phase separations in liquid samples or grading in solid samples may bias sample results.

4.2 In order to prevent possible detector contamination, aqueous samples should be contained in a plastic bag or other suitable device to ensure secondary containment, with the first container being the durable sample container such as a Marinelli beaker or plastic “jar.” In the event of a spill, the detector must be cleaned immediately, and backgrounds must be measured.

4.3 High activity samples may cause excessive dead time in detectors and should be analyzed utilizing a geometry that increases the sample to detector distance, thereby decreasing the observed count rate. Optionally, a portion of sample is diluted using inert sand and re-prepared in the desired geometry.

4.4 Detector electronics must be kept cool while counting is in progress. Liquid nitrogen is stored in a dewar at the base of the instrument for this purpose. The level must be maintained by regularly filling the dewar with liquid nitrogen. System performance is greatly affected by temperature fluctuations, and damage to detectors can result from operating without proper cooling.

4.5 Many radioisotopes emit gamma rays that are indistinguishable (by energy) from other gamma-emitting radioisotopes. One such example, Ra-226, emits a predominant gamma ray very near that of a gamma ray emitted by U-235. Common gamma spectroscopy systems cannot easily identify the source of the gamma ray. For this reason, interfering gamma rays should be excluded from use for quantitation. Alternatively, if the interfering gamma rays are used for quantitation, the results must be qualified as potentially biased due to conflicts with other radionuclides.

5. Safety

5.1 Procedures must be carried out in a manner that protects the health and safety of all personnel.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves will be cleaned immediately.

5.3 When mixing or diluting acids, always add the acid slowly to water and swirl. Dilution of acids must always be done in a hood. Appropriate eye protection, gloves, and lab coat must be worn.

5.4 Exposure to radioactivity and chemicals must be maintained as low as reasonably achievable therefore, unless they are known to be non-hazardous and/or non-radioactive, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 In order to minimize the potential for cross contamination of high and low levels of radioactive samples, good housekeeping and good laboratory practices are essential and must be strictly adhered to.

5.6 Organic samples of unknown content must be handled with extreme caution and under the direct instruction of a senior analyst. Direct treatment of organic matrices with strong oxidizing chemicals such as nitric acid and/or hydrogen peroxide is strictly prohibited.

5.7 Hydrofluoric acid is particularly hazardous because a serious skin exposure may cause no immediate sensation of pain. The acid penetrates the skin and spreads internally, causing tissue damage deep under the skin. The resulting burn is painful, difficult to treat, and easily infected. Gloves must be checked for pinhole leaks before use. They must be rinsed before they are removed and must be discarded after use. HF burn gel shall be put on suspected HF burns after flushing (except the eyes) until medical help can be obtained. Medical attention shall be sought even if suspicions arise after working hours. Contact the group leader immediately for further information if an HF burn is suspected.

5.8 In addition, HF vapors are also hazardous. Exposure can cause permanent damage. Breathing HF vapors even for a short time and at a low temperature can be injurious to the respiratory system, and even fatal. All such direct contact must be avoided.

5.9 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the SDS files maintained in the laboratory.

5.10 Refer to the Pace Analytical Services, LLC. – Pittsburgh Chemical Hygiene Plan/Safety Manual for the specific safety requirements to be followed when working in the laboratory.

5.11 The toxicity and carcinogenicity of each reagent used in this procedure has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. At a minimum, personal protective equipment must include a lab coat, gloves, and safety glasses.

5.12 Analysts must be familiar with the Safety Data Sheets (SDS) for all chemicals and reagents used in this procedure, and the location of the SDS within the laboratory.

6. Definitions

6.1 Hardware equipment and software terms are defined in the applicable operating manuals by the equipment and/or software manufacturer.

6.2 Refer to the current Quality Manual for definitions.

7. Responsibilities and Distribution

7.1 General Manager/Assistant General Manager (GM/AGM)

7.1.1 The GM/AGM has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the laboratory involving the collection and reporting of analytical data.

7.1.2 The GM/AGM and Senior Quality Manager/Quality Manager have final review and approval authority for all SOPs prepared within the laboratory.

7.2 Senior Quality Manager/Quality Manager (SQM/QM)

7.2.1 The SQM/QM will maintain a master file of all SOPs applicable to the operations departments.

7.2.2 The SQM/QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The SQM/QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members read, follow, and are adequately trained in the use of the SOPs

7.3.2 The Department Manager/Supervisor coordinates the preparation and revision of all SOPs within the department whenever a procedure changes.

7.3.3 The Department Manager/Supervisor provides initial approval of all SOPs within the department.

7.3.4 The Department Manager/Supervisor makes recommendations for SOP revision to the SQM/QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each person may make recommendations to the Department Manager/Supervisor for revising SOPs as the need arises.

7.4.3 Personnel are responsible for ensuring that any deviations from this SOP are reported to the Department Manager/Supervisor.

8. Sample Collection, Preservation, and Handling

8.1 Refer to the applicable SOP and certified test method for sample collection and preservation requirements. The list of applicable SOPs and reference methods is located in Sections 2.2 and 2.3.

8.2 Aqueous samples should be bagged to prevent leaking that may contaminate detectors.

8.3 Solid samples should be sealed in order to prevent detector contamination in the event that the sample is dropped.

8.4 The maximum hold time for most analytes measured by this SOP is 180 days from sample collection to sample analysis. For I-131, the hold time is 8 days from samples collection to sample analysis.

9. Equipment and Supplies

9.1 High Purity Germanium (HPGe) “p” type, “n” type and Low-Energy Germanium (LeGe) or Low-Energy Photon Spectrometer (LEPS) type detectors.

9.2 Computer Data Analysis system run on a Canberra instrument-compatible computer. Canberra utilizes multiple software applications joined together to form the Genie 2000/Procount software package. For issues/processes not addressed within this SOP, refer to the instrument manual current revision.

9.3 Ortec GammaVision® software. Ortec GammaVision®-compatible computer. For issues/processes not addressed within this SOP, refer to the instrument manual current revision.

9.4 Front End Electronic components:

9.4.1 High Voltage Power Supply: supplies power to detectors.

9.4.2 Analog to Digital converter: converts analog voltage from crystal to digital readout.

9.4.3 Multi Channel Analyzer (MCA): Detector acquisition and control is performed through an MCA. The MCA is supported through a combination of hardware and software and functions as the analyzer. It is the link between spectra and the computer system.

9.5 Kim wipes® or lint free cloths.

9.6 Plastic bags.

10. Reagents and Standards

10.1 Reagents should be prepared from reagent grade chemicals, unless otherwise specified below. Reagent (DI) water must be at least ASTM Type II quality or better. NOTE: Consult Safety Data Sheets for the properties of these reagents, and how to work with them.

10.2 Distilled or deionized water, ASTM Type II generated as specified in Pace SOP ENV-SOP-GBUR-0008, current revision.

10.3 Liquid nitrogen, ACS grade, for detector cooling.

11. Calibration and Quality Control

Note: Refer to the instrument operations manual for instructions regarding specific system setup options.

11.1 Daily Checks

11.1.1 Daily or prior to use, a continuing calibration verification (CCV) check source is counted for five minutes to determine detector function, assessing the energy, efficiency (activity), and resolution (FWHM) calibrations.

11.1.2 High Purity Germanium Detectors with associated electronics are sensitive to temperature variations within the count room environment. The probable effect of variations in temperature is the slight drifting of gamma peaks in the high-energy range (>1MeV) of the analytical spectrum. Marginal shifts in the ambient temperature do not cause spectral shifts that would negatively impact analytical results. In order to optimize gamma spectral analysis, the system fine amplifier gain may be adjusted to correct for minor peak drifting. This process applies exclusively to Ortec gamma detectors.

11.1.3 Gain Adjustment

11.1.3.1 Place the check source used for instrument performance checks on the endcap of the applicable detector. Perform a manual count of the check source while observing the spectral location of the 1332.5 keV peak of Co-60. Adjust the system fine gain incrementally in order to position the peak at channel 5330. Record the fine gain adjustment value in the detector Maintenance Logbook.

11.1.3.2 Clear the analysis spectrum and re-start the qualitative count of the check source. Confirm the location of the 1332.5 keV peak to be centered at channel 5330. Clear the analysis spectrum and perform performance checks as documented below.

11.1.4 Each energy, efficiency (activity), and resolution (FWHM) is assessed using defined tolerances for each parameter. For the efficiency (activity) assessment, the defined tolerance is used as a total allowable deviation for the count source. For control purposes, the tolerance is divided by 3.0 to generate a standard tolerance deviation. Warning limits are set at +/- 2.0 standard tolerance deviations and control limits are set at +/- 3.0 standard tolerance deviations. The assessments of peak energy and resolution (FWHM) are not statistical measurements. For these variables, tolerances have been set based on manufacturer's recommendations. Limits have been set to establish a warning and control boundaries.

11.1.5 Min/Max control limits are established at +/- 3% for efficiency. This tolerance was chosen based upon the requirements cited in the DOD QSM Table B-17 (MARLAP 18.5.6.2)

11.1.6 The low warning limit for energy has been established as -0.25 keV difference from the known peak energy. The low control limit has been established as -0.50 keV from the known peak energy. The high warning limit and high control limit for energy have been established as 0.25 keV and 0.50 keV, respectively.

11.1.7 The control assessment for resolution is measured as a ratio of the source check peak resolution versus the calibration-defined resolution. The low warning limit for resolution (FWHM) has been established at 0.9 with a low control limit at 0.8. The high warning limit and high control limit for resolution (FWHM) have been established as 1.2 and 1.5 respectively.

11.1.8 A minimum five minute daily background of the empty shield is conducted and compared to the running median background counts to determine if the detector shield has been contaminated.

11.1.8.1 The control limit for the daily background count has been established statistically using a representative population of background counts. Warning and control limits have been established for each detector system with warning limits established at +/- 2.0 standard deviations of the system total background count rate in units of counts per second and control limits set at +/- 3.0 standard deviations of the system total background count rate in units of counts per second.

11.1.9 To perform the daily check, place the designated check source in the sample holder onto the shield, and close the cover. For the Canberra system: Select QC, then CALIBRATION CHECK. Choose the appropriate detector from the dropdown list. Select QCC-A (or the appropriate detector-specific file), then Control Det A (or the appropriate detector-specific control program), followed by OK to initiate the five-minute count. For the Ortec system: Double-click appropriate desktop icon (Det “#” QA Daily Check). Click “OK” at the following prompt.

11.1.10 Upon completion, the QC report will automatically be generated. QC reports are stored electronically and may be retrieved for performance troubleshooting. Data from each QC assessment are automatically loaded into the QA database for automated assessment and charting.

11.1.11 The analyst must verify that the detector meets the control criteria. To determine system acceptance for use, review the instrument check printouts for the assessment criteria OR review the control chart for each performance parameter monitored. QA assessment is software controlled within each counting system type. Control limits are statistical for activity assessments and are based on generally recognized tolerances for resolution and peak location.

11.1.12 Any daily check not meeting the control criteria must be recounted. Check the positioning of the source within the detector and verify the correct placement of the check source prior to initiating a recount. Two consecutive acceptable recounts are required for the detector to be in service. If the recount is unsuccessful, the detector must be locked out until a successful daily check is performed. If a detector fails several consecutive daily checks, the cause must be investigated. Consult with a senior analyst on how to proceed.

11.2 Monthly Background Measurement

11.2.1 Every month, at a minimum, (or within thirty days of sample analysis, at a minimum) an extended background count is completed for use in sample analysis. Additionally, backgrounds must be re-acquired following calibration, detector cleaning due to confirmed contamination, or maintenance. Typically, extended background counts are performed weekly. For all sample analyses, the prior (but most recent) background must be used for sample analysis.

11.2.2 Clean the detector shields prior to counting backgrounds with a lint free cloth dampened with ASTM Type II DI water.

11.2.3 Ensure daily checks have been performed and detectors have passed control criteria prior to performing background counts.

11.2.4 Canberra System:

11.2.4.1 For the Canberra system: Start counts by selecting COUNT and Start A LONG BACKGROUND COUNT. Choose the appropriate detector when prompted, followed by LONG BKG and NO SPECIFIC GEOMETRY. Select OK to begin the acquisition. Select OK in the following window, since all of the criteria has been pre-selected. The detector will begin counting. The shield cover must remain closed during the count.

11.2.4.2 When counting is complete, a background report will automatically be generated.

11.2.5 Ortec System:

11.2.5.1 For the Ortec system, ensure that the detector shield is empty. Perform step 12.1.6 as indicated below, acquiring an empty chamber count using a count time of 1000 minutes (60,000 seconds). The convention for naming the background count is LB (Long-background) Detector Number (DX), date of counting (MMDDYY). A background count performed for detector 2 on June 1, 2015 would be named, “LBD2060115.”

11.2.5.2 The Ortec Background Spectrum must be analyzed using each combination of detector/geometry calibration/library to be used for sample analysis.

11.2.5.3 Upon completion of the background count, recall the background spectrum into the processing “buffer.” To apply the appropriate calibration file: from GV toolbar (Fig 1. below), click CALIBRATION and select RECALL CALIBRATION. From the list of archived calibration files, select the file for the appropriate geometry for which to create the background analysis file. Next, select the appropriate nuclide library. From the GV toolbar, click LIBRARY and click SELECT.

11.2.5.4 Click ANALYZE, place cursor over SETTINGS and select SAMPLE TYPE. A new window will appear into which

sample data will be entered. From the SAMPLE tab (Fig 2.), click BROWSE, near the file entry blank, and select the appropriate .sdf file. Also from the SAMPLE tab, select the appropriate library and calibration files.

11.2.5.5 For the background spectral analysis, the sample size and decay correction date are not necessary. The "Peak-Background Correction" (PBC) file created for the background analysis only requires the energy calibration file which relates peak channel to energy and the library file which relates peak energy to detected analyte. At the bottom of the window select CLOSE and click YES, when prompted to save.

11.2.5.6 Lastly, from the GV toolbar, click ANALYZE and ANALYZE ENTIRE SPECTRUM IN MEMORY. If the printer output has been selected, the analyzed report will be printed.

11.2.5.7 To create the individual "Peak-Background-Correction" (PBC) files, click "ANALYZE" on the GV menu bar. Select "SETTINGS". Select "Peak Background Corrections", then "Select PBC" Choose the file for a recently-completed PBC file and select "OPEN."

11.2.5.8 Using the cursor, depress the "Cut" button repeatedly until all analytes have been removed from the active PBC file. Once all analytes have been removed, select the window in the very upper left-hand corner of the PBC box. Select the "Show Background Analysis" option.

11.2.5.9 The system will show all of the available un-formatted output "UFO" files for each sample spectrum previously analyzed. Find and choose the .UFO file for the analyzed background file you wish to create the PBC file from. The .UFO file will have the name of the background spectrum with a .UFO extension. For the example cited in section 11.2.5.1 above the .UFO file will correspond as "LBD2060115.UFO."

11.2.5.10 Once the .UFO file has been high-lighted, select the window in the very upper left-hand corner of the PBC window. Select, "Save PBC table as"…." Type in the name for the new detector/geometry/library PBC combination and select, "Save."

11.2.6 For each detector platform, the analyst must check the report and compare it to previous long backgrounds to determine if contamination is present.

11.2.7 Background changes must be tracked to determine if detectors need more vigorous cleaning. All detectors which do not pass the control criteria must be locked out to prevent accidental use during sample analysis.

11.2.8 The background count for detectors failing control criteria may be re-acquired following maintenance to improve background performance, including reassessment of potential contamination sources and re-cleaning of the detector shields.

11.3 Detector Calibration

11.3.1 Efficiency, energy, and FWHM calibrations for specific counting geometries must be completed initially or following major system maintenance, such as detector replacement. Calibration for specific counting geometries must be performed following major analytical SOP changes that would change the final geometric configuration of the final counting source. For example, an analytical change resulting in counting an aqueous sample in a 1.0L Marinelli beaker to counting an aqueous sample in a 0.5L Marinelli beaker requires calibration for the additional geometry.

11.3.2 Calibrations must be performed using the same protocols as used in sample analysis, with adjustment to sample count time being the only factor to change. Calibration instructions for each analysis type are included in the current revision of each applicable SOP. The list of applicable SOPs and reference methods is located in Sections 2.2 and 2.3 of this SOP.

11.3.3 Although the gamma analysis software contains features which would allow manual integration of regions of interest, this feature has been disabled. Manual integrations of peaks is not allowed.

11.3.4 Gamma Spectroscopy Instrument Calibration Requirements

11.3.4.1 Energy calibrations are performed prior to geometry-specific efficiency calibrations. The energy calibration documents the peak channel number to the peak energy. Geometry efficiency calibrations relate the peak energy to the detector response as percent of emissions observed versus emitted.

11.3.4.2 A minimum of 10000 net counts for each nuclide of interest utilized in the calibration source must be obtained. Nuclides of interest should be chosen in order to encompass various energy ranges consistent with those encountered in routine sample counting. Typically, a minimum of ten nuclides, are utilized in a calibration source. For each geometry-specific efficiency calibration performed, a known standard reference material (SRM) in an identical configuration is counted and assessed using the statistical control limits used for Laboratory Control Samples (LCS) in the related Gamma analysis SOP. Sources used for the initial calibration verifications of a newly-established calibration must incorporate the use of a SRM that is not related to the calibration source parent solution. Subsequent annual calibration verifications are performed as specified in sections 11.3.4.4 and 11.3.4.5.

11.3.4.3 Data are analyzed by the Genie 2000/Procount® or Ortec GammaVision® software package.

11.3.4.4 Calibrations must be verified annually for all aqueous geometries, including those used for drinking water analysis. For drinking water analyses, the same source utilized for the initial calibration may be used for verifying the calibration. A newly-prepared verification source may be used for DW calibration verification if the original calibration source is no longer available. For other aqueous geometries, annual calibration verification is performed using a known standard reference material (SRM) un-related to the initial calibration source. The verification source is prepared in an identical configuration as the initial calibration source and is counted and assessed using the statistical control limits used for Laboratory Control Samples (LCS) in the related Gamma analysis SOP. In all instances, a minimum of three of the nuclides used in the initial calibration must be used to verify the calibration. The three nuclides should span the energy range (low, mid, high) of the initial calibration, for example Am-241(Pb-210), Cs-137, and Co-60. The verification source result for all three nuclides, individually, must be within 10% of the known nuclide concentration for the verification to be acceptable.

11.3.4.5 For all other calibration geometries and matrices, calibrations must be verified annually. Calibration verifications are performed using sources un-related to the initial SRM used for calibration. Calibration standard reference materials (SRMs) such as spiked soils are purchased in limited quantities that do not allow simultaneous creation of all solid calibration sources used by the lab. For this reason, SRM material is often recycled to perform all of the necessary geometry calibration verifications. A minimum of three of the nuclides representative of the initial calibration energy range must be used to verify the calibration. The three nuclides should span the energy range (low, mid, high) of the initial calibration, for example Am-241(Pb-210), Cs-137, and Co-60. The verification source result for all three nuclides must be within 10% of the known nuclide concentration for the verification to be acceptable.

12. Operating Procedures

12.1 Sample Counting and Processing

12.1.1 Before beginning any counts, the detector run log information must be completed. This information includes: the date, analyst, and passing detectors.

12.1.2 Prior to counting, ensure that daily checks have been completed satisfactorily and the detector is free of check sources and contamination.

12.1.3 Insert the sample to be counted and record the detector in which it will be counted in the gamma instrument run log. Record all sample

information in the run log. Place sample into the detector and close the shield lid.

12.1.4 For the Canberra system: select COUNT and START AND COUNT from the Procount-ESP Screen. Select the detector, then choose the ANALYTICAL SEQUENCE FILE (ASF), which will determine the criteria by which the sample will be analyzed. Choose the geometry, then select OK to start the acquisition. Complete the sample information form, and select OK. A report will be generated automatically upon count completion.

12.1.5 For analysis of nuclear dosimetry chain samples, it is imperative that peak-fitting algorithms are optimized to ensure accuracy and precision. The primary peak for Co-58 analysis is located at 810.6 keV. An interfering peak of unknown origin is located near 821.4 keV. Lower peak sensitivity settings may cause inclusion of the 821.4 keV peak for the Co-58 peak at 810.6 keV, causing a high-biased result. This issue is controlled through proper assignment of the peak sensitivity setting. The default peak sensitivity setting has been established as 8.0. The sample spectra for nuclear dosimetry chain samples must be reviewed manually, with the 821.4 keV peak reviewed on-screen to ensure optimal peak fitting. Visual inspection of peaks without an optimal fit will have a noted inclusion of the peak located at 821.4 keV. Samples with this unacceptable characteristic must be re-analyzed manually including a peak-sensitivity adjustment until visual inspection confirms an acceptable peak-fit. Confirmation of the peak sensitivity assessment is documented on the respective gamma analysis report by adding a check-mark to the recorded peak sensitivity setting, with the assessors initials and date.

12.1.6 For the Ortec system: Double-click the appropriate desktop icon (Det "#" Sample). When prompted, enter the requested sample information. After entering the time, in seconds, select CLOSE. Finally, click OK on the following popup. Upon completion of sample counting, the user will be required to manually process data

Fig 1. (GV toolbar)

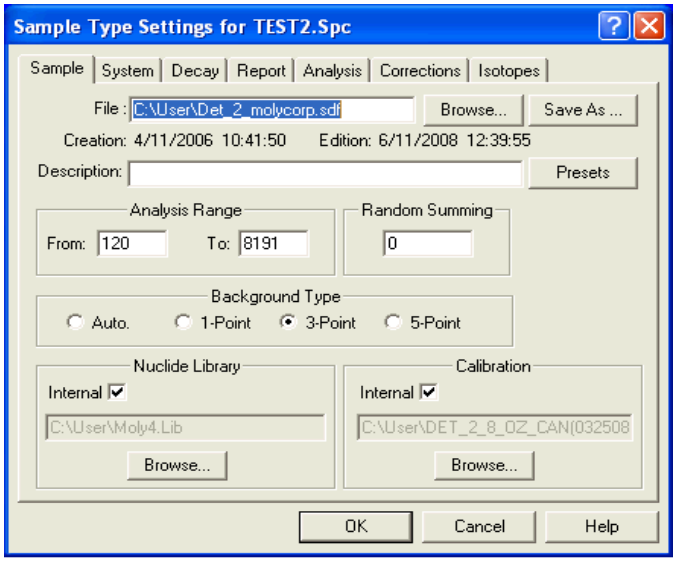

Fig 2. (Sample Tab)

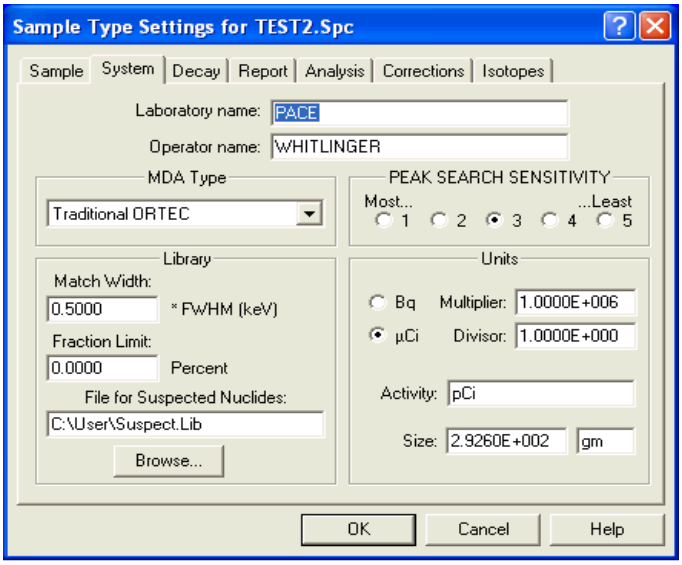

Fig 3. (System Tab)

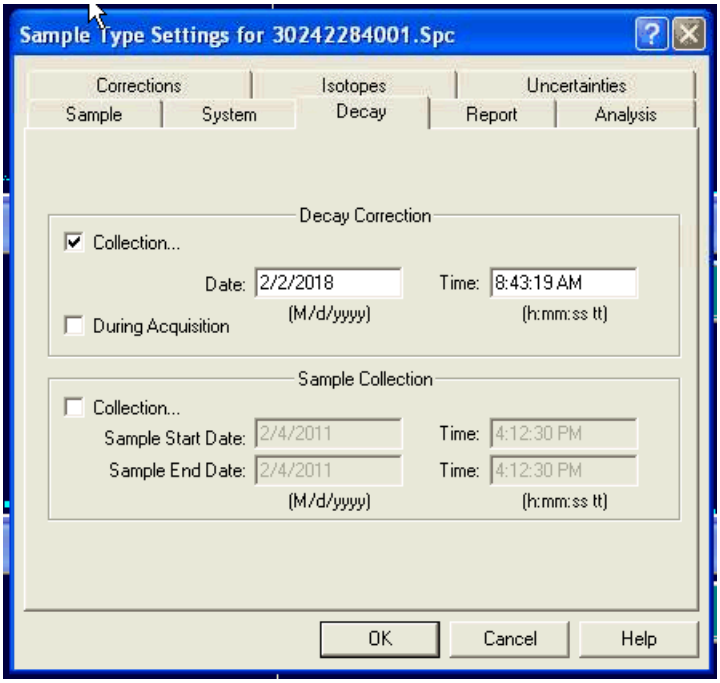

Fig 4. (Decay Tab)

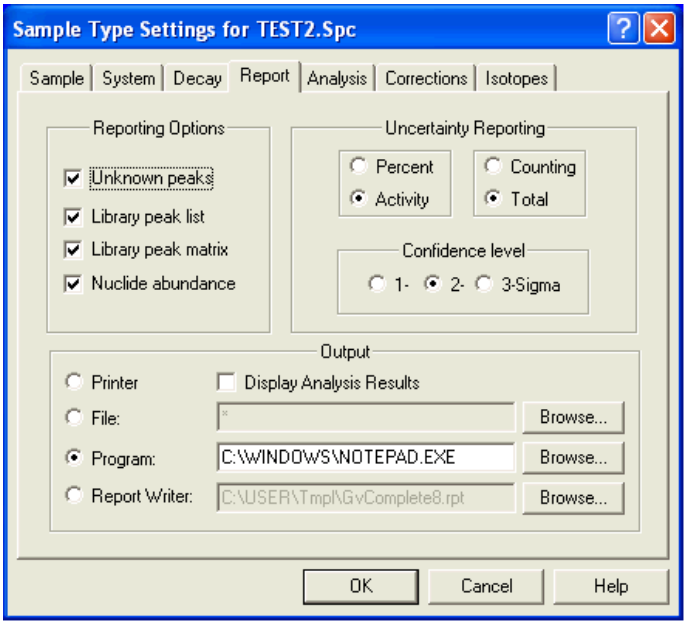

Fig 5. (Report Tab)

12.1.7 To process data from the Ortec system, the analyst must first recall the desired spectrum, using the GammaVision(GV)® program. To apply the appropriate calibration file: from GV toolbar (Fig 1.), click CALIBRATION and select RECAL INFORMATION. From the list of

archived calibration files, select the most recent file for the appropriate geometry. Next, select the appropriate nuclide library. From the GV toolbar, click LIBRARY and click SELECT.

12.1.8 Click ANALYZE, place cursor over SETTINGS and select SAMPLE TYPE. A new window will appear into which sample data will be entered. From the SAMPLE tab (Fig 2.), click BROWSE, near the file entry blank, and select the appropriate .sdf file. Also from the SAMPLE tab, select the appropriate library and calibration files.

12.1.9 From the “System” tab (Fig 3.), enter the sample size, in grams/Liters. From the “Decay” tab (Fig 4.), enter the sample collection date and time. From the “Report” tab (Fig. 5), select the output option, printer or file. At the bottom of the window select CLOSE and click YES, when prompted to save.

12.1.10 Finally, from the GV toolbar, click ANALYZE and ANALYZE ENTIRE SPECTRUM IN MEMORY. If the printer output has been selected, the analyzed report will be printed.

12.1.11 The gamma report must be reviewed by the analyst, and the spectrum must be viewed and compared to the report. Sign the report and enter the calculated activities into LIMS for the final report.

12.1.12 Manual integrations of peaks is not allowed and the feature for this has been disabled.

12.2 Maintenance

12.2.1 Detector

12.2.1.1 Detectors can be cleaned and maintained with ASTM Type II DI water and lint free cloths, or KImwipes®.

12.2.1.2 Removal and replacement of any detector requires a new calibration be established and must be recorded in the equipment maintenance logbook.

12.2.1.3 Detector temperature must be maintained with liquid nitrogen. Maintaining the level of liquid nitrogen in the dewar under each detector is crucial for system operation.

12.2.2 Major Instrument Maintenance

12.2.2.1 Consult with a senior analyst prior to performing troubleshooting steps to identify the source of system problems. Refer to the instrument manual for guidance on diagnosing system problems.

12.2.2.2 Consult with the manufacturer for troubleshooting major system problems.

12.3 All maintenance functions involving power disruptions to the instrument must be documented in the appropriate instrument maintenance logbook at the time of occurrence.

13. Calculations

13.1 Refer to the Canberra "Spectroscopy Applications Algorithms and Software Verification and Validations Manual 07-0368, September 1991" for analysis calculation documentation.

14. Quality Control

14.1 See Section 11.0 of this SOP for system calibration and for system Quality Control requirements.

14.2 Analytical batch Quality Control is documented for each analyte in the applicable SOP. The list of applicable SOPs and reference methods is located in Section 2.2 and 2.3.

14.3 Corrective Actions for Out-Of-Control Data

14.3.1 Method Blank (Reagent Blank) (MB/RB) – Individual samples that do not meet the acceptance criteria must be reanalyzed. If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

14.3.2 Duplicate (DUP) – The duplicate sample is typically a duplicate count of the Laboratory Control Sample (LCS) DUP analysis that fails the replicate test must be reanalyzed to determine if analytical failure or sample heterogeneity was the cause of the problem.

14.3.3 Matrix Spike Recovery (MS) – MS samples are not typically analyzed for gamma spectral content due to inability of the lab to homogenize spike material with sample media. If performed, MS recoveries that do not meet the acceptance criteria must have that sample reanalyzed. The batch may be reportable if the acceptance criteria for the LCS is met. If a Matrix Spike Duplicate is also analyzed and the recovery is comparable to the MS, the results are reported and noted in the final report. Calculations of MS activity include source decay correction to account for decay between the spike solution source certificate reference date/time and the MS sample collection date/time.

14.3.3.1 The analyst must evaluate the MS results to attempt to determine the cause of the failure and the appropriate action to take based on that evaluation. All decisions made must be documented.

14.3.4 Matrix Spike Duplicate (MSD) - If an MSD is analyzed and the recovery is comparable to the MS, the results are reported with qualification in the final report.

14.3.5 Laboratory Control Sample (LCS) – The LCS used for gamma-spectral analysis is a static source of relative consistent content of project samples, matching the geometric configuration of prepared project samples. If an LCS analysis does not meet the acceptance criteria, the entire analytical batch must be re-prepped and reanalyzed. Calculations of LCS activity include source decay correction to account for decay between the LCS spike solution certificate reference date/time and the LCS sample analysis date/time.

14.3.5.1 The results of the batch may be reported, with qualification in the final report, if the LCS recoveries are high and the

sample results within the batch are less than the reporting limit.

14.3.6 Laboratory Control Sample Duplicate (LCSD) – The LCSD is typically a replicate count of the static LCS source described in section 14.3.5. If a LCSD does not meet the recovery acceptance criteria, the entire analytical batch must be reanalyzed.

14.3.6.1 The results of the batch may be reported, with qualification, if the LCS recoveries are high and the sample results within the batch are less than the reporting limit, and duplicate precision meets the acceptance criteria.

14.3.7 If there is no additional sample available for reanalysis, evaluate the usefulness of the data in the final report.

15. Method Performance

15.1 Laboratory control samples (LCS) are analyzed with each batch.

15.2 Each analyst must read and understand this procedure with written documentation maintained electronically.

15.3 An initial demonstration of capability (IDOC) study must be performed. A record of the IDOC will be maintained for each analysts.

15.4 On an annual basis, each analyst will complete a continuing demonstration of capability (CDOC).

16. Pollution Prevention and Waste Management

16.1 Place radioactive waste into appropriate receptacles.

16.2 Discard acidified samples and unusable standards into proper waste drains.

16.3 Dispose of waste materials in accordance to type: Non-hazardous, hazardous, non-radioactive, radioactive or mixed.

17. References

17.1 ASTM E181-93, Standard Test Methods for Detector Calibration and Analysis of Radionuclides, ASTM Standards, Vol. 12.02.

17.2 User's Manual, Model 480726 Genie-ESP System, September, 2000.

17.3 Advanced Concept's Manual, Model 480198 Genie-VMS Spectroscopy System, September 2000.

17.4 Command Descriptions Manual, Model 480198 Genie-V<MS Spectroscopy System, September, 2000.

17.5 Crystal Reports, Version 8.5, Seagate, 2001.

17.6 User's Manual, Model 480206 Genie-VMS Quality Assurance Software, September, 2000.

17.7 User's manual, Model 480720 PROcount-ESP, September, 2000.

17.8 User's Manual Maestro-32 MCA Emulator, Ortec, Version 6.05, 2002.

17.9 Programmer's Guide, Model 480198 Genie-VMS Spectroscopy System, September, 2000.

17.10 Nuclide Identification Algorithms and Software Verification and Validation Manual, 07-0464-02, Canberra Industries, November 1993.

17.11 Peak Search Program Algorithm Manual, 07-0064, Canberra Industries, March 1985.

17.12 Spectroscopy Applications Algorithms and Software Verification and Validation Manual, 07-0368, September 1991.

17.13 Table of Radioactive Isotopes, Brown and Firestone, Shirley editor, John Wiley & Sons, 1986.

17.14 Krieger, H. L. and Whittaker, E. L., Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, "Gamma Emitting Radionuclides in Drinking Water," Method 901.1, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, August, 1980.

17.15 "Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)", July 2004, Final.

17.16 Department of Defense Quality System Manual for Environmental Laboratories (DoD QSM), current version.

17.17 *EML Procedures Manual*, HASL-300, 27th Edition, Volume 1, 1990, Method 4.5.2.3 – Gamma.

17.18 Pace SOP ENV-SOP-GBUR-0044 (Laboratory Equipment), current revision.

17.19 Pace SOP ENV-SOP-GBUR-0079 (Gamma Spec Prep), current revision.

17.20 Pace SOP ENV-SOP-GBUR-0080 (Neutron Dosimetry), current revision.

17.21 Pace SOP ENV-SOP-GBUR-0081 (Cs-137 Dosimeter), current revision.

17.22 Pace SOP ENV-SOP-GBUR-0082 (I-129), current revision.

17.23 Pace SOP ENV-SOP-GBUR-0008, current revision (Deionized Water Quality and Suitability).

17.24 National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, Program Policy and Structure (most recently approved revision).

17.25 TNI Standard, Requirements for Laboratories Performing Environmental Analysis, current version.

17.26 Pace Analytical Services, LLC. - Pittsburgh Laboratory Quality Assurance Manual, current version.

18. Tables, Diagrams, Flowcharts, Appendices, etc.

18.1 See the operations manual supplied by the manufacturer for diagrams and tables associated with the operation or maintenance of gamma spectroscopy detectors.

19. Method Modifications

19.1 Not Applicable.

20. 20. Revisions

Document Number	Reason for Change	Date
PGH-R-023-5	1. Table of contents added. 2. Section 1 modified to specify location of referenced documents. 3. Section 2 modified to specify hardware and software as required by DOD QSM. 4. Section 3 modified to incorporate “resolution” term in conjunction with FWHM calibration. Long Background count time corrected to minimum of 1000 minutes. Long Background frequency defined to reflect specific requirements. 5. Section 4.2 modified to clarify secondary containment of aqueous count geometries for prevention of cross-contamination. 6. Section 6 Revised to discuss the location of definitions for terms related to the equipment hardware and system software. 7. Section 8 modified to remove extraneous analysis sample analysis protocols. Specification that geometries containing solid sample should be sealed. 8. Section 9 modified to describe computer requirements for the two analysis platforms used currently 9. Section 11 modified to cite requirement for daily performance check assessment by analyst. Also, order of calibrations is documented to require energy calibration prior to geometry-specific efficiency calibrations. 10. Section 15, 19 and 20 added. 11. Section 15 renamed as Method Performance. Method performance requirements added. 12. Section 17: Added Method 901.1 reference 13. Section 19 renamed as Method Modifications	18May2012
PGH-R-023-6	1. Annual Review and Update (2013). 2. Added specifications for DI water as ASTM Type II DI water and included reference to SOP PGH-C-027, the SOP that documents the DI water production and testing process. 3. Section 11.1.2 Specified the requirement of a minimum five minute daily background check for gamma instruments. 4. Section 11.2.1 specified that extended background counts used for sample analyses are performed monthly at a minimum but specified that backgrounds are typically run weekly. 5. Section 11.3.3.3 added Ortec GammaVision software to the list of software used for calibration calculations. 6. Section 17.19 Added reference to *EML Procedures Manual*, HASL-300, 27th Edition, Volume 1, 1990, Method 4.5.2.3 – Gamma.	25Jun2013
PGH-R-023-7	1. Annual SOP Review (2014) 2. Section 2.2 and 2.3 - Included reference to Pace SOPs and methods for analyses performed by gamma counting. 3. Section 11 – Updated for verification procedure and acceptance criteria. 4. Section 11 – Updated to include aqueous and Drinking	13Jul2014

Document Number	Reason for Change	Date
	Water calibration and other geometry calibration verification requirements. 5. Document updated to include reference to all applicable Pace SOP and method references for analyses where a gamma detector/system is utilized. 6. Section 17 – Updated to include Pace SOP and method references related to gamma spectroscopy counting. 7. Reformatted document.	
PGH-R-023-8	1. Section 11 (11.1.2) updated to include process for amplifier gain adjustments for Ortec gamma detectors.	20Feb2015
PGH-R-023-9	1. Corrected formatting in Section 8. 2. Section 9.1, defined Gamma Detector Types. 3. Section 9.2 and 9.3, added suggestion to consult the respective instrument manuals for issues not covered by this SOP. 4. Section 11.1.5, revised SOP to indicate that hard-copy performance check data are being stored electronically. Printouts are no longer stored. 5. Section 11.2.5, added procedure for performing long background counts on the Ortec system. 6. Section 13.3, added clarifying information regarding the LCS and duplicate counts.	03Dec2015
PGH-R-023-10	1. Section 2.8 – Added for decay correction of results per nuclide based on the nuclide library. 2. Section 8.4 – Hold time for gamma nuclides and I-131. 3. Section 11.3.3 and 12.1.11– Manual integration feature disabled and manual integration of peaks is prohibited. 4. Section 12.- Re-labeled as section 13 Calculations 5. Section 14.3.3 and 14.3.5 – Updated to discuss decay correction of spiking solutions. 6. Sections 13 through 19, re-labeled section 14 through 20.	21Dec2016
PGH-R-023-11	1. 1.Section 12.1.5 added to document the peak analysis process utilized for nuclear dosimetry samples.	13Feb2017
S-PGH-R-023-rev.12	1) Sections 11.3.4.4 and 11.3.4.5 revised to specify calibration verification requirements for Drinking Waters following the guidance from the Manual for the Certification of Drinking Water Laboratories. Calibration verifications for all other matrices revised to follow guidance from the current TNI standard. 2) Figure 4 updated to be correct figure. The previous figure was a duplicate of Figure 3. 3) Section 14.3.6 updated to correct reference to section 14.3.5, not 13.3.5.	02Feb2018
ENV-SOP-GBUR-0078 Rev 01	1. Section 11.1.5 modified to require a daily efficiency check tolerance of 3% as required by the DOD QSM. 2. Periodic review as required for compliance. 3. Sections 2,10, 11, and 17 modified to update current SOP IDs. 4. Updated section 14.3.3.1. 5. Updated section 15, removed references to LMS.	22Feb2019

APPENDIX D-4

PACE ENERGY SERVICES SOPS

Document Information

Document Number: ENV-SOP-PITTS-0027 **Revision:** 01

Document Title: Sample Receiving

Department(s): Client Services

Previous Document Number: S-PAE-C-003-rev.03

Date Information

Effective Date: 04 Jun 2019

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-PITTS-0027 **Revision:** 01

Title: Sample Receiving

All dates and times are in Central Time Zone.

ENV-SOP-PITTS-0027

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Ruth Welsh (003453) Charlotte Washlaski (003467)	Assistant General Manager Quality Manager	04 Jun 2019, 08:39:43 AM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Charlotte Washlaski (003467)	Quality Manager	04 Jun 2019, 08:39:55 AM	Approved
Ruth Welsh (003453)	Assistant General Manager	04 Jun 2019, 10:09:00 AM	Approved

1. Purpose/Identification of Method

The purpose of this Standard Operating Procedure is to outline the procedures for sample receipt and storage.

2. Summary of Method

2.1. This SOP describes all aspects of sample receipt, sample management and sample storage.

3. Scope and Application

3.1. **Personnel**: This Standard Operating Procedure applies specifically to the Sample Receipt Technician and/or his or her representative during activities of sample receipt. This Standard Operating Procedure also applies to the Client Service Office and bottle preparation personnel.

4. Applicable Matrices

4.1. Not applicable to this SOP.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Not applicable to this SOP.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Not applicable to this SOP.

8. Definitions

Aliquot: a portion of a sample

Background Radiation: naturally occurring radiation.

Chain of Custody Form: record that documents the possession of the samples from the time of collection to receipt in the laboratory. The record may include: number and types of containers; the mode of collection; time of collection; preservation; requested analyses; and sampler's printed name and signature.

Holding Time: the maximum time that samples may be held prior to analysis.

Non-Conformance: samples or sample documentation that are received with incorrect, incomplete, or inadequate information or properties.

Preservation: refrigeration and/or reagents added prior to sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Shall: denotes a requirement that is mandatory.

Short Holding Time: samples that must be analyzed within 48 hours or less of sample collection.

Temperature Blank: a bottle of water that accompanies the samples in each cooler. This blank is used to monitor cooler temperature upon receipt of samples in the laboratory.

Trip Blank: a set of 40mL VOA vials filled with deionized water that travel with samples to be analyzed for target analytes of concern. These samples are analyzed to determine if cross contamination occurred during transport.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. Computer

9.2. Printer

9.3. LIMS

9.4. Sink

9.5. Storage Refrigerators with thermometers

9.6. Temperature Gun

9.7. pH Strips

9.8. Disposable pipettes

9.9. Disposable plastic containers

9.10. Safety glasses

9.11. Chemical protective gloves

9.12. Cut resistant gloves

9.13. Auto-retractable utility knives

9.14. Radiation Screening Instrument

The instrument used for scanning coolers and packages for radiation is an S.E. International Monitor 4 powered by a 9 volt battery.

The Monitor 4 Radiation instrument is calibrated annually by S.E. International by pulse generator and is typically ± 15% of full scale relative to Cesium 137.

There are many natural factors which affect background radiation levels at any given time the instrument is turned on.

10. Reagents and Standards

10.1. Methylene Chloride (DCM)

11. Calibration and Standardization

11.1. Not applicable to this SOP.

12. Procedure

The following policy and procedures are in place to ensure that all samples and chains of custody accepted at PAES are thoroughly inspected and all discrepancies are fully documented. A Client Service Representative shall contact the client in the event that there is any discrepancy involving the

condition or the documentation of samples, upon receipt, that may affect the sample's integrity or the analytical process.

A permanent record of sample receipt shall be maintained electronically in the Laboratory Information Management System (LIMS). At a minimum, that record will include: (1) Client Name; (2) Project Name; (3) Date and time of sample receipt; (4) Unique laboratory identification code; (5) Name or initials of the person making the entries; and (6) requested analyses.

12.1. **Sample Acceptance Policy**

A printed copy of the Sample Acceptance Policy (see Attachment I) is forwarded to sample collection personnel as a part of their bottle order shipment.

12.2. **Sample Receipt Procedure**

- Prior to signing shipping documents from courier, ensure that the number of packages listed on the shipping documents corresponds with the number of packages actually delivered.
- The courier must document existing discrepancies before the Sample Receipt Technician accepts the packages. Document the discrepancy on a Non-Conformance Form and forward it to the Client Service Office for immediate action.
- Put on safety glasses and protective gloves before handling, opening, or unpacking packages and coolers that contain environmental samples.
- Prior to cooler inspection and opening, determine if any coolers were received from any DOE or DOD facilities. These coolers and packages must be scanned for radiation using the Radiation Alert Monitor 4 according to the following procedures:

  Turn the Monitor 4 Radiation Instrument to the ON position.

  Check the battery by sliding the range switch to the Battery icon position. The needle should move to the meter area marked battery at the right side of the meter display. If the meter indicates a low battery, outside of the battery area, turn the instrument off and replace the battery with a 9 volt battery.

  Set the range switch in the X1 position and take a background reading away from the proximity of the packages. The reading should be <0.1mR/hr, as indicated on the dial.

  Record the date, time, battery check, and background reading in the radiation instrument log. This documentation shall be done at least once a day when the radiation instrument is used.

  Hold the back of the instrument toward the cooler beginning at a distance of 1 foot and slowly close the distance to one inch. **If the instrument shows a reading above background, greater than 0.1mR/hr, leave the room and close both doors. The Technical Director will take appropriate action to remove and/or isolate the cooler.**

- Inspect all coolers and packages for damaged or broken custody seals. Note any discrepancies on a Non-Conformance Form.
- Open the cooler and expose the sample bottles. Hold the back of the radiation instrument over the samples within the cooler to a proximity of 1 inch. If there is no reading above background, greater than 0.1mR/hr, continue with the sample receipt process. **If the instrument shows a reading above background, take the same steps as above.**

- Record the cooler temperature on the cooler receipt form as soon as possible upon opening the cooler. The temperature in the cooler should be above freezing but <6°C. If the temperature is not within those parameters, note the discrepancy on a Non-Conformance Form and indicate whether ice was present or not. Sign the chain of custody on the date of receipt.

  Special NPDES requirements: For samples requiring analyses for NPDES monitoring, a minimum of one bottle from each sampling location will be checked for temperature upon receipt. The temperature will be recorded either on the chain of custody form or the cooler receipt form. A list of NPDES-related clients will be maintained in sample login to assist with identification. This list will be reviewed and updated as necessary, annually at a minimum.

  Special Requirements for Samples Originating in WV - Measure the temperature of each sample container using the IR gun and document any container that is outside of the acceptable range of above freezing but less than 6 degrees C.

- Inspect each sample and sample label while removing it from the cooler. Samples containers should be intact. At a minimum, sample labels should be completed with the following information:

  Sample Number
  Date and time of Collection
  Site Name

  If samples cannot be properly identified by label inspection, note the discrepancy on a Non-Conformance Form.

- If samples were received in grouped sets, keep the sets grouped together as they are unpacked. If samples were not received in sets, organize them into sets while unpacking.
- Match the sample identifications to the Chain of Custody. Note any discrepancies on a Non-Conformance Form.
- If the project requirements specify data reporting above PAES' standard level, the technician must be aware that each group of 20 samples may have at least one duplicate and one spike set. Note any discrepancies on a Non-Conformance Form.
- Check to see if field and trip blanks are present and identified. Document all missing or potentially missing samples on a Non-Conformance Form.
- Check the Chain of Custody to ensure that all samples are entered and the specific analysis is listed for each bottle. Note all discrepancies on a Non-Conformance Form.
- Check appropriate samples for proper sample preservative using pH paper according to the procedure outlined in Section 12.5 of this Standard Operating Procedure. Samples that are improperly preserved are to be documented using a Non-Conformance Form.
- If samples for Petroleum Forensics are received, follow the instructions on Attachments IX and X to properly identify sample matrix and analysis.
- Complete Cooler Receipt form (Attachment V) for each package opened when a standard Pace Chain of Custody is not used.
- If a request is made by the client to hold samples, a Sample on Hold Process Sheet (Attachment VII) will be generated and kept with the samples.
- Ensure that all sample receipt documentation is complete.

- Once the cooler is emptied, remove all tape, labels and other packing materials and place the coolers with the lids opened in the hallway to dry prior to storage.

12.2.1. **Quarantined Soil Receipt Procedure**

This procedure is applicable to all soil samples received from a foreign country or the following US states and/or territories (check the USDA/APHIS website periodically for updates to this list):

- Alabama
- Arkansas
- California
- Florida
- Georgia
- Louisiana
- Idaho
- Mississippi
- New Mexico
- New York
- North Carolina
- Oklahoma
- Puerto Rico
- South Carolina
- Tennessee
- Texas

Client Service personnel are responsible to determine if soil samples coming to the laboratory have originated from a restricted area as defined above.

Client Service will complete a Foreign and Domestic Soil Sample Processing form. (Attachment IV) This form will be printed on orange paper to make it easy to identify.

This form is forwarded to Sample Receiving to alert them of the possibility of sample receipt.

Once the project is received and verified through the Foreign and Domestic Soil Sample Processing form, the samples are logged into the LIMS as usual and a Regulated Domestic and Foreign Soils checklist (Attachment VIII) is completed and placed into the project folder.

When sample labels are applied to the containers, an orange dot is also applied to the sample container lids so that the analysts will know that the samples require special processing.

The orange form becomes part of the permanent file in the waste coordinators office and is used upon project completion to document proper disposal treatment of samples.

Refer to the SOP for Regulated Soil Handling for exact procedure for handling regulated soils.

12.2.2. **Weekend Sample Receipt Procedures**

If the Sample Receipt Technician is not present, the weekend analyst will follow the abbreviated sample receipt process below in order to comply with sample holding times. The complete sample receipt process will occur during normal business hours the following Monday.

- If coolers were received from DOD or DOE facilities, scan those coolers for radiation prior to and during opening following instructions above.
- Remove samples that have short holding times for immediate analysis.
- Leave a detailed message with Sample Receipt Technician on what bottles were taken. This may be done via email, voicemail, or written note.

12.2.3. **After Hours Receipt Procedures**

Because the Sample Receipt Technician is not typically present before or after normal business hours, samples that are received during those times shall be placed into the cooler in the Sample Receiving area until the Sample Receipt Technician processes them on the following business day. If a client wishes to have samples processed outside of normal business hours they must make those arrangements with PAES Client Service Office prior to sample delivery. The Client Service Manager must approve those arrangements in writing.

12.2.4. **Sample Receipt Discrepancies**

If there is any discrepancy, problem, or situation with the samples or the above steps that is out of the ordinary, a Non-Conformance Form must be completed immediately and submitted through the proper channels as specified in Section 12.4 of this Standard Operating Procedure.

After all sample receipt documentation has been completed and the samples have been thoroughly examined, the Sample Receipt Technician creates a batch file and begins the process of Sample Log-In in accordance with the LIMS Standard Operating Procedure.

12.3. **Non-Conformance Forms**

The Non-Conformance Form is PAES' primary documentation tool for sample receipt problems or discrepancies that require client contact or corrective action. It is imperative that Non-Conformance Forms are completed accurately and submitted to the Client Service Office in a timely manner.

Any non-standard requirements that were not negotiated in advance of sample receipt such as rapid-turnaround, particular reporting limits, or particular sample disposal instructions must be documented on a Non-Conformance Form.

Non-Conformance Forms are to be completed by the Sample Receipt Technician under the following conditions:

- Broken containers
- Label information inadequate to properly identify samples
- Information on COC inadequate to properly log-in samples
- Missing or extra samples
- Conflict between bottle labels and COC (except as noted below)
- Samples received past holding times (except as noted below)
- Improperly preserved samples
- Any other circumstances that are out of the ordinary

Exceptions: In the following situation, non-conformance forms are not required:

- Samples received for pH analyses are always received outside of the specified holding time; therefore a non-conformance form is not required. A notice in the narrative portion of the final report must indicate that samples for pH were received out of hold.

12.3.1. **Non-Conformance Form Submissions and Handling**

The Client Service Office is to be notified as soon as possible when a Non-Conformance Form is issued. Client Service is to expedite their completion of the Non-Conformance Process and return the documentation to the Sample Receipt Technician as quickly as possible. The original Non-Conformance Form is to be placed in the project file.

12.3.2. **Non-Conformance Completion**

A Non-Conformance Form is to be completed by Sample Receiving personnel as follows:

- Complete date, client name, name of person who received samples, and time of sample receipt.
- Using the lines on the form, ensure adequate information is provided to explain the non-conformance.
- Add additional information, if necessary, on the back of the Non-Conformance Form.
- Submit form to Client Service Office.

The bottom half of the form is to be completed by the Client Service Office as follows:

- Client Service shall document the action taken on the form.
- Client Service will then initial and date the form at the bottom.
- The form will then be returned to Sample Receiving personnel who will check it for completeness.
- Sample Receiving personnel will then log in the samples accordingly, and write the PAES project number on the top of the non-conformance form and place the original in the project file where it becomes a permanent part of the project file.

12.4. **Checking Sample Preservative**

In order for water samples to be considered valid, they must be either cooled and/or chemically preserved according to the type of analyses each sample will undergo. All appropriate samples for analyses that require chemical preservatives shall be checked upon log-in for proper preservative.

The following are not tested for a preservative prior to analysis:

- volatiles in 40 ml vials (either for SW-846 8260, EPA 624 or fuel oxygenates)
- dissolved gases (either light hydrocarbons, permanent gases or MEE; by AM20GAx or RSK175)
- volatile fatty acids (AM21 or AM23G)

All other water samples are to be tested through the use of the narrow range pH paper as per Table 12.4.

Table 12.4 Acceptable pH range by preservative

Preservative	Acid	Neutral	Base
Nitric Acid (HNO_3)	<2	-	-
Sulfuric Acid (H_2SO_4)	<2	-	-
Hydrochloric Acid (HCl)	<2	-	-
Benzyl alkonium chloride (BAK)	-	4-8	-
Unpreserved	-	4-8	-
Sodium hydroxide (NaOH)	-	-	>12
Sodium hydroxide and Zinc acetate (NaOH + ZnAc)	-	-	>12
Trisodium Phosphate	-	-	>10

12.4.1. **Procedures for Checking Sample Preservative**

- Ensure proper personal protective equipment is being worn, i.e. lab coat, safety glasses and protective gloves.
- Open sample container to be tested and pull a small amount of the sample into a disposable pipette.
- Squeeze the aliquot into a clean disposable plastic dish.
- Immerse the pH paper into the aliquot in the plastic dish. Narrow range pH paper will be used. The paper is selected based upon the preservative as presented in Table 12.5.
- Compare the pH paper to the chart to determine the pH range of the sample aliquot.

- The pH check shall be documented in detail by writing the full client sample id, the preservative, the pH and the pH strip lot number next to it on the pH screening form (Attachment VI). If a sample has more than one container with the same preservative, just put an A, B, … suffix after the sample name. For example, if there are 4 sulfide bottles for sample MW-1 the cooler receipt form would have written on it:
  MW-1A NaOH+ pH 12.9
  MW-1B NaOH+ pH 13.0
  MW-1C NaOH+ pH 13.0
  MW-1D NaOH+ pH 12.9
- Dispose of the used pipette and dish. Use a new set for each bottle tested.

12.4.2. **Preservative Check Documentation**

All samples that are checked for preservative will be documented manually on the Cooler Receipt Form and pH screening form. These forms become a permanent part of the record and are maintained for a minimum of five years.

12.5. **Sample Storage**

Samples shall be stored according to the conditions specified by preservation protocols. The storage conditions shall be maintained, monitored, and documented. Samples shall be stored away from all standards, reagents, food and other potentially contaminating sources. Samples shall be stored in segregated areas to prevent cross contamination.

12.5.1. **Sample Storage Temperature Documentation and Responsibility**

Samples which require thermal preservation shall be stored under refrigeration or frozen. Digital thermometers that record maximum and minimum temperatures are used to insure that sample integrity is not compromised by transient temperature excursions between thermometer readings. It is the Sample Receipt Technician's responsibility to record that maximum and minimum and to reset thermometer on each work day. A temperature of just above freezing but below 6°C is acceptable for a refrigerator that has been closed overnight. A temperature of -10 to -20°C is acceptable for a freezer. The temperature logs are to be maintained in the Sample Receipt Technician's Office.

12.5.2. **Corrective Action for Refrigerator Temperature Beyond Control Limits**

If the temperature is outside of the acceptable temperature range limits, the Sample Receipt Technician must immediately notify the Laboratory Manager. Maintenance will be arranged through the Laboratory Manager or his representative. If it is apparent that the proper sample temperature cannot be maintained in the area needing maintenance, then every effort will be made to move samples to another cooler that is functioning within the temperature control limits.

12.5.3. **Samples Requiring Extra Security**

If the Sample Receipt Technician has previously been notified by the PAES' project manager that the samples require high security, the Sample Receipt Technician is to complete an internal chain of custody form for each bottle type using our standard chain of custody form. Once the log-in process is complete the samples are to be placed in a cooler in a secure room. A sample tracking record with the appropriate bottle type circled shall be posted on the outside of the cooler. Only PAES personnel will have access to that area, and will sign out those samples when they are taken for analysis. Employees who have signed out samples will keep them in their possession at all times, or in a secure area, until such time as the analysis is complete or the remainder of the sample(s) and/or extract(s) is/are returned to the original locked location. A sample tracking record form is displayed in Attachment III.

13. Quality Control

13.1. Not applicable to this SOP.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. Not applicable to this SOP.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. Safety glasses are required in all lab areas, including Sample Receiving. All personnel are required to wear appropriate personal protective equipment, which includes, but is not limited to, safety glasses, lab coat and protective gloves. Cut resistant gloves are to be used when using auto-retractable knives or broken glass. Coolers shall be opened in a well ventilated area. If odors are detected upon opening, the cooler shall be closed and moved to an area with a fume hood before proceeding with the sample receipt procedures.

23. Waste Management

23.1. Not applicable for this SOP.

24. Pollution Prevention

24.1. Not applicable for this SOP.

25. References

25.1. Radiation Alert, Operation Manual for the Monitor 4, Monitor $EC, and MC1K.

25.2. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: Sample Acceptance Policy

26.2. Attachment II: Non-Conformance Form

26.3. Attachment III: Sample Tracking Record

26.4. Attachment IV: Foreign and Domestic Soil Sample Processing Form

26.5. Attachment V: Cooler Receipt Form

26.6. Attachment VI: pH Screening Form

26.7. Attachment VII: Sample on Hold Process Sheet

26.8. Attachment VIII: Regulated Domestic and Foreign Soils Checklist

26.9. Attachment IX: Petroleum-Sample Matrix Identification Instructions

26.10. Attachment X: Petroleum-Sample Login Table

27. Revisions

Document Number	Reason for Change	Date
Section 12.3	Added Sample on Hold Process Sheet	1/30/2017
Section 12.3.1	Added references to Regulated Domestic and Foreign Soils Checklist and SOP-S-002 for Regulated Soil Handling.	1/30/2017
Attachments	Added Attachments VII, VIII, IX, X	1/30/2017
Section 12.3.3	Changed Lab Manager to Client Service Manager	2/2/2017
Section 12.3	Added reference to the new Petroleum Forensics Attachments	2/2/2017
Table 12.5	Changed acceptable pH range to >10 for tri sodium phosphate to agree with notes put on the case narratives of final reports.	2/2/2017
S-PAE-C-003-rev.01 Attachment I	Updated with new sample acceptance policy	7/25/2017
S-PAE-C-003-rev.01 Section 12.1	Removed this section, as it is an attachment to the SOP	7/25/2017
S-PAE-C-003-rev.01 Section 12.5	Checking sample preservation-deleted anion and cation analyses	7/25/2017
S-PAE-C-003-rev.02	Added the documentation of pH strip lot numbers to Section 12. Updated the pH Screening Form to include the documentation of the pH strip lot numbers.	7/6/2018

ENV-SOP-PITTS-0027 rev.00	Removed references to old SOP numbers. Updated Regulated soil Section to include a note to check the website for periodic changes to the map and to remove Arizona from the list. Added WV requirement for checking temperature of every sample to Section 12. Removed cover page and Table of Contents to fit into MC. Added task of empyting coolers and removing all labels and tape and letting dry in the hallway.	6/3/2019

Attachment I
Sample Acceptance Policy

Pace Analytical® Energy Services	Document Name: Sample Acceptance Policy	Document Revised: July 24, 2017 Page 12 of 1
	Document No.: F-PAE-Q-017-rev.01	Issuing Authority: PAES Quality office

PAES Sample Acceptance Policy

In accordance with regulatory guidelines, PAES complies with the following sample acceptance policy for all samples received.

If the samples do not meet the sample receipt acceptance criteria outlined below, the Pace facility is required to document all non-compliances, contact the client, and either reject the samples or fully document any decisions to proceed with analyses of samples that do not meet these criteria. Any results reported from samples not meeting these criteria are noted in the case narrative of the final report.

Sample Acceptance Policy requirements:

1. Sample containers must have unique client identification designations, and dates and times of collection, that are clearly marked with indelible ink on durable, water-resistant labels. The client identifications must match those on the chain-of-custody (COC);
2. There must be clear documentation on the COC, or related documents such as the Cooler Receipt form, that lists the unique sample identification, sampling site location (city, state), date and time of sample collection, and name and signature of the sample collector;
3. There must be clear documentation on the COC, or related documents, that lists the requested analyses, the preservatives used, sample matrix, and any special remarks concerning the samples (i.e., data deliverables, samples are for evidentiary purposes, field filtration, etc.);
4. Samples must be in appropriate sample containers. If the sample containers show signs of damage (i.e., broken or leaking) or if the samples show signs of contamination, the samples will not be processed without prior client approval;
5. Samples must be correctly preserved upon receipt, unless the method requested allows for laboratory preservation. If the samples are received with inadequate preservation, and the samples cannot be preserved by the lab appropriately, the samples will not be processed without prior client approval;
6. Samples must be received within required holding time. Any samples with hold times that are exceeded will not be processed without prior client approval; Clients are requested to notify PAES client services if samples with short holding times are being shipped;
7. Samples must be received with sufficient sample volume or weight to proceed with the analytical testing. If insufficient sample volume or weight is received, analysis will not proceed without client approval;
8. All samples that require thermal preservation are considered acceptable if they are received at a temperature within 2°C of the required temperature, or within the method-specified range. For samples with a required temperature of 4°C, samples with a temperature ranging from just above freezing to 6°C are acceptable. Samples that are delivered to the lab on the same day they are collected are considered acceptable if the samples are received on ice. Any samples that are not received at the required temperature will not be processed without prior client approval.
9. Some specific clients may require custody seals. **For these clients**, samples or coolers that are not received with the proper custody seals will not be processed without prior client approval.
10. Samples must pass the radiation screening according to the criteria set forth in the SOP for Sample Receiving.
11. Coolers that arrive with hazard labels on them, for which PAES is not equipped or certified, will not be accepted. A chart listing these hazards is posted in Sample Receiving.

Attachment II

NON-CONFORMANCE FORM

PAES Work Order #: _____

Date: _____ Time of Receipt: _____ Receiver: _____

Client: _____

REASON FOR NON-CONFORMANCE:

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

ACTION TAKEN:

Client name: _____ Date: _____ Time: _____

_____

_____

_____

_____

_____

_____

_____

Client Service Initials: _____ Date: _____

Attachment III

Sample Tracking Record

Client Name: _____ **Page** _____ **of** _____

Client Project Number: _____

Bottle Type **Circle or Highlight** (Sample Receiving Only)	VOA	VFA	TIC	Hydrogen			
	G. Chem.	LLVFA	Soils	CSIA			
	TOC/DOC	Cations	Diss. Gas	Petroleum			
	Sulfide	Anions	Vapor	Molecular			

Sample Receiving only to mark above dotted line

Sample Numbers	**Removed from Storage**			**Bottle**	**Returned or Placed in Storage**		
	By	**Date**	**Time**	**Type**	**By**	**Date**	**Time**

Enter Bottle Type From List Above In Proper Column

Sample Tracking Record

Client Name: _____ **Page** _____ **of** _____

Client Project Number: _____

Sample Receiving only to mark above dotted line

Sample Numbers	Removed from Storage			Bottle Type	Returned or Placed in Storage		
	By	Date	Time		By	Date	Time

Enter Bottle Type From List Above In Proper Column

Attachment IV

Foreign and Domestic Soil Sample Processing

Client Name: _____
Client Contact Name: _____
Project Name: _____
Expected Date of Arrival: _____
State/Country of Origin: _____
PAES WO#: _____
Subcontracted? Yes / No Lab _____
Heat treated/Disposal Date: _____

Comments:

_____
_____
_____
_____
_____
_____
_____

Soil samples received for the above mentioned project, must be disposed of as per USDA specifications.
These samples must be tracked through the lab by using the NEON ORANGE dot stickers. Upon completion of analytical testing, soil samples that have the NEON ORANGE dot stickers, must be kept in the waste room, separated from the others.

After completion of the analytical program and generation of the final report, please return this form to the Waste Coordinator for filing and disposal purposes.

Attachment V
Cooler Receipt Form

Client Name: _____ **Project:** _____ **Lab Work Order:** _____

A. **Shipping/Container Information** (circle appropriate response)

Courier: FedEx UPS USPS Client Other:_____

Air bill Present: Yes No

Tracking Number:_____

Custody Seal on Cooler/Box Present: Yes No **Seals Intact:** Yes No

Cooler/Box Packing Material: Bubble Wrap Absorbent Foam Other:_____

Type of Ice: Wet Blue None **Ice Intact:** Yes Melted

Cooler Temperature:_____ **Radiation Screened:** Yes No

Chain of Custody Present: Yes No

Comments:_____

B. **Laboratory Assignment/Log-in** (check appropriate response)

	YES	NO	N/A	Comment Reference non-Conformance
Chain of Custody properly filled out				
Chain of Custody relinquished				
Sampler Name & Signature on COC				
Containers intact				
Were samples in separate bags				
Sample container labels match COC Sample name/date and time collected				
Sufficient volume provided				
PAES containers used				
Are containers properly preserved for the requested testing? (as labeled)				
If an unknown preservation state, were containers checked? Exception: VOA's coliform				If yes, see pH form.
Was volume for dissolved testing field filtered, as noted on the COC? Was volume received in a preserved container?				
Headspace present?				

Comments:_____

Cooler contents examined/received by :_____ **Date:**_____

Project Manager Review :_____ **Date:**_____

F-PAE-Q-009-rev.01, 3Oct2017

Attachment VI

pH SCREENING FORM

Client _____ **Client Project** _____

PAES WO# _____

Completed by _____

Date _____

Page ___ of ___

No.	Sample	Preservative							pH	pH strip lot number
		HNO_3	H_2SO_4	HCl	None	BAK	NaOH	NaOH+ ZnAc		

Attachment VII

SAMPLE ON HOLD (SAVE) PROCESS SHEET

Requested by: _____ Date Requested: _____

Client Name: _____

Contact person(s): _____

Phone Number: _____

Client project name/number: _____

Sample name(s)/number(s): _____

_____

_____

_____

_____

Save in walk-in cooler: Y or N (circle one) Save till date: _____

Samples will be held for 30 days unless otherwise stated. After 30 days, the sample(s) will be discarded or returned to the client. (If requested in writing by the client.)

Comments: _____

_____

_____

_____

_____

_____

_____

_____

_____

Sample custodian signature: _____ Date: _____

Copy of original COC with Project Number must accompany this form.

F-PAE-Q-025-rev.00, 15JAN2015

Attachment VIII
Regulated Domestic and Foreign Soils Checklist

Project #: _____ **Time:** _____

Initials: _____ **Date:** _____

Origin (Circle One): **Domestic** **Foreign**

If "Domestic", State of Origin (Circle One) AL AR AZ CA FL GA ID LA MI MS NC NM NY OK OR SC TN TX WA

If "Foreign", Country of Origin: _____

Note: Soils from Hawaii and Puerto Rico are of Foreign Origin

Sample analysis will take place at (Circle all that apply):

PAES Subcontract Laboratory

Name of Subcontract Laboratory: _____

	Action	Completed
1) Did "Regulated" sticker get placed on Samples?	Regulated sticker must be placed onto each sample container.	Yes / No
2) If samples were sent to a subcontract laboratory, do they hold a valid Soil Permit and Compliance Agreement from the USDA? If not being subcontracted please circle NA.	Subcontract Laboratories are required to hold a valid Soil Permit and Compliance Agreement before we can send soil samples to them. Verify validity by contacting and getting a copy of it	Yes / No / NA
3) Were Samples placed in designate container in Walk-In Cooler?	Regulated samples retained at PAES Laboratory must be stored in designated containers in the Walk-In Cooler.	Yes / No
4) Were there signs of breakage or leakage? If no please complete 5, circle NA for 6 and move to 7. If yes please circle NA for 5, and move to 6.	Check for broken glass or loose soil in the cooler.	Yes / No
5) Were ice and melt water separated from cooler and disposed of properly? (No signs of breakage or leakage)	Foreign and Domestic Sources: Ice and melt water can be disposed of by dumping down the sink.	Yes / No / NA
6) Were ice and melt water separated from cooler and disposed of properly? (Signs of breakage or leakage)	Foreign and Domestic Sources: Ice and melt water must be baked at 140°C then cooled and dumped down the sink. Soils must be disposed of by baking and then placing in appropriate waste barrel.	Yes / No / NA
7) Was the cooler decontaminated?	Soak cooler for 30 minutes with 1:10 bleach solution, drain in sink, let cooler air dry.	Yes / No

Comments:

Attachment IX

How to test if sample matrix is PRODUCT or WATER?

Petroleum Samples

1. Look at the chain-of-custody (COC) to see what analyses are being requested and what matrix is listed on the COC by the client
2. Look at the sample containers to see what the client sent
3. Follow table to determine if 'TEST' needs to be completed
4. If 'TEST' is required, grab a clean 2mL glass vial
5. Grab clean glass pipette and DCM container vial
6. Pipette ~1mL of DCM in the clean 2mL vial
7. Grab a disposable glass pipette (do not use same pipette for different samples)
8. Pipette ~1mL of sample in the clean 2mL vial with the DCM already in it, shake it slightly
9. Determine if there is a separation of phases
10. If there is a line, the sample is a water (bring folder up to PM so that the correct analyses are chosen)
11. If there is no line, the sample dissolved with DCM and matrix is a product
12. If still unsure of matrix, ask analyst or PM to come down and analyze further
13. Place 2mL vial with sample mixture in disposal container when finished

Attachment X

MATRIX TYPE

ANALYSIS

	PRODUCT (Oil/Gasoline/Diesel)	SOIL (Soil/Dirt/Sediment/Wipe)	AQUEOUS (Water)
C3-C36 or Whole Oil or ASTM D3328	TEST	X	X
Fuel Oxygenates Or EPA 1625M	TEST	X	X
Organic Leads Or OrgPb/EDB/ MMT	TEST	X	X
Simulated Distillation Or ASTM D2887	TEST	X	X
Full Scan Or C8+ Hydrocarbon Or ASTM D5739	TEST	OK	TEST
C3-C10 Or PIANO GC/MS	TEST	OK	TEST
PAH	TEST	OK	TEST

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Document Title: Waste Handling and Management

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Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

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All dates and times are in Central Time Zone.

ENV-SOP-PITTS-0023

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Charlotte Washlaski (003467)	Quality Manager	25 Apr 2019, 01:06:03 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Charlotte Washlaski (003467)	Quality Manager	25 Apr 2019, 01:18:59 PM	Approved

1. Purpose/Identification of Method

1.1. Pace Analytical Services, Inc. (Pace) acknowledges its obligation to the responsible management of the environment and its resources. Pace Management is committed to operating in such a way that meets or exceeds the state and federal laws governing waste management and encourages the use of best practices to reduce, reuse and recycle waste material where possible. This Standard Operating Procedure (SOP) documents the systems, processes and procedures that Pace Analytical Energy Services uses to manage generated wastes.

1.2. It is Pace's policy to minimize the amount of hazardous waste it produces and to reduce the hazardous properties of those wastes whenever practical within regulatory compliance. This can be achieved by periodic auditing of all processes producing hazardous waste; reduction of sample volume delivered by the client; return of excess sample material to clients whenever practical and economical; investigation of new technologies that might require smaller volumes of sample. or produce fewer or less hazardous by-products; implementation of lab cleaning procedures that reduce the volume of cleaning residue; recycling of hazardous materials; and investigation of new treatment technologies that are comprehensively destructive or are effective in reducing the volume or hazardous qualities of the wastes produced.

2. Summary of Method

2.1. Pace facilities that generate waste must initially contact the EPA to obtain an ID number. Each unique type of generated waste is classified and characterized into waste streams according to procedures in 40 CFR 261. The amount of waste the facility generates determines the Generator Status of a lab, which in turn determines how long and how much waste can accumulate. Pace Analytical Energy Services is ultimately responsible for the waste it generates, and is required to obey any and all regulations during the process of creating, accumulating, disposing, and releasing waste to a TSDF for final disposal. Documentation is kept to prove all regulations have been obeyed.

3. Scope and Application

3.1. Personnel: The policies and procedures contained in this SOP are applicable to all personnel responsible for all aspects of waste handling and management.

3.2. This SOP is applicable to all processes at Pace Analytical Energy Services that involve generated waste, and is designed to assist its operations in adhering to regulations set forth in the following federal statutes: Resource Conservation and Recovery Act (RCRA), Clean Water Act (CWA), Toxic Substances Control Act (TSCA), and DOT Title 49, and Transportation (parts 100-199). Particular attention is given to local pretreatment standards covering discharges to publicly owned treatment works (POTW) when performing elementary neutralization on acidic and basic waste. The local standards are based in part upon provisions in the National Pretreatment Standards and Prohibited Discharge Standards.

3.3. The degree to which RCRA regulations apply to Pace facilities is dependent upon the generator status of the operation. Under the federal rules (state requirements may be more stringent or give the classes a slightly different name) there are three different classes of hazardous waste generators based upon the amount of waste generated in a month to month time frame.

3.4. **Waste Generator Class Limits:**

Hazardous Waste Generator Class	Quantity of Hazardous Waste Generated per Month	Generated Monthly Acute Hazardous Waste	Maximum Allowable Hazardous Waste Quantity on-site	Maximum Permitted Waste Accumulation Time
Cond. Exempt Small Quantity	<100kg	<1 kg	<1000kg	Unlimited
Small Quantity	100-1000kg	<1 kg	<6000kg	180 days (270 days if the waste must be sent >200 miles to TSDF)
Large Quantity	>1000kg	>1kg	Unlimited	90 days

3.5. **Parameters**: Not applicable to this SOP.

4. Applicable Matrices

4.1. Not applicable to this SOP.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Not applicable to this SOP.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Not applicable to this SOP.

8. Definitions

8.1. **Acutely Hazardous Waste** - A waste which is hazardous as identified with an (H) Hazard Code in the lists of Hazardous Waste in 40 CFR Part 261, Subpart D, Sections 261.30, 261.31 and 261.33.

8.2. **Animal and Plant Health Inspection Service (APHIS)** - an agency of the USDA responsible for protecting animal health, animal welfare, and plant health. APHIS is the lead agency for collaboration with other agencies to protect U.S. agriculture from invasive pests and diseases.

8.3. **Clean Air Act** - The Federal Clean Air Act, 42 U.S.C. 7401, and amendments thereto amending 42 U.S.C. 1857 et.seq.

8.4. **Conditionally Exempt Small Quantity Generator** - A generator who produces no more than 100 kilograms of hazardous waste or one kilogram of acutely hazardous waste (or a total of 100 kilograms of any residue or contaminated soil, waste or other debris resulting from the cleanup of a spill, into or on any land or

water, or any acute hazardous waste) in a calendar month. The total amount of hazardous waste which may be accumulated on-site is 1000 kilograms.

8.5. **Confined Space** – A space that is large enough and so configured that an employee can bodily enter and perform assigned work; and has limited or restricted means for entry or exit (for example, tanks, vessels, silos, storage bins, hoppers, vaults, and pits are spaces that may have limited means of entry); and is not designed for continuous employee occupancy.

8.6. **Container** - Any device material is stored, transported, treated, disposed of, or otherwise handled.

8.7. **Contingency Plan** - A document setting out an organized, planned, and coordinated course of action to be followed in case of fire, explosion, or release of hazardous waste or hazardous waste constituents which could threaten human health or the environment.

8.8. **Designated Hazardous Waste Storage Area** - Area used to hold hazardous waste for a temporary period, at the end of which the hazardous waste is treated, disposed of, or stored elsewhere. This is the storage area into which hazardous waste from the laboratory (e.g., satellite waste) is moved.

8.9. **DOT** - The United States Department of Transportation.

8.10. **DTSC** – Department of Toxic Substances Control.

8.11. **Elementary Neutralization Unit** – A device which: (1) is used for neutralizing wastes which are hazardous only because they exhibit the corrosivity characteristic defined in 40 CFR 261.22 or are listed in Subpart D of Part 261; and (2) meets the definition of tank, container, transport vehicle, or vessel in 40 CFR 260.10.

8.12. **EPA** - The United States Environmental Protection Agency.

8.13. **EPA Hazardous Waste Number** - The EPA number assigned to each EPA hazardous waste identified in 40 CFR Part 260, Subpart D - Lists of Hazardous Wastes.

8.14. **EPA Identification Number** - The site-specific number assigned to each generator, transporter, and TSDF upon approval of a notification form.

8.15. **Federal Clean Water Act** - 33 U.S.C. 1251, et. Seq.

8.16. **Foreseeable Emergency** - Any fire, explosion, or sudden or non-sudden release of hazardous waste or hazardous waste constituents to the air, soil, or surface water, which could threaten human health or the environment.

8.17. **Generator** - Any person, by site who owns or operates a facility where hazardous waste is generated, i.e. Pace Analytical Services (Pace).

8.18. **Hazardous Waste Coordinator** - The Pace employee responsible for creating, guiding, and implementing all hazardous waste management operations.

8.19. **Hazardous Waste** - As defined in 40 CFR Part 261, Subparts B and C, a solid, semi-solid, liquid or contained gaseous waste, or any combination of these wastes.

8.19.1. Which, because of either quantity, concentration, physical, chemical, or infectious characteristics may:

8.20.1.1. Cause or contribute to an increase in mortality or an increase in irreversible or incapacitating reversible illness; or

8.20.1.2. Pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, disposed of or otherwise mismanaged.

8.19.2. Or which has been identified as having a characteristic of hazardous waste by the EPA using the criteria established under 40 CFR Part 261, Subpart C, or as listed under Sections 261.31, 261.32, 261.33, and 261.34. Such wastes include, but are not limited to, those which are reactive, toxic, corrosive, ignitable, irritants, strong sensitizers or which generate pressure through decomposition, heat or other means. Such wastes do not include radioactive substances that are regulated by the Atomic Energy Act of 1954, as amended. A waste is considered hazardous if it is listed or it fits into one of four categories. These categories are as follows:

8.20.2.1. Ignitable – (40 CFR 261.21, Waste Code D001) A flash point of less than 60°C/140°F.

8.20.2.2. Corrosive – (40 CFR 261.22, Waste Code D002) A pH of less than 2.0 or greater than 12.5.

8.20.2.3. Reactive – (40 CFR 261.23, Waste Code D003) Reactive wastes exhibit one or more of the following characteristics:

8.20.2.3.1. It is unstable and can undergo a violent change without detonating.

8.20.2.3.2. It can react violently with water.

8.20.2.3.3. When mixed with water it can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.

8.20.2.3.4. It is cyanide or sulfide bearing waste that, when exposed to pH conditions between 2.0 and 12.5, can generate gases, vapors, or fumes that can present a danger to human health or the environment.

8.20.2.3.5. It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

8.20.2.3.6. It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.

8.20.2.3.7. It is a forbidden explosive as defined in 49 CFR 173.51, or a Class A explosive as defined in 49 CFR 173.53, or a Class B explosive as defined in 49 CFR 173.88.

8.20.2.4. Toxic – (40 CFR 261.24, Waste Codes D004-D043) A solid waste that contains a toxic concentration of a contaminant listed in 40 CFR 261.24, Table 1. A toxic waste is given any and all D-codes that apply to the particular material.

8.20. **Hazardous Waste Constituent** - A substance, compound, or element listed as hazardous waste in EPA 40 CFR 261.

8.21. **Lab Pack Material** - A hazardous waste that does not match a listed Pace waste stream category.

8.22. **Large Quantity Generator (LQG)** - Any generator who generates at a rate greater than 1000 kilograms of hazardous waste per month.

8.23. **Manifest** - As defined in 40 CFR Part 262, Subpart B, namely "the form used for identifying the origin, quantity composition, routing and destination of hazardous waste".

8.24. **Plant Protection and Quarantine (PPQ)** – A program within APHIS which attempts to safeguard agriculture and natural resources in the U.S. against the entry, establishment, and spread of animal and plant pests and noxious weeds.

8.25. **Regulated Soil** – Soil from foreign countries, U.S. territories and areas within states that are under Federal quarantine that can be moved into or through continental U.S. only if conditions and safeguards prescribed by the USDA and APHIS are met.

8.26. **Sample** - Except as provided below in 8.27.7.2.3, any solid waste, water, soil, or air that is collected for the sole purpose of being tested to determine its characteristics or composition.

8.26.1. Samples are not subject to any requirements of 40 CFR Part 261.5 or Parts 262 through 267 or Part 270 or Part 124 or to the notification requirements of Section 3010 of RCRA, when:

8.27.1.1 The sample is being transported to a laboratory for the purpose of testing; or

8.27.1.2 The sample is being transported back to the sample collector after testing; or

8.27.1.3 The sample is being stored by the sample collector before transport to a laboratory for testing; or

8.27.1.4 The sample is being stored in a laboratory before testing; or

8.27.1.5 The sample is being stored in a laboratory after testing but before it is returned to the sample collector; or

8.27.1.6 The sample is being stored temporarily in the laboratory after testing for a specific purpose (for example, until conclusion of a court case or enforcement action where further testing of the sample may be necessary).

8.26.2. In order to qualify for the exemption in 8.27.1.1 and 8.27.1.2 above, a sample collector shipping samples to a laboratory and a laboratory returning samples to a sample collector must:

8.27.7.1. Comply with U.S. Department of Transportation (DOT), U.S. Postal Service (USPS), or any other applicable shipping requirements; or

8.27.7.2. Comply with the following requirements if the sample collector determines that DOT, USPS, or other shipping requirements do not apply to the shipment of the sample:

8.27.7.2.1. Assure that the following information accompanies the sample:

8.27.7.2.1.1. The sample collector's name, mailing address, and phone number;

8.27.7.2.1.2. The laboratory's name, mailing address, and phone number;

8.27.7.2.1.3. The quantity of the sample;

8.27.7.2.1.4. The date of shipment; and

8.27.7.2.1.5. A description of the sample.

8.27.7.2.2. Package the sample so that it does not leak, spill, or vaporize from its packaging.

8.27.7.2.3. This exemption does not apply if the laboratory determines that the waste is hazardous but the laboratory is no longer meeting any of the conditions stated in 8.27.1 above.

8.27. **Satellite Waste or Laboratory Satellite Waste** - Hazardous waste generated by Pace that is at or near any point of generation and under the control of the operator. Satellite accumulation provisions allow generators to accumulate up to 55 gallons of hazardous waste (or 1 quart of acute hazardous waste) in containers without starting the storage clock as described in Section 3.4.

8.28. **Satellite Waste Container** - Any portable device used to accumulate laboratory generated waste prior to transfer to the hazardous waste storage area.

8.29. **Small Quantity Generator (SQG)** - A generator who produces no more than 1000 kilograms of hazardous waste (or a total of 1000 kilograms of any residue or contaminated soil, waste or other debris resulting from the cleanup of a spill, into or on any land or water, or any acute hazardous waste) in a calendar month. The total amount of hazardous waste which may be accumulated on-site is 6000 kilograms.

8.30. **TSDF** - A Treatment/Storage/Disposal Facility.

8.31. **Universal Waste** – Commonly used items that are hazardous but can be recycled. These include fluorescent lights, computer monitors, etc.

8.32. **Waste Stream** - The generic profile of chemical and physical properties that satellite wastes exhibit.

9. Equipment and Supplies (Including Computer Hardware and Software)

The following equipment is mandatory under RCRA guidelines unless otherwise denoted. Periodic review (not to exceed monthly) of availability of equipment and supplies below should be conducted to maintain an adequate and viable supply.

9.1. **Chemical Spill Control Neutralizers**: The waste room stores three types of bulk dry spill neutralizers: solvent, acid and base. They may be utilized by placing the dry neutralizer onto a liquid chemical spill. Neutralization is indicated by a prevalent color change.

9.2. **Communication Device**: Required for emergency notification of spill, fire, etc.

9.3. **Drums**: Common types of waste drums used for storing and shipping hazardous wastes are polyethylene, steel-polyethylene lined, and steel. Sizes are typically 5gal, 15gal, 30gal, and 55gal. Drums used for liquids typically are closed top with an opening to pour the solvent through a funnel, while drums used for solids or lab packs are open-top.

9.4. **Fire Alarm Pull Station**: A fire alarm pull station must be in close proximity to the hazardous waste room. The alarm may be activated by pulling the switch. Other alarm systems may be utilized as long as all personnel are trained on the procedures.

9.5. **Fire Extinguisher**: An extinguisher with a rating appropriate to the waste being stored in the area must be in close proximity to the hazardous waste room.

9.6. **Labels**: A multitude of labels are provided to ensure compliant labeling. They may be purchased or prepared manually.

9.7. **Liquid Chemical Neutralizers**: Liquid chemical neutralizers (base and acid) may be used to neutralize a contained hazardous liquid. This may be done by slowly adding the neutralizer to the liquid.

9.8. **Spill Control Pads**: Spill pads are used to soak up hazardous liquids. They do not neutralize spills. They are especially effective for cleaning up oily materials. Various pads are available for aqueous and petroleum based liquids.

9.9. **Spill Control Pillows**: Spill pillows may be used to soak up large amounts of liquid chemical spills. No neutralization occurs.

9.10. **Spill Dikes**: vary depending on the size and type of room: Their purpose is to encircle a spill, barring the spread of a hazardous chemical. They will also absorb liquids, but do not neutralize spills.

10. Reagents and Standards

10.1. Not applicable to this SOP.

11. Calibration and Standardization

11.1. Not applicable to this SOP.

12. Procedure

12.1. All Pace facilities that generate hazardous waste must have a Generator's US EPA Identification Number. The ID number is obtained through the applicable EPA region's office by completing EPA form 8700-12, and must be completed before generating any hazardous waste.

12.1.1. Pace only utilizes transporters and treatment, storage, or disposal facilities (TSDFs) that have EPA identification numbers for hazardous waste handling and meet the TSDF transfer requirements.

12.1.2. A new ID number is necessary when changing locations as the number is tied to the facility address.

12.1.3. This facility's US EPA Identification Number is PAD987397239.

12.2. The laboratory generates wastes originating from several source types: materials and chemicals used to prepare and analyze samples (e.g., solvents, acids), unconsumed liquid and solid samples, certain types of batteries, mercury from lamps and broken thermometers and automobile waste. Unconsumed samples may include laboratory-contaminated sample residue (both liquid and soil) generated as part of digestion, extraction, etc., procedures used to prepare samples for analysis.

12.2.1. This facility is classified as a Conditionally Exempt Small Quantity Generator.

12.3. Hazardous waste classification is the most critical step in establishing an effective, compliant waste-handling program. Laboratory wastes are classified using the criteria set forth under RCRA for ascertaining non-hazardous versus hazardous status, and this criterion is listed in the definition of hazardous waste in 8.20.

12.4. The following are the waste streams resulting from materials and chemicals used in the laboratory operation. Applicable information for each is given pertaining to packing, labeling, or listing on a manifest. A description of how the wastes are created, and the preferred method of final disposal for each, is included. The overriding principle in hazardous waste classification is application of a conservative formula based on all known or suspected hazards related to a waste material. While this formula may result in some materials being disposed as hazardous when in fact, they are non-hazardous (e.g., false positive), the formula will not be compromised in the interest of reducing the amount of waste produced. This will minimize any risk of a material being disposed of erroneously as non-hazardous when it, by definition, is a hazardous waste.

12.4.1. **Corrosive waste** is generated in the majority of the departments in the laboratory. This waste stream consists primarily of spent or excess aqueous reagent solutions generated from preservatives, acid digestions of metals, impinger solutions or other corrosive solutions generated in the course of analysis. The predominant corrosives include hydrochloric acid, nitric acid and sulfuric acid, but corrosives also include bases. Varying concentrations of metals may be present dependent upon the composition of the reagents added. This waste stream only has the hazardous quality of being corrosive; therefore, if a waste has any additional hazardous waste quality (e.g., Toxic or Ignitable) it cannot be mixed with this stream. This stream is most commonly treated onsite.

Corrosive Waste	
DOT Shipping Name	RQ Waste, Corrosive Liquid, N.O.S (i.e. corrosive material)
EPA Waste #	D002
Container	Various
Average pH	<2.0, >12.5
Disposal Method	Treatment by Neutralization
Label	Corrosive

12.4.2. The **Chlorinated Waste Stream** consists primarily of methylene chloride with a very small amount of other organic solvents derived from extraction procedures performed on samples and from rinsing glassware.

Chlorinated Solvents	
DOT Shipping Name	RQ Hazardous Waste, Toxic Liquid, N.O.S (i.e. dichloromethane, acetone, methanol)
EPA Hazard Codes	U080, F001/F002
Container	Various
Average pH	7.0
Disposal Method	Haz Waste Hauler
Label	Toxic, Chlorinated

12.4.3. . The **Product Sample Waste Stream** consists primarily of unused client product samples. This stream is containerized and placed with a TSDF for disposal.

12.5. Some waste can become complicated when attempting to classify as non-hazardous or hazardous due to the list of hazardous constituents contained in sections 40 CFR 261.30-261.35 including a majority of analytes of interest routinely analyzed in Pace laboratories. Definitions have been established for each of the F, K. P, and U lists covering hazardous waste originating from non-specific sources, specific sources and discarded commercial chemical products, off-specification species, container residues, and spill residues. The application of listed hazardous wastes and substances is intended for manufacturing processes involving pure products, by-products, wastes generated as part of the production process and cleanup of materials contaminated from a spill of the listed commercial chemical product or manufacturing chemical intermediate. See Attachment I for common F-listed wastes.

12.5.1. Hazardous waste classification of unconsumed samples by listed hazardous waste criteria is not commonly applied in laboratory operations. Examples of sample types which would be identified as listed hazardous wastes include the following:

12.5.1.1. Samples containing 5% or more (by volume) of halogenated and non-halogenated "spent solvents:" (e.g., drum sample with > 10% TCE);

12.5.1.2. Pure product and two phase solution samples containing a listed chemical product or manufacturing intermediate (e.g., drum sample);

12.5.1.3. Samples from specific sources listed in section 261.32 (e.g., bottom sediment sludge from the treatment of wastewaters from wood-preserving processes that use creosote and/or pentachlorophenol - K001);

12.5.1.4. Samples representing any residue or contaminated soil, water or other debris resulting from the cleanup of a spill into or on any land or water of any commercial chemical product or manufacturing chemical intermediate having a generic name listed in section 261.33, or any residue or contaminated soil, water or other debris resulting from the cleanup of a spill, into or on any land or water, of any off-specification chemical product and manufacturing chemical intermediate which, if it met specifications, would have the generic name listed in section 261.33.

12.5.2. For the wastes listed in 12.5.1.1 and 12.5.1.2, disposal can be achieved by individually lab packing them or combining with other compatible hazardous wastes.

12.5.3. The remaining two sample types in 12.5.1.3 and 12.5.1.4 would also require lab packing for disposal. However, it is important to note that in order for the laboratory to ascertain that the samples were derived from a specific listed source or from a spill of a listed chemical, they must be so informed by the industrial concern or lead agency (e.g., EPA, state regulators) submitting the sample for analysis. If a water or soil sample contains a listed hazardous waste substance whose origin is unknown or uncertain to the lead agency, then that sample is not classified as a listed hazardous waste. Rather in this case, determination of a hazardous waste classification can only be obtained by the waste exhibiting a characteristic of hazardous waste (e.g., ignitability, corrosivity, reactivity).

12.5.4. Due to the fact that the majority of samples analyzed by Pace do not meet the well-defined criteria for identifying "listed" hazardous waste, disposal classification of unconsumed samples will be based upon characteristics of hazardous waste:

12.5.4.1. Non-Hazardous - Analysis results indicate an absence of contaminants; unless contaminants listed under the hazardous disposal categories are parts of the requested sample analysis.

12.5.4.2. Hazardous – Analysis results indicate presence of contaminants (Attachment III) or sample analysis requires hazardous materials and contaminants. Samples in this category are segregated from others and disposed of as hazardous according to laboratory procedures.

12.5.4.3. PCB Waste - Generated exclusively by samples contaminated with greater than trace levels of polychlorinated biphenyls ($\geq$ 50ppm). Samples containing 50ppm (total) or higher of PCBs must be segregated and disposed of as PCB waste.

12.5.4.4. Waste Oil/Paint - Samples which are predominantly of an oil matrix (e.g., highly viscous organic liquid) or paint (solvent and pigment blend) are segregated and disposed in a separate container. Though these samples are defined as nonhazardous, oil samples are a special case and never disposed as nonhazardous.

12.5.5. USDA-APHIS-PPQ Regulated Soils (Regulated Soils) are a special case of sample strictly controlled under quarantine regulations 7 CFR 330 because they can readily provide a pathway for a variety of dangerous organisms throughout the United States. The movement of soil into the United States from foreign sources and from certain regulated areas within the continental U.S. is restricted unless permitted by APHIS under specific conditions and safeguards.

12.5.5.1. Any laboratory that plans to handle Regulated Soils must have an approved Soil Permit or Regulated Soil Agreement from USDA-APHIS-PPQ.

12.5.6. Though Pace is obligated to ensure nonhazardous discharge complies with requirements set by applicable publicly owned treatment works (POTW), Pace is not obligated to run every available analysis on every sample for proper waste classification. Consequently, samples are characterized according to the preservatives added, the requested analytical testing data, and any knowledge of the sample provided by the client. When sample analysis is canceled/not completed, those untested samples only need be characterized by the preservatives added and any knowledge of the sample that is obtained by the client.

12.6. Consolidation of wastes from the laboratory proceeds via two distinct routes covering either laboratory-generated hazardous wastes or excess unconsumed samples.

12.6.1. Laboratory Accumulation and Satellite Waste Containers

12.6.1.1. Waste materials from routine lab procedures are collected in containers of appropriate construction, placed in convenient locations at the point of generation. Under RCRA guidelines, these are defined as satellite containers.

12.6.1.2. The amount of hazardous waste stored in the laboratory at the individual satellite areas cannot exceed 55 gallons (liquid) or 550 lbs (solid) per waste stream, for non-acute hazardous waste.

12.6.1.3. Satellite waste containers must be labeled in accordance with all regulations, including:

12.6.1.3.1. Designation of the contents to be hazardous waste with the words "Hazardous Waste" clearly legible.

12.6.1.3.2. The waste stream description (e.g., acid waste).

12.6.1.3.3. A hazard label (e.g., corrosive).

12.6.1.4. The satellite containers must be maintained such that evolution of chemical vapors is precluded. This requires that the container be closed at all times, except when adding or emptying hazardous waste to and from the container.

12.6.1.5. The most critical point in the waste handling system is when a person (e.g., analyst, technician) places a waste material into a satellite container. Here, the characteristics or listing of the waste and the waste stream must both be known to match. For this reason, only material from approved procedures should be placed in the compatible satellite containers. All materials from experimental procedures, unknown or out of the ordinary sources, or from spill cleanups must be characterized and described to the Hazardous Waste Coordinator, who determines the proper method of disposal.

12.6.1.6. Full satellite containers must be transferred to the proper accumulation drum within 3 calendar days. Lab collection containers must not be filled to the top of the opening. Space must be left to prevent splashing of hazardous material when containers are emptied and to allow for expansion and contraction within the drum during transport.

12.6.1.7. Satellite containers for liquid hazardous waste must have secondary containment made of material that could successfully contain the entire satellite container's contents.

12.6.2. Unconsumed Sample Disposal

12.6.2.1. Client samples are stored on-site for a defined period of time after the final analytical report is generated and prior to sample disposal. The purpose of sample storage is to provide the client time to review the analytical report and determine if the samples require additional testing or need to be returned to the client. Samples are not considered a waste during this time according to 40 CFR 261.4(d)(vi).

12.6.2.1.1. Sample storage time is 30 days from final report. Other sample storage hold times may be assigned for specific contractual requirements.

12.6.2.1.2. During sample storage, the process and sample status must be obvious to employees, customers and auditors. This transparency is imperative to ensure samples are considered active test specimens to be retained until they are categorized as a waste for disposal.

12.6.2.2. Samples which cannot be returned to the client for disposal are characterized according to section 12.4. Samples are characterized by one of three methods:

12.6.2.2.1. Analytical results are evaluated against characterization criteria established for the sample waste stream. The samples which exhibit waste characteristics as previously outlined are segregated and denoted per laboratory/facility policies. OR:

12.6.2.2.2. Samples are scanned out of EPIC Pro (LIMS), if available, as RCRA nonhazardous to be disposed as the waste stream is normally handled unless the sample tested over RCRA limits, in which the LIMS will prompt the employee that the sample is scheduled for Hazardous disposal, and is segregated from the nonhazardous samples. OR:

12.6.2.2.3. Samples of a certain type are all "assumed" to be hazardous, and all are placed into an accumulation drum with all required RCRA labeling for that waste stream.

12.6.2.3. Samples are pulled from storage and disposed of according to local lab processes. The analysts are responsible for the disposal of analyzed samples that are non-hazardous.

12.7. Transferring Satellite Waste to the Waste Storage/Accumulation Area

12.7.1. All transfers of satellite waste to waste drums must be made by the Hazardous Waste Coordinator or designated, trained personnel. When a satellite waste container is full, the Hazardous Waste Coordinator, or designee must be notified. Regular disposal events may be scheduled to dispose satellite waste on a continuous basis.

12.7.2. Find the correct waste drum by referring to the Hazardous Waste placard and hazard label. Mixing solvents that are not compatible could result in a hazardous reaction.

12.7.3. Ensure there is enough capacity in the drum to hold all the content that will be dispensed.

12.7.4. Check to make sure there is a ground connection before opening a solvent waste drum.

12.7.5. Open and slowly pour the contents of the satellite container into the proper waste drum using an appropriate solvent resistant funnel.

12.7.6. Replace the cap on the bunghole and carefully screw the cap on but do not tighten the cap.

12.8. Unconsumed Soil Samples

12.8.1. All soil samples are to be placed into the soil drum in the waste room after the 30 day after final report storage requirement. Separate according to USDA requirements and heat to 105C if necessary.

12.9. Elementary Neutralization

12.9.1. Dilute corrosive solutions (e.g., preserved metals samples) which do not exhibit any hazardous characteristics other than being corrosive, may be neutralized. Elementary neutralization is exempt from RCRA permitting requirements for on-site hazardous waste treatment. While exempt under RCRA guidelines, before utilizing this practice to reduce off-site treatment or disposal of wastes, local pretreatment and discharge standards must be met for publicly owned treatment works (POTW).

12.9.2. The discharges listed below are prohibited under the National Pretreatment Standards and Prohibited Discharge Standards:

12.9.2.1. Pollutants causing fire or explosion (waste with a flashpoint < 60°C);

12.9.2.2. Corrosive wastes with pH less than 2 or greater than 12.5;

12.9.2.3. Solid or viscous pollutants that could potentially block the system;

12.9.2.4. Oxygen-demanding pollutants;

12.9.2.5. Wastes which generate toxic gases.

12.9.3. Wastes that are generated by the laboratory that have a pH of less than 2 and greater than 12.5 shall be neutralized to a pH of not less than 6 and not greater than 8 prior to sewer disposal using the following procedure. Acids and bases shall always be neutralized separately.

12.9.3.1. Put on safety glasses, inner gloves and over gloves (PVC).

12.9.3.2. Place a large plastic bucket into a fume hood and turn the fume hood on.

12.9.3.3. Set the sash height according to the arrows on the front of the hood.

12.9.3.4. Place approximately 1 liter of tap water into the bucket.

12.9.3.5. Slowly pour the acid or base into the bucket.

12.9.3.6. Add soda ash (acids) or sodium bicarbonate (acids or bases) approximately a tablespoon at a time, allowing the reaction to stop prior to adding more.

12.9.3.7. Check the pH frequently.

12.9.3.8. When the pH meets the above specifications, the solution is amenable to sewer disposal according to the following instructions.

12.9.4. The only laboratory chemicals and waste that are amenable to sewer disposal are the ones that are deemed non-hazardous, or corrosive wastes that have been treated. Non-hazardous aqueous samples are amenable to sewer disposal. Any time samples or neutralized wastes are disposed using the sanitary sewer; the tap shall be run for a minimum of fifteen minutes.

12.9.4.1. Turn on the cold water in the sink where the waste will be poured 5 minutes prior to the start of disposal to flush the lines.

12.9.4.2. While keeping the cold water on, slowly pour the waste into the sink. Triple-rinse the waste container. The container can then be placed in the trash.

12.9.4.3. When all of the corrosive wastes have been disposed, keep the water running for an additional 15 minutes to flush the lines before turning off the water.

12.10. Waste Storage Container Requirements

12.10.1. Drums in the hazardous waste storage area are labeled consistent with both DOT and EPA regulations concerning hazardous materials and wastes.

12.10.2. Labels must be easily visible and legible (e.g., a drum must not be labeled and then placed in such a way that the label cannot be seen).

12.10.3. The Accumulation Start Date must be recorded on the drum. The date should reflect the first time waste was added to the drum and not the date when the waste was generated in the laboratory.

12.10.3.1. Once a waste is removed from the point of generation to a hazardous waste staging area, the clock is started for storage time prior to disposal.

12.10.3.2. Drums must be picked up by TSDF for disposal before accumulation time exceeds RCRA requirement for lab's generator status.

12.10.4. The hazardous waste staging room must be arranged in such a fashion to assure direct access pathways in the event of foreseeable emergency and for safe waste transfer. A minimum aisle space of three feet must be maintained at all times to access hazardous waste containers.

12.10.5. All hazardous waste drums and containers must be securely closed when not in use. All volatile and flammable hazardous waste liquid containers must be securely grounded at all times. Drums

containing these liquids should also be manipulated with non-sparking tools and fitted with a drum venting bung, to assure that excess pressure build-ups are safely released.

12.10.6. All liquid waste stream containers must be provided with secondary containment devices. Such containment devices must be made of materials compatible with each waste, and they must be free of leaks. The waste storage room may act as secondary containment as long as the room has been constructed to safely and effectively contain a hazardous waste spill.

12.10.6.1. Secondary containers must exceed the total volume of the largest container stored in each containment device for indoor storage.

12.10.7. Compatibility of wastes must be considered in arranging storage areas. For example, acid waste should never be stored adjacent to basic waste, particularly cyanide wastes. Further examples are outlined in 40 CFR 264, Appendix V.

12.10.8. The hazardous waste staging area is controlled so unauthorized personnel are not able to access the room or contents.

12.10.9. The maximum volume of acutely hazardous waste (e.g., P-listed wastes) that can be accumulated in the laboratory is one quart. The volumetric measurement of one quart is based upon container size in which the waste is stored and not the actual amount (volume) of waste present. An example of how this one quart limit can inadvertently be exceeded involves the disposal of a neat standard of 2,4-dinitrophenol into a one gallon bottle. While the neat standard itself may only constitute 1-2mL, the volume as defined under RCRA would be one gallon, thus the laboratory would be out of compliance.

12.11. Waste Documentation and Reporting

12.11.1. All drums containing hazardous waste are recorded in a logbook or database. The information contained in this log is useful when filling out EPA biennial reports and for retaining an accurate description of how much waste has been accumulated. The following information is entered into the logbook/database;

12.11.1.1. The drum number;

12.11.1.2. The date filling the drum was started;

12.11.1.3. The drum capacity (e.g., 55-gallon, etc.);

12.11.1.4. The manifest number associated with the drum's disposal.

12.11.2. The following hazardous waste records must be maintained a minimum of five years and should be retained indefinitely:

12.11.2.1. Drum tracking logs;

12.11.2.2. Sample Reports;

12.11.2.3. Sample disposal information and waste records on computer disc;

12.11.2.4. Analytical records relating to sample waste stream profiling and characterization;

12.11.2.5. Labpack inventory logs;

12.11.2.6. Biennial Reports, Exception Reports, or other reports filed for compliance reasons;

12.11.2.7. Records related to unresolved enforcement action must be retained indefinitely until such a time that the matter is resolved;

12.11.2.8. Facility Certificates of Destruction or Recycling.

12.11.3. A Waste Manifest is the documentation form that must accompany all shipments of hazardous waste while in transit.

12.11.3.1. A Hazardous Waste Manifest Cover Sheet (*F-ALL-W-DRAFT-rev.00 or local replacement*) will be utilized to ensure waste transfer from generator to TSDF fulfills all legal requirements.

12.11.3.2. The manifest is be signed and dated by a DOT trained Pace employee responsible for the shipment and the transporter. The transporter will leave 2-3 of these "two-signature page" copies of the manifest.

12.11.3.3. Within 35 days you will receive a three-signature page (generator, transporter, facility) showing the waste reached its intended destination.

12.11.3.3.1. If you do not receive the three signature page within 35 days of shipment, call the facility to find out why you have not received it. If you do not receive the three-signature page within 60 days you must file an exception report.

12.11.3.4. All manifests must be kept for a minimum of three years.

12.11.4. The central accumulation staging room must have a documented inspection weekly and satellite waste containers must have documented inspection as part of the monthly laboratory inspection. The inspections should ensure all regulations are obeyed; see sections 12.10 and 12.6.1 for accumulation storage and satellite rules.

12.11.4.1. A record of the inspections must be kept in an inspection log or summary.

12.11.4.2. Records must be maintained for at least three years from the date of inspection. At a minimum, the records must indicate:

12.11.4.2.1. The date and time of the inspection;

12.11.4.2.2. The name and signature of the inspector (typically will be Hazardous Waste Coordinator);

12.11.4.2.3. A notation of the observations made (can be in a check-off format, e.g., fire extinguisher: charged _X_ requires recharging __);

12.11.4.2.4. The date and nature of any repairs or other remedial actions.

13. Quality Control

13.1. Not applicable to this SOP.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. The analyst must read and understand this procedure with written documentation maintained in his/her training file.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A formal safety plan is also available to all employees. Safety glasses are required in all lab areas. Gloves and eye protection should be routinely worn when handling reagents or samples. When qualified employees are transferring wastes, additional protection such as goggles, face shield, and lab apron are recommended.

22.2. Safety Data Sheets are located in a central location and should be consulted prior to handling samples and standards.

22.3. A hazard assessment must be completed for waste areas to ensure proper PPE are utilized.

23. Waste Management

23.1. Not applicable to this SOP.

24. Pollution Prevention

24.1. Not applicable to this SOP.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. 40CFR261-268, Code of Federal Regulations Chapter 1, Subchapter I – Solid Waste.

25.3. 29CFR171-174, Code of Federal Regulations, Transportation.

25.4. Federal Plant Pest Regulations, Part 330.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: RCRA Requirements for Labs as a Function of Generator Status.

26.2. Attachment II: Hazard Codes for Common F-List Wastes (solvents).

26.3. Attachment III: TCLP Contaminant List with Concentration Limits.

26.4. Attachment IV: Hazardous Waste Label for Accumulation Drum (example).

26.5. Attachment V: Satellite Container Inspection Form (example).

26.6. Attachment VI: Waste Accumulation Room Inspection Form (example).

26.7. Attachment VII: Hazardous Waste Manifest Cover Sheet.

27. Revisions

Document Number	Reason for Change	Date
SOT-ALL-W-002-rev.05	Section 8.20.2.4: Added definition of Toxic. Section 12.5.5: Added more detail to USDA Regulated Soils. Section 12.6.2.1: Defined sample storage hold times. Added Section 12.11.3.1 and Attachment VIII– Hazardous Waste Manifest Cover Sheet info. Clarity added throughout that liquid waste containers need secondary containment, not all waste containers. Referenced sections and regulations corrected.	14Nov2013
SOT-ALL-W-002-rev.06	Section 8.27: reorganized for clarity and fixed reference section errors. Section 8.28: updated definition. Sections 12.5.5 and 12.5.5.1: updated to reference new, local version of Regulated Soil Handling SOT. Section 12.5.6: clarification added that Pace labs must obey discharge rules. Section 12.6.2.2.4: added red text paragraph regarding removal of sample labels for ESI clients. Removed old Attachment IV (soil regulations map) because it was outdated and this topic is covered in Regulated Soil SOP.	24Mar2015
ENV-SOP-PITTS-023	Removed cover page and Table of Contents to conform to MC.	4/8/2019

Attachment I: RCRA Requirements for Labs as a Function of Generator Status

Requirement (40CFR)	CESQG	SQG	LQG
Waste Determination (262.11)	Applicable	Applicable	Applicable
Generation Rate Limits (261.5 and 262.34)	<100 kg/mo	100-1,000 kg/mo	1,000 kg/mo or greater
Accumulation Quantity Limit w/o Permit (261.5 and 262.34)	Not to exceed 1,000 kg at any time. Not to exceed 1 kg acute at any time	not to exceed 6,000 kg at any time	No limit
Accumulation Time (261.5 and 262.34)	No limit	180 days or 270 if waste is to be transported over 200 miles.	90 days
EPA ID Number (262.12)	Not required***; possible state requirement	Required	Required
Mark Containers with Start Date (262.34)	Not applicable	Applicable	Applicable
Mark Containers "Hazardous Waste" (262.34(a))	Not applicable	Applicable	Applicable
Air Emission Standards 40 CFR 265 Subpart CC	Not applicable	Not applicable	Applicable
Satellite Accumulation (262.34(c))	Not applicable	Applicable	Applicable
Use Manifests (262, Subpart B)	Not required; possible state requirement	Required	Required
Exception Reporting (262.42)	Not required	Required after 60 days. No TSDF notification requirement.	Required after 45 days. Notification of TSDF within 35 days.
Biennial Report (262.41)	Not required	Not required; possible state requirement	Required
Contingency Plan (265, Subpart D)	Not required, but OSHA (29 CFR 1910.38) requires emergency planning	Basic planning required in accordance with the standards in 262.34(d)(4) and (5) and 265, Subpart C as well as OSHA regulations	Full written plan in accordance with 265 Subpart D, is required by 262.34(a)(4) and OSHA regulations
RCRA Personnel Training (262.34 and 265.16)	Not required, but recommended	Basic training required by 262.34(d)(5)(iii)	Full compliance with the training requirements in 265.16 is required by 262.34(a)(4)

Requirement (40CFR)	CESQG	SQG	LQG
Storage Requirements (without permit) (262.34 and 265)	None, but OSHA regulations under 29 CFR 1910, Subparts H and N, apply, particularly 29 CFR 1910.106	Compliance with technical standards in Part 265, Subparts I and J; for containers and tanks is required by 262.34(d)(2) and (3) and OSHA regulations	Compliance with technical standards in Part 265, Subparts I, J, W, and DD, is required by 262.34(a)(1) and OSHA regulations
Recordkeeping Requirements (262.40)	Waste determinations and generation log required (notification of regulated waste activity, training records, manifests, and land disposal restriction notifications recommended)	Notification of regulated waste activity, waste determinations, generation log, manifests, land disposal restriction notifications, exception reports, and correspondence with local emergency responders (written contingency plan, weekly container inspection & periodic equipment maintenance logs, and RCRA training records recommended)	Notification of regulated waste activity, waste determinations, generation log, manifests, land disposal restriction notifications, exception reports, biennial reports, correspondence with local emergency responders, RCRA training records, and written contingency plan required (weekly container inspection is required & periodic equipment maintenance logs is recommended)
Waste "Designated Facility"	State-approved or RCRA permitted facility or legitimate recycler	RCRA-permitted facility or legitimate recycler	RCRA-permitted facility or legitimate recycler
Land Disposal Restrictions (268.7)	Possible state requirement	Applicable	Applicable

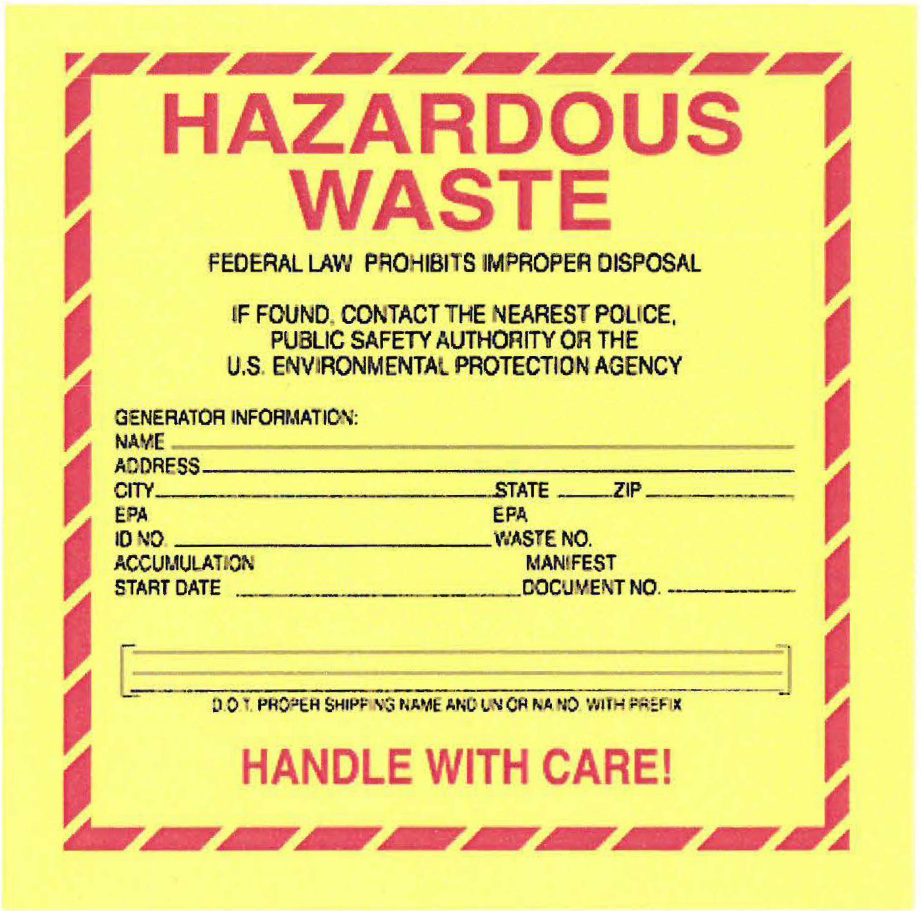
Attachment II: Common F-Listed Solvents

Waste Name	Hazardous Waste Code(s)	Waste Name	Hazardous Waste Code(s)
Acetone	F003	Methylene Chloride	F001, F002
Benzene	F005	Methyl ethyl ketone (MEK)	F005
iso-Butanol	F005	Methyl isobutyl ketone	F003
n-Butyl alcohol	F003	Nitrobenzene	F004
Carbon Disulfide	F005	2-Nitropropane	F005
Carbon Tetrachloride	F001	Orthodichlorobenzene	F002
Chlorobenzene	F002	Pyridine	F005
Chlorinated fluorocarbons (CFC)s	F001	Tetrachloroethylene	F001, F002
Cresols	F004	Toluene	F005
Cresylic acid	F004	1,1,1-Trichloroethane	F001, F002
Cyclohexanone	F003	1,1,2-Trichloeoethane	F002
2-Ethoxyethanol	F005	1,1,2-Trichloro-1,2,2-trifluoroethane	F002
Ethyl acetate	F003	Trichloroethylene	F001, F002
Ethyl benzene	F003	Trichloroflourormethane	F002
Ethyl ether	F003	Xylene	F003
Methanol	F003		

Attachment III: TCLP Contaminant List

Waste ID #	Contaminant	Conc (mg/L)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin	0.02
D013	Lindane	0.4
D014	Methoxychlor	10.0
D015	Toxaphene	0.5
D016	2,4-D	10.0
D017	2,4,5-TP Silvex	1.0
D018	Benzene	0.5
D019	Carbon Tetrachloride	0.5
D020	Chlordane	0.03
D021	Chlorobenzene	100.0
D022	Chloroform	6.0
D023	o-Cresol	200.0
D024	m-Cresol	200.0
D025	p-Cresol	200.0
D026	Cresol	200.0
D027	1,4-Dichlorobenzene	7.5
D028	1,2-Dichloroethane	0.5
D029	1,1-Dichloroethylene	0.7
D030	2,4-Dinitrotoluene	0.13
D031	Heptachlor	0.008
D032	Hexachlorobenzene	0.13
D033	Hexachlorobutadiene	0.5
D034	Hexachloroethane	3.0
D035	Methyl ethyl ketone	200.0
D036	Nitrobenzene	2.0
D037	Pentachlorophenol	100.0
D038	Pyridine	5.0
D039	Tetrachloroethylene	0.7
D040	Trichlorethylene	0.5
D041	2,4,5-Trichlorophenol	400.0
D042	2,4,6-Trichlorophenol	2.0
D043	Vinyl Chloride	0.2

Attachment IV: Hazardous Waste Label for Accumulation Drum (Example)



Attachment V: Satellite Container Inspection Form

Waste Container ID	Clearly Labeled as "Hazardous Waste" with Waste Stream	Liquid Waste has Secondary Containment	Closed when not in use
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No
	Yes / No	Yes / No	Yes / No

If any of the above fields are a "NO", please document how the container was brought back into compliance.

Comments: _____

_____

_____

Inspector Signature _____ **Date:** _____

Reviewer Signature _____ **Date:** _____

ATTACHMENT VI: WASTE ACCUMULATION ROOM INSPECTION FORM

Containers closed when not in use	**Labels Easily Seen and Legible**	**Drums have Accumulation Start Date**	**Storage Amounts and Limits Obeyed**[1]	**Secondary Containment** for Liquid Waste	**Adequate Aisle Space**	**Available Emergency Equip. and Materials**	**Signature and Date of Inspection**	**Corrective Action for NO Answers**
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		
Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No	Yes / No		

1: Accumulation limits are 90 days for LQG, and 180 days for SQG. SQG may have no more than 6000kg waste at any time.

ATTACHMENT VII: HAZARDOUS WASTE MANIFEST COVER SHEET

HAZARDOUS WASTE PICKUP DATE: _____

MANIFEST NUMBER(S)	3-SIGN. MANIFEST RETURN DATE
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

2-SIGNATURE FORM/PICK-UP CHECKLIST

- ☐ DRUMS REQUESTED FOR PICKUP/PRESENT MATCHES MANIFEST
- ☐ HAZARD CODES ARE CORRECT FOR EACH WASTE STREAM
- ☐ PACE REPRESENTATIVE AND TRANSPORTER SIGNATURE PRESENT

35 DAYS FROM PICKUP DATE: _____

If the three signature page has not been received within 35 days, contact the disposal facility to determine where the shipment is and request a copy of the three signature page.

If the three signature page has not been received within 45 days, you are required to file an exception report with the local regulating authority.

ALL 3-SIGNATURE MANIFEST(S) RECEIVED DATE _____

- ☐ FILE COVER SHEET, 3-SIG AND 2-SIG FORMS TOGETHER IN FOLDER, BINDER OR BY PAPER-CLIP. RETAIN FOR AT LEAST 3 YEARS

WASTE COORDINATOR: _____

DATE COMPLETED: _____

Document Information

Document Number: ENV-SOP-PITTS-0018 **Revision:** 01

Document Title: AM20GAx

Department(s): MNA

Previous Document Number: S-PAE-RISK-004-rev.01

Date Information

Effective Date: 30 Apr 2019

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Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-PITTS-0018 **Revision:** 01
Title: AM20GAx

All dates and times are in Central Time Zone.

ENV-SOP-PITTS-0018

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Charlotte Washlaski (003467)	Quality Manager	30 Apr 2019, 05:58:42 AM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Ruth Welsh (003453)	Assistant General Manager	29 Apr 2019, 02:43:34 PM	Approved
Charlotte Washlaski (003467)	Quality Manager	30 Apr 2019, 05:58:56 AM	Approved
Mark Mikesell (003456)	Manager - Lab Services	30 Apr 2019, 09:22:36 AM	Approved

1. Purpose/Identification of Method

Method AM20GAx is used to determine the concentration of biodegradation indicator gases in vapor samples.

2. Summary of Method

2.1. The sample gas is analyzed with a gas chromatograph capable of simultaneous analysis of all of the target analytes from a single gas sample. A single injection of gas from integral, simultaneously filled sample loops is used to assure consistent injection volume. The uniform sample size achieved using the sample loop assures consistent and accurate results. The permanent gases are analyzed using a thermal conductivity detector (TCD). The light hydrocarbons are analyzed using a flame ionization detector (FID). Hydrogen is analyzed using a reduction gas detector (RGD). The data are transferred to a microcomputer, converted to digital format, stored, and processed using a chromatography data system.

3. Scope and Application

3.1. **Personnel**: This method is recommended for use by, or under the supervision of, analysts experienced in sample preparation, the operation of gas chromatographs and in the interpretation of chromatograms.

3.2. **Parameters:**

Light Hydrocarbons	CAS Number	Permanent Gases	CAS Number
Methane	74-82-8	Carbon Dioxide	124-38-9
Ethane	74-84-0	Oxygen	7782-44-7
Ethene	74-85-1	Nitrogen	7727-37-9
Propane	74-98-6	Methane	74-82-8
Propene	115-07-1	Carbon Monoxide	630-08-0
n-Butane	106-97-8	Hydrogen	1333-74-0
iso-Butane	75-28-5	Total Inorganic Carbon*	
Acetylene	74-86-2		

*Total inorganic carbon (TIC) is converted to carbon dioxide using the steps outlined in SOP ENV-SOP-PITTS-0016. The sample is then analyzed for carbon dioxide according to this SOP. Any differences in method are specified in the appropriate section.

4. Applicable Matrices

4.1. Sample vapor can be provided to the laboratory or generated by the laboratory through three matrices; vapor as directly sampled, headspace vapor generated from an aqueous sample using SOP ENV-SOP-PITTS-0016, or bubble-strip vapor generated from an aqueous source volume using SOP ENV-SOP-PITTS-0015.

5. Limits of Detection and Quantitation

5.1. Reporting Limits

The reporting limits for this analysis are listed in Table 5.0 below. Method detection limit studies are run annually in accordance with PAES Standard Operating Procedure for the Determination of Method Detection Limits and PQLs (ENV-SOP-PITTS-0009). MDL studies are also performed

when there is reason to suspect that method sensitivity has changed. The MDL studies are kept on file in the Quality Systems Office.

Reporting Limits
Table 5.0

Analyte	Reporting Limit Vapor (units)	Reporting Limit Bubble (units)	Reporting Limit Water (units)
Carbon Monoxide	0.20 %	0.10 mg/L	1.0 mg/L
Carbon Dioxide	0.20 %	2.00 mg/L	5.0 mg/L
Oxygen	0.20 %	0.15 mg/L	0.50 mg/L
Nitrogen	0.50 %	0.40 mg/L	2.0 mg/L
Hydrogen	1.0 ppmv	1.0 nM	10 nM
Acetylene	0.20 ppmv	0.500 ug/L	0.50 ug/L
Methane	1.0 ppmv	0.10 ug/L	0.50 ug/L
Ethane	0.10 ppmv	0.010 ug/L	0.10 ug/L
Ethene	0.10 ppmv	0.010 ug/L	0.10 ug/L
Propane	0.10 ppmv	0.025 ug/L	0.10 ug/L
Propene	0.20 ppmv	0.025 ug/L	0.10 ug/L
Iso-Butane	0.20 ppmv	0.025 ug/L	0.20 ug/L
n-Butane	0.20 ppmv	0.025 ug/L	0.20 ug/L
TIC	N/A	N/A	10 mg $CaCO_{3/L}$

6. Interferences

6.1. The most likely source of "interference" is ambient air. Due to the relatively high concentrations of oxygen and nitrogen, a very small amount of air as a contaminant will dramatically affect the results. The collector of samples must take great care and only use the sample containers outlined in this SOP. Substituting alternate preservatives or septa than those outlined here, can result in biased concentrations (high or low), depending on the specific compounds of interest. Also, the analyst must take great care to ensure that the presence of air has been eliminated from any integral step in the analysis process, prior to making injections into the gas chromatograph.

6.2. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. An unrestricted flow (instrument flush) of pure carrier gas from a 10 psig source should be allowed to flow through each sample loop for a minimum of 2 minutes prior to each analysis. As required, the analyst should demonstrate the absence of carryover contamination by analysis of the contents of the sample loop when purged with carrier gas. This demonstration should be performed when carryover contamination is suspected (after high samples). In the event that 'ghost peaks' (peaks similar to previous sample) appear when a pure carrier gas sample is analyzed (method blank), measures should be taken to eliminate the carryover contamination.

6.3. Another potential contaminant is very low concentrations of methane, ethane and ethane generated in field blanks that are not properly treated in the field. Even "purified" water purchased for field use is likely to have substantial light hydrocarbon or permanent gases concentrations. If field blanks are desired, arrangements should be made with PAES customer service representatives when the bottle order is placed. These vials must be treated as samples at all times. That means they must stay on ice in the field.

6.4. The gas matrix for this analysis minimizes the opportunity for matrix effects. If the client suspects possible matrix affect, they should request that matrix spike (MS) and matrix spike duplicate (MSD) analyses be conducted and should supply sufficient sample volume. Since matrix effects are extremely site dependent, the MS and MSD are not part of the regular analytical quality assurance program.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Samples directly collected as a vapor or prepared with the bubble strip technique are shipped and received at a positive pressure, which eliminates a cross-contamination issue during sample shipment. It is preferred that these samples be shipped without cooling, however it is not a sample receipt non-conformance if these samples are packed in ice (sample may experience slight loss in pressure.) These samples are stored in the laboratory at room temperature (23°C±4°). The pressure in the vials is not checked upon receipt in the laboratory because of the inherent risk of losing sample, or inadvertently introducing atmospheric gases, when the septum is pierced. The number of times the septum is pierced should be as few as possible. See Section 12.2 for a discussion on how the laboratory checks vial pressure. Holding time these samples is fourteen days from the date of collection.

7.2. Water samples should be cooled upon collection and stored at a temperature of just above freezing but below 6°C. Holding time for water samples is fourteen days from the date of collection.

- Water samples for light hydrocarbon analyses are collected in 40ml clear glass VOA vials with zero headspace and preserved with tri-sodium phosphate (TSP). The vials are pre-preserved by an approved vendor. TSP is added as the dodecahydrate at 250 mg/40 ml vial. This results in a sample pH > 10.
- Water samples collected for either permanent gases or permanent gases and light hydrocarbon analyses are collected in 40ml amber VOA vials with zero headspace and preserved with benzalkonium chloride (BAK) solution. The vials are pre-preserved by an approved vendor. BAK is added as a liquid, with 0.20ml of base solution added to each 40ml vial. The base solution is prepared at a ratio of 9 grams BAK per 1 liter of water. This solution acts as a microbial inhibitor and does not influence the buffered state of the sample.
- Water samples collected for Total Inorganic Carbon are collected in 40ml clear glass VOA vials without additional preservation.
- All vial types used for sample collection shall be capped with butyl septa.

8. Definitions

8.1. **Analytical Batch:** A batch consists of twenty or fewer client samples, submitted to the laboratory for analysis.

8.2. **Instrument Flush:** The front end of the sample loop is flushed with ultra high purity helium injected into the loop directly from the cylinder to remove possible interference by ambient air and to avoid cross contamination between samples.

8.3. **Method Blank:** An injection that consists of ultra-high purity helium. The method blank is free from the analytes of interest.

8.4. **Laboratory Control Sample:** A sample of laboratory grade deionized water spiked with verified known amounts of analytes. A LCS is used to assess the performance of the measurement system.

8.5. **Matrix Spike and Matrix Spike Duplicate:** A sample prepared by adding a known concentration of target analyte to a specific amount of sample. Matrix spikes are used to determine the effect of sample matrix on a method's recovery efficiency.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. Materials

- Syringes: Disposable Plastic (BD Medical; 3,5,10,30 and 60ml or equivalent)
- Headspace vials (Approved vendor; 10, 20 or 160ml clear glass with butyl septa or equivalent)
- Certified Gas Standards (AirGas, or equivalent)
- 23 Gauge stainless steel needles (Precision Glide Needles or equivalent)
- Traceable Memory Monitoring Thermometer (Fisher Scientific part # 0666411)

9.2. Operating Conditions

Room Temperature:	23°C±4°
Oven Temperature:	210°C (rest/bake-off)
Oven Temperature:	100°C (Isothermal program)
Detector Temperature:	Not Applicable (non-programmable)
Injector Temperature:	Not Applicable (non-programmable)
Quantification Software:	Thermo-Fisher/Dionex Chromeleon

The remaining conditions related to column configuration and ultra-high purity (UHP) gas delivery are unique to each gas chromatograph currently supporting the performance of this SOP and can be made available upon request.

10. Reagents and Standards

- Sodium Bicarbonate;$NaHCO_3$ (ACS Grade, ThermoFisher or another approved vendor)
- Ultra-High Purity Gases (Helium, Nitrogen, Hydrogen and compressed air)
- Certified Commercial Gas Standards

Commercial Standards used for calibration or other method specific quality assurance criteria shall be received and documented in accordance with laboratory SOP ENV-SOP-PITTS-0010; Standard Operating Procedure for Reference Materials and Reagents. The laboratory shall assign dates of expiration according to the following schedule:

- Single Analyte: Neat Gas at +99% purity: 60 months from date received
- Single Analyte: Fixed concentration with balance gas: 36 months from date opened
- Multiple Analytes: Fixed concentrations with balance gas: 24 months from date opened

The light molecular weight gases this analysis measures are known to be particularly stable. If they breakdown the breakdown products will be seen during the use of these standards and any such observation should be reported to the laboratory manager and the standard should not be used unless it is returned to service by the laboratory manager. The expiration date assigned by the vendor is based on different criteria then the laboratory uses, so expiration dates will be assigned according to the above schedule. While an inaccurate standard content would lead to an error in standardization, such an error is more likely to occur from the delivery equipment used to transfer the aliquot from the standard tank to the GC. For this reason this analysis requires particular emphasis be placed on second source verification of all calibrations. This verification process is an excellent way to monitor the validity of standards and serves as a continual check of the laboratory assigned expiration dates.

Reagents are stored at room temperature (23°C±4°) and all standards are prepared fresh for each use immediately prior to each analysis. Standards are made up from compressed gas cylinders.

11. Calibration and Standardization

11.1. Vial Preparation

Headspace vials used for instrument calibration standards for this method are prepared as follows:

- Collect enough vials to complete the calibration procedure. Assure that the vials have been documented and pass acceptance criteria noted in the SOP for Support Equipment, ENV-SOP-PITTS-0008.
- Crimp and cap each vial, with stopper type butyl septa.
- Evacuate each vial to vacuum. Attach vials to the vacuum manifold for 10 minutes to achieve evacuation.
- Flush each vial to atmospheric pressure with the balance gas appropriate for the analytes being calibrated. (See Table 11.1)

Table 11.1

Detector	Balance Gas
FID	Nitrogen
TCD	Helium
RGD	Nitrogen

11.2. Preparing Calibration Standards

Though it may be preferred to prepare all standards or other quality sources with Teflon lined, locking gas tight, glass syringes, it has been the laboratories experience that these syringes are not the most practical for day-to-day operations. Therefore, the laboratory shall use plastic syringes for all day-to-day use measurements' following verification of accuracy and imprecision as outlined within SOP for Support Equipment, as noted previously.

The instrument is initially calibrated (ICAL) using dilutions of custom certified gas mixes. The calibration standards are made up in the following concentrations as specified in Tables 11.2 A, B, C, and D. Due to the nature of preparing custom gas standards, the component concentration can fluctuate between purchased lots. This is accounted for during method/calibration development. The values below are very close approximations.

Calibration standards are prepared by using the procedures below:

- Prepare the correct number of vials for the detector being calibrated.
- Remove the specified amount of standard by extracting it from the standard mix gas cylinder using a syringe and injecting it into a prepared vial.
- Add the specified amount of vial balance gas to the same vial.
- The dilution factor of one is achieved by directly injecting the standard gas mix from the cylinder into the GC.

Table 11.2 A
Light Hydrocarbons by FID
(Methane, Ethane, Ethene, Butane, Propane, Propene and Acetylene)

Stock-1000ppmv Hydrocarbon Mix in Nitrogen from AirGas, or equivalent.
Stock-1000ppmv Acetylene in Nitrogen, AirGas, or equivalent.

Std Level	Conc. (PPMV)	Std	Make-up Gas
Level 9	0.040	2cc (W/S#8)	248cc UHP Nitrogen (w/serum bottle)
Level 8	0.100	1cc (W/S#8)	49cc
Level 7	0.200	2cc (W/S#8)	48cc
Level 6	0.500	4cc (W/S#8)	36cc
Level 5	2.00	2cc (W/S#7)	38cc
Level 4	10.0	10cc (W/S#7)	30cc
Level 3	40.0	2cc (each stock)	46cc
Level 2	125	5cc (each stock)	30cc
Level 1	500	21cc (each stock)	Into an evacuated vial
W/S#7	40.0	8cc (each stock)	184cc (w/160cc serum bottle)
W/S#8	5.00	1cc (each stock)	198cc (w/160cc serum bottle)

Table 11.2 B
Hydrogen by RGD

Stock-100 PPMV Hydrogen in Nitrogen, AirGas, or equivalent.

Level	Conc.	Std	Make-up Gas
Working Sol #4	2.00	1cc Stock	49cc
Level 1	50.0	21cc Stock	21cc
Level 2	20.0	10cc Stock	40cc
Level 3	10.0	5cc Stock	45cc
Level 4	5.00	2cc Stock	38cc
Level 5	2.00	1cc Stock	49cc
Level 6	0.500	10cc Working Sol #4	30cc
Level 7	0.200	4cc Working Sol #4	36cc

Table 11.2 C

Permanent Gases by TCD
(Oxygen, Carbon Dioxide, Nitrogen, Methane, Carbon Monoxide)

Stock-Multi-component Mix at various conc. in Nitrogen, AirGas, or equivalent.

Level	Std	Make-up Gas
Working Sol #5	1cc Stock	49cc
1	As received from cylinder	0
2	21cc Stock	21cc
3	5.0cc Stock	45cc
4	1.0cc Stock	49cc
5	0.5cc Stock	49.5cc
6	10cc Working Sol #5	40cc

Table 11.2 D
Permanent Gases by TCD
(Carbon Dioxide, Methane, Ethane, Ethene)

Stock-Single component sources, 100% Stock by AirGas, or equivalent.

Std Level	Conc. (PPMV)	Std	Make-up Gas
Working Sol #6	20,000	5cc each comp	230cc (w/serum bottle)
Level 1	200,000 CO_2 100,000 MEE	10cc CO_2 5cc MEE	25cc
Level 2	50,000	2.5cc each comp	40cc
Level 3	10,000	25cc Working Sol #6	25cc
Level 4	2,000	5.0cc Working Sol #6	45cc
Level 5	400	1.0cc Working Sol #6	49cc

12. Procedure

12.1. Sample Preparation

- Samples that are collected as direct vapors, for example from a soil gas survey or from the headspace of a microcosm sample, do not require additional preparation.
- Samples that are collected using the Bubble Strip Sampling Technique, PAES Sampling Method SM9 (ENV-SOP-PITTS-0015), do not require additional preparation prior to analysis.
- Samples that are collected as waters and are to be analyzed for dissolved gases must be prepared using PAES Standard Operating Procedure PM01C (ENV-SOP-PITTS-0016).

12.2. Analysis

- If the sample is prepared via SOP ENV-SOP-PITTS-0016, it can be injected from the syringe in which it is prepared by inserting the needle of the syringe through the septum on the "sample in" port. If the sample is a calibration standard, a bubble strip sample (SM9), or a direct vapor, the septum inlet to the "sample in" port of the GC must be removed and a luer-lock needle receptacle is plumbed to the "sample in" port. A needle is attached to the luer-lock receptacle and inserted through the septa of the calibration standard, bubble stripped sample, or direct vapor sample.

- In order to initiate analysis and introduce the sample into the GC sample loop, a needle is attached to the entry port on the GC and inserted through the sample septum. The flow through the sample loop is monitored by a flow meter connected to the sample-loop vent-port on the gas chromatograph. When a vial is sufficiently filled, the ball in the flow meter will shoot to the top of the column. This indicates that there is sufficient pressure in the vial to fill the sample loop. If the loop is not properly pressurized, this is reflected on the flow meter immediately. The ball in the flow meter will go up the column part way and drop back to the bottom. This indicates there is not sufficient pressure in the sample vial. If this happens, the analyst will remove the vial from the inlet port and vent any remaining positive pressure from the vial. The analyst will then add a measured volume of UHP Helium, resulting in dilution. This is then injected into the instrument. The lack of sufficient pressure in the vial and the means of sample injection are then documented on the case narrative.
- Once the flow out of the sample loop ceases (3 seconds if SOP ENV-SOP-PITTS-0016 is used) the sample loop valves are activated. Once the sample loop valves have been activated, the ports to and from the sample loop are flushed with ultra-high purity helium injected into the loop directly from the cylinder to remove any interference from ambient air and to avoid cross contamination between samples.
- Once all designated samples and associated quality assurance injections have been made to the GC, the instrument is placed into the "bake-out" configuration. With carrier gas continuously flushing through the GC, the temperature on the oven is manually turned up to 210 degrees Celsius or as high as the instrument column oven can maintain. This assures column integrity for consistent day-to-day operations.

13. Quality Control

13.1. Calibration

Initial calibration is accomplished by analyzing multiple standards of appropriate concentration ranges, as outlined in Section 11.2, for each detector being readied for sample analysis.

Acceptance Criteria: A linear fit to an area response versus concentration plot is formed with the origin forced to zero and the calibration is accepted for use if r^2, the coefficient of determination is $\geq$ 0.995. If this criterion cannot be met using a linear fit, a quadratic fit can be used. For the quadratic fit, the acceptance criteria is also $r^2 \geq 0.995$.

Corrective Action: If the acceptance criteria specified above is not met, the instrument is examined for a cause and a new set of calibration standards are analyzed.

13.2. Initial Calibration Verification

The ICV is prepared from an alternate source, than that used for the ICAL standards. The concentration of the ICV is in the middle of the calibration range and is close to that of the ICAL midpoint, but because of the nature of gas standard it is not at exactly that concentration. The ICV standard immediately follows the initial calibration.

Acceptance Criteria: Acceptance criterion for the ICV is an instrument response within ± 15% drift. Since the instrumentation used routinely monitors the percent recoveries and in this instance percent drift is equal to percent recovery less 100%, the control limits are 85%-115% recovery.

Corrective Action: If the instrument response for the ICV standard is outside the acceptance window of 85-115%, the analyst will not analyze samples until either the reason is determined and the problem is corrected, or a new multi-point calibration is analyzed and an acceptable ICV is run using that calibration.

13.3. Initial Calibration Blank

An initial calibration blank follows the ICV. The blank is made up of the instrument flush. Target compounds must not be detected above the reporting limits. For DoD projects the results of the ICB must be < ½ RL.

Corrective Action: If the blank does not meet the acceptance criterion, another blank is injected. If the second analysis also falls outside acceptance criteria, analysis is halted, and the issue corrected.

13.4. Continuing Calibration Verification

The CCV is prepared from an alternate source, than that used for the ICAL standards. The concentration of the CCV is in the middle of the calibration range and is close to that of the ICAL midpoint, but because of the nature of gas standard it is not at exactly that concentration. The CCV is analyzed at the beginning and end of each analytical shift and after every 15 field samples.

Acceptance Criteria: Acceptance criterion for the CCV is an instrument response within ± 15% drift. Since the instrumentation used routinely monitors the percent recoveries and in this instance percent drift is equal to percent recovery less 100%, the control limits are 85%-115% recovery.

Corrective Action: If the CCV fails, a new CCV is prepared and analyzed. If the new CCV falls within the acceptance criterion, analysis continues. If the new CCV fails, the instrument shall be recalibrated, and all samples since the last acceptable calibration verification shall be reanalyzed.

13.5. Continuing Calibration Blank

A CCB follows each CCV. The blanks are made up of the instrument flush. The acceptance criterion for the blank is the result must be less than the reporting limits for all target compounds. For DoD projects the results for the CCB must be < ½ RL.

Corrective Action: If the blank does not meet the acceptance criterion, another blank is injected. If the second analysis also falls outside acceptance criteria, analysis is halted, and the issue corrected.

13.6. Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

13.6.1. Direct Vapor/Bubblestrip/Water Samples:

The LCS and LCSD are prepared at a mid-range concentration. The type of LCS/LCSD depends upon the original matrix of the sample. For samples that arrive as vapors, the LCS/LCSD is injected as a gas. For samples that arrive as waters, DI water is spiked with a gas mixture of target analytes and prepared the same as the samples. Both an LCS and an LCSD are to be run with each analytical batch.

Note: Deionized source water for LCS/LCSD should be "degassed" prior to the addition of the source headspace.

13.6.2. Total Inorganic Carbon Samples

Mix approximately 0.20g $NaHCO_3$ into 200ml laboratory grade DI water, prepare according to the TIC procedures outlined in SOP ENV-SOP-PITTS-0016 and analyzed in duplicate as a sample. The true value of the spike is calculated as follows:

$$\text{mg/L } CaCO_3 = \frac{Mass(g)NaHCO_3}{H_2O(ml)} X \frac{100.09}{84.01} X(1{,}000{,}000)$$

Acceptance Criteria: Percent recovery is to be between 80-120% and RPD (Relative Percent Difference) is to be less than or equal to 20%.

Corrective Action: If the LCS fails, a new LCS is prepared and analyzed. If the new LCS falls within the acceptance criterion, analysis continues. If the new LCS fails, analysis is stopped and the overall procedural system is checked for error. Once the cause is determined, analysis continues and if necessary, discussion placed to the case narrative.

13.7. Method Blank:

A method blank is analyzed with each analytical batch. Water that is free of the principle atmospheric components of nitrogen and oxygen is very difficult to make and similarly difficult to store. Toward that end, the blanks are made up of instrument flush for all of the gases except for blanks for TIC. TIC blanks are made up of deionized water. The acceptance criterion for the blank is the result must be less than the reporting limits for all target compounds. For DoD projects the results for the method blank must be < ½ RL.

Corrective Action: If the blank does not meet the acceptance criterion, another blank is injected. If the second analysis also falls outside acceptance criteria, analysis is halted, and the issue corrected.

13.8. Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

13.8.1. Water Samples:

For water samples, MS and MSDs are prepared, analyzed, and reported when clients' request and send sufficient numbers of aliquots to prepare them (e.g. one 40 ml vial each for the MS and another for the MSD). The source used for MS/MSD will be based upon the methane concentration of the original field sample being spiked; depending upon the detector used for the methane determination.
Source water is spiked with a gas mixture of target analytes and prepared the same as the field samples.

13.8.2. Total Inorganic Carbon MS and MSD

Weigh and mix well, approximately 0.04g $NaHCO_3$ directly into the 40ml voa vials provided for MS and MSD, and prepare according to the TIC procedures outlined in SOP ENV-SOP-PITTS-0016. The true value of the spike is calculated as noted, section 13.6.2.

Acceptance Criteria: Percent recovery is to be between 70-130% and RPD (Relative Percent Difference) is to be less than or equal to 20%.

Corrective Action: If the matrix spike and spike duplicate fail but all the other quality control samples are within the acceptance criteria, matrix interference is noted in the Case Narrative.

14. Data Analysis and Calculations

14.1. The output of the chromatograph is directed to a microcomputer where the signal is converted to digital format, stored, and processed using a chromatography data system.

14.2. Assignment of Retention Time and Windows

Following completion of the calibration injections, each instrument or column in use for the procedure must establish specific retention times and retention time windows for all target analytes being monitored. These shall be set to the calibration according to the following procedures:

Note: The steps outlined are applicable to the Thermo Fisher/Dionex Chromeleon data acquisition software.

14.2.1. Retention Times

Each calibration is performed over a range of concentrations. The analyst shall choose a single calibration concentration between the mid-point and high-point concentrations, for setting the absolute retention time for each analyte. Do not use the high-point concentration. Transfer the times (minutes) from the chosen concentration into the calibration table. Entered values are to be three significant figures.

Note: The exact retention times may vary day-to-day as a function of column type, column age and column history. The analyst must monitor daily continuing calibration verifications to assure accurate assignment of peak identifications. The analyst may also use the data system settings of the calibration table to assist in this application.

14.2.2. Retention Time Windows

The analyst shall set absolute retention time windows based upon data interpretation of the second highest calibration concentration. The procedure is as follows:

Determine the peak width, at base line level, for each analyte; this is a monitored peak variable available with the data system. For each analyte, enter a value of ½ the peak width into the calibration table, rounded to two significant figures. Set the data system to interpret these entered values as ± the absolute retention time. If the value entered creates a window that overlaps with other peaks in close proximity, divide the window value by 2 until the overlap is resolved.

Retention time windows must be calculated for each instrument and column used. New retention time windows must be established when a new column is installed. This procedure is used because the standard procedure discussed in method SW846-8000B, Section 7.6 is not appropriate for the packed column chromatography of low molecular weight gases.

14.3. Total Inorganic Carbon Result Calculation

The final result is calculated as follows:

TIC as mg/L $CaCO_3$= ($\%CO_2$)((Volume headspace)(2.08)+43.3)

14.4. Use the calculation below for the percent recovery of the LCS/LCSD and ICV/CCV:

$$Percent\ \mathrm{Recovery} = \frac{MeasuredValue}{TrueValue} \times 100$$

14.5. Use the calculation below for the percent recovery of the MS/MSD:

$$Percent\ \mathrm{Recovery} = \left[\frac{SpikeAdjustedValue - OriginalValue}{SpikeTrueValue}\right] \mathrm{x}100$$

14.6. Use the calculation below for the relative percent difference (RPD) of the LCSD and MSD:

$$RPD = \left|\frac{(C1 - C2)}{((C1 + C2).x0.5)}\right| \mathrm{x}100$$

Where: C1=concentration of the original injection for each target component
C2=concentration of the duplicate injection for each target component

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Because the results from this method frequently require the analyst to use manual integration, manual integration is included as part of the training. Because of the nature of the instrument, the range of integrated concentrations and the low specificity of the detectors, it is often necessary to perform manual integration even on the laboratory control samples. As part of the training, the analysts must:

- Retain an electronic copy of the original chromatogram that was integrated by the automated settings of the instrument software. (This is done automatically by the Chromeleon software.)
- Document on the hard copy Case Narrative a justification for the manual integration and circle "YES" in the box in the lower right corner of the narrative sheet.
- The analyst shall present in hardcopy printout, all data for review in accordance to requirements outlined in SOP ENV-SOP-PITTS-0036, Manual Integration.
- The reviewer shall thoroughly examine the data and when satisfied, check the appropriate box on the case narrative form and place their initials where designated.
- If there are questions about the manual integration, the data reviewer shall review the original chromatogram from the data system.
- If agreement is obtained from the data reviewer that the manual integration was indeed necessary, the reviewer shall document on the same hard copy Case Narrative (lower left corner) that the manual integration was reviewed and the justification stands.
- If the reviewer disagrees with either the necessity of the integration or the specific manipulations done in the integration, the specific objections should be discussed with the analyst and the manual integration techniques should be further discussed and emphasized.

15.2. The analytes of this method are indicators. Every attempt to achieve and deliver precise results is made. However, it is realized that for indicator parameters measuring the range of the analyte concentration (i.e. is the concentration of methane gas >1 mg/l or < 0.1 mg/l) is the primary goal of employing these analyses. The calibration range is chosen to extend over most of the bio-indicator concentration range. If the concentration of an analyte exceeds that of the highest calibration standard, while employing a linear calibration fit, but does not saturate the instrument response, the concentration is calculated by assuming detector response linearity and using an extrapolation of the calibration plot. If the instrument response is saturated or the concentrations are determined from a quadratic calibration fit, the sample is diluted to bring the analyte concentration into the calibration range.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. If the requirements set forth in Section 13 are not met, the analytical program will be terminated until the cause is determined and a solution is affected. All samples associated with out of control quality control samples (with the exception of matrix interference) must be reanalyzed provided sufficient sample containers have been provided by the client. If quality control acceptance criteria cannot be met using the corrective action above, a detailed check of the analytical system is made. Reagents, standards, and other quality control samples are re-prepared and analyzed. If problems persist, sample analysis will be halted and the Laboratory Manager shall be contacted immediately to determine the cause and implement corrective action.

Any data submitted with unacceptable quality control sample results shall be qualified in a case narrative. The narrative should indicate the out of control event that occurred, the corrective action that was taken, and any other pertinent information to inform the client of exactly what occurred.

18. Method Performance

18.1. Analysts who use this method have been certified for the method by running Initial Demonstration of Proficiency (IDOP) Samples in accordance with PAES Standard Operating Procedure for Administering and Documenting Training in Laboratory Procedures and Instrumentation (SOP ENV-SOP-PITTS-0014). IDOPs are run any time there is significant change to an instrument, method, or in the training procedure for training a new analyst.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Instrument maintenance should be followed as suggested in the manufacturer's operation manual and in the laboratory SOP for Equipment Maintenance (ENV-SOP-PITTS-0005).

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. Safety glasses are required in all laboratory areas. Safety Data Sheets (SDS) for all compounds used in this procedure are available in the laboratory. The major hazard in this laboratory is stick from needles. All needles must be capped when not in use and when moving about the laboratory. The proper way of capping a needle is to place the cap on the laboratory bench and direct the needle into the cap. A needle is never to be directed into a cap while the cap is being held. For further information regarding safety issues, please refer to the company Chemical Hygiene Plan.

23. Waste Management

23.1. Unused portions of samples are kept for 30 days following final report generation. The samples are then removed from the laboratory and disposed of according to the SOP for Waste Disposal.

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains information on pollution prevention.

25. References

Citing a reference does not imply that all of the recommendations and/or requirements in those cited methods is required in this Standard Operating Procedure. This section simply refers to sources that were consulted to gather information or knowledge in order to write an informed technical procedure.

U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste. SW-846, 3rd ed., Office of Solid Waste and Emergency Response, Washington, DC. 1986.

Newel, B.S., RSK-SOP-175, Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples using GC Headspace Equilibration Technique. Revision No. 0, August 1994.

American Society for Testing and Materials, Standard Practice for Analysis of Reformed Gas by Gas Chromatography. Annual Book of ASTM Standards. Vol. 14.02, 1994.

Kampbell, D.H. and Vandegrift, S.A., Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique. Journal of Chromatographic Science. Vol. 36 May 1998.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
Section 14	Redefine sections to include actual calculations	11/16/2016
ENV-SOP-PITTS-0018 Rev00	Removed front cover page and Table of Contents to conform to MC. Added verbiage to Section 6.1 to include importance of using provided containers/preservatives. Added to QC Section 13.3, 13.5 and 13.7, "If second analysis also falls outside acceptance criteria, analysis is halted, and the issue is corrected." Added reference to Equipment Maintenance SOP to Section 20. Added details of linear and quadratic fits to Section 15.2. Updated all SOP references throughout document to account for new numbering system through MC.	4/26/2019

APPENDIX D-5

PACE KANSAS SOPS

Document Information

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Notes

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ENV-SOP-LENE-0021 Sample Management

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Gregory Busch (003971)	Quality Manager	29 Nov 2018, 01:15:51 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Charles Girgin (002243)	General Manager	02 Dec 2018, 02:24:26 PM	Approved
Eric Brockett (008554)	Working Supervisor	21 Jan 2019, 10:41:16 AM	Approved

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to outline the procedures involved with the receipt, login, storage, and disposal of samples received by Pace Analytical Services, LLC, Kansas (PASI-KS).

2. Summary of Method

2.1. Samples are delivered to the laboratory via several delivery mechanisms. Samples received are checked for adherence to the Sample Acceptance Policy with any discrepancies noted. Discrepancies are communicated to the client for their acknowledgement and decision making.

2.2. The Laboratory Information Management System (LIMS) assigns all samples with a unique sample number and manages the analyses assigned to each sample.

2.3. Samples are labeled with the appropriate information and staged in refrigerated sample storage coolers if temperature preservation is required or on open shelves for samples not requiring sub-ambient temperature preservation. Samples will remain under these conditions until prepared and/or analyzed. Samples received under United States Department of Agriculture (USDA) protocols need to be stored separately (please refer to the lab's Regulated Soils SOP, if applicable).

2.4. Samples and associated sub-samples (digestates, extracts, etc.), with the exception of Air cans, are maintained for a minimum of 45 days from receipt of samples unless otherwise requested by the client or other regulatory agency.

2.5. Samples are disposed of in accordance with local laboratory regulatory requirements and the laboratory's waste handling procedures and any USDA regulated soil requirements.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP apply to all personnel involved in the receipt, login, storage, and disposal of samples.

3.2. A sample acceptance policy is contained within the Procedure section that outlines guidelines for acceptable sample conditions. Any deviation from these guidelines requires detailed documentation within the report, usually as a footnote, or on the chain-of-custody, or SCURF and may require client contact.

3.3. **Parameters**: Not applicable to this SOP.

4. Applicable Matrices

4.1. Not applicable to this SOP.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Samples may be prone to cross contamination from others within the same delivery group or from other client projects. The sample receiving personnel must make every effort to minimize cross- contamination.

6.2. Preservation checks are one of the most likely situations where cross-contamination may occur. Materials used in the process must be specific to each sample and may not used for multiple samples.

6.3. Samples are stored under specific conditions and in specific locations, typically per the requirements of the analytical method. However, consideration must be given to samples that are uniquely different from others. Samples that are anticipated to be severely contaminated must be segregated from others in anticipation that the high levels of contaminants may cross-contaminate others in close proximity. USDA samples must also be distinctly segregated for storage.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Acceptable sample preservation, containers, and hold times are listed in Attachment IV of this SOP. They may also be located in the Pace Quality Assurance Manual, the laboratory's method SOPs or in the applicable test method. Samples are stored separately from all standards and reagents and any known highly contaminated samples.

NOTE: To avoid contamination, no food or drink products can be located near the areas where samples are unpacked, labeled, or staged.

7.2. Sample Storage – See Section 12.3 for general storage guidelines.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

8.2. **COC - Chain-of-Custody:** a form used to record the field identification of samples collected, analyses requested, date and time of collection, sample preservation used, and traceability of samples from time of collection until delivery to the laboratory. This is a legal document.

8.3. **LIMS - Laboratory Information Management System:** a computer system used to manage the flow and traceability of environmental samples and associated data within the laboratory.

8.4. **Matrix:** the bulk characteristics of a sample. See Table 8.1 below.

8.5. **SDS - Safety Data Sheet:** contains information on chemicals used in the laboratory.

8.6. **Sample Custody:** a sample is considered to be in someone's custody if:

8.6.1. It is in one's physical possession;

8.6.2. It is in someone's view, after being in someone's physical possession;

8.6.3. It is kept in a secured area, restricted to authorized personnel only.

8.7. **SCURF - Sample Condition Upon Receipt Form:** a form used to record the condition of samples received in the laboratory.

8.8. **SRF – Sample Receipt Form:** form generated by LIMS system after a project is logged in. Contains sample and project information.

8.9. **UN Number -** identification numbers preceded by the letters UN are associated with proper shipping names considered appropriate for international and domestic transportation. These shipping names along with the identification numbers are located in the Federal Register (49CFR172.101).

Table 8.1 Matrix Cross-Reference

NELAC/TNI defined matrix	Corresponding EPIC Pro matrices
Air and Emissions: Whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbant tube, impinger solution, filter, or other device.	Air (AR)
Aqueous: any aqueous sample excluded from the definition of Drinking Water or Saline/Estuarine. Includes surface water, ground water effluents, and TCLP or other extracts.	Water (WT)
Biological tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.	Tissue (TS) or Tissue Dry (TD)
Chemical Waste: a product or by-product of an industrial process that results in a matrix not previously defined.	Oil (OL) or Other (OT)
Drinking Water: any aqueous sample that has been designated a potable or potentially potable water source.	Drinking Water (DW)
Non-aqueous liquid: any organic liquid with < 15% settleable solids.	Other (OT)
Saline/Estuarine: any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake.	Water (WT)- not assigned as a separate matrix.
Solids: includes soils, sediments, sludges and other matrices with > 15% settleable solids.	Solid (SL)
(No corresponding matrix to wipes; wipes would be included in with solids)	Wipe (WP) or Swab (SW)

9. Equipment and Supplies

Table 9.1 – Equipment and Supplies

Equipment/Supplies	Description	Vendor/Item #
Sample Labels		
Thermometers	Infrared, digital, NIST traceable	
Sample storage cooling units	Capable of holding required storage temperatures	
COC forms		N/A
SCUR forms		N/A
pH paper		
Label Printer		
LIMS computer system	EPIC Pro	
Disposable pipettes		
Sample containers		
Residual chlorine strips	For UCMR, capable of measuring 0.1mg/L of chlorine	
Narrow range pH paper	For UCMR, capable of distinguishing pH of 7.9 from 8	
Narrow range pH paper	For hexavalent chromium, capable of distinguishing pH between 9.3-9.7	
Lead acetate paper		
Temperature blank		

10. Reagents and Standards

10.1. All reagents used in this procedure must be labeled with:

10.1.1. Laboratory reagent identification number;

10.1.2. Unless otherwise noted, the name and concentration of the reagent;

10.1.3. Date the reagent was received, opened and, as needed, prepared;

10.1.4. Person preparing reagent;

10.1.5. Expiration date.

10.2 Table 10.1 – Sample Preservation Reagents

Reagent	Formula	Concentration
Sulfuric Acid	**H_2SO_4**	**1:1**
Nitric Acid	**HNO_3**	**1:1**
Hydrochloric Acid	**HCl**	**1:1**
Sodium Hydroxide	**NaOH**	**50% or Pellets**
Sodium Thiosulfate	**$Na_2S_2O_3 \cdot 5H_2O$**	
Zinc Acetate Solution (for sulfide)	**$Zn(CH_3CO_2)_2$ + NaOH**	**1N $Zn(CH_3CO_2)_2$ + 50% NaOH**
Methanol	**CH_3OH**	**Purge and Trap Grade**
Ascorbic Acid (for cyanide)	**$C_6H_8O_6$**	**Conc. or dilute**
Sodium Bisulfate	**$NaHSO_4$**	**5 mL**
a,a,a-Trifluorotoluene	**$C_6H_5CF_3$**	**2.5mg/L**
Ammonium sulfate/ ammonium hydroxide (for hexavalent chromium)	**$(NH4)_2SO_4$ / NH_4OH**	**33g $(NH4)_2SO_4$ + 6.5 mL NH_4OH / 100 mL Water**

10.3. For acids, bases and other reagents obtained from other laboratory departments, this information is located in the appropriate hardcopy or electronic standards/reagent preparation log. In the event that these reagents are managed within the Sample Receiving group, the department must maintain its own reagent preparation log.

10.4. Some Pace labs use preserved sample containers. In this case, documentation must be maintained for bottleware and preservation traceability.

10.2. For acids, bases and other reagents obtained from other laboratory departments, this information is located in the department reagent preparation log. In the event that these reagents are managed within the Sample Receiving group, the department must maintain its own reagent preparation log.

10.3. PASI-KS uses pre-preserved sample containers. Certificates of Analysis (CoA) documentation must be maintained for bottleware and preservation traceability.

11. Calibration and Standardization

11.1. Thermometers, IR-Guns, and other equipment used for measuring temperatures must be calibrated according to SOP ENV-SOP-LENE-0030 **Support Equipment**, or its equivalent revision or replacement.

12. Procedure

12.1. Sample Receipt

12.1.1. The laboratory receives client samples via three major methods: mail/commercial delivery service, Pace Analytical courier/field services and hand delivery.

12.1.2. Courier services may be used to pick up client samples on either a regular schedule or on an as-needed basis as communicated by Project Managers or by the client.

12.1.2.1. When the client is present during courier pick-up, the client signs the chain-of-custody (COC) relinquishing custody to the courier. The courier signs the COC as accepting the samples and provides the client with a copy of the COC. When the courier returns to the lab with the client samples, the courier signs the COC as relinquishing the samples to the lab.

12.1.2.2. If the client is not present during courier pick-up, the courier signs the COC as accepting the samples and leaves a copy of the COC for the client. If the COC is sealed inside the cooler, the courier will not sign the COC. If a client also has a sample log in use, the courier must sign and date the log when the samples are picked up. When the courier returns to the lab with the client samples, the courier signs the COC as relinquishing the samples to the lab. The date/time of delivery to the lab by the courier is the official date/time received by the lab (analogous to the official date/time of receipt by an outside commercial carrier or courier).

12.1.2.3. To ensure the sample security, the Pace courier custody seals all the coolers being picked up and the courier vehicle is locked at each client pick-up location. IMPORTANT: Pace Analytical courier/field services personnel must open the sample coolers and verify there is adequate ice in the coolers before transporting or shipping to the laboratory.

12.1.2.4. The lab must provide pertinent information to the person or persons responsible for taking and transporting samples. This information includes sampling procedures (where applicable), and information on storage and transport of samples, including any information on factors that may influence the test results.

12.1.3. **Lab COC Procedures**: The COC (see example Attachment II) is signed immediately upon receipt of the samples from the client. If the client drops off the samples, a copy of the signed COC is given to the client at that time. If samples are received via commercial carrier or mail delivery, the COC should be signed immediately when the cooler or package is opened and ultimately placed in the project file. The delivery date and time is considered the date/time received.

12.1.4. **Sample Acceptance Policy -** Copies of the Sample Acceptance Policy must be provided, in the form of a letter, fax, or e-mail to each client or sampler, as necessary. Samples are considered acceptable if they meet the criteria listed in the Sample Acceptance Policy (see Attachment I)

12.1.4.1.1. Some labs may have agreements with clients regarding exceptions to the client contact requirements for sample acceptance policy deviations. If a lab has such agreements, two conditions must be met: 1) the agreement must be a formal document showing client approval; 2) the lab must qualify the final report as appropriate to their applicable regulatory bodies.

12.1.5. **Measuring temperature when temperature blank present:** Open the cooler and verify the temperature of the samples by taking the temperature of the temperature blank. The temperature of the cooler must be taken using a NIST-traceable thermometer. The thermometer is placed into the temperature blank. After 5 minutes, the thermometer is read to the nearest 0.5°C increment and recorded.

12.1.6. **Measuring temperature when NO temperature blank present:** If there is no temperature blank in the cooler, measure the temperature of a representative sample bottle or cooler melt water. A representative sample will reflect an "average" condition of the samples in the cooler and, depending on the manner in which they are packed, may not necessarily be in direct contact with the cooling material.

12.1.6.1. Procedure using a stick thermometer: If an IR gun is not used, the temperature of the cooler must be taken using a NIST-traceable thermometer. If there is no temperature blank, the thermometer is placed into the melt water of the cooler for approximately 5 minutes. After 5 minutes, the thermometer is read to the nearest 0.5°C increment and recorded. If no ice is present, a sample aliquot (non-volatile) is poured into a small container and the temperature of the sample is taken.

12.1.6.2. Procedure using an IR gun: If an IR gun is used, the temperature must be taken from an opaque surface such as the bottle label. Measurements taken through a transparent surface (clear or amber glass) may not be reliable and must incorporate a specific temperature correction factor for that surface reading.

12.1.7. Record the uncorrected and corrected cooler temperatures on the COC (example in Attachment II) and/or SCUR form (example in Attachment III). In addition, record the type of "ice" used for packing the cooler (e.g., wet ice, "blue ice", gel packs, etc.).

12.1.8. If samples within a project are spread over multiple coolers and one or more of the coolers are outside of the temperature criteria, then the contents of the cooler must be itemized and the samples and sample containers affected by the out-of-control temperature must be listed on the SCUR form for qualification in the final report. This itemization must be retained in the project file for future reference.

12.1.9. Unpack the cooler and COC. Organize the samples, grouped by client sample ID, according to the order on the COC. Review COC against samples to make sure the bottles received match the analysis requested. All anomalies must be recorded on the SCUR form.

12.1.10. For USDA samples, the cooler and all contents must be decontaminated (refer to Regulated Soil SOP for procedure). For non-USDA samples, discard any ice or water that remains in the cooler and the packing material used to secure the samples. Water or ice should be discarded down a drain that connects to the local sewer. Packing materials should be placed in the garbage. If a sample container was broken, the contents remaining in the cooler MUST be discarded in a manner consistent with the hazardous waste handling standard operating procedure.

12.1.11. **pH Verification Instructions:**

12.1.11.1. The pH of the sample must be verified on all preserved sample bottles requiring pH preservation (see exceptions below).

12.1.11.2. Open each preserved bottle (except as noted below). Use a new disposable pipette, a stirring rod or another inert utensil to withdraw a small portion of the sample. Dispense the aliquot on a sample specific pH strip and check the pH.

12.1.11.3. NOTE: Do not check the pH of samples for coliform, volatiles, Total Organic Carbon (TOC), Wisconsin Diesel Range Organics (WI-DRO), oil and grease, or hexane extractable materials (HEM). These analyses will be checked by the analyst at the bench and must not be opened by sample management personnel.

Table 12.1 – General pH Preservation Requirements by Preservative

Sample Preservatives	Sample pH Requirement
Hydrochloric Acid (HCl)	must be less than 2
Nitric Acid (HNO_3)	must be less than 2
Sulfuric Acid (H_2SO_4)	must be less than 2
Sodium Hydroxide (NaOH)	must be greater than 12
Zinc Acetate and Sodium Hydroxide (NaOH)	must be greater than 9

12.1.11.4. If the pH for a sample container that is supposed to be preserved is not within the required range, indicate the anomaly on the SCUR form or on the COC. If a sample does not require preservation, write N/A in the applicable section of the SCUR form.

12.1.12. **pH Preservation Adjustments:**

12.1.13.1. If a sample container does not meet the pH preservation required, the pH of the sample must be recorded on the COC or SCUR. Additional preservative is added so that the preservative content is < 1% of the sample container volume. For example:

12.1.13.1.1. For a 100mL container, a maximum of 1mL of preservative may be added;

12.1.13.1.2. For a 250mL container, a maximum of 2.5mL of preservative may be added;

12.1.13.1.3. For a 500mL container, a maximum of 5mL of preservative may be added;

12.1.13.1.4. For a 1L container, a maximum of 10mL of preservative may be added.

12.1.13.2. The appropriate preservative is added to the sample container, the sample is mixed and the pH is taken again. The new pH reading is also recorded on the COC or SCUR along with the amount, type and lot number of the preservative added. In addition, the sample container is marked with the preservative added, volume added, date, time and initials of the technician. For Metals analyses specifically, the lab must wait 24 hours after pH adjustment to pH < 2 before sample preparation can begin.

12.1.13.3. The sample SCUR or Non-conformance form must contain the documentation of additional sample preservation (preservative ID, date, time, initials and volume added).

12.1.13. **Total Residual Chlorine Verification Instructions -** Total residual chlorine must be verified at the time of receipt or at the bench as required by the method or individual state regulatory agency for certain analyses (see Table 12.2). Do not check the sample bottles for those analyses listed in 12.1.10.

12.1.14.1. Open the appropriate sample container. Utilizing a new disposable pipette, stirring bar or other inert utensil; withdraw a small portion of the sample. Dispense the aliquot on a sample specific residual chlorine test strip.

12.1.14.2. If any chlorine is detected, regardless of amount, note the information on the COC, SCUR or analytical bench sheet.

12.1.14.3. Insert lab procedure for treatment of samples when residual chlorine is present and method requires removal.

Table 12.2 – Analyses requiring Residual Chlorine Verification

Analyses
Ammonia (NH_3) EPA 350.1
Nitrate (NO_3) EPA 353.2
Biochemical Oxygen Demand (BOD) SM5210B
Cyanides SM4500 CN and EPA 335.4
Dioxin 1613B
PBDE 1614
PCBs 1668A
EPA 508.1
EPA 549.2
EPA 515.3
EPA 548.1
EPA 608, 608.3
EPA 610
EPA 625

12.1.14. **Checking for Sulfide in Cyanide analyses:** Test for sulfide by placing a drop of sample onto a piece of lead acetate paper. Darkening of the paper indicates the presence of sulfide. Follow specific method instructions for removing sulfide from samples.

12.1.15. Note any discrepancies pertaining to samples as defined by the sample acceptance policy detailed above on the COC or SCUR. Any discrepancies involving temperature, preservation, hold time, collection dates and times, sample volume, sample containers, and unclear analysis, must be reported to project management as soon as possible.

12.1.16. For short hold samples, the laboratory is notified and the samples are staged per section 12.3.

Table 12.3 – Analyses with Hold Times Less Than 72 Hours

Short Hold Time	Analyses	Details
15 minutes	Field Parameters	pH, Dissolved Oxygen, Residual Chlorine
15 minutes	Ferrous Iron	
8 Hours	Total/Fecal Coliform (MPN, MF), Enterococci, Fecal Streptococci MPN	Non-potable water only
8 Hours	Heterotrophic Plate Count (HPC)	
24 Hours	Hexavalent Chromium	
24 Hours	Fecal Sludge MPN	
24 Hours	Odor	
30 Hours	Total Coliform (Presence / Absence)	
48 Hours	Color	
48 Hours	MBAS	
48 Hours	Nitrate (unpreserved)	If Preserved, reported as NO3+NO2
48 Hours	Nitrite (unpreserved)	If Preserved, reported as NO3+NO2
48 Hours	Ortho –phosphate	
48 Hours	Settable Solids	
48 Hours	Turbidity	
48 Hours	VOA - Soils by Unpreserved EPA5035	Jars, Encores, Sleeves
48 Hours	Gross Alpha (NJ 48hr method)-waters	EPA NJAC 7:18-6
48 Hours	UV254	
48 Hours	Asbestos	
48 Hours	Chlorophyll A	48 hours to filtration
72 Hours	3030C Metals	
72 Hours	Volatiles – Air TO-18	Tedlar bag or equivalent

12.2. **Sample Login**

12.2.1. All samples received by the laboratory must be logged into the LIMS. Rush projects and/or projects with short holds should be prioritized. After these projects have been addressed, projects should be addressed on a first in, first out basis.

12.2.1.1. Samples must be logged into the LIMS so the samples can be uniquely identified (lab sample identification numbers). These lab sample ID numbers are used to track the prep and analysis activities of the samples, as well as identify the sub-samples, digestates, extracts, and other sample byproducts. This laboratory code maintains an unequivocal link with the unique client field sample ID code assigned to each sample.

12.2.2. Generate sample labels.

12.2.2.1. Generate sample labels and Sample Receipt Form (SRF) (see Attachment III).

12.2.3. Attach the sample labels to the appropriate sample bottles.

12.2.3.1. Do not attach labels to soil sample collected in tared vials. Vials for each sample are put into a Ziploc bag and the labels loosely placed inside. .

12.2.4. If any samples require analyses performed outside of the laboratory, prepare the samples for subcontracting according to the procedures listed in the SOP describing the subcontracting of analytical services, ENV-SOP-LENE-0009 **Subcontracting Samples**, or equivalent revision or replacement.

12.2.5. The Project Manager, Project Coordinator, or designated Client Services personnel must review and verify the following information by comparing the COC to SRF. Some of this information may not be provided by the client and those fields should be left blank:

12.2.7.1. Report Recipient;

12.2.7.2. Invoice Recipient;

12.2.7.3. Additional Report Recipient;

12.2.7.4. PO#;

12.2.7.5. Project Name;

12.2.7.6. Project Number;

12.2.7.7. Requested Due Date;

12.2.7.8. Sample ID;

12.2.7.9. Matrix;

12.2.7.10. Collection Date & Time;

12.2.7.11. Received Date & Time;

12.2.7.12. Analysis: Double check compound lists;

12.2.7.13. Price;

12.2.7.14. Region Codes;

12.2.7.15. Work Region % Split (for Pace internal subcontracted work).

12.3. **Sample Storage**

12.3.1. Once unpacked, samples will be logged into the LIMS in a timely manner and returned to appropriate storage conditions as soon as possible. Labs must make every effort to keep samples under the required thermal conditions during the login process. For the exceptional case where samples are not logged in the day they were received, they must be stored under appropriate temperature-controlled conditions until login takes place. In all cases, the sample temperatures must be taken as soon after receipt as possible (before samples are placed into storage) and the samples stored so as to maintain the required storage conditions while awaiting log-in.

12.3.1.1. For ESI BP-XA projects, samples must be kept in the cooler while being processed. If not kept in the cooler, the temperature must be checked and documented every 20 minutes during processing.

12.3.2. Once logged into the LIMS and labeled, samples are placed in the appropriate storage areas. Specific temperature requirements are outlined in the analytical methods, but general guidelines are outlined below:

12.3.2.1. Short hold samples are placed in the short hold storage area or delivered directly to the laboratory.

12.3.2.2. Biological tissue samples are staged by receiving date or project number on shelves in a freezer for all types of analyses.

12.3.2.3. Summa canisters and Tedlar bags are stored on designated shelving at ambient temperature.

12.3.2.4. Volatiles- Aqueous samples are stored by receiving date or by project number in a segregated volatiles cooler. Associated trip blanks are stored with the samples.

12.3.2.5. Volatiles- Soil and other solid samples received preserved in methanol are stored by receiving date or by project number in a segregated volatile cooler. Associated trip blanks are stored with the samples.

12.3.2.6. Volatiles- Soil and other solid samples received preserved with a stir bar, or deionized water and a stir bar, are stored by receiving date or by project number in a segregated volatiles freezer. Associated trip blanks are stored with samples.

12.3.2.7. Volatiles- Soil and other solid samples received in 4oz containers or similar bottleware must be preserved within 48 hours. In order to preserve these samples, it is necessary to collect a 5g aliquot of the sample and transfer it to a 40mL vial. One of the following preservation options must be utilized:

12.3.2.7.1. The 5g aliquot is preserved with a stir bar, 5mL of deionized water and a stir bar, or 5mL of sodium bisulfate and a stir bar and stored in a freezer until analysis, or;

12.3.2.7.2. Within 48 hours of collection in the field, the 5g aliquot must be immediately extracted with 5mL of methanol and stored in a segregated volatiles cooler until analysis, or;

12.3.2.7.3. Within 48 hours of collection in the field, the 5g aliquot can be preserved with 10mL of deionized water and a stir bar, stored in a segregated volatile cooler and analyzed within 48 hours of collection.

12.3.2.8. Volatiles- Soil and other solid samples received in Encore samplers must be managed within 48 hours of collection by freezing the Encore or extruding it.

12.3.2.8.1. If extruding the sample into a 40mL vial containing a stir bar or a stir bar and 10mL of deionized water, then the sample is stored in the segregated volatile freezer until analysis.

12.3.2.8.2. If extruding the sample into methanol, then the sample is extracted within 48 hours of collection and the sample is stored in a segregated volatile cooler until analysis.

12.3.2.8.3. NOTE: if samples are not received within 48 hours of collection or are not received with enough time to process the samples correctly within 48 hours of collection, this must be noted in a way that will be visible on the final report (e.g., footnote in LIMS).

12.3.2.9. General Chemistry/Semi-volatiles- Waters and other liquid samples are staged by receiving date or by project number on the shelves in the appropriate sample storage cooler.

12.3.2.10. General Chemistry/Semi-volatiles- Soils and other solid samples are staged by receiving date or by project number on the shelves in the appropriate sample storage cooler.

12.3.2.11. Metals Solids and Liquids: These samples are staged by receiving date or by project number on designated shelving in the laboratory or appropriate designated area. These samples may be stored at ambient temperature unless Mercury or Hexavalent Chromium analysis is needed. If Mercury or Hexavalent Chromium analysis will be performed, the samples are staged by receiving date or by project number in the appropriate sample storage cooler. Samples requiring low level mercury analysis by Method 1631 are taken to the clean room for preservation and ambient storage.

12.4. Internal Chain-of-Custody: When an analyst removes samples from a storage unit, the ICOC form must be completed in the applicable ICOC logbook. The following items must be documented: lab sample ID, analyst initials, date and time samples are removed, and sample container type. Project number is optional and only necessary when it is needed to uniquely identify a specific sample container. Once the analyst is finished with the sample, the sample must be returned to the applicable storage unit. The analyst must again document the necessary information in the ICOC logbook (date and time samples are returned to the storage unit and the analyst's initials). If the sample was entirely consumed, then document with the appropriate comment code.

12.5. Internal Chain-of-Custody: Similar steps must be taken for sample by-products such as extracts, digestates, and leachates. Once a sample is prepared for analysis, sample custody of the sample by-product must be transferred to the appropriate analytical group sample storage unit. Analytical staff must document in their ICOC logbook when removing and returning the sample by-products from and to the analytical sample storage location. If the sample by-product is entirely consumed during analysis, then document with the appropriate comment code.

12.6. **Sample Retention and Disposal**

12.6.1. If samples must be returned to customers, the lab must take special care to ensure that the samples are not damaged during any handling, testing, storing, or transporting processes.

12.6.2. Samples may need to be retained longer than the normal sample retention time (45 days from sample receipt). Reasons for this extended sample retention include: customer, program, or contract requirements so that samples can be retained in a secure location for the customers that is designated as a long-term storage area.

12.6.3. Disposal of unconsumed samples: Refer to the laboratory SOPs regarding waste handling and disposal: **Waste Handling and Management ENV-SOP-LENE-0127**, and USDA **Regulated Soil ENV-SOP-LENE-0132**, or current revisions or replacements.

13. Quality Control

13.1. For any sample received at the laboratory that does not meet the sample acceptance, hold time or preservation criteria, the client must be contacted by project management and advised of the situation**.** .

13.1.1. If the client instructs the laboratory to proceed with the analysis, all appropriate personnel/departments must be informed and the client approval must be documented on the SCURF or COC. Data will be appropriately qualified.

13.1.2. The client may also instruct the laboratory to preserve the samples at the laboratory prior to proceeding with analysis. This must be documented on the COC or the SCURF, and should be noted in the final laboratory report.

13.2. All supporting documentation related to sample custody must be retained by the laboratory. This includes: memorandums, fax transmissions, the original COC, all paperwork received with the COC, the completed SCUR form and copies of email transmissions. Please contact the laboratory QM/SQM for documentation retention time frames required.

13.3. Documenting Discrepancies during receipt of samples:

13.3.1. The following are examples of client discrepancies that need to be documented on the appropriate paperwork (e.g., SCURF):

13.3.1.1. Lost samples/insufficient sample volume;

13.3.1.2. Broken or missing bottles;

13.3.1.3. Missing COC;

13.3.1.4. Mislabeled bottles;

13.3.1.5. Preservation error;

13.3.1.6. Missing sample related details (date, time, sample type).

13.3.1.7. Headspace in VOA vials (>6mm)

13.3.1.8. Tared vials labeled in the field.

13.3.2. Pace sample management discrepancies will be documented on the SCURF, COC or within the project files. Discrepancies attributable to errors and omissions on the part of the laboratory will be addressed and resolved through the formal corrective action process.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Not applicable.

21. Troubleshooting

21.1. Not applicable.

22. Safety

22.1. Hazards and Precautions - Use extreme caution in handling samples and wastes as they may be hazardous. Each reagent and chemical used in this method should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats, safety glasses, and ventilation hoods. Safety Data Sheets (SDS) are on file and available to all personnel.

22.2. All personnel involved in sample management are responsible for complying with OSHA and DOT regulations. These regulations pertain to the safe handling and/or shipping of the chemicals specified in this procedure. Refer to the Sample Control Supervisor for any questions or concerns related to the safe handling and shipment of hazardous materials.

22.3. Other laboratory safety requirements are contained in the Chemical Hygiene Plan/Safety Manual. Immediate questions can also be addressed with the local Safety Officer.

23. Waste Management

23.1. Not applicable to this SOP.

24. Pollution Prevention

24.1. Not applicable to this SOP.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA, current revision.

25.5. American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1995, Standard Methods for the Examination of Water and Wastewater, A.E. Greenberg, L.W. Clesceri, A.D. Eaton and M.A.H. Franson, eds., 19th ed., American Public Health Association, Washington D.C.

25.6. U.S. Environmental Protection Agency, 1983, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

25.7. U.S. Environmental Protection Agency, 1988, Methods for Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.

25.8. Code of Federal Regulations- most recent version.

25.9. Method Update Rule- most recent version.

25.10. ASTM D7365-09a, Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I – Example Chain of Custody Form

26.2. Attachment II – Example Sample Condition Upon Receipt Form

26.3. Attachment III – Example Sample Receipt Form (SRF)

26.4. Attachment IV – Pace Approved Sample Containers, Preservation.

27. Revisions

Document Number	Reason for Change	Date
ALL-C-001-rev.0	New Procedure	July 12, 2004
ALL-C-001rev.1	Grammatical/Removal of outdated information	March 30, 2005
KS-C-001-rev.0	Grammatical/Removal of outdated information	April 23, 2007
S-KS-C-001-rev.1	Grammatical/Removal of outdated information	November 26, 2008
S-KS-C-001-rev.2	Section 8.1 – Removed note. Table 9.1 – Added adhesive labels. Section 12.1 – Check temperature of single sample. Changed green label to ink dot. Added headspace procedure. Removed client-specific QC from policy. Table 12.3 – Added Table 12.4 – Added TNRCC 1005, removed USDA-regulated soils. Section 13.3 – Revised list of headspace-sensitive analyses.	January 12, 2010
S-KS-C-001-rev.3	Section 6 – Added definition for ESI Tech Spec. Section 7 – Revised Distribution. Section 12 – COC completion for hand-delivered samples. Record quantity, type of containers and pH checks on COC. Record time samples are outside cold storage on the SCURF for ESI Tech Spec projects.	January 26, 2011
S-KS-C-001-rev.4	General: Used template SOT-ALL-C-001-rev.03 and converted it into the new SOP format. Inserted local information and procedures. Section 12.5 – Added SEKS procedures	January 9, 2013
S-KS-C-001-rev.5	Section 12.1.4.1 – Added blue dot on sample lids to indicate ICOC needed Section 12.4 – Added ICOC procedure Section 12.6 – Revised SEKS procedure to match current practice	February 21, 2014
S-KS-C-001-rev.6	Updated to the latest prescribed format. Table 10.1: Removed NaOH from the list of reagents. Table 12.2, Added BOD/CBOD/SBOD Section 12.1.11 – Removed TOC and Phenols from list of pH exceptions Section 12.1.14 – Tared vials labeled in field must be documented on SCURF. Section 12.2.3 – Don't put labels on tared VOA vials. Section 13.3.1.8 – Tared vials labeled in field must be documented on SCURF.	November 14, 2014
S-KS-C-001-rev.7	Table 9.1- Added test papers Table 10.1 – Added Sodium Thiosulfate Table 10.2- Added working reagents Table 10.3 – Added Standard Storage Conditions Section 12.1.11 – Added testing for residual chlorine and sulfides Section 12.1.2 – Added instructions for removal of residual chlorine Section 12.1.6- Added language to measure most representative sample for temperature instead of a temp blank if the cooler is packed improperly. Section 26 – Removed Cooler Receiving Log Section 27 - References – Added ASTM D7365-09a	May 10, 2016
S-KS-C-001-rev.8	Table 10.1 – Added sodium thiosulfate solution. Section 12.1.12.4- Removed H_2O_2 addition. Table 12.1 – NaOH preservation requirement changed to > 10. Attachment II – Update SCUR form.	May 25, 2016

ENV-SOP-LENE-0021-01	SOP – Removed Cover page, TOC and headers: revised the footer language and removed the uncontrolled document numbering line. General: made administrative edits that do not affect the policies or procedures within the document. Table 8.1: updated to match 2016 TNI Standard. Section 12.1.2.3: removed language regarding custody seals. Section 12.1.4: removed all Sample Acceptance Policy language in lieu of Attachment I. Section 12.1.4.1: added paragraph in red text for those labs that have exception agreements with clients. Sections 12.1.5, 12.1.6: reworded for clarity. Section 12.1.11, 12.1.13, 12.1.14: changed some text from red to black. Section 12.2.5: new section added requiring the state of origin to be documented. New Attachment I: Added Sample Acceptance Policy from form F-ALL-C-006. Old Attachment III: removed example SRF. Old Attachment IV: removed bottle/preservation table and all references to it within the SOP.SOP – Revised to Pace LLC Section 2.2 – Added USDA and Air Cans Section 6.3 – Added USDA Table 8.1 – Replaced Table 9.1 – Replaced Table 10.1 – Replaced Section 12 – Replaced with Corporate template Section 13.2 -- Revised	November 29, 2018

Attachment I – Sample Acceptance Policy (from F-ALL-C-006)

In accordance with regulatory guidelines, Pace Analytical facilities comply with the following sample acceptance policy for all samples received.

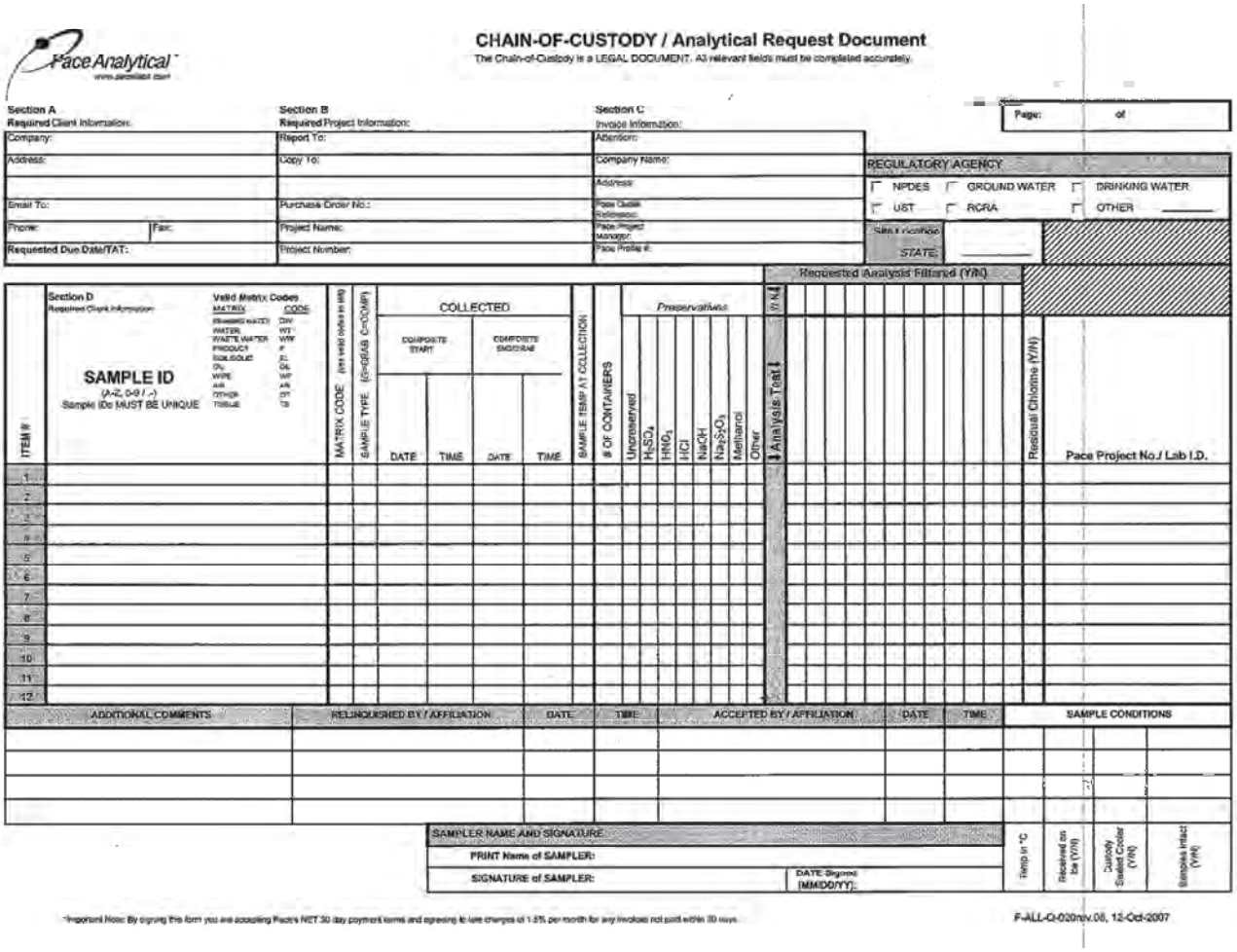
If the samples do not meet the sample receipt acceptance criteria outlined below, the Pace facility is required to document all non-compliances, contact the client, and either reject the samples or fully document any decisions to proceed with analyses of samples that do not meet these criteria. Any results reported from samples not meeting these criteria are appropriately qualified on the final report.

Sample Acceptance Policy requirements**:**

1. Sample containers must have unique client identification designations, and dates and times of collection, that are clearly marked with indelible ink on durable, water-resistant labels. The client identifications must match those on the chain-of-custody (COC);
2. There must be clear documentation on the COC, or related documents such as the Sample Condition Upon Receipt (SCUR) form, that lists the unique sample identification, sampling site location (including state; some regulations may require city, county, etc.), date and time of sample collection, and name and signature of the sample collector;
3. There must be clear documentation on the COC, or related documents, that lists the requested analyses, the preservatives used, sample matrix, and any special remarks concerning the samples (i.e., data deliverables, samples are for evidentiary purposes, field filtration, etc.);
4. Samples must be in appropriate sample containers. If the sample containers show signs of damage (i.e., broken or leaking) or if the samples show signs of contamination, the samples will not be processed without prior client approval;
5. Samples must be correctly preserved upon receipt, unless the method requested allows for laboratory preservation. If the samples are received with inadequate preservation, and the samples cannot be preserved by the lab appropriately, the samples will not be processed without prior client approval;
6. Samples must be received within required holding time. Any samples with hold times that are exceeded will not be processed without prior client approval;
7. Samples must be received with sufficient sample volume or weight to proceed with the analytical testing. If insufficient sample volume or weight is received, analysis will not proceed without client approval;
8. All samples that require thermal preservation are considered acceptable if they are received at a temperature within 2°C of the required temperature, or within the method-specified range. For samples with a required temperature of 4°C, samples with a temperature ranging from just above freezing to 6°C are acceptable. Samples that are delivered to the lab on the same day they are collected are considered acceptable if the samples are received on ice. Any samples that are not received at the required temperature will not be processed without prior client approval.
9. For all compliance **drinking water** samples, analyses will be rejected at the time of receipt if they are not received in a secure manner, are received in inappropriate containers, are received outside the required temperature range, are received outside the recognized holding time, are received with inadequate identification on sample containers or COC, or are improperly preserved (with the exception of VOA samples- tested for pH at time of analysis and TOC- tested for pH in the field).

Some specific clients may require custody seals. **For these clients**, samples or coolers that are not received with the proper custody seals will not be processed without prior client approval.

Attachment II – Example Chain-of-Custody Form



Pace Analytical

CHAIN-OF-CUSTODY / Analytical Request Document

The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately.

Section A — Required Client Information: Company; Address; Email To; Phone; Fax; Requested Due Date/TAT:

Section B — Required Project Information: Report To; Copy To; Purchase Order No.; Project Name; Project Number:

Section C — Invoice Information: Attention; Company Name; Address; Pace Quote Reference; Pace Project Manager; Pace Profile #:

Page: of

REGULATORY AGENCY: NPDES, GROUND WATER, DRINKING WATER, UST, RCRA, OTHER; Site Location STATE:

Requested Analysis Filtered (Y/N)

ITEM #	Section D — Required Client Information: SAMPLE ID (A-Z, 0-9 / ,) Sample IDs MUST BE UNIQUE	Valid Matrix Codes: MATRIX / CODE — DRINKING WATER DW; WATER WT; WASTE WATER WW; PRODUCT P; SOIL/SOLID SL; OIL OL; WIPE WP; AIR AR; OTHER OT; TISSUE TS	MATRIX CODE (Enter valid codes in this column)	SAMPLE TYPE (G=GRAB C=COMP)	COLLECTED: COMPOSITE START DATE	COMPOSITE START TIME	COMPOSITE END/GRAB DATE	COMPOSITE END/GRAB TIME	SAMPLE TEMP AT COLLECTION	# OF CONTAINERS	Preservatives: Unpreserved; H_2SO_4; HNO_3; HCl; NaOH; $Na_2S_2O_3$; Methanol; Other	Analysis Test Y/N	Residual Chlorine (Y/N)	Pace Project No./ Lab I.D.
1														
2														
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12														

ADDITIONAL COMMENTS	RELINQUISHED BY / AFFILIATION	DATE	TIME	ACCEPTED BY / AFFILIATION	DATE	TIME	SAMPLE CONDITIONS

SAMPLER NAME AND SIGNATURE

PRINT Name of SAMPLER:

SIGNATURE of SAMPLER: DATE Signed (MM/DD/YY):

Temp in °C | Received on Ice (Y/N) | Custody Sealed Cooler (Y/N) | Samples Intact (Y/N)

*Important Note: By signing this form you are accepting Pace's NET 30 day payment terms and agreeing to late charges of 1.5% per month for any invoices not paid within 30 days.

F-ALL-Q-020rev.06, 12-Oct-2007

Attachment III – Example Sample Condition Upon Request Form

Pace Analytical® www.pacelabs.com

Sample Condition Upon Receipt

Client Name: _____

Courier: FedEx ☐ UPS ☐ VIA ☐ Clay ☐ PEX ☐ ECI ☐ Pace ☐ Xroads ☐ Client ☐ Other ☐

Tracking #: _____ Pace Shipping Label Used? Yes ☐ No ☐

Custody Seal on Cooler/Box Present: Yes ☐ No ☐ Seals intact: Yes ☐ No ☐

Packing Material: Bubble Wrap ☐ Bubble Bags ☐ Foam ☐ None ☐ Other ☐

Thermometer Used: _____ **Type of Ice:** Wet Blue None

Cooler Temperature (°C): **As-read** _____ **Corr. Factor** _____ **Corrected** _____

Date and initials of person examining contents:

Temperature should be above freezing to 6°C

Chain of Custody present:	☐Yes ☐No ☐N/A	
Chain of Custody relinquished:	☐Yes ☐No ☐N/A	
Samples arrived within holding time:	☐Yes ☐No ☐N/A	
Short Hold Time analyses (<72hr):	☐Yes ☐No ☐N/A	
Rush Turn Around Time requested:	☐Yes ☐No ☐N/A	
Sufficient volume:	☐Yes ☐No ☐N/A	
Correct containers used:	☐Yes ☐No ☐N/A	
Pace containers used:	☐Yes ☐No ☐N/A	
Containers intact:	☐Yes ☐No ☐N/A	
Unpreserved 5035A / TX1005/1006 soils frozen in 48hrs?	☐Yes ☐No ☐N/A	
Filtered volume received for dissolved tests?	☐Yes ☐No ☐N/A	
Sample labels match COC: Date / time / ID / analyses	☐Yes ☐No ☐N/A	
Samples contain multiple phases? Matrix:	☐Yes ☐No ☐N/A	
Containers requiring pH preservation in compliance? (HNO_3, H_2SO_4, HCl<2; NaOH>9 Sulfide, NaOH>10 Cyanide) (Exceptions: VOA, Micro, O&G, KS TPH, OK-DRO)	☐Yes ☐No ☐N/A	
Cyanide water sample checks: Lead acetate strip turns dark? (Record only)	☐Yes ☐No	
Potassium iodide test strip turns blue/purple? (Preserve)	☐Yes ☐No	
Trip Blank present:	☐Yes ☐No ☐N/A	
Headspace in VOA vials (>6mm):	☐Yes ☐No ☐N/A	
Samples from USDA Regulated Area: State:	☐Yes ☐No ☐N/A	
Additional labels attached to 5035A / TX1005 vials in the field?	☐Yes ☐No ☐N/A	

Client Notification/ Resolution: Copy COC to Client? Y / N Field Data Required? Y / N

Person Contacted: _____ Date/Time: _____

Comments/ Resolution: _____

Project Manager Review: _____ Date: _____

F-KS-C-003-Rev.10, August 18, 2016

Attachment IV – Pace Analytical Approved Sample Containers, Preservation

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Acidity	SM2310B	Water	Plastic/Glass	≤ 6°C	14 Days
Actinides	HASL-300	Water		pH<2 HNO_3	180 Days
Actinides	HASL-300	Solid		None	180 Days
Alkalinity	SM2320B/310.2	Water	Plastic/Glass	≤ 6°C	14 Days
Alkylated PAHs		Water		≤ 6°C; pH<2 1:1 HCl (optional)	14/40 Days preserved; 7/40 Days unpreserved
Alkylated PAHs		Solid		≤ 10°C	1 Year/40 Days
Total Alpha Radium (see note 3)	9315/903.0	Water	Plastic/Glass	pH<2 HNO_3	180 days
Total Alpha Radium (see note 3)	9315	Solid		None	180 days
Anions (Br, Cl, F, NO_2, NO_3, o-Phos, SO_4, bromate, chlorite, chlorate)	300.0/300.1/SM4110B	Water	Plastic/Glass	≤ 6°C; EDA if bromate or chlorite run	All analytes 28 days except: NO_2, NO_3, o-Phos (48 Hours); chlorite (immediately for 300.0; 14 Days for 300.1). NO_2/NO_3 combo 28 days.
Anions (Br, Cl, F, NO_2, NO_3, o-Phos, SO_4, bromate, chlorite, chlorate)	300.0	Solid	Plastic/Glass	≤ 6°C	All analytes 28 days except: NO_2, NO_3, o-Phos (48 hours); chlorite (immediately). NO_2/NO_3 combo 28 days.
Anions (Br, Cl, F, NO_2, NO_3, o-Phos, SO_4	9056	Water/ Solid	Plastic/Glass	≤ 6°C	28 days
Aromatic and Halogenated Volatiles (see note 1)	8021	Solid	5035 vial kit	See note 1	14 days
Aromatic and Halogenated Volatiles	602/8021	Water	40mL vials	pH<2 HCl; ≤ 6°C; $Na_2S_2O_3$ if Cl present	14 Days (7 Days for aromatics if unpreserved)
Acid Volatile Sulfide	Draft EPA 1629	Solid	8oz Glass	≤ 6°C	14 Days
Bacteria, Total Plate Count	SM9221D	Water	Plastic/WK	≤ 6°C; $Na_2S_2O_3$	24 Hours
Base/Neutrals and Acids	8270, 8121	Solid	8oz Glass	≤ 6°C	14/40 Days
Base/Neutrals and Acids	625/625.1/8270/8121	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Base/Neutrals, Acids & Pesticides	525.2	Water	1L Amber Glass	pH<2 HCl; ≤ 6°C; Na sulfite if Cl present	14/30 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Biomarkers		Water	≤ 6°C; pH<2 1:1 HCl (optional)	14/40 Days preserved; 7/40 Days unpreserved	≤ 6°C; pH<2 1:1 HCl (optional)
Biomarkers		Solid	≤ 10°C	1 Year/40 Days	≤ 10°C
BOD/cBOD	SM5210B	Water	Plastic/Glass	≤ 6°C	48 hours
BTEX/Total Hydrocarbons	TO-3	Air	Summa Canister	None	14 Days
BTEX/Total Hydrocarbons	TO-3	Air	Tedlar Bag or equivalent	None	48 Hours
Cation/Anion Balance	SM1030E	Water	Plastic/Glass	None	None
Cation Exchange	9081	Solid	8oz Glass	None	unknown
Chloride	SM4500Cl-C,E	Water	Plastic/Glass	None	28 Days
Chlorine, Residual	SM4500Cl-D,E,G/330.5/Hach 8167	Water	Plastic/Glass	None	15 minutes
Chlorophyll	SM10200H	Water	Opaque bottle or aluminum foil		
COD	SM5220C, D/410.4/Hach 8000	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Coliform, Fecal	SM9222D	Water	100mL Plastic	≤ 6°C	6 Hours
Coliform, Fecal	SM9222D	Solid	100mL Plastic	≤ 6°C	6 Hours
Coliform, Total and Escherichla (E. coli)	SM9223B	Water	100mL Plastic	≤ 10°C	48 Hours after collection; results from samples analyzed 30-48 Hours after collection must be qualified as analyzed >30 hours
Color	SM2120B,E	Water	Covered Plastic/Acid Washed Amber Glass	≤ 6°C	24 Hours
Condensable Particulate Emissions	EPA 202	Air	Solutions	None	6 Months
Cyanide, Reactive	SW846 chap.7	Water	Plastic/Glass	None	28 Days
Cyanide, Reactive	SW846 chap.7	Solid	Plastic/Glass	None	28 Days
Cyanide, Total and Amenable	SM4500CN-A,B,C,D,E,G,I,N/9010/9012/335.4	Water	Plastic/Glass	pH≥12 NaOH; ≤ 6°C; $Na_2S_2O_3$ if Cl present	14 Days (24 Hours if sulfide present-applies to SM4500CN only)
Diesel Range Organics- Alaska DRO	AK102	Solid	8oz Glass	≤ 6°C	14/40 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Diesel Range Organics- Alaska DRO	AK102	Water	1L Glass	pH<2 HCl; ≤ 6°C	14/40 Days
Diesel Range Organics- TPH DRO	8015	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Diesel Range Organics- TPH DRO	8015	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Diesel Range Organics- TPH DRO	8015	Tissue	1L Amber Glass	≤ - 10°C	1 Year if frozen/40 Days
Diesel Range Organics- NwTPH-Dx	Nw-TPH-Dx	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Diesel Range Organics- NwTPH-Dx	Nw-TPH-Dx	Water	1L Amber Glass	pH <2 HCl; ≤ 6°C	14/40 Days; 7 Days from collection to extraction if unpreserved
Diesel Range Organics- Wisconsin DRO	WI MOD DRO	Solid	Tared 4oz Glass Jar	≤ 6°C	10/47 Days
Diesel Range Organics- Wisconsin DRO	WI MOD DRO	Water	1L Amber Glass	≤ 6°C	14/40 Days
Dioxins and Furans	1613B	Solid	8oz Glass	≤ -10°C	1 year
Dioxins and Furans	1613B	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	1 year
Dioxins and Furans	1613B	Fish/ Tissue	Aluminum foil	< -10°C	1 year
Dioxins and Furans	8290	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	30/45 Days
Dioxins and Furans	8290	Solid	8oz Glass	≤ 6°C	30/45 Days
Dioxins and Furans	8290	Fish/ Tissue	Not specified	< -10°C	30/45 Days
Dioxins and Furans	TO-9	Air	PUF	None	30/45 Days
EDB/DBCP (8011) EDB/DBCP/1,2,3-TCP (504.1)	504.1/8011	Water	40mL vials	≤ 6°C; $Na_2S_2O_3$ if Cl present	14 Days
Explosives	8330/8332	Water	1L Amber Glass	≤ 6°C	7/40 Days
Explosives	8330/8332	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Extractable Petroleum Hydrocarbons (aliphatic and aromatic)	MA-EPH	Water	1L Amber Glass	pH<2 HCl; ≤ 6°C	14/40 Days
Extractable Petroleum Hydrocarbons (aliphatic and aromatic)	MA-EPH	Solid	4oz Glass Jar	≤ 6°C	7/40 Days
Ferrous Iron	SN3500Fe-D	Water	Glass	None	Immediate
Flashpoint/Ignitability	1010	Liquid	Plastic/Glass	None	28 Days
Fluoride	SM4500Fl-C,D	Water	Plastic	None	28 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Gamma Emitting Radionuclides	901.1	Water	Plastic/Glass	pH<2 HNO_3	180 days
Gasoline Range Organics	8015	Water	40mL vials	pH<2 HCl	14 Days
Gasoline Range Organics	8015	Solid	5035 vial kit	See note 1	14 days
Gasoline Range Organics-Alaska GRO	AK101	Solid	5035 vial kit	See 5035 note*	28 Days if GRO only (14 Days with BTEX)
Gasoline Range Organics-Alaska GRO	AK101	Water	40mL vials	pH<2 HCl; ≤ 6°C	14 Days
Gasoline Range Organics-NwTPH-Gx	Nw-TPH-Gx	Water	40mL vials	pH<2 HCl; ≤ 6°C	7 Days unpreserved; 14 Days preserved
Gasoline Range Organics-NwTPH-Gx	Nw-TPH-Gx	Solid	40mL vials	≤ 6°C; packed jars with no headspace	14 Days
Gasoline Range Organics-Wisconsin GRO	WI MOD GRO	Water	40mL vials	pH<2 HCl; ≤ 6°C	14 Days
Gasoline Range Organics-Wisconsin GRO	WI MOD GRO	Solid	40mL MeOH vials	≤ 6°C in MeOH	21 Days
Gross Alpha (NJ 48Hr Method)	NJAC 7:18-6	Water	Plastic/Glass	pH<2 HNO_3	48 Hrs
Gross Alpha and Gross Beta	9310/900.0	Water	Plastic/Glass	pH<2 HNO_3	180 Days
Gross Alpha and Gross Beta	9310	Solid	Glass	None	180 Days
Haloacetic Acids	552.1/552.2	Water	40mL Amber vials	NH_4Cl; ≤ 6°C	14/7 Days if extracts stored ≤ 6°C or 14/14 Days if extracts stored at ≤ -10°C
Hardness, Total ($CaCO_3$)	SM2340B,C/130.1	Water	Plastic/Glass	pH<2 HNO_3	6 Months
Heterotrophic Plate Count (MPC)	SM9215B	Water	100mL Plastic	≤ 6°C	24 Hours
Herbicides, Chlorinated	8151	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Herbicides, Chlorinated	8151	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Herbicides, Chlorinated	515.1/515.3	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	14/28 Days
Hexavalent Chromium	7196/218.6/SM3500Cr-C,D	Water	Plastic/Glass	≤ 6°C	24 Hours
Hexavalent Chromium	7196 (with 3060A)	Solid		≤ 6°C	24 Hours after extraction
Hydrogen Halide and Halogen Emissions	EPA 26	Air	Solutions	None	6 Months
Ignitability of Solids	1030	Non-liquid Waste	Plastic/Glass	None	28 Days
Lead Emissions	EPA 12	Air	Filter/Solutions	None	6 Months

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
KS TPH LRH	8260	Solid	40mL vial	10 mL MeOH	28 days
KS TPH LRH	8260	Water	40 mL amber/clear glass	HCL	14 days
KS TPH MRH/HRH	8015	Solid	Amber glass	None	14/40 days
KS TPH MRH/LRH	8015	Water	500 mL Amber glass	HCL	10/40 days
KS TPH MRH/LRH (Reduced Volume)	8015	Water	40 mL Amber glass	HCL	10/40 days
Lipids	Pace Lipids	Tissue	Plastic/Glass	≤ -10°C	1 Year if frozen
Mercury, Low-Level	1631E	Solid	Glass (wide-mouth)	≤ 6°C	28 Days; 1 Year if frozen
Mercury, Low-Level	1631E	Water	Fluoropolymer bottles (Glass if Hg is only analyte being tested)	12N HCl or BrCl	48 Hours for preservation or analysis; 28 Days to preservation if sample oxidized in bottle; 90 Days for analysis if preserved
Mercury, Low-Level	1631E	Tissue	Plastic/Glass	≤ - 10°C	28 Days if frozen
Mercury	7471	Solid	8oz Glass Jar	≤ 6°C	28 days
Mercury	7470/245.1/245.2	Water	Plastic/Glass	pH<2 HNO_3	28 Days
Mercury	7471/245.6	Tissue	Plastic/Glass	≤ - 10°C	28 Days if frozen
Metals (GFAA)	7000/200.9	Water	Plastic/Glass	pH<2 HNO_3	6 Months
Metals (ICP)	NIOSH 7300A/7303	Air	Filters	None	6 Months
Metals (ICP/ICPMS)	6010/6020	Solid	8oz Glass Jar	None	6 months
Metals (ICP/ICPMS)	6010/6020/200.7/200.8	Water	Plastic/Glass	pH<2 HNO_3	6 Months
Metals (ICP/ICPMS)	6020	Tissue	Plastic/Glass	≤ -10°C	6 Months if frozen
Methane, Ethane, Ethene	8015 modified	Water	40mL vials	HCl	14 Days
Methane, Ethane, Ethene	RSK-175	Water	40mL vials	HCl	14 Days
Methane, Ethane, Ethene	EPA 3C	Air	Summa Canister	None	14 Days
Methane, Ethane, Ethene	EPA 3C	Air	Tedlar Bag or equivalent	None	48 Hours
Methanol, Ethanol	8015 modified	Water	40mL vials	≤ 6°C	14 Days
Methanol, Ethanol	8015 modified	Solid	2oz Glass	≤ 6°C	14 Days
Nitrogen, Ammonia	SM4500NH3/350.1	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Nitrogen, Kjeldahl (TKN)	351.2	Solid	Plastic/Glass	≤ 6°C	28 Days
Nitrogen, Kjeldahl (TKN)	SM4500-Norg/351.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Nitrogen, Nitrate	SM4500-NO3/352.1	Water	Plastic/Glass	≤ 6°C	24 Hours preferred
Nitrogen, Nitrate & Nitrite combination	353.2	Solid	Plastic/Glass	≤ 6°C	28 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Nitrogen, Nitrate & Nitrite combination	SM4500-NO3/353.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Nitrogen, Nitrite or Nitrate separately	SM4500-NO2/353.2	Water	Plastic/Glass	≤ 6°C	48 Hours
Nitrogen, Organic	SM4500-Norg/351.2	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Non-Methane Organics	EPA 25C	Air	Summa Canister	None	14 Days
Non-Methane Organics	EPA 25C	Air	Tedlar Bag or equivalent	None	48 Hours
Odor	SM2150B	Water	Glass	≤ 6°C	24 Hours
Oil and Grease/HEM	1664A/SM5520B/9070	Water	Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Oil and Grease/HEM	9071	Solid	Glass	≤ 6°C	28 Days
PBDEs	1614	Water	1L Amber Glass	≤ 6°C	1 Year/1 Year
PBDEs	1614	Solid	Wide Mouth Jar	≤ 6°C	1 Year/1 Year
PBDEs	1614	Tissue	Aluminum Foil	≤ -10°C	1 Year/1 Year
PCBs and Pesticides, Organochlorine (OC)	TO-4/TO-10	Air	PUF	None	7/40 Days
PCBs and Pesticides, Organochlorine (OC)	608, 608.3	Water	1L Amber Glass		Pest: 7/40 Days; PCB: 1 Year/1 Year
Pesticides, Organochlorine (OC)	8081, 508	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Pesticides, Organochlorine (OC)	8081	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Pesticides, Organochlorine (OC)	8081	Tissue	8oz Glass Jar	≤ -10°C	1 Year if frozen/40 Days
Pesticides, Organophosphorous (OP)	8141	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Pesticides, Organophosphorous (OP)	8141	Water	1L Amber Glass	pH 5-8 with NaOH or H_2SO_4; ≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
PCBs (Aroclors)	8082	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	1 Year/1 Year
PCBs (Aroclors)	8082	Solid	8oz Glass Jar	≤ 6°C	1 Year/1 Year
PCBs (Aroclors)	8082	Tissue	Plastic/Glass	≤ -10°C	1 Year if frozen/1 Year
PCB Congeners	1668A	Water	1L Amber Glass	≤ 6°C but above freezing	1 Year/1 Year

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
PCB Congeners	1668A	Solid	4-8oz Glass Jar	≤ 6°C but above freezing	1 Year/1 Year
PCB Congeners	1668A	Tissue	4-8oz Glass Jar	≤ -10°C	1 Year/1 Year
Oil Range Organics- ORO		Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Oil Range Organics- ORO		Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Oxygen, Dissolved (Probe)	SM4500-O	Water	Glass	None	15 minutes
Paint Filter Liquid Test	9095	Water	Plastic/Glass	None	N/A
Particulates	PM-10	Air	Filters	None	6 Months
Permanent Gases	EPA 3C	Air	Summa Canister	None	14 Days
Permanent Gases	EPA 3C	Air	Tedlar Bag or equivalent	None	48 Hours
pH	SM4500H+B/9040	Water	Plastic/Glass	None	15 minutes
pH	9045	Solid	Plastic/Glass	None	Contact local lab
Phenol, Total	420.1/420.4/9065/9066	Water	Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Phosphorus, Orthophosphate	SM4500P/365.1/365.3	Water	Plastic	Filter; ≤ 6°C	Filter within 15 minutes, Analyze within 48 Hours
Phosphorus, Total	SM4500P/ 365.1/365.3/365.4	Water	Plastic/Glass	pH<2 H_2SO_4; ≤ 6°C	28 Days
Phosphorus, Total	365.4	Solid	Plastic/Glass	≤ 6°C	28 Days
Polynuclear Aromatic Hydrocarbons (PAH)	TO-13	Air	PUF	None	7/40 Days
Polynuclear Aromatic Hydrocarbons (PAH)	8270 SIM	Solid	8oz Glass Jar	≤ 6°C	14/40 Days
Polynuclear Aromatic Hydrocarbons (PAH)	8270 SIM	Water	1L Amber Glass	≤ 6°C; $Na_2S_2O_3$ if Cl present	7/40 Days
Polynuclear Aromatic Hydrocarbons (PAH)	8270 SIM	Tissue	Plastic/Glass	≤ -10°C	1 Year if frozen/40 Days
Radioactive Strontium	905.0	Water	Plastic/Glass	pH<2 HNO_3	180 days
Radium-226	903.0/903.1	Water	Plastic/Glass	pH<2 HNO_3	180 days
Radium-228 (see note 3)	9320/904.0	Water	Plastic/Glass	pH<2 HNO_3	180 days
Radium-228 (see note 3)	9320	Solid			
Residual Range Organics- Alaska RRO	AK103	Solid	8oz Glass	≤ 6°C	14/40 Days
Saturated Hydrocarbons	SOP S-MN-O-567	Water	≤ 6°C; pH<2 1:1 HCl (optional)	14/40 Days preserved; 7/40 Days unpreserved	≤ 6°C; pH<2 1:1 HCl (optional)
Saturated Hydrocarbons	SOP S-MN-O-567	Solid	≤ 10°C	1 Year/40 Days	≤ 10°C
Silica, Dissolved	SM4500Si-D	Water	Plastic	≤ 6°C	28 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Solids, Settleable	SM2540F	Water	Glass	≤ 6°C	48 Hours
Solids, Total	SM2540B	Water	Plastic/Glass	≤ 6°C	7 Days
Solids, Total	SM2540G	Solid	Plastic/Glass	≤ 6°C	7 Days
Solids, Total (FOC, OM, Ash)	ASTM D2974	Solid	Plastic/Glass	≤ 6°C	7 Days
Solids, Total Dissolved	SM2540C	Water	Plastic/Glass	≤ 6°C	7 Days
Solids, Total Suspended	SM2540D/USGS I-3765-85	Water	Plastic/Glass	≤ 6°C	7 Days
Solids, Total Volatile	160.4/SM2540E	Water	Plastic/Glass	≤ 6°C	7 Days
Solids, Total Volatile	160.4	Solid	Plastic/Glass	≤ 6°C	7 Days
Specific Conductance	SM2510B/9050/120.1	Water	Plastic/Glass	≤ 6°C	28 Days
Stationary Source Dioxins and Furans	EPA 23	Air	XAD Trap	None	30/45 Days
Stationary Source Mercury	EPA 101	Air	Filters	None	6 Months, 28 Days for Hg
Stationary Source Metals	EPA 29	Air	Filters	None	6 Months, 28 Days for Hg
Stationary Source PM10	EPA 201A	Air	Filters	None	6 Months
Stationary Source Particulates	EPA 5	Air	Filter/Solutions	None	6 Months
Sulfate	SM4500SO4/9036/ 9038/375.2/ASTM D516	Water	Plastic/Glass	≤ 6°C	28 Days
Sulfide, Reactive	SW-846 Chap.7	Water	Plastic/Glass	None	28 Days
Sulfide, Reactive	SW-846 Chap.7	Solid	Plastic/Glass	None	28 Days
Sulfide, Total	SM4500S/9030	Water	Plastic/Glass	pH>9 NaOH; ZnOAc; ≤ 6°C	7 Days
Sulfite	SM4500SO3	Water	Plastic/Glass	None	15 minutes
Surfactants (MBAS)	SM5540C	Water	Plastic/Glass	≤ 6°C	48 Hours
Total Organic Carbon (TOC)	SM5310B,C,D/9060	Water	Glass	pH<2 H_2SO_4 or HCl; ≤ 6°C	28 Days
Total Organic Carbon (TOC)	9060/Walkley Black	Solid	Glass	≤ 6°C	14 Days
Total Organic Halogen (TOX)	SM5320/9020/9021	Water	Glass; no headspace	≤ 6°C	14 Days
Tritium	906.0	Water	Glass	None	180 days
Turbidity	SM2130B/180.1	Water	Plastic/Glass	≤ 6°C	48 Hours
Total Uranium	908.0/ASTM D5174-97	Water	Plastic/Glass	pH<2 HCl	180 days
Volatile Petroleum Hydrocarbons (aliphatic and aromatic)	MA-VPH	Water	40mL vials	pH<2 HCl; ≤ 6°C	14 Days preserved
Volatile Petroleum Hydrocarbons (aliphatic and aromatic)	MA-VPH	Solid	4-8oz Glass Jar	≤ 6°C; packed jars with no headspace	7/28 Days
Volatiles	TO-14	Air	Summa Canister	None	30 Days

Parameter	Method	Matrix	Container	Preservative	Max Hold Time
Volatiles	TO-14	Air	Tedlar Bag or equivalent	None	48 Hours
Volatiles	TO-15	Air	Summa Canister	None	30 Days
Volatiles	8260	Solid	5035 vial kit	See note 1	14 days
Volatiles	8260	Water	40mL vials	pH<2 HCl; ≤ 6°C; $Na_2S_2O_3$ if Cl present	14 Days
Volatiles	8260	Conc. Waste	5035 vial kit or 40mL vials	≤ 6°C	14 Days
Volatiles	624, 624.1	Water	40mL vials	pH<2 HCl; ≤ 6°C; $Na_2S_2O_3$ if Cl present	14 Days (7 Days for aromatics if unpreserved)
Volatiles (see note 2)	524.2	Water	40mL vials (in duplicate)	pH<2 HCl; ≤ 6°C; Ascorbic acid or $Na_2S_2O_3$ if Cl present[2]	14 Days

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Notes

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Pace Analytical™

STANDARD OPERATING PROCEDURE

WASTE HANDLING AND MANAGEMENT

Reference Methods: N/A

SOP Number:	S-KS-S-002-rev.7
Effective Date:	Date of final signature
Supersedes:	S-KS-S-002-rev.6
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APPROVALS

Laboratory General Manager — Date: 1/11/18

Laboratory Quality Manager — Date: 1-9-18

Laboratory Waste Coordinator — Date: 1/9/18

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date

1. Purpose/Identification of Procedure

1.1. Pace Analytical Services (Pace) acknowledges its obligation to the responsible management of the environment and its resources. Pace senior management is committed to operating in such a way that meets or exceeds the state and federal laws governing waste management and encourages the use of best practices to reduce, reuse and recycle waste material where possible. This Standard Operating Procedure (SOP) documents the systems, processes and procedures that this location uses to manage generated wastes.

1.2. It is Pace's policy to minimize the amount of hazardous waste it produces and to reduce the hazardous properties of those wastes whenever practical within regulatory compliance. This can be achieved by periodic auditing of all processes producing hazardous waste; reduction of sample volume delivered by the client; return of excess sample material to clients whenever practical and economical; investigation of new technologies that might require smaller volumes of sample, or produce fewer or less hazardous by-products; implementation of lab cleaning procedures that reduce the volume of cleaning residue; recycling of hazardous materials; and investigation of new treatment technologies that are comprehensively destructive or are effective in reducing the volume or hazardous qualities of the wastes produced.

2. Summary of Method

2.1. Pace facilities that generate waste must initially contact the EPA to obtain an ID number. Each unique type of generated waste is classified and characterized into waste streams according to procedures in 40 CFR 261. The amount of waste the facility generates determines the Generator Status of a lab, which in turn determines how long and how much waste can accumulate. Pace is ultimately responsible for the waste it generates, and is required to obey any and all regulations during the process of creating, accumulating, disposing, and releasing waste to a TSDF for final disposal. Documentation is kept to prove all regulations have been obeyed.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel responsible for all aspects of waste handling and management.

3.2. This SOP is applicable to all processes that involve generated waste, and is designed to assist its operations in adhering to regulations set forth in the following federal statutes: Resource Conservation and Recovery Act (RCRA), Clean Water Act (CWA), Toxic Substances Control Act (TSCA), and DOT Title 49, and Transportation (parts 100-199). Particular attention is given to local pretreatment standards covering discharges to publicly owned treatment works (POTW) when performing elementary neutralization on acidic and basic waste. The local standards are based in part upon provisions in the National Pretreatment Standards and Prohibited Discharge Standards.

3.3. The degree to which RCRA regulations apply to Pace facilities is dependent upon the generator status of the operation. Under the federal rules (state requirements may be more stringent or give the classes a slightly different name) there are three different classes of hazardous waste generators based upon the amount of waste generated in a month to month time frame.

3.4. **Waste Generator Class Limits (federal categories, some locations may have different titles):**

Hazardous Waste Generator Class	Quantity of Hazardous Waste Generated per Month	Generated Monthly Acute Hazardous Waste	Maximum Allowable Hazardous Waste Quantity on-site	Maximum Permitted Waste Accumulation Time
Cond. Exempt Small Quantity	<100kg	<1 kg	<1000kg	Unlimited
Small Quantity	100-1000kg	<1 kg	<6000kg	180 days (270 days if the waste must be sent >200 miles to TSDF)
Large Quantity	>1000kg	>1kg	Unlimited	90 days

3.5. **Parameters**: Not applicable to this SOP.

4. Definitions

4.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

4.2. **Acutely Hazardous Waste** - A waste which is hazardous as identified with an (H) Hazard Code in the lists of Hazardous Waste in 40 CFR Part 261, Subpart D, Sections 261.30, 261.31 and 261.33.

4.3. **Animal and Plant Health Inspection Service (APHIS)** - an agency of the USDA responsible for protecting animal health, animal welfare, and plant health. APHIS is the lead agency for collaboration with other agencies to protect U.S. agriculture from invasive pests and diseases.

4.4. **Clean Air Act** - The Federal Clean Air Act, 42 U.S.C. 7401, and amendments thereto amending 42 U.S.C. 1857 et.seq.

4.5. **Conditionally Exempt Small Quantity Generator** - A generator who produces no more than 100 kilograms of hazardous waste or one kilogram of acutely hazardous waste (or a total of 100 kilograms of any residue or contaminated soil, waste or other debris resulting from the cleanup of a spill, into or on any land or water, or any acute hazardous waste) in a calendar month. The total amount of hazardous waste which may be accumulated on-site is 1000 kilograms.

4.6. **Confined Space** – A space that is large enough and so configured that an employee can bodily enter and perform assigned work; and has limited or restricted means for entry or exit (for example, tanks, vessels, silos, storage bins, hoppers, vaults, and pits are spaces that may have limited means of entry); and is not designed for continuous employee occupancy.

4.7. **Container** - Any device material is stored, transported, treated, disposed of, or otherwise handled.

4.8. **Contingency Plan** - A document setting out an organized, planned, and coordinated course of action to be followed in case of fire, explosion, or release of hazardous waste or hazardous waste constituents which could threaten human health or the environment.

4.9. Day Containers - A “day accumulation container” is any container with a capacity of no more than 6 gallons that is used to accumulate hazardous waste at a work area or work station, and that is under the direct control of the operator of the work area or station.

4.10. **Designated Hazardous Waste Storage Area** - Area used to hold hazardous waste for a temporary period, at the end of which the hazardous waste is treated, disposed of, or stored elsewhere. This is the storage area into which hazardous waste from the laboratory (e.g., satellite waste) is moved.

4.11. **DOT** - The United States Department of Transportation.

4.12. **DTSC** – Department of Toxic Substances Control.

4.13. **Elementary Neutralization Unit** – A device which: (1) is used for neutralizing wastes which are hazardous only because they exhibit the corrosivity characteristic defined in 40 CFR 261.22 or are listed in Subpart D of Part 261; and (2) meets the definition of tank, container, transport vehicle, or vessel in 40 CFR 260.10.

4.14. **EPA** - The United States Environmental Protection Agency.

4.15. **EPA Hazardous Waste Number** - The EPA number assigned to each EPA hazardous waste identified in 40 CFR Part 260, Subpart D - Lists of Hazardous Wastes.

4.16. **EPA Identification Number** - The site-specific number assigned to each generator, transporter, and TSDF upon approval of a notification form.

4.17. **Federal Clean Water Act** - 33 U.S.C. 1251, et. Seq.

4.18. **Foreseeable Emergency** - Any fire, explosion, or sudden or non-sudden release of hazardous waste or hazardous waste constituents to the air, soil, or surface water, which could threaten human health or the environment.

4.19. **Generator** - Any person, by site who owns or operates a facility where hazardous waste is generated, i.e. Pace.

4.20. **Hazardous Waste Coordinator** - The Pace employee responsible for creating, guiding, and implementing all hazardous waste management operations.

4.21. **Hazardous Waste** - As defined in 40 CFR Part 261, Subparts B and C, a solid, semi-solid, liquid or contained gaseous waste, or any combination of these wastes.

4.21.1. Which, because of either quantity, concentration, physical, chemical, or infectious characteristics may:

4.21.2. Cause or contribute to an increase in mortality or an increase in irreversible or incapacitating reversible illness; or

4.21.3. Pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, disposed of or otherwise mismanaged.

4.21.4. Or which has been identified as having a characteristic of hazardous waste by the EPA using the criteria established under 40 CFR Part 261, Subpart C, or as listed under Sections 261.31, 261.32, 261.33, and 261.34. Such wastes include, but are not limited to, those which are reactive, toxic, corrosive, ignitable, irritants, strong sensitizers or which generate pressure through decomposition, heat or other means. Such wastes do not include radioactive substances that are regulated by the Atomic Energy Act of 1954, as amended. A waste is considered hazardous if it is listed or it fits into one of four categories. These categories are as follows:

4.21.4.1. Ignitable – (40 CFR 261.21, Waste Code D001) A flash point of less than 60°C/140°F.

4.21.4.2. Corrosive – (40 CFR 261.22, Waste Code D002) A pH of less than 2.0 or greater than 12.5.

4.21.4.3. Reactive – (40 CFR 261.23, Waste Code D003) Reactive wastes exhibit one or more of the following characteristics:

4.21.4.3.1. It is unstable and can undergo a violent change without detonating.

4.21.4.3.2. It can react violently with water.

4.21.4.3.3. When mixed with water it can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.

4.21.4.3.4. It is cyanide or sulfide bearing waste that, when exposed to pH conditions between 2.0 and 12.5, can generate gases, vapors, or fumes that can present a danger to human health or the environment.

4.21.4.3.5. It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

4.21.4.3.6. It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.

4.21.4.3.7. It is a forbidden explosive as defined in 49 CFR 173.51, or a Class A explosive as defined in 49 CFR 173.53, or a Class B explosive as defined in 49 CFR 173.88.

4.21.4.4. Toxic – (40 CFR 261.24, Waste Codes D004-D043) A solid waste that contains a toxic concentration of a contaminant listed in 40 CFR 261.24, Table 1. A toxic waste is given any and all D-codes that apply to the particular material.

4.22. **Hazardous Waste Constituent -** A substance, compound, or element listed as hazardous waste in EPA 40 CFR 261.

4.23. **Lab Pack Material -** A hazardous waste that does not match a listed Pace waste stream category.

4.24. **Large Quantity Generator (LQG) -** Any generator who generates at a rate greater than 1000 kilograms of hazardous waste per month.

4.25. **LIMS -** Laboratory Information Management System. The database program that contains analysis data and automatically flags samples for hazardous disposal when certain criteria are met.

4.26. **Manifest -** As defined in 40 CFR Part 262, Subpart B, namely "the form used for identifying the origin, quantity composition, routing and destination of hazardous waste".

4.27. **Plant Protection and Quarantine (PPQ)** – A program within APHIS which attempts to safeguard agriculture and natural resources in the U.S. against the entry, establishment, and spread of animal and plant pests and noxious weeds.

4.28. **Regulated Soil** – Soil from foreign countries, U.S. territories and areas within states that are under Federal quarantine that can be moved into or through continental U.S. only if conditions and safeguards prescribed by the USDA and APHIS are met.

4.29. **Sample -** Except as provided below in 4.27.2.2.3, any solid waste, water, soil, or air that is collected for the sole purpose of being tested to determine its characteristics or composition.

4.29.1. Samples are not subject to any requirements of 40 CFR Part 261.5 or Parts 262 through 267 or Part 270 or Part 124 or to the notification requirements of Section 3010 of RCRA, when:

4.29.1.1. The sample is being transported to a laboratory for the purpose of testing; or

4.29.1.2. The sample is being transported back to the sample collector after testing; or

4.29.1.3. The sample is being stored by the sample collector before transport to a laboratory for testing; or

4.29.1.4. The sample is being stored in a laboratory before testing; or

4.29.1.5. The sample is being stored in a laboratory after testing but before it is returned to the sample collector; or

4.29.1.6. The sample is being stored temporarily in the laboratory after testing for a specific purpose (for example, until conclusion of a court case or enforcement action where further testing of the sample may be necessary).

4.29.2. In order to qualify for the exemption in 4.27.1.1 and 4.27.1.2 above, a sample collector shipping samples to a laboratory and a laboratory returning samples to a sample collector must:

4.29.2.1. Comply with U.S. Department of Transportation (DOT), U.S. Postal Service (USPS), or any other applicable shipping requirements; or

4.29.2.2. Comply with the following requirements if the sample collector determines that DOT, USPS, or other shipping requirements do not apply to the shipment of the sample:

4.29.2.2.1. Assure that the following information accompanies the sample:

4.29.2.2.1.1. The sample collector's name, mailing address, and phone number;

4.29.2.2.1.2. The laboratory's name, mailing address, and phone number;

4.29.2.2.1.3. The quantity of the sample;

4.29.2.2.1.4. The date of shipment; and

4.29.2.2.1.5. A description of the sample.

4.29.2.2.2. Package the sample so that it does not leak, spill, or vaporize from its packaging.

4.29.2.2.3. This exemption does not apply if the laboratory determines that the waste is hazardous but the laboratory is no longer meeting any of the conditions stated in 4.27.1 above.

4.30. **Satellite Waste or Laboratory Satellite Waste -** Hazardous waste generated by Pace that is at or near any point of generation and under the control of the operator. Satellite accumulation provisions allow generators to accumulate up to 55 gallons of hazardous waste (or 1 quart of acute hazardous waste) in containers without starting the storage clock as described in Section 3.4.

4.31. **Satellite Waste Container -** Any portable device used to accumulate laboratory generated waste prior to transfer to the hazardous waste storage area.

4.32. **Small Quantity Generator (SQG) -** A generator who produces no more than 1000 kilograms of hazardous waste (or a total of 1000 kilograms of any residue or contaminated soil, waste or other debris resulting from the cleanup of a spill, into or on any land or water, or any acute hazardous waste) in a calendar month. The total amount of hazardous waste which may be accumulated on-site is 6000 kilograms.

4.33. **TSDF -** A Treatment/Storage/Disposal Facility.

4.34. **Universal Waste** – Commonly used items that are hazardous but can be recycled. These include fluorescent lights, computer monitors, etc.

4.35. **Waste Stream -** The generic profile of chemical and physical properties that satellite wastes exhibit.

5. Procedure

5.1. All Pace facilities that generate hazardous waste must have a Generator's US EPA Identification Number. The ID number is obtained through the applicable EPA region's office by completing EPA form 8700-12, and must be completed before generating any hazardous waste.

5.1.1. Pace only utilizes transporters and treatment, storage, or disposal facilities (TSDFs) that have EPA identification numbers for hazardous waste handling and meet the TSDF transfer requirements.

5.1.2. A new ID number is necessary when changing locations as the number is tied to the facility address.

5.1.3. This facility's US EPA Identification Number is KSD984972992.

5.2. The laboratory generates wastes originating from several source types: materials and chemicals used to prepare and analyze samples (e.g., solvents, acids), unconsumed liquid and solid samples, certain types of batteries, mercury from lamps and broken thermometers and automobile waste. Unconsumed samples may include laboratory-contaminated sample residue (both liquid and soil) generated as part of digestion, extraction, etc., procedures used to prepare samples for analysis.

5.2.1. Based on table 3.4, this facility is classified as a Large Quantity Generator.

5.3. Hazardous waste classification is the most critical step in establishing an effective, compliant waste-handling program. Laboratory wastes are classified using the criteria set forth under RCRA for ascertaining non-hazardous versus hazardous status, and this criterion is listed in the definition of hazardous waste in 4.20.

5.4. The following are the waste streams resulting from materials and chemicals used in the laboratory operation. Applicable information for each is given pertaining to packing, labeling, or listing on a manifest. A description of how the wastes are created, and the preferred method of final disposal for each, is included. The overriding principle in hazardous waste classification is application of a conservative formula based on all known or suspected hazards related to a waste material. While this formula may result in some materials being disposed as hazardous when in fact, they are non-hazardous (e.g., false positive), the formula will not be compromised in the interest of reducing the amount of waste produced. This will minimize any risk of a material being disposed of erroneously as non-hazardous when it, by definition, is a hazardous waste.

5.4.1. **Corrosive waste** is generated in the majority of the departments in the laboratory. This waste stream consists primarily of spent or excess aqueous reagent solutions generated from preservatives, acid digestions of metals, impinger solutions or other corrosive solutions generated in the course of analysis. The predominant corrosives include hydrochloric acid, nitric acid and sulfuric acid, but corrosives also include bases. Varying concentrations of metals may be present dependent upon the composition of the reagents added. This waste stream only has the hazardous quality of being corrosive; therefore, if a waste has any additional hazardous waste quality (e.g., Toxic or Ignitable) it cannot be mixed with this stream. This stream is treated onsite.

Corrosive Waste	
DOT Shipping Name	RQ Waste, Corrosive Liquids, N.O.S (i.e. corrosive material)
EPA Waste #	D002
Container	LIST CONTAINER
Average pH	<2.0, >12.5
Disposal Method	Treatment by Neutralization
Label	Corrosive

5.4.2. **COD Waste** is specific waste that results from COD analysis. This waste comes from used and expired COD vials of samples and reagent. This stream has sulfuric acid, mercuric sulfate, potassium dichromate, and silver sulfate.

COD Waste	
DOT Shipping Name	RQ,UN2922,WASTE CORROSIVE LIQUIDS, TOXIC, N.O.S.,8(6.1),PGII,(MERCURIC SULFATE, SULFURIC ACID),(D009 D011),ERG#154
EPA Waste #	D002, D007, D009, D011

Container	30 gallon poly drum (30DF)
Average pH	<2
Disposal Method	Reclamation, Stabilization, Landfill
Label	Corrosive, Toxic

5.4.3. **Oily Water** is a general waste that is used throughout the laboratory to dispose of waste solvents such as methanol and hexane, and used reagents, oil samples, liquids that have been deemed unsuitable for neutralization by visual inspection and liquid waste samples that have the toxic characteristic by RCRA guidelines. Waste samples are considered RCRA toxic if they are liquid and the LIMS database flags the sample for over the TCLP limits for any D-code except D009 (mercury). Liquid samples that are flagged for D009 are handled in the TKN waste stream.

Oily Water	
DOT Shipping Name	RQ,UN1993,WASTE FLAMMABLE LIQUIDS, N.O.S.,3,PGII,(HEXANE, METHANOL),(D004 D011),ERG#128
EPA Waste #	F003, D001, D004, D005, D006, D007, D008, D010, D011, D018, D022, D035, D038,D040
Container	55 gallon Steel drum (55 DM)
Average pH	7
Disposal Method	Fuel Blending
Label	Flammable, Toxic

5.4.4. **TKN Waste** is a specific waste that includes the effluent from the TKN digestion process. This waste will include liquid samples that have the D009 (Mercury) characteristic as flagged by our LIMS.

TKN Waste	
DOT Shipping Name	RQ, UN3264, Waste corrosive liquid, acidic, inorganic, n.o.s., (mercuric sulfate, sulfuric acid), 8, PG II, (D009)
EPA Waste #	D002, D009
Container	30 gallon poly drum (30 DF)
Average pH	<2
Disposal Method	Reclamation, Stabilization, Landfill
Label	Corrosive, Toxic

5.4.5. **Chlorinated Reuse Product*** is the used chlorinated solvent from the organic preparation of extractables and rinse operations in various parts of the laboratory. This is not considered waste by the state of Kansas nor the federal government. It consists of 95+% dichloromethane. This material is shipped, as is, to WRR in Eau Clair, WI.

Chlorinated Reuse Product	
DOT Shipping Name	UN2929, Toxic liquids, flammable, organic, n.o.s (dichloromethane methanol), 6.1(3), PGII, ERG#160 & ERG#131

EPA Waste #	D001
Container	30 gallon poly drum (30 DF)
Average pH	NA
Disposal Method	Reuse
Label	Flammable, Toxic
*	See Attachment VI

5.4.6. **Glass Vials** is a loose pack of sample extracts in dichloromethane and hexane form the semivolatile laboratory.

Glass Vials	
DOT Shipping Name	RQ,UN1993,WASTE FLAMMABLE LIQUIDS, N.O.S.,3,PGII,(METHANOL, HEXANE, METHYLENE CHLORIDE),(F001 F003),ERG#128
EPA Waste #	F001, F003
Container	30 gallon poly drum (30 DF)
Average pH	NA
Disposal Method	Incineration
Label	Flammable, Toxic

5.4.7. **Mercury Debris** is a combination of broken mercury thermometers, debris from any clean up required, and solid samples that have the D009 (Mercury) characteristic as flagged by our LIMS.

Mercury Debris	
DOT Shipping Name	RQ,UN3288,WASTE TOXIC SOLID, INORGANIC, N.O.S.,6.1,PGIII,(MERCURY CONTAMINATED DEBRIS AND DEVICES),(D009),ERG#151
EPA Waste #	D009
Container	5 gallon poly drum (05 DF)
Average pH	NA
Disposal Method	Reclamation, Stabilization, Landfill
Label	Toxic

5.4.8. **USDA Soils Loose Pack** is regulated soil that originates from foreign countries, Puerto Rico or certain designated areas of the United States. These soils are marked for special handling and disposal upon arrival.

USDA Regulated Soils	
DOT Shipping Name	NON-DOT/NON-RCRA REGULATED

EPA Waste #	NA
Container	55 gallon steel drum (55 DM)
Average pH	NA
Disposal Method	Incineration at a USDA compliant facility
Label	USDA Regulated

5.4.9. **Sodium Sulfate** is waste sodium sulfate, paper filters and soil that has been soaked in dichloromethane. This waste is generated in the preparation of semivolatile extracts.

Sodium Sulfate	
DOT Shipping Name	RQ,NA3077,HAZARDOUS WASTE, SOLID, N.O.S.,9,PGIII,(SODIUM SULFATE WITH METHYLENE CHLORIDE),(F002),ERG#171
EPA Waste #	F002
Container	55 gallon steel drum (55 DM)
Average pH	NA
Disposal Method	Incineration
Label	Miscellaneous (Category 9)

5.4.10. **Hazardous Solid Samples** are samples that have been tested for TCLP and have exceeded the regulatory limits or are deemed unsuitable for landfill (Paint/Grease etc.) by visual inspection. Waste solid samples are considered RCRA toxic if they are solid and the LIMS database flags the sample for over the TCLP limits for any D-code except D009 (mercury). Solid samples that are flagged for D009 are handled in the Mercury Debris waste stream.

Hazardous Solid Samples	
DOT Shipping Name	RQ,UN3288,WASTE TOXIC SOLID, INORGANIC, N.O.S.,6.1,PGIII,(PAINT, #2 OIL SLUDGE),(D004 D006),ERG#151
EPA Waste #	D004,D006,D007,D008,D018,D040
Container	20 gallon poly drum (20 DF)
Average pH	NA
Disposal Method	Incineration
Label	Toxic

5.4.11. **NHS/Crushed Glass** is a combination of crushed glass and crushed non-hazardous soil samples. This waste stream is tested at least quarterly or if a particular drum warrants at the discretion of the disposal technician.

NHS/Crushed Glass	
DOT Shipping Name	NON-DOT/NON-RCRA REGULATED
EPA Waste #	NA
Container	55 gallon Steel drum (55 DM)

Average pH	NA
Disposal Method	Landfill
Label	NA

5.4.12. **Light Bulbs Universal Waste** is fluorescent bulbs that are taken out of service.

Light Bulbs Universal Waste	
DOT Shipping Name	NON-DOT UNIVERSAL WASTE- LAMPS
EPA Waste #	NA
Container	Fiber Boxes
Average pH	NA
Disposal Method	Reclamation
Label	NA

5.4.13. **Used Oil** is oil from vacuum pumps in the laboratory. Oil samples from unknown/client sources are excluded as the source is generally unknown.

Used Oil	
DOT Shipping Name	NON-DOT REGULATED MATERIAL USED OIL PER 40 CFR 279
EPA Waste #	NA
Container	5 gallon steel drum (05 DM)
Average pH	NA
Disposal Method	Fuel/Reclamation
Label	NA

5.4.14. **COMPUTER PARTS FOR RECYCLING** includes monitors, circuit boards and other computer parts.

COMPUTER PARTS FOR RECYCLING	
DOT Shipping Name	NON-DOT/NON-RCRA REGULATED
EPA Waste #	NA
Container	Fiber Boxes
Average pH	NA
Disposal Method	Reclamation
Label	NA

5.4.15. **Batteries** are lithium ion batteries from various sources in the laboratory.

Batteries	
DOT Shipping Name	Batteries, Dry, Containing Potassium Hydroxide, Solid, (Universal Waste), 0, PG III
EPA Waste #	NA
Container	Fiber Boxes
Average pH	NA
Disposal Method	Reclamation
Label	NA

5.4.16. **PCB Lab Pack** contains expired or unused PCB standards, solid and oil samples identified by the LIMS as being above 50PPM PCB.

PCB lab Pack	
DOT Shipping Name	RQ, UN1993, WASTE FLAMMABLE LIQUIDS, N.O.S. MIXTURE, (BENZENE, TOLUENE), 3, PG III (POLYCHLORINATED BIPHENYLS)
EPA Waste #	D001, D018, U165, U220, U239
Container	5 gallon poly drum (05 DF)
Average pH	NA
Disposal Method	Incineration
Label	Flammable, Toxic

5.4.17. **PCB Extracts** is a loose pack of expired and unused sample extracts containing 50% sulfuric acid and 50% Hexane. These extracts are expected to contain some PCBs but, overall be below the 50 ppm threshold. They are incinerated at a facility licensed to handle PCBs out of caution.

PCB Extracts	
DOT Shipping Name	UN2924, WASTE FLAMMABLE LIQUIDS, CORROSIVE, N.O.S., (HEXANE, SULFURIC ACID), 3, (8), PG II
EPA Waste #	D001, D002
Container	30 gallon poly drum (30 DF)
Average pH	<2
Disposal Method	Incineration
Label	Flammable, Corrosive

5.5. Some waste can become complicated when attempting to classify as non-hazardous or hazardous due to the list of hazardous constituents contained in sections 40 CFR 261.30-261.35 including a majority of analytes of interest routinely analyzed in Pace laboratories. Definitions have been established for each of the F, K. P, and U lists covering hazardous waste originating from non-specific sources, specific sources and discarded commercial chemical products, off-specification species, container residues, and spill residues. The application of listed hazardous wastes and substances is intended for manufacturing processes involving pure products, by-products, wastes generated as part of the production process and cleanup of materials contaminated from a spill of the listed commercial chemical product or manufacturing chemical intermediate. See Attachment II for common F-listed wastes.

5.5.1. Hazardous waste classification of unconsumed samples by listed hazardous waste criteria is not commonly applied in laboratory operations. Examples of sample types which would be identified as listed hazardous wastes include the following:

5.5.1.1. Samples containing 5% or more (by volume) of halogenated and non-halogenated “spent solvents:” (e.g., drum sample with > 10% TCE);

5.5.1.2. Pure product and two phase solution samples containing a listed chemical product or manufacturing intermediate (e.g., drum sample);

5.5.1.3. Samples from specific sources listed in section 261.32 (e.g., bottom sediment sludge from the treatment of wastewaters from wood-preserving processes that use creosote and/or pentachlorophenol - K001);

5.5.1.4. Samples representing any residue or contaminated soil, water or other debris resulting from the cleanup of a spill into or on any land or water of any commercial chemical product or manufacturing chemical intermediate having a generic name listed in section 261.33, or any residue or contaminated soil, water or other debris resulting from the cleanup of a spill, into or on any land or water, of any off-specification chemical product and manufacturing chemical intermediate which, if it met specifications, would have the generic name listed in section 261.33.

5.5.2. For the wastes listed in 5.5.1.1 and 5.5.1.2, disposal can be achieved by individually lab packing them or combining with other compatible hazardous wastes.

5.5.3. The remaining two sample types in 5.5.1.3 and 5.5.1.4 would also require lab packing for disposal. However, it is important to note that in order for the laboratory to ascertain that the samples were derived from a specific listed source or from a spill of a listed chemical, they must be so informed by the industrial concern or lead agency (e.g., EPA, state regulators) submitting the sample for analysis. If a water or soil sample contains a listed hazardous waste substance whose origin is unknown or uncertain to the lead agency, then that sample is not classified as a listed hazardous waste. Rather in this case, determination of a hazardous waste classification can only be obtained by the waste exhibiting a characteristic of hazardous waste (e.g., ignitability, corrosivity, reactivity).

5.5.4. Due to the fact that the majority of samples analyzed by Pace do not meet the well-defined criteria for identifying "listed" hazardous waste, disposal classification of unconsumed samples will be based upon characteristics of hazardous waste:

5.5.4.1. Non-Hazardous - Analysis results indicate an absence of contaminants; unless contaminants listed under the hazardous disposal categories are parts of the requested sample analysis.

5.5.4.2. Hazardous – Analysis results indicate presence of contaminants (Attachment III) or sample analysis requires hazardous materials and contaminants. Samples in this category are segregated from others and disposed of as hazardous according to laboratory procedures.

5.5.4.3. PCB Waste - Generated exclusively by samples contaminated with greater than trace levels of polychlorinated biphenyls ($\geq$ 50ppm). Samples containing 50ppm (total) or higher of PCBs must be segregated and disposed of as PCB waste.

5.5.4.4. Waste Oil/Paint - Samples which are predominantly of an oil matrix (e.g., highly viscous organic liquid) or paint (solvent and pigment blend) are segregated and disposed in a separate container. Though these samples are defined as nonhazardous, oil samples are a special case and never disposed as nonhazardous. Note: Bottle caps and liners do not typically contain sample residuals and can be disposed of directly through the non-hazardous building refuse.

5.5.5. USDA-APHIS-PPQ Regulated Soils (Regulated Soils) are a special case of sample strictly controlled under quarantine regulations 7 CFR 330 because they can readily provide a pathway for a variety of dangerous organisms throughout the United States. The movement of soil into the

United States from foreign sources and from certain regulated areas within the continental U.S. is restricted unless permitted by APHIS under specific conditions and safeguards.

5.5.5.1. Any laboratory that handles Regulated Soils must have an approved Compliance Agreement from USDA-APHIS-PPQ, and labs that handle foreign soils must have an approved Permit to Receive Soil. See updated revision of *Regulated Soil Handling SOT-ALL-S-003 or local version* for all information regarding the handling of these materials.

5.5.6. Though Pace is obligated to ensure nonhazardous discharge complies with requirements set by applicable publicly owned treatment works (POTW) and local regulations, Pace is not obligated to run every available analysis on every sample for proper waste classification. Consequently, samples are characterized according to the preservatives added, the requested analytical testing data, and any knowledge of the sample provided by the client. When sample analysis is canceled/not completed, those untested samples are characterized by the preservatives added and any knowledge of the sample that is obtained by the client.

5.6. Consolidation of wastes from the laboratory proceeds via two distinct routes covering either laboratory-generated hazardous wastes or excess unconsumed samples.

5.6.1. Laboratory Accumulation and Satellite Waste Containers

5.6.1.1. Waste materials from routine lab procedures are collected in containers of appropriate construction, placed in convenient locations at the point of generation. Under RCRA guidelines, these are defined as satellite containers.

5.6.1.2. The amount of hazardous waste stored in the laboratory at the individual satellite areas cannot exceed 55 gallons (liquid) or 550 lbs (solid) per waste stream, for non-acute hazardous waste.

5.6.1.3. Satellite waste containers must be labeled in accordance with all regulations, including:

5.6.1.3.1. Designation of the contents to be hazardous waste with the words “Hazardous Waste” clearly legible.

5.6.1.3.2. The waste stream description (e.g., acid waste).

5.6.1.3.3. A hazard label (e.g., corrosive).

5.6.1.4. The satellite containers must be maintained such that evolution of chemical vapors is precluded. This requires that the container be closed at all times, except when adding or emptying hazardous waste to and from the container.

5.6.1.5. The most critical point in the waste handling system is when a person (e.g., analyst, technician) places a waste material into a satellite container. Here, the characteristics or listing of the waste and the waste stream must both be known to match. For this reason, only material from approved procedures should be placed in the compatible satellite containers. All materials from experimental procedures, unknown or out of the ordinary sources, or from spill cleanups must be characterized and described to the Hazardous Waste Coordinator, who determines the proper method of disposal.

5.6.1.6. Full satellite containers must be transferred to the proper accumulation drum within 3 calendar days. Lab collection containers must not be filled to the top of the opening. Space must be left to prevent splashing of hazardous material when containers are emptied and to allow for expansion and contraction within the drum during transport.

5.6.1.7. Satellite containers for liquid hazardous waste must have secondary containment made of material that could successfully contain the entire satellite container's contents.

5.6.2. Unconsumed Sample Disposal

5.6.2.1. Client samples are stored on-site for a defined period of time after the final analytical report is generated and prior to sample disposal. The purpose of sample storage is to provide the client time to review the analytical report and determine if the samples require additional testing or need to be returned to the client. Samples are not considered a waste during this time according to 40 CFR 261.4(d)(1)(vi).

5.6.2.1.1. The default sample storage time is **"365 days from Login."** Therefore, the maximum sample storage time is one (1) year from the login date. Other sample storage hold times may be assigned for specific contractual requirements.

5.6.2.1.2. When the final report is generated for a work order, the laboratory information management system (EPIC Pro) updates the samples' disposal date code from 365 days from login to 30 days from report. This update does not change our default storage but allows for samples to be disposed before the maximum time is reached, but only after the sample has been held for a period of time defined in the local Sample Management SOP (S-KS-C-001-rev.08) AND restrictions are not placed on the sample via the LIMS from the PACE project manager (in accordance with client specific contractual requirements).

5.6.2.1.3. During sample storage, the process and sample status must be obvious to employees, customers and auditors. This transparency is imperative to ensure samples are considered active test specimens to be retained until they are categorized as a waste for disposal.

5.6.2.2. Samples which cannot be returned to the client for disposal are characterized according to section 5.4. Samples are characterized by one of three methods:

5.6.2.2.1. Analytical results are evaluated against characterization criteria established for the sample waste stream. The samples which exhibit waste characteristics as previously outlined are segregated and denoted per laboratory/facility policies. The completed form is then forwarded to the Hazardous Waste Coordinator, who in turn uses the information to coordinate removal of unconsumed samples from active sample storage by the log-in staff. OR:

5.6.2.2.2. Samples are scanned out of EPIC Pro (LIMS) as RCRA nonhazardous to be disposed as the waste stream is normally handled unless the sample tested over RCRA limits, in which the LIMS will prompt the employee that the sample is scheduled for Hazardous disposal, and is segregated from the nonhazardous samples. OR:

5.6.2.2.3. Samples of a certain type are all "assumed" to be hazardous, and all are placed into an accumulation drum with all required RCRA labeling for that waste stream.

5.6.2.2.4. Labs that analyze samples under an ESI Technical Specifications document are required to physically remove labels from ESI samples prior to waste disposal.

5.6.2.3. Samples may be pulled from cold storage when the EPA recommended hold time has passed and placed in short term storage without climate control. As samples become available for disposal (generally seven weeks from sample receipt) the samples are scanned into an internal COC in LIMS designed for disposal. Samples are scanned into a NONHAZARDOUS COC. If the sample is designated for Hazardous disposal (RCRA, Hg, PCB) a pop up will alert the operator and require action before disposal can continue.

5.7. Transferring Satellite Waste to the Waste Storage/Accumulation Area

5.7.1. All transfers of satellite waste to waste drums must be made by the Hazardous Waste Coordinator or designated, trained personnel. When a satellite waste container is full, the Hazardous Waste Coordinator, or designee must be notified. Regular disposal events may be scheduled to dispose satellite waste on a continuous basis.

5.7.2. Find the correct waste drum by referring to the Hazardous Waste placard and hazard label. Mixing solvents that are not compatible could result in a hazardous reaction.

5.7.3. Ensure there is enough capacity in the drum to hold all the content that will be dispensed.

5.7.4. Check to make sure there is a ground connection before opening a solvent waste drum.

5.7.5. Open and slowly pour the contents of the satellite container into the proper waste drum using an appropriate solvent resistant funnel.

5.7.6. Replace the cap on the bunghole and carefully screw the cap on but do not tighten the cap.

5.8. Unconsumed Soil Samples

5.8.1. Soil samples are scanned into a nonhazardous internal COC document in the LIMS. If a sample is listed as hazardous the operator is alerted and must take action before continuing. The hazardous samples are loose packed into the Hazardous Solid Sample waste stream and the non-hazardous samples are crushed into a 55 gallon steel drum for landfill. This waste stream is tested at least quarterly or if a particular drum warrants at the discretion of the disposal technician.

5.9. Elementary Neutralization

5.9.1. Dilute corrosive solutions (e.g., preserved metals samples) which do not exhibit any hazardous characteristics other than being corrosive, may be neutralized. Elementary neutralization is exempt from RCRA permitting requirements for on-site hazardous waste treatment. While exempt under RCRA guidelines, before utilizing this practice to reduce off-site treatment or disposal of wastes, local pretreatment and discharge standards must be met for publicly owned treatment works (POTW). See Attachment VII.

5.9.2. The discharges listed below are prohibited under the National Pretreatment Standards and Prohibited Discharge Standards:

5.9.2.1. Pollutants causing fire or explosion (waste with a flashpoint < 60°C);

5.9.2.2. Corrosive wastes with pH less than 2 or greater than 12.5;

5.9.2.3. Solid or viscous pollutants that could potentially block the system;

5.9.2.4. Oxygen-demanding pollutants;

5.9.2.5. Wastes which generate toxic gases.

5.9.3. The Pace Analytical, Lenexa Kansas, Neutralization tank is located in the Waste Disposal Area and consists of a 55 gallon drum physically plumbed into the sewer with a closeable pipe. During normal operation the drain is closed. The opening of the tank is fitted with 5 gallon bucket to act as a sieve to catch solid material and an oil adsorbent pillow from New Pig is in place to prevent organics such as oil from entering the tank. When the tank is deemed full, the operator removes the bucket and tests the pH to determine a base line. Because of the nature of material disposed in the laboratory this base line is nearly always <2. The operator will add an appropriate amount of 50% NaOH from a commercially purchased drum. The tank is agitated and the pH tested. This procedure is repeated until the pH is between 5.5 and 10.5 (per Johnson County Specifications. See Attachment VII.) If the pH is overshot the operator will add high acid (metals digitates works well.) content to balance the pH. Once the pH meets specifications a tap downstream is opened to create a flush and the tank drain is opened. When the tank is empty the drain and tap are closed, the bucket replaced and the system is ready for use.

5.10. Waste Storage Container Requirements

5.10.1. Drums in the hazardous waste storage area are labeled consistent with both DOT and EPA regulations concerning hazardous materials and wastes (see Attachment IV for example of label).

5.10.2. Closure instructions must be available for all containers used to transport hazardous materials. If a container in the accumulation area is the same one the waste will be shipped away in, the Waste Coordinator must obtain the closure instructions from the provider of the containers.

5.10.3. Labels must be easily visible and legible (e.g., a drum must not be labeled and then placed in such a way that the label cannot be seen).

5.10.4. The Accumulation Start Date must be recorded on the drum. The date should reflect the first time waste was added to the drum and not the date when the waste was generated in the laboratory.

5.10.4.1. Once a waste is removed from the point of generation to a hazardous waste staging area, the clock is started for storage time prior to disposal.

5.10.4.2. Drums must be picked up by TSDF for disposal before accumulation time exceeds RCRA requirement for lab's generator status (see section 3.4).

5.10.5. The hazardous waste staging room must be arranged in such a fashion to assure direct access pathways in the event of foreseeable emergency and for safe waste transfer. A minimum aisle space of three feet must be maintained at all times to access hazardous waste containers.

5.10.6. All hazardous waste drums and containers must be securely closed when not in use. All volatile and flammable hazardous waste liquid containers must be securely grounded at all times. Drums containing these liquids should also be manipulated with non-sparking tools and fitted with a drum venting bung, to assure that excess pressure build-ups are safely released.

5.10.7. All liquid waste stream containers must be provided with secondary containment devices. Such containment devices must be made of materials compatible with each waste, and they must be free of leaks. The waste storage room may act as secondary containment as long as the room has been constructed to safely and effectively contain a hazardous waste spill.

5.10.7.1. Secondary containers must exceed the total volume of the largest container stored in each containment device for indoor storage.

5.10.8. Compatibility of wastes must be considered in arranging storage areas. For example, acid waste should never be stored adjacent to basic waste, particularly cyanide wastes. Further examples are outlined in 40 CFR 264, Appendix V.

5.10.9. The hazardous waste staging area is controlled so unauthorized personnel are not able to access the room or contents.

5.10.10. The maximum volume of acutely hazardous waste (e.g., P-listed wastes) that can be accumulated in the laboratory is one quart. The volumetric measurement of one quart is based upon container size in which the waste is stored and not the actual amount (volume) of waste present. An example of how this one quart limit can inadvertently be exceeded involves the disposal of a neat standard of 2,4-dinitrophenol into a one gallon bottle. While the neat standard itself may only constitute 1-2mL, the volume as defined under RCRA would be one gallon, thus the laboratory would be out of compliance.

5.11. Waste Documentation and Reporting

5.11.1. All drums containing hazardous waste are recorded in a logbook or database. The information contained in this log is useful when filling out EPA biennial reports and for retaining an accurate description of how much waste has been accumulated. The following information is entered into the logbook/database;

5.11.1.1. The drum number;

5.11.1.2. The date filling the drum was started;

5.11.1.3. The drum capacity (e.g., 55-gallon, etc.);

5.11.1.4. The manifest number associated with the drum's disposal.

5.11.2. The following hazardous waste records must be maintained a minimum of five years and should be retained indefinitely:

5.11.2.1. Drum tracking logs;

5.11.2.2. Sample Reports;

5.11.2.3. Sample disposal information and waste records on computer disc;

5.11.2.4. Analytical records relating to sample waste stream profiling and characterization;

5.11.2.5. Labpack inventory logs;

5.11.2.6. Biennial Reports, Exception Reports, or other reports filed for compliance reasons;

5.11.2.7. Records related to unresolved enforcement action must be retained indefinitely until such a time that the matter is resolved;

5.11.2.8. Facility Certificates of Destruction or Recycling.

5.11.3. A Waste Manifest is the documentation form that must accompany all shipments of hazardous waste while in transit.

5.11.3.1. A Hazardous Waste Manifest Cover Sheet (*F-ALL-W001-rev.00 or local replacement*) will be utilized to ensure waste transfer from generator to TSDF fulfills all legal requirements.

5.11.3.2. The manifest is be signed and dated by a DOT trained Pace employee responsible for the shipment and the transporter. The transporter will leave 2-3 of these "two-signature page" copies of the manifest.

5.11.3.3. Within 35 days you will receive a three-signature page (generator, transporter, facility) showing the waste reached its intended destination.

5.11.3.3.1. If you do not receive the three signature page within 35 days of shipment, call the facility to find out why you have not received it. If you do not receive the three-signature page within 45 days you must file an exception report with KDHE

5.11.3.4. All manifests must be kept for a minimum of three years.

5.11.4. The central accumulation staging room must have a documented inspection weekly and satellite waste containers must have documented inspection as part of the monthly laboratory inspection. The inspections should ensure all regulations are obeyed; see sections 5.10 and 5.6.1 for accumulation storage and satellite rules.

5.11.4.1. A record of the inspections must be kept in an inspection log or summary.

5.11.4.2. Records must be maintained for at least three years from the date of inspection. At a minimum, the records must indicate:

5.11.4.2.1. The date and time of the inspection;

5.11.4.2.2. The name and signature of the inspector (typically will be Hazardous Waste Coordinator);

5.11.4.2.3. A notation of the observations made (can be in a check-off format, e.g., fire extinguisher: charged _X_ requires recharging __);

5.11.4.2.4. The date and nature of any repairs or other remedial actions.

5.11.5. Annual Generation Reports are required to be filed with KDHE:

5.11.5.1. Large Quantity Generators must file a biennial report with the local state or EPA Region. , The report must be submitted by March 1st, on the even year. The report is submitted on EPA Form 8700-13A and can be downloaded from the EPA website at http://www.epa.gov/epawaste/inforesources/data/biennialreport/index.htm. The downloaded instructions should be an adequate guide, although as a general set of requirements, the report must include the following items:

5.11.5.1.1. Laboratory name, address, and EPA identification number;

5.11.5.1.2. The calendar year covered in the report;

5.11.5.1.3. The name, address and EPA identification number for each TSDF used during the calendar year;

5.11.5.1.4. A description, EPA hazardous waste number (e.g., F002), DOT hazard class and quantity of each waste shipped off-site for treatment and disposal. This must be listed by the TSDF used;

5.11.5.1.5. Description of the efforts made during the year to reduce or minimize the amount and toxicity of waste generated;

5.11.5.1.6. The signed certification statement on Page 3 of the Site Identification Form.

6. Training, Expectations, and Supplemental Information

6.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

6.2. **Equipment and Supplies** - The following equipment is mandatory under RCRA guidelines unless otherwise denoted. Periodic review (not to exceed monthly) of availability of equipment and supplies below should be conducted to maintain an adequate and viable supply.

6.2.1. **Chemical Spill Control Neutralizers**: The waste room stores three types of bulk dry spill neutralizers: solvent, acid and base. They may be utilized by placing the dry neutralizer onto a liquid chemical spill. Neutralization is indicated by a prevalent color change.

6.2.2. **Communication Device**: Required for emergency notification of spill, fire, etc.

6.2.3. **Drums**: Common types of waste drums used for storing and shipping hazardous wastes are polyethylene, steel-polyethylene lined, and steel. Sizes are typically 5gal, 15gal, 30gal, and 55gal. Drums used for liquids typically are closed top with an opening to pour the solvent through a funnel, while drums used for solids or lab packs are open-top. The UN rating for all containers must be suitable if the waste is to be transported under DOT regulations.

6.2.4. **Emergency Drench Shower**: Shower should deliver water approximately twenty gallons per minute with a non-interruptible flow. It may be turned on by pulling the shower handle down. It may be turned off by pushing the handle back to the 'off' position.

6.2.5. **Emergency Lighting** (as needed): The waste room is outfitted with emergency lighting that goes on if power fails.

6.2.6. **Exit Signs** (as needed): Exit signs are provided on all waste room doors. These signs are self-illuminating.

6.2.7. **Fire Alarm Pull Station/Evacuation Alarm**: A fire alarm pull station must be in close proximity to the hazardous waste room. The alarm may be activated by pulling the switch. Other alarm systems may be utilized as long as all personnel are trained on the procedures and the process can effectively notify facility employees of an emergency.

6.2.8. **Fire Extinguisher**: An extinguisher with a rating appropriate to the waste being stored in the area must be in close proximity to the hazardous waste room.

6.2.9. **Labels**: A multitude of labels are provided to ensure compliant labeling. They may be purchased or prepared manually.

6.2.10. **Liquid Chemical Neutralizers**: Liquid chemical neutralizers (base and acid) may be used to neutralize a contained hazardous liquid. This may be done by slowly adding the neutralizer to the liquid.

6.2.11. **Spill Control Pads**: Spill pads are used to soak up hazardous liquids. They do not neutralize spills. They are especially effective for cleaning up oily materials. Various pads are available for aqueous and petroleum based liquids.

6.2.12. **Spill Control Pillows**: Spill pillows may be used to soak up large amounts of liquid chemical spills. No neutralization occurs.

6.2.13. **Spill Dikes**: vary depending on the size and type of room: Their purpose is to encircle a spill, barring the spread of a hazardous chemical. They will also absorb liquids, but do not neutralize spills.

6.2.14. Add in equipment and supplies as needed per local lab requirements.

6.3. **Attachments**

6.3.1. Attachment I: RCRA Requirements for Labs as a Function of Generator Status.

6.3.2. Attachment II: Hazard Codes for Common F-List Wastes (solvents).

6.3.3. Attachment III: TCLP Contaminant List with Concentration Limits.

6.3.4. Attachment IV: Hazardous Waste Label for Accumulation Drum (example).

6.3.5. Attachment V: Waste Inspection Form (example).

6.3.6. Attachment VI: Continued Use Concurrance.

6.3.7. Attachment VII– Wastewater Discharge Standards

6.3.8. Attachment VIII: Hazardous Waste Manifest Cover Sheet.

6.3.9. Attachment XI: Nonvolatile Water Sample Disposal Process

6.3.10. Attachment X: Volatile Water Sample Disposal Process

6.3.11. Attachment XI: Soil Sample Disposal Process

6.3.12. Attachment XII: Oil Sample Disposal Process

7. References

7.1. Pace Chemical Hygiene/Safety Manual-most current version.

7.2. Pace Quality Assurance Manual- most current version.

7.3. National Environmental Laboratory Accreditation Conference (NELAC) Standard- most current version.

7.4. The NELAC Institute (TNI) Standard- most current version applicable to each lab.

7.5. Department of Defense (DoD) Quality Systems Manual- most current version.

8. Revisions

Document Number	Reason for Change	Date
ALL-KS-S-002-rev.1	New	November 6, 2006
ALL-KS-S-002-rev.2	Sections 1-11 - Added Section 12 – Added Chlorinated Reuse Product. Extensively revised to reflect present practices. Table 1 – Added Attachments 1-3 - Added	March 5, 2009
ALL-KS-S-002-rev.3	Incorporated corporate template content and format to local SOP. Addressed non-hazardous disposal.	February 10,2011
ALL-KS-S-002-rev.4	SOP - Updated to latest prescribed format. Section 8.19 – Removed “EP Toxic” Table 12.1 – Revised shipping names for PCB. Section 12.5 – Added multiple phases to hazard determination Attachment 8 – Deleted USDA Regulated Soil Maps	July 9, 2013
ALL-KS-S-002-rev.5	SOP - Updated to latest prescribed format. Section 12 – Substituted reference to USDA Regulated Soil SOP. Section 20 – Added glass crusher items. Section 22 – Added glass crusher items. Attachment 4 – Updated to reflect current practice. Attachment 5 – Updated to reflect current practice.	March 18, 2015
ALL-KS-S-002-rev.6	Section 20 – Add requirement for cut-resistant gloves.	May4, 2015
ALL-KS-S-002-rev.7	SOP - Updated to latest prescribed format. Section 5.4.1 through 17 Updated waste streams Appendix V updated Waste Inspection Checklist	October 31, 2017

Attachment I: RCRA Requirements for Labs as a Function of Generator Status

Requirement (40CFR)	CESQG	SQG	LQG
Waste Determination (262.11)	Applicable	Applicable	Applicable
Generation Rate Limits (261.5 and 262.34)	<100 kg/mo	100-1,000 kg/mo	1,000 kg/mo or greater
Accumulation Quantity Limit w/o Permit (261.5 and 262.34)	Not to exceed 1,000 kg at any time. Not to exceed 1 kg acute at any time	not to exceed 6,000 kg at any time	No limit
Accumulation Time (261.5 and 262.34)	No limit	180 days or 270 if waste is to be transported over 200 miles.	90 days
EPA ID Number (262.12)	Not required***; possible state requirement	Required	Required
Mark Containers with Start Date (262.34)	Not applicable	Applicable	Applicable
Mark Containers "Hazardous Waste" (262.34(a))	Not applicable	Applicable	Applicable
Air Emission Standards 40 CFR 265 Subpart CC	Not applicable	Not applicable	Applicable
Satellite Accumulation (262.34(c))	Not applicable	Applicable	Applicable
Use Manifests (262, Subpart B)	Not required; possible state requirement	Required	Required
Exception Reporting (262.42)	Not required	Required after 60 days. No TSDF notification requirement.	Required after 45 days. Notification of TSDF within 35 days.
Biennial Report (262.41)	Not required	Not required; possible state requirement	Required
Contingency Plan (265, Subpart D)	Not required, but OSHA (29 CFR 1910.38) requires emergency planning	Basic planning required in accordance with the standards in 262.34(d)(4) and (5) and 265, Subpart C as well as OSHA regulations	Full written plan in accordance with 265 Subpart D, is required by 262.34(a)(4) and OSHA regulations
RCRA Personnel Training (262.34 and 265.16)	Not required, but recommended	Basic training required by 262.34(d)(5)(iii)	Full compliance with the training requirements in 265.16 is required by 262.34(a)(4)
Storage Requirements (without permit) (262.34 and 265)	None, but OSHA regulations under 29 CFR 1910, Subparts H and N, apply, particularly 29 CFR 1910.106	Compliance with technical standards in Part 265, Subparts I and J; for containers and tanks is required by 262.34(d)(2) and (3) and OSHA regulations	Compliance with technical standards in Part 265, Subparts I, J, W, and DD, is required by 262.34(a)(1) and OSHA regulations

Requirement (40CFR)	CESQG	SQG	LQG
Recordkeeping Requirements (262.40)	Waste determinations and generation log required (notification of regulated waste activity, training records, manifests, and land disposal restriction notifications recommended)	Notification of regulated waste activity, waste determinations, generation log, manifests, land disposal restriction notifications, exception reports, and correspondence with local emergency responders (written contingency plan, weekly container inspection & periodic equipment maintenance logs, and RCRA training records recommended)	Notification of regulated waste activity, waste determinations, generation log, manifests, land disposal restriction notifications, exception reports, biennial reports, correspondence with local emergency responders, RCRA training records, and written contingency plan required (weekly container inspection is required & periodic equipment maintenance logs is recommended)
Waste "Designated Facility"	State-approved or RCRA permitted facility or legitimate recycler	RCRA-permitted facility or legitimate recycler	RCRA-permitted facility or legitimate recycler
Land Disposal Restrictions (268.7)	Possible state requirement	Applicable	Applicable

Attachment II: Common F-Listed Solvents

Waste Name	Hazardous Waste Code(s)		Waste Name	Hazardous Waste Code(s)
Acetone	F003		Methylene Chloride	F001, F002
Benzene	F005		Methyl ethyl ketone (MEK)	F005
iso-Butanol	F005		Methyl isobutyl ketone	F003
n-Butyl alcohol	F003		Nitrobenzene	F004
Carbon Disulfide	F005		2-Nitropropane	F005
Carbon Tetrachloride	F001		Orthodichlorobenzene	F002
Chlorobenzene	F002		Pyridine	F005
Chlorinated fluorocarbons (CFC)s	F001		Tetrachloroethylene	F001, F002
Cresols	F004		Toluene	F005
Cresylic acid	F004		1,1,1-Trichloroethane	F001, F002
Cyclohexanone	F003		1,1,2-Trichloeoethane	F002
2-Ethoxyethanol	F005		1,1,2-Trichloro-1,2,2-trifluoroethane	F002
Ethyl acetate	F003		Trichloroethylene	F001, F002
Ethyl benzene	F003		Trichloroflourormethane	F002
Ethyl ether	F003		Xylene	F003
Methanol	F003			

Attachment III: TCLP Contaminant List

Waste ID #	Contaminant	Conc (mg/L)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin	0.02
D013	Lindane	0.4
D014	Methoxychlor	10.0
D015	Toxaphene	0.5
D016	2,4-D	10.0
D017	2,4,5-TP Silvex	1.0
D018	Benzene	0.5
D019	Carbon Tetrachloride	0.5
D020	Chlordane	0.03
D021	Chlorobenzene	100.0
D022	Chloroform	6.0
D023	o-Cresol	200.0
D024	m-Cresol	200.0
D025	p-Cresol	200.0
D026	Cresol	200.0
D027	1,4-Dichlorobenzene	7.5
D028	1,2-Dichloroethane	0.5
D029	1,1-Dichloroethylene	0.7
D030	2,4-Dinitrotoluene	0.13
D031	Heptachlor	0.008
D032	Hexachlorobenzene	0.13
D033	Hexachlorobutadiene	0.5
D034	Hexachloroethane	3.0
D035	Methyl ethyl ketone	200.0
D036	Nitrobenzene	2.0
D037	Pentachlorophenol	100.0
D038	Pyridine	5.0
D039	Tetrachloroethylene	0.7
D040	Trichlorethylene	0.5
D041	2,4,5-Trichlorophenol	400.0
D042	2,4,6-Trichlorophenol	2.0
D043	Vinyl Chloride	0.2

Attachment IV: Hazardous Waste Label for Accumulation Drum (Example)

ATTACHMENT V: WASTE INSPECTION FORM

Week of: 01/01/2018

	Accumulation Start Date on Container?	Container Condition Acceptable?	Liquid Wastes Have Secondary Containment?	Container bears Hazardous Waste label?	Description of Contents on label?	Containers Found Closed?	Aisle Space Sufficient to Access Waste?	Incompatible Wastes Segregated?	Area Housekeeping OK?	Comments
Volatiles										
Solvent Satellite Container										
Used Oil Container										
Metals										
Instrument Effluents (5)										
Extractions										
Solvent Day Containers										
Solvent Satellite Containers										
Wet Chemistry										
COD Waste Container										
Flashpoint Waste Container										
Instrument Effluents										
Solvent Satellite Container										
TKN Waste Container										
GC Semivolatiles										
GC Vials (2)										
MS Semivolatiles										
Solvent Containers										
Used Oil Container										

Disposal Area										Date/Time	Comments
Disposal Servicing Area											
Sodium Sulfate											
Waste Storage Shed											

Inspecting Technician _____

Reviewer _____

Attachment VI: Continued Use Concurrence

KANSAS

DEPARTMENT OF HEALTH
AND ENVIRONMENT
Division of Environment

Kathleen Sebelius, Governor
Roderick L. Bremby, Secretary

www.kdheks.gov

November 18, 2008

Jeff Orth
Pace Analytical Services, Inc.
9608 Loiret Blvd
Lenexa, KS 66219

RE: Continued Use concurrence request

Dear Mr. Orth:

The Kansas Department of Health and Environment (KDHE) Bureau of Waste Management (BWM) has reviewed the additional information provided in your June 10, 2008 e-mail and the information provided by the Wisconsin Department of Natural Resources in their October 29, 2008 e-mail. The information was provided as part of your April 4, 2008 request for concurrence that your waste methylene chloride can be reused by WRR Environmental Services Co., Inc. in Eau Claire, Wisconsin. Based on the information provided, KDHE concurs with your position that the material is being re-used and is therefore a product, not a waste.

Your cooperation with the solid and hazardous waste management program is appreciated. If you have any questions or concerns regarding this matter, please call me at 785-296-1604.

Sincerely,

Rebecca Wenner
Compliance and Enforcement Unit Chief
Bureau of Waste Management

Cc: Jim Rudeen, BWM
Bill Bider,BWM
NEDO

BUREAU OF WASTE MANAGEMENT
CURTIS STATE OFFICE BUILDING, 1000 SW JACKSON ST., STE. 320, TOPEKA, KS 66612-1366
Voice 785-296-1600 Fax 785-296-8909 www.kdheks.gov/waste

Attachment VII– Wastewater Discharge Standards

The following is excerpted from the Johnson County Code of Regulations for Sanitary Sewer Use, 2003 Edition:

ARTICLE 4 PRETREATMENT

PART C. WASTEWATER DISCHARGE STANDARDS

Section 1. General. The Director shall have the authority to limit volume, rate, strength, or nature of wastewater discharge to any public sanitary sewer by any user. Pollutants, substances, or wastewater prohibited by this subpart shall not be processed or stored in such a manner that they could be discharged to the POTW.

Section 2. Prohibited Discharges. No person or user shall introduce into any public sanitary sewer or into the sewerage system any pollutant which causes pass through, interference or significant inhibition of microbial activity, nor shall any person or user introduce any of the following into any public sanitary sewer or the sewerage system:

(a) Any gasoline, benzene, naphtha, fuel oil, or other liquid, solid, or gas which could potentially create a fire or explosion hazard in the sewerage system, including, but not limited to, waste streams with a closed cup flash point of less than 140° F (60°C) using the test methods specified in 40 C.F.R. § 261.21 or which exceed a five percent lower explosive limit (5% LEL) measured as methane.

(b) Pollutants which result in the presence of toxic gases, vapors, or fumes within the sewerage system in a quantity that may cause acute human health and/or safety problems.

(c) Any discharge containing toxic or poisonous solids, liquids, or gases in sufficient quantity, either singly or by interaction with other wastes, to injure or interfere with any wastewater treatment process, constitute a hazard to humans or animals, create a public nuisance, or create any hazard in the receiving waters of the wastewater treatment plant.

(d) Any discharge having a pH less than 5.5 or greater than 10.5, unless the Director has approved an exception under the provisions of Article 4.A.2(c).

(e) Solid or viscous substances of fats, wax, grease or oils in quantities or form capable of obstructing the flow in sewers, or otherwise result in interference.

(f) Heat in amounts which will inhibit biological activity in the treatment works resulting in interference, but in any case heat in such quantities that the temperature at the POTW exceeds 104°F (40°C), unless the Director has approved an exception under the provisions of Article 4.A.2(c). In no case shall the Director approve an exception that exceeds 150°F (65°C).

(g) Any discharge from significant industrial users permitted under the authority of Article 4 of this Code containing fats, wax, grease or oils, whether emulsified or not, containing substances which may solidify or become viscous at temperatures between 32°F (0°C) and 150°F (65°C), and which exceed 200 mg/L, unless another numeric limit or measurement methodology is approved by the Director under the provisions of Article 4.A.2(c). This discharge requirement does not apply to food service facilities as defined in Article 2 of this Code.

(h) Any petroleum oil, non-biodegradable cutting oil, or products of mineral oil origin in amounts that will cause interference or pass through.

(i) Any silver-bearing wastewater from photo-finishing processes not treated with a silver recovery unit prior to discharge.

ATTACHMENT VII– WASTEWATER DISCHARGE STANDARDS (CONT.)

(j) Any discharge containing iron, chromium, copper, zinc, and similar objectionable or toxic substances; or wastes exerting an excessive disinfection requirement or adversely affecting sludge disposal methods utilized by the Unified Wastewater Districts, to such degree that any such material measured at the source exceeds the limits established by the Environmental Department for such materials.

(k) Any discharge of odor-producing substances in concentrations exceeding the limits which may be established by the Director as necessary, after treatment of the composite wastewater to meet the requirements of state, federal, or other public agencies of jurisdiction for such discharge to the receiving waters.

(l) Any radioactive wastes or isotopes except in compliance with limits established by the Director or in compliance with applicable state or federal regulations.

(m) Any pollutant, including oxygen-demanding pollutants, released in a discharge at a flow rate and/or pollutant concentration which will cause interference with a treatment facility, and/or a significant load on the sewerage works.

(n) Any pollutant which causes excessive discoloration, such as, but not limited to, dye wastes, vegetable tanning solutions, and water-based inks which consequently impart color to the POTW's effluent, thereby causing it to violate its NPDES permit.

(o) Any discharges which cause unusual volumes of flow, mass and/or concentration of wastes constituting slug loadings.

(p) Any discharge which does not comply with the applicable categorical pretreatment standards set out in 40 C.F.R., Chapter I, Subchapter N, Parts 405-471, now in effect or as may later be amended.

(q) Any approved trucked or hauled wastes, except at discharge points designated by the Unified Wastewater Districts.

(r) Storm water, surface water, ground water, roof runoff, subsurface drainage, swimming pool drainage and non-contact cooling water, unless the Director approves an exception under the provisions of Article 4.A.2(c).

(s) Discharge of any substance which, if otherwise disposed of, would be a hazardous waste under 40 C.F.R. § 261, is prohibited unless the Director approves an exception under the provisions of Article 4.A.2(c).

(t) Any discharge which, in the opinion of the Director, causes the POTW's daily operation and maintenance schedule to be significantly disrupted.

ATTACHMENT VIII: HAZARDOUS WASTE MANIFEST COVER SHEET

HAZARDOUS WASTE PICKUP DATE: _____

MANIFEST NUMBER(S)	3-SIGN. MANIFEST RETURN DATE
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

2-SIGNATURE FORM/PICK-UP CHECKLIST

- ☐ DRUMS REQUESTED FOR PICKUP/PRESENT MATCHES MANIFEST
- ☐ HAZARD CODES ARE CORRECT FOR EACH WASTE STREAM
- ☐ PACE REPRESENTATIVE AND TRANSPORTER SIGNATURE PRESENT

35 DAYS FROM PICKUP DATE: _____

If the three signature page has not been received within 35 days, contact the disposal facility to determine where the shipment is and request a copy of the three signature page.

If the three signature page has not been received within 45 days, you are required to file an exception report with the local regulating authority.

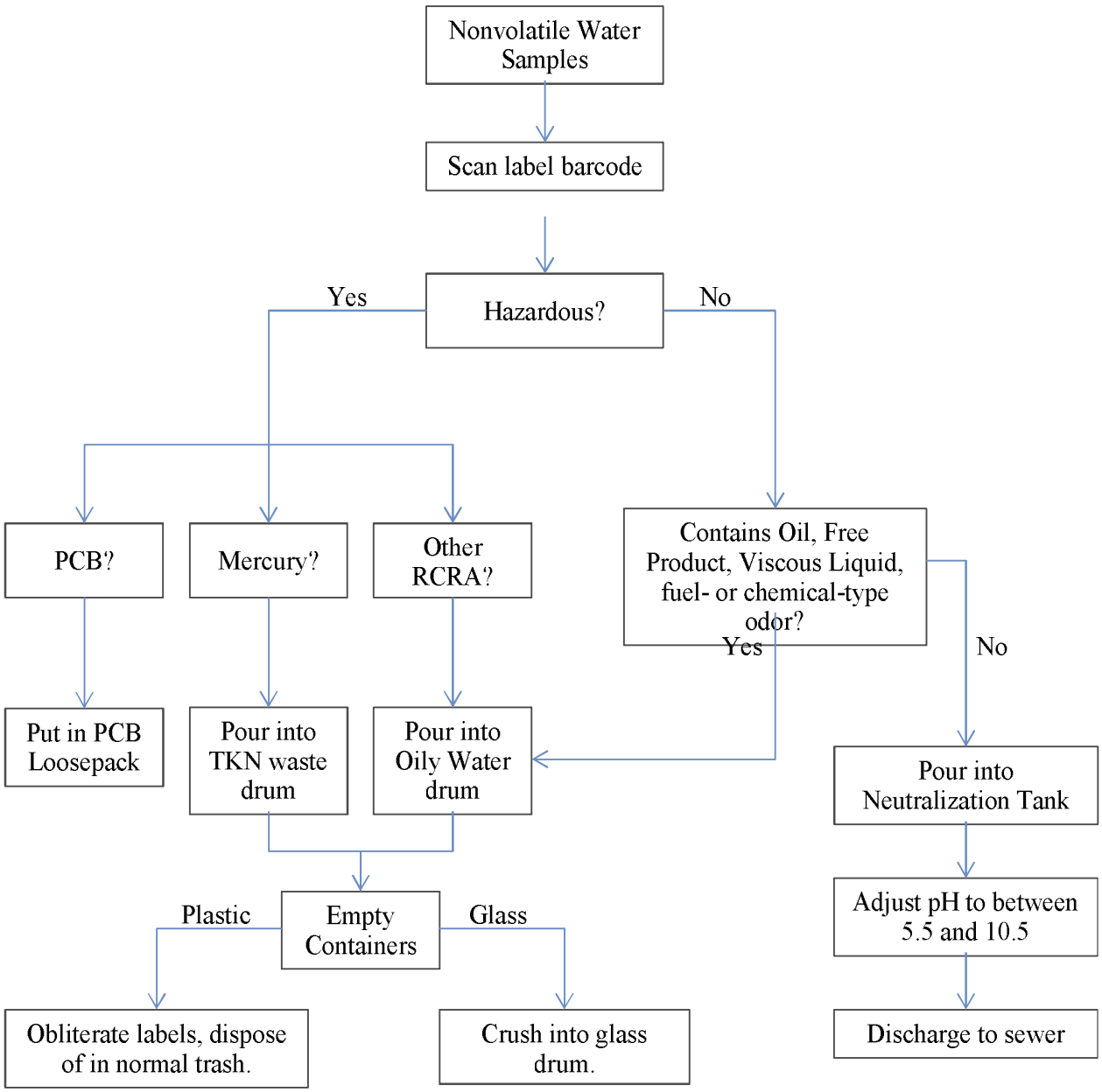
ALL 3-SIGNATURE MANIFEST(S) RECEIVED DATE_____

- ☐ FILE COVER SHEET, 3-SIG AND 2-SIG FORMS TOGETHER IN FOLDER, BINDER OR BY PAPER-CLIP. RETAIN FOR AT LEAST 3 YEARS

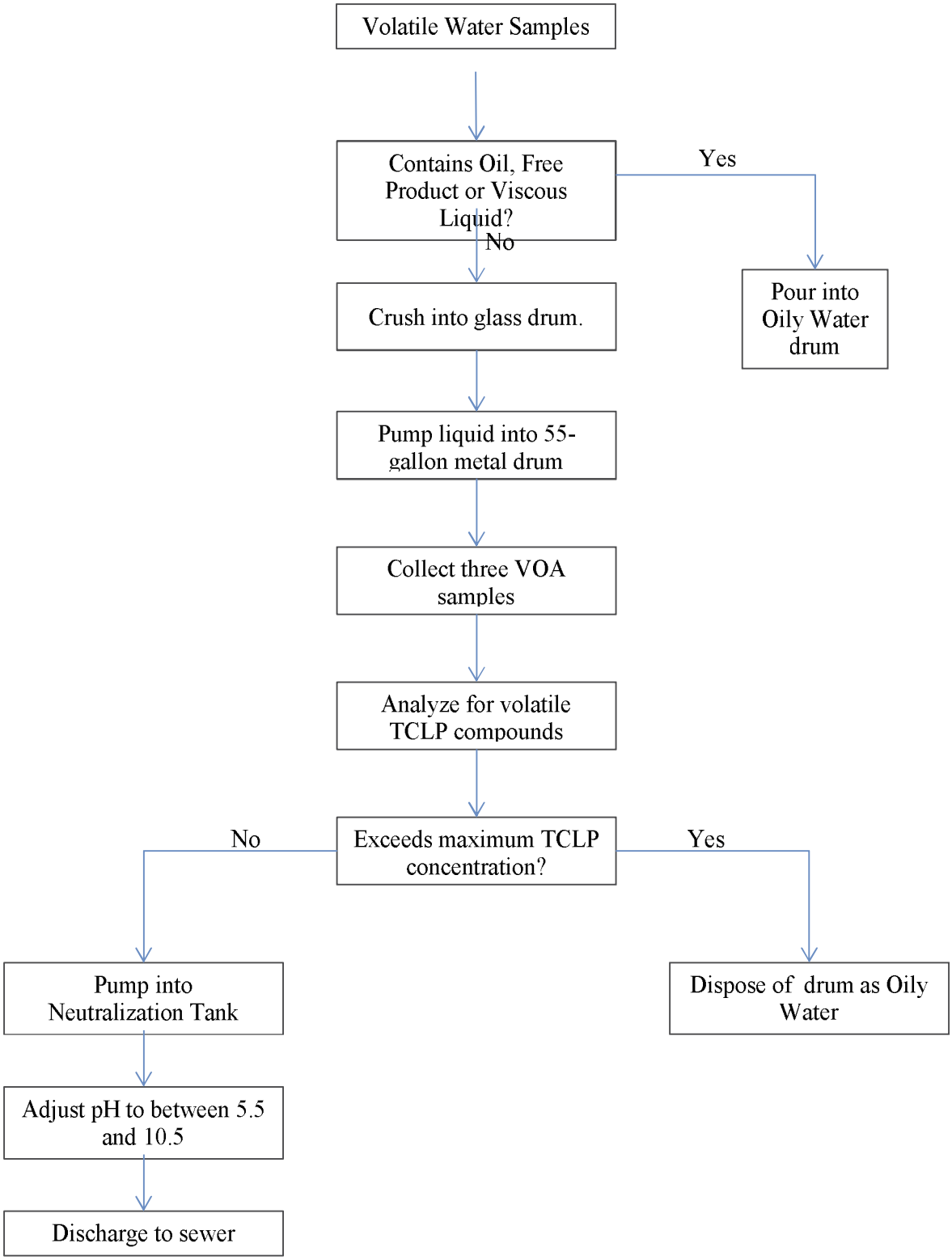
WASTE COORDINATOR:_____

DATE COMPLETED:_____

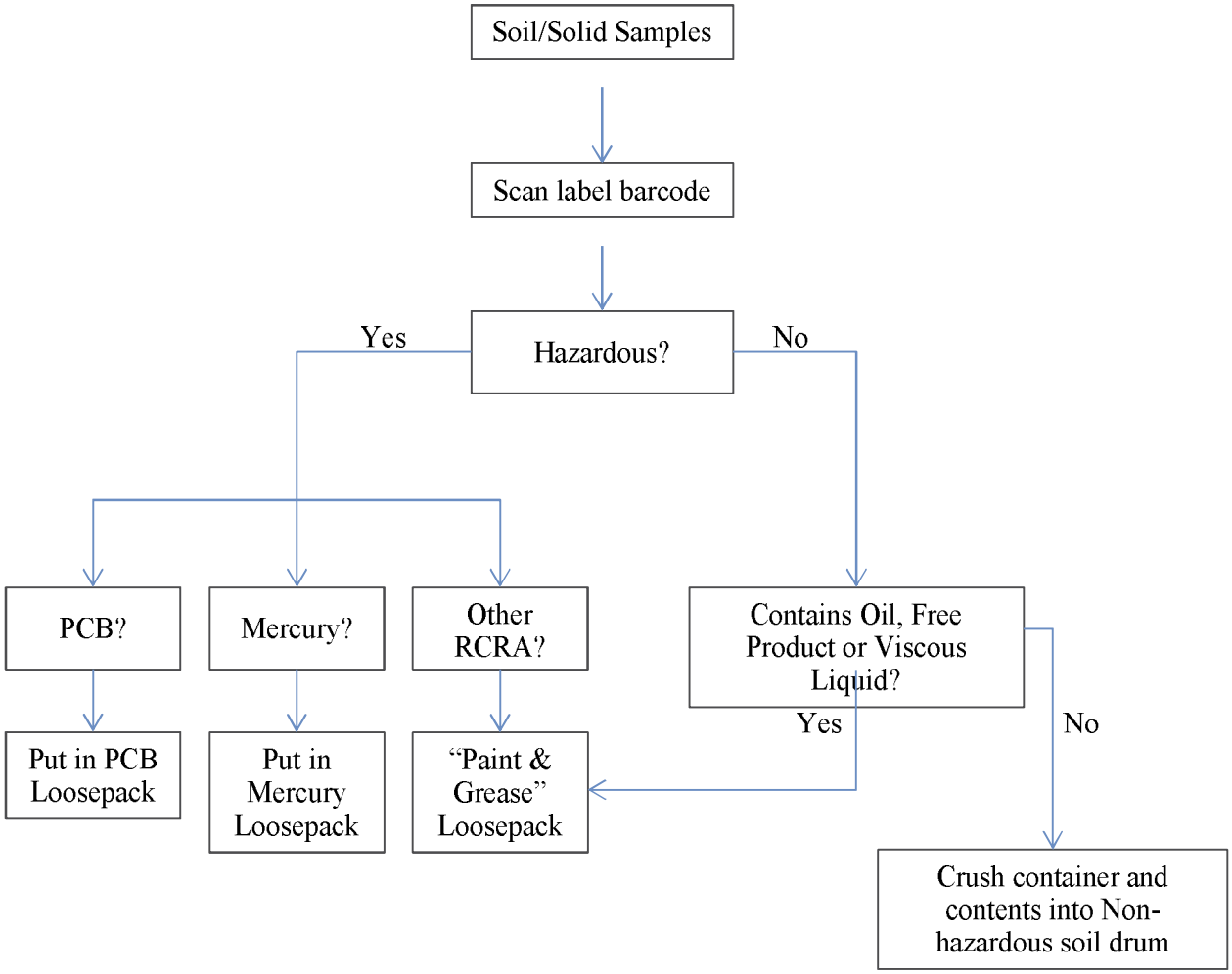
Attachment IX: Nonvolatile Water Sample Disposal Process



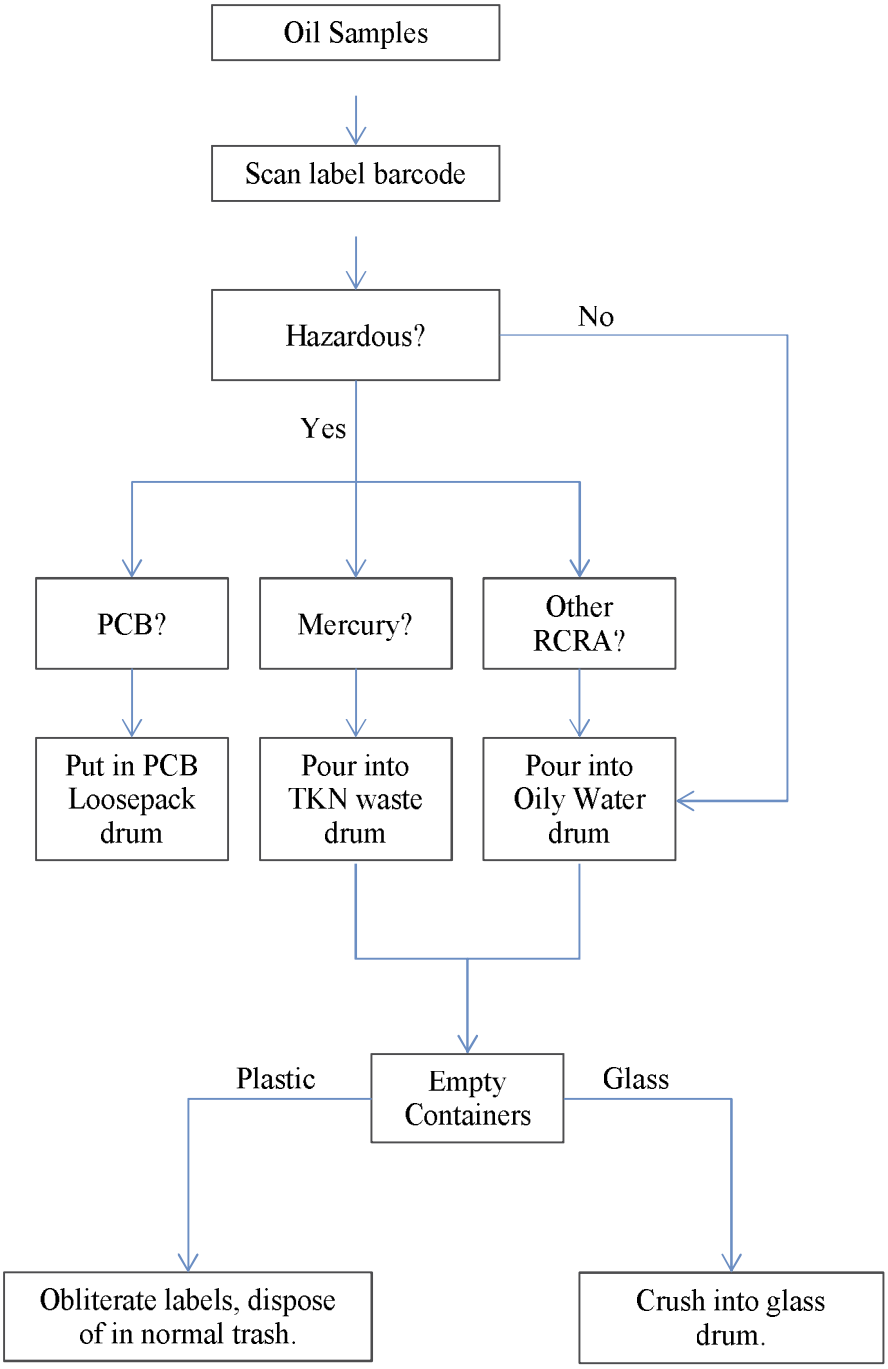
Attachment X: Volatile Water Sample Disposal Process



Attachment XI: Soil Sample Disposal Process


Soil/Solid Samples
Scan label barcode
Hazardous?
Yes
No
PCB?
Mercury?
Other RCRA?
Contains Oil, Free Product or Viscous Liquid?
Yes
No
Put in PCB Loosepack
Put in Mercury Loosepack
"Paint & Grease" Loosepack
Crush container and contents into Non-hazardous soil drum

Attachment XII: Oil Sample Disposal Process



Document Information

Document Number: ENV-SOP-LENE-0039 **Revision:** 02

Document Title: Separatory Funnel Extraction

Department(s): Organic Prep

Previous Document Number: S-KS-O-029-rev.09

Date Information

Effective Date: 22 Jan 2019

Next Review Date: 22 Jan 2021 **Last Review Date:**

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-LENE-0039 **Revision:** 02
Title: Separatory Funnel Extraction

All dates and times are in Central Time Zone.

ENV-SOP-LENE-0039 L/L Extraction

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Gregory Busch (003971)	Quality Manager	16 Jan 2019, 05:09:48 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Charles Girgin (002243)	General Manager	17 Jan 2019, 07:39:47 AM	Approved
Harry Borg (005736)	Manager - Lab Services	21 Jan 2019, 02:39:17 PM	Approved

1. Purpose/Identification of Method

1.1. The purpose of this SOP is to provide a laboratory specific procedure for extracting non-volatile and semi-volatile organic compounds from aqueous samples in a separatory funnel while meeting the requirements specified in EPA Method 3510C.

2. Summary of Method

2.1. A measured volume of sample (usually about 1L for regular volume, 500ml for Kansas TPH and about 100mL for reduced volume) is serially extracted with solvent in a separatory funnel. Some extractions also require the monitoring and adjusting of the pH of the sample. The extract is separated from the sample and is concentrated, followed by cleanup or analysis.

3. Scope and Application

3.1. Personnel: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method or non-analytical process.

3.2. Parameters: This SOP applies to the extraction from aqueous samples of semivolatile compounds (BNAs), PCBs, Chlorinated hydrocarbons and petroleum hydrocarbons.

4. Applicable Matrices

4.1. This SOP is applicable to most water samples. Common matrices are ground and surface water, wastewater, and other aqueous samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix-related modifications must be documented within the analytical data.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Solvents, reagents and glassware can all contribute to compound artifacts or raised baselines; both conditions that can affect chromatography. Analyzing method blanks is therefore crucial in determining the presence of contaminants.

6.2. Phthalate esters are common contaminant products in many products in the lab. All plastic products should be avoided when performing this method.

7. Sample Collection, Preservation, Shipment and Storage

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	1 liter with a minimum of 100 mL. Amber glass container with Teflon-lined lid (preferably widemouth).	Refer to determinative method.	≤6°C (not frozen)	Extract within 7 days of collection. Kansas TPH 14 days after collection PCB only: Extract within 1 year from collection.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

9. Equipment and Supplies

Table 9.1 Equipment and Supplies

Supply	Vendor	Model / Version	Comments
N-EVAP™	Organomation Associates	112	Nitrogen Evaporator
S-EVAP™	Organomation Associates	120	Solvent Evaporator
TurboVap®	Biotage	TurboVap® II	Six place concentration work station
200mL Tube w/ 1.0mL stem	Biotage	TurboVap® II / 45817	TurboVap® sample stem tube
Clear Bath®	Fisher	105535 / 15-459-20	Water treatment for TurboVap
Shaker table	Eberbach	6010	
3-D Floor Shaker	Glas-Col, LLC	099A VS5504	
Analytical Balance	Ohaus	SP202	Capable of measuring ±0.01g
Boiling Chips	Fisher	09-191-20	PTFE
Concentrator tubes	Fisher	K570051-1025	10-mL capacity
Funnels	Fisher	10-371C	HDPE
Glass beakers	Fisher	02-539K	Kimax; 250-mL.
Pasteur pipettes	Fisher	22-378-893	5.75”
Screw Top Glass Vials	Fisher	Various	1 mL, 4 mL, 12 mL,
Separatory Funnels	Fisher	10-437-25E	2-L, PTFE
Separatory Funnels	Fisher	10-437-25B	250-mL, PTFE
Test tubes	Fisher	14-959-35AA	16x100mm, threaded w/marking spot
Autosampler vials	Fisher	03-391-9	Fisher Brand; ~2mL, amber glass.
Micro-syringes	Fisher	Various	Hamilton; gas-tight, various sizes.
Funnels	Fisher	10-371C	Polypropylene
Graduated cylinders	Fisher	Various	Class A, 1000-, 250-, 100-mL.
Kuderna-Danish (K-D) flasks	Fisher	NC9599012	500-mL with ground glass joints.
K-D concentrator tubes	Fisher	K570012-0500	with ground glass fitting.
Snyder columns	Fisher	K503000-0121	3-ball variety.
Keck clip	Fisher	05-880D	For securing K-D joints
Filter paper	Fisher	09-790-12G	P-8
pH paper	Fisher	Type CF / 09-876-17	Whatman; 0-14 range.
Glass stirring rods	Fisher	11-380D	For breaking up emulsions.

10. Reagents and Standards

Table 10.1 Reagents and Standards

Reagent/Standard	Concentration/ Description	Vendor/ Item #
Acetone	Fisher Optima™ grade	Fisher / A929
Hexane	Fisher Optima™ grade	Fisher / H303
Methylene chloride	Fisher Optima™ grade	Fisher / D151
Methanol	Fisher Optima™ grade	Fisher / A454
Reagent water	ASTM Type II water	SOP S-KS-Q-011 (latest revision)
Sodium chloride	USP/FCC	Fisher / S640
Sodium hydroxide pellets	ACS Reagent grade	Fisher/ S318
Sodium sulfate, anhydrous	ACS Reagent grade	Fisher / S415
Sulfuric acid solution	1:1 solution; Ricca Chemical	Fisher / 8180-16

10.1. Sodium hydroxide solution (10N)

10.1.1. Dissolve 40g of sodium hydroxide pellets in 100 mL of reagent water.

11. Calibration and Standardization

11.1. The analytical balance used during this procedure must be calibrated prior to use each day. Refer to the current revision of *Support Equipment* (S-ALL-Q-013).

12. Procedures

12.1. **Extraction of Regular Volume (>100mL) Samples**

12.1.1. Inspect all required glassware to ensure it is clean and undamaged.

12.1.2. If the glassware is wet rinse first with methanol, this step is not necessary if the glassware is already dry. Then rinse the glassware three rinses with methylene chloride followed by a final rinse with methanol.

12.1.3. Allow the samples to warm to room temperature. Prepare two additional sample aliquots to serve as an MS and MSD.

12.1.4. Prior to measurement of the water sample volume, perform a visual inspection of the sample. There are three different sample types that you are likely to encounter:

- Sample with minimal sediment content.
- Sample with more than one-quarter inch of sediment on the bottom of the container.
- Bi-phasic or multi-phasic sample containing two or more layers.

12.1.5. Water sample with minimal sediment

12.1.5.1 Mark the level of sample on the outside of the bottle with a marker, briefly shake each sample to re-suspend settled solids and pour the sample into the 2-L separatory funnel (if the sample volume is ≤500 mL, then adjust to 1-L with reagent water). Kansas TPH uses 500ml for all samples and QC.

- **NOTE:** If only a portion of the contents of the sample container is going to be extracted, and not the entire contents of the sample container, then briefly shake the container to homogenize the contents and measure the portion used in a graduated cylinder.

12.1.5.2 Pipet 1.0 mL of the appropriate surrogate spiking solution into the sample bottle for Method 3510 and spike into the separatory funnel for EPA 625.1 and 608.3 (also add 1.0 mL of the matrix spiking standard if this is a matrix spike).

- Use this step only if catechol, 3- or 4-methylcatechol are to be determined: Add sufficient sodium chloride (NaCl) to the 1 liter of sample to fully saturate the liquid (this will be approximately 300 grams of sodium chloride per liter of sample). There should be sufficient NaCl added such that, after shaking to dissolve, the separatory funnel still contains some NaCl crystals. If no NaCl crystals can be detected add more NaCl. This same process must be completed for the Blank, LCS, MS and MSD.
- Proceed to pH adjustment step.

12.1.5.3 Check and record the pH of any sample aliquots that will be analyzed for Methods 8082, 8270C and Kansas TPH by removing a few drops with a disposable pipette for application to pH strips. Refer to Tables in section 24 for the proper extraction pH.

12.1.5.4 Adjust and record sample aliquot pH (if necessary) with 1:1 sulfuric acid solution or 10N sodium hydroxide solution.

12.1.5.5 Add 60 mL of methylene chloride to the sample container, cap, and briefly shake. Transfer the solvent to the 2-L separatory funnel.

- **NOTE:** If only a portion of the contents of the sample container was measured out in a graduated cylinder, and not the entire contents of the sample container, then add 60 mL of methylene chloride to the graduated cylinder by pouring down the side while rotating the cylinder.

12.1.5.6 Refill the sample bottle to the mark with water and then measure the volume of sample that was in the bottle with a graduated cylinder.

12.1.5.7 Proceed with further procedures as described in sections 12.1.8 through 12.1.12

12.1.6. Water sample with more than one-quarter inch of sediment

12.1.6.1 Immediately notify your Supervisor and the Project Manager to determine if the sediment must be analyzed separately.

12.1.6.2 Carefully decant the water from the container to the 1-L graduated cylinder ensuring minimal sediment is transferred.

12.1.6.3 Record the volume at the bottom of the meniscus up to a maximum volume of 1-L. and pour the sample into the separatory funnel (if the sample volume is ≤500 mL, then adjust to 1-L with reagent water, with the exception of the Kansas TPH method leave all at 500ml).

12.1.6.4 Pipet 1.0 mL of the surrogate spiking solution into the graduated cylinder for Method 3510 and spike into the separatory funnel for EPA 625.1 and 608.3 (also add 1.0 mL of the matrix spiking standard if this is a matrix spike).

- Use this step only if catechol, 3- or 4-methylcatechol are to be determined: Add sufficient sodium chloride (NaCl) to the sample to fully saturate the liquid (this will be approximately 300 grams of sodium chloride per liter of sample). There should be sufficient NaCl added such that, after shaking to dissolve, the separatory funnel still contains some NaCl crystals. If no NaCl crystals can be detected add more NaCl. This same process must be completed for the Blank, LCS, MS and MSD.
- Proceed to pH adjustment step.

12.1.6.5 Check and record the pH of any sample aliquots that will be analyzed for Methods 8082, or 8270C by removing a few drops with a disposable pipette for application to pH strips. Refer to Tables in section 24 for the proper extraction pH.

12.1.6.6 Adjust and record sample aliquot pH (if necessary) with 1:1 sulfuric acid solution or 10N sodium hydroxide solution.

12.1.6.7 Add 60 mL of methylene chloride to the graduated cylinder by pouring down the side while rotating the cylinder. Finally, transfer the solvent to the separatory funnel.

12.1.6.8 Proceed with further procedures as described in sections 12.1.8 through 12.1.12

12.1.7. Bi-phasic or multi-phasic sample

12.1.7.1 Immediately notify your Supervisor and Project Manager and determine which phase(s) is to be tested.

12.1.7.2 Carefully pour the sample from the container to a pre-rinsed 2-L separatory funnel. For the bi-phasic sample, the top layer will typically contain the lower density organics and the lower layer the aqueous. If more than one phase is present, a series of miscibility evaluations may be necessary in order to determine the phase types present.

12.1.7.3 Drain the lower or aqueous phase into the 1-L graduated cylinder, record the volume to the bottom of the meniscus and pour the sample into the separatory funnel (if the sample volume is ≤500 mL, then adjust to 1-L with reagent water).

12.1.7.4 . Pipet 1.0 mL of the surrogate spiking solution into the sample (also add 1.0 mL of the matrix spiking standard if this is a matrix spike).

- Use this step only if catechol, 3- or 4-methylcatechol are to be determined: Add sufficient sodium chloride (NaCl) to fully saturate the liquid (this will be approximately 300 grams of sodium chloride per liter of sample). There should be sufficient NaCl added such that, after shaking to dissolve, the separatory funnel still contains some NaCl crystals. If no NaCl crystals can be detected add more NaCl. This same process must be completed for the Blank, LCS, MS and MSD.
- Proceed to pH adjustment step.

12.1.7.5 Check and record the pH of any sample aliquots that will be analyzed for Methods 8082, or 8270C by removing a few drops with a disposable pipette for application to pH strips. Refer to Tables in section 26 for the proper extraction pH.

12.1.7.6 Adjust and record sample aliquot pH (if necessary) with 1:1 sulfuric acid solution or 10N sodium hydroxide solution.

12.1.7.7 Add 60 mL of methylene chloride to the graduated cylinder by pouring down the side while rotating the cylinder. Finally, transfer the solvent to the 2-L separatory funnel.

12.1.7.8 From the first 2-L separatory funnel used, drain the remaining top layer or organic phase into the original sample container and cap.

12.1.7.9 Proceed with further procedures as described in sections 12.1.8 through 12.1.12

12.1.8. Add (2) 1-L aliquots of reagent water to separatory funnels to serve as the Method Blank and LCS. Add 1.0 mL of the surrogate spiking solution to the MB and LCS and 1.0 mL of the matrix spiking standard to the LCS. Adjust and record pH's (if necessary) with 1:1 sulfuric acid solution or 10N sodium hydroxide solution and add 60 mL of methylene chloride to each.

12.1.9. Shake each sample by hand for approximately 10-30 seconds with periodic venting into a hood to release gas pressure.

12.1.10. Extract the sample by shaking the funnel for three minutes on the 3-D Floor Shaker at 150 rpm for the 2 liter separatory funnels and 170 rpm for the 250 ml separatory funnels. Allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means.

12.1.11. Drain the methylene chloride extract through a funnel containing filter paper and sodium sulfate into a Kuderna-Danish/ concentrator tube setup.

12.1.12. Add a second 60-mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the K-D flask. Perform a third extraction in the same manner.

12.2. **Extraction of TCLP/SPLP Leachates**

12.2.1. Inspect all required glassware to ensure it is clean and undamaged.

12.2.2. If the glassware is wet rinse first with methanol, this step is not necessary if the glassware is already dry. Then rinse the glassware three rinses with methylene chloride followed by a final rinse with methanol.

12.2.3. Allow the leachates to warm to room temperature. The leachates are collected in 500 mL amber glass bottles; only 100 mL is used for extraction, with the remainder of the leachate held in reserve and for QC samples.

12.2.4. Place 250-mL separatory funnels onto a ring stand and label appropriately, allowing one funnel for each sample leachate and one each for the MB, LCS, MS.

12.2.5. Pour 100 mL of the TCLP (or SPLP) Extraction Fluid (same lot as was used to leach the samples) into the separatory funnels marked MB and LCS. Note: Since the sample leachate bottle contains more volume than is processed, spiking cannot be done into those bottles.

12.2.6. Pour 100 mL of each sample leachate into its respective separatory funnel and 100 mL of the sample leachate selected for spiking into the separatory funnel labeled MS.

12.2.7. Inject 1.0 mL of TCLP surrogate spiking solution into all sample leachates, MB, LCS, and MS.

12.2.8. Inject 1.0 mL of TCLP matrix spiking standard into the separatory funnels labeled LCS and MS.

12.2.9. Check and record the pH of all leachates and QC samples. Adjust and record pH's to <2 with 1:1 sulfuric acid solution (approx. 1-2 mL)

12.2.10. Add 60 mL of methylene chloride to each 100-mL graduated cylinder used to measure samples by pouring down the side while rotating the cylinder then transfer to the respective separatory funnel.

12.2.11. Shake each sample by hand for approximately 30 seconds with periodic venting into a fume hood to release gas pressure.

12.2.12. Extract the sample by shaking the funnel for three minutes on the 3-D Floor Shaker at 170 rpm. Allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means.

12.2.13. As a backup option the separatory funnels may be placed on the shaker table and shake on low setting for 3 minutes.

12.2.14. Return separatory funnels to the ring stands and allow the organic layer to separate.

12.2.15. If an emulsion layer is still present after 10 minutes, gently knock the outside of the separatory funnel with a small aluminum rod, or centrifuge the samples in 40-mL VOA vials.

12.2.16. Drain the methylene chloride extract through a funnel containing filter paper and sodium sulfate into a Kuderna-Danish/concentrator tube setup.

12.2.17. After draining the samples, rinse the sodium sulfate in each funnel with approx. 10-15 mL of methylene chloride.

12.2.18. Add a second 60-mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the K-D flask. Perform a third extraction in the same manner.

12.2.19. Using 10N NaOH, adjust and record the pH to >11 on all samples.

12.2.20. Serially extract three times with 60 mL of methylene chloride, as outlined in Section 12.2.17.

12.3. **Extraction of Reduced Volume (≤100mL) Samples**

12.3.1. Inspect all required glassware to ensure it is clean and undamaged.

12.3.2. If the glassware is wet rinse first with methanol, this step is not necessary if the glassware is already dry. Then rinse the glassware three rinses with methylene chloride followed by a final rinse with methanol.

12.3.3. Allow the samples to warm to room temperature. Prepare two additional sample aliquots to serve as an MS and MSD.

12.3.4. Prior to measurement of the water sample volume, perform a visual inspection of the sample. There are three different sample types that you are likely to encounter:

- Sample with minimal sediment content.
- Sample with more than one-quarter inch of sediment on the bottom of the container.
- Bi-phasic or multi-phasic sample containing two or more layers.

12.3.5. <u>Water sample with minimal sediment</u>

12.3.5.1 Mark the level of sample on the outside of the bottle with a marker, briefly shake each sample to re-suspend settled solids. Pipet 1.0 mL of the appropriate surrogate spiking solution into the sample (also add 1.0 mL of the matrix spiking standard if this is a matrix spike). Spike Method 625 and 608 samples into the separatory funnel containing the sample.

12.3.5.2 Pour the sample (or sample with spikes) into the 250-mL separatory funnel (if the sample volume is ≤50 mL, then adjust to 100 mL with reagent water).

12.3.5.3 Add 15 mL of methylene chloride to the sample container, cap, and briefly shake. Transfer the solvent to the 250-mL separatory funnel.

12.3.5.4 Refill the sample bottle to the mark with water and measure the volume of sample that was in the bottle with a graduated cylinder.

12.3.5.5 Proceed with further procedures as described in sections 12.3.8 through 12.3.12

12.3.6. <u>Water sample with more than one-quarter inch of sediment</u>

12.3.6.1 Immediately notify your Supervisor and the Project Manager to determine if the sediment must be analyzed separately.

12.3.6.2 Carefully decant the water from the container to a 100-mL graduated cylinder ensuring minimal sediment is transferred.

12.3.6.3 Record the volume at the bottom of the meniscus.

12.3.6.4 Pipet 1.0 mL of the surrogate spiking solution into the graduated cylinder (also add 1.0 mL of the matrix spiking standard if this is a matrix spike) and pour the sample into the separatory funnel (if the sample volume is ≤50 mL, then adjust to 100 mL with reagent water).

12.3.6.5 Add 15 mL of methylene chloride to the graduated cylinder by pouring down the side while rotating the cylinder. Finally, transfer the solvent to the separatory funnel.

12.3.6.6 Proceed with further procedures as described in sections 12.3.8 through 12.3.12

12.3.7. Bi-phasic or multi-phasic samples

12.3.7.1 Immediately notify your Supervisor and Project Manager and determine which phase(s) is to be tested.

12.3.7.2 Carefully pour the sample from the container into a 250-mL separatory funnel. Bi-phasic samples will typically have the lower-density organics in the top layer and the lower layer will be aqueous. If more than one phase is present, a series of miscibility evaluations may be necessary in order to determine the phase types present.

12.3.7.3 Drain the lower or aqueous phase into the 250-mL graduated cylinder, record the volume to the bottom of the meniscus and pour the sample into the separatory funnel (if the sample volume is ≤50 mL, then adjust to 100 mL with reagent water).

12.3.7.4 Pipet 1.0 mL of the surrogate spiking solution into the sample (also add 1.0 mL of the matrix spiking standard if this is a matrix spike).

12.3.7.5 Add 15 mL of methylene chloride to the graduated cylinder by pouring down the side while rotating the cylinder. Finally, transfer the solvent to the separatory funnel.

12.3.7.6 From the first 250-mL separatory funnel used, drain the remaining top layer or organic phase into the original sample container and cap.

12.3.7.7 Proceed with further procedures as described in sections 12.3.8 through 12.3.12

12.3.8. Add (2) 100-mL aliquots of reagent water to separatory funnels to serve as the Method Blank and LCS. Add 1.0 mL of the surrogate spiking solution to the MB and LCS and 1.0 mL of the matrix spiking standard to the LCS. Add 15 mL of methylene chloride to each.

12.3.9. Shake each sample by hand for approximately 10-30 seconds with periodic venting into a hood to release gas pressure.

12.3.10. Extract the sample by shaking the funnel for three minutes on the 3-D Floor Shaker at 170 rpm. Allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means.

12.3.11. As a backup option the separatory funnels may be placed on the shaker table and shake on low setting for 3 minutes. (For reduced volume OA2 samples and QC, shake all separatory funnels for an additional 1 minute by hand after the table shake.)

12.3.12. Allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include: stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means.

12.3.13. Drain the methylene chloride extract through a funnel containing filter paper and sodium sulfate into a Kuderna-Danish/ concentrator tube setup for reduced volume 8270SIM samples. (Use TurboVap tubes for reduced volume OA2, 8015, and MO TPH-DRO/ORO samples.)

12.3.14. Add a second 15-mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the K-D flask or TurboVap tube. Perform a third extraction in the same manner.

12.4. **Extract Concentration (Kuderna-Danish Method)**

12.4.1. Quantitatively transfer the extract to a Kuderna-Danish (K-D) flask, fitted with a concentrator tube, and add 1-2 clean boiling chips. Attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL methylene chloride to the top.

12.4.2. Place the K-D apparatus on a hot water bath (~70°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 20 to 25 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 4 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 minutes. **Note: The K-D temperature range should be set between 60 to 80 degrees with a target of 70 degrees C. At the target range of 70 the concentrator balls should have sufficient chatter and not be flooding. If there is not sufficient chatter or the balls are flooding contact the appropriate supervisor for guidance.**

12.4.3. Rinse the Snyder column with 2-3 mL of the final solvent while rotating the KD apparatus 360°. Remove the Snyder column and rinse the K-D flask and its upper and lower joints into the concentrator tube with 1 to 2 mL of the final solvent.

12.4.4. If a solvent exchange is required (as indicated in Tables in section 26):

- concentrate the extract to approximately 10 mL and add 10 mL of hexane,
- repeat the process of concentration and exchange solvent addition,
- concentrate to approximately 10ml and move to final extract concentration step (N-

EVAP)

12.5. **Final Extract Concentration (N-EVAP)**

12.5.1. Place the concentrator tube in a warm water bath (~35°C) and further evaporate the solvent volume to approximately ½ of the target final volume (Tables in section 24) with a gentle stream of nitrogen. The extract must never be allowed to become dry. If it does, contact your supervisor immediately.

12.5.2. Rinse down sides of concentrator tube with extract and transfer to final vial type (2ml or 10ml) as appropriate for the target final volume. Add more final solvent to the concentrator tube and again rinse the sides and transfer this to the final vial type (try to keep original extract and extra solvent below final solvent volume. Adjust final extract volume to the appropriate volume by either adding more solvent or using N-EVAP to blow down to final volume is you over shot the true final volume. (It is critical that this volume is precise)

12.5.3. If the final extract will not be analyzed immediately, it must be stored in accordance with the determinative method.

12.6. **TurboVap Extract Concentration**

12.6.1. The concentrator tubes are rinsed with methylene chloride prior to use.

12.6.2. Verify that the TurboVap temperature bath is set at 40°C (This should always remain at 40°C on each TurboVap). The TurboVaps should be turned on first thing in the morning if they are going to be used during the dayshift, so the water can get equilibrated to 40°C.

12.6.3. The TurboVap temperature must be recorded on the laboratory bench sheet.

12.6.4. While under the fume hood, quantitatively transfer the entire sample extract into a labeled TurboVap tube (Take care as not to fill the tube full, it must have at a minimum 1 ¾ inch of head space. This will insure that during the Turbovap process splashing and cross contamination does not occur.) Note: Do not pour sample extract into the tubes while they are in the TurboVap.

12.6.5. Ensure that the nitrogen flow has been shut off using the nitrogen cylinder gas regulator knob.

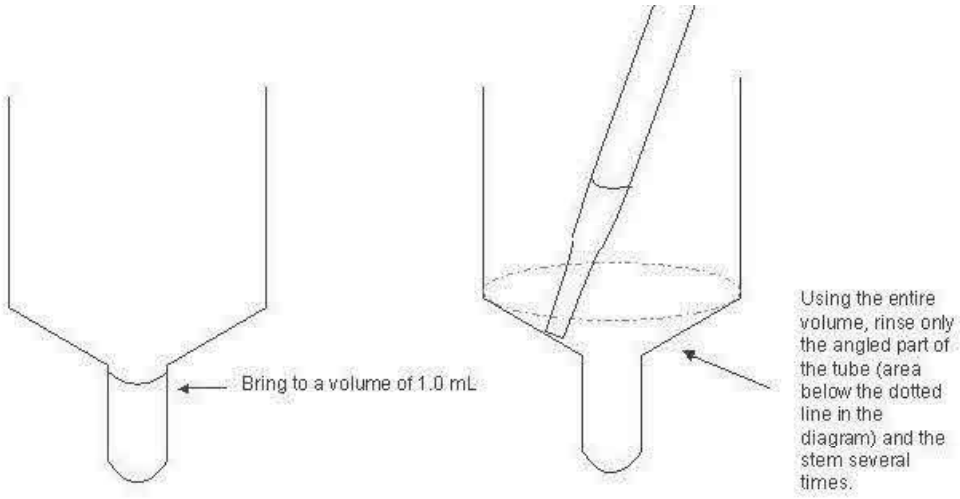
12.6.6. Place tubes into the TurboVap and close the lid.

12.6.7. Slowly turn on the nitrogen tank regulator. Start each TurboVap cell that has a sample in it. Check the pressure of each cell, they should be between 17-20 PSI (if these are not within this range contact your supervisor). Then verify that the timer on each TurboVap is set to 20 minutes. 20 minutes is a nominal time for the solvent methylene chloride to concentrate at our current volumes) If lower volumes are used, the timer times must be re-verified and changed if needed. Note: This is a very critical step. The nitrogen is creating a vortex shearing along the sides of the TurboVap tube. This facilitates rinsing of the tube walls as the sample concentrates, which results in better recoveries of analytes.

12.6.8. When the 20 minute timer sounds, you must check the volume in the TurboVap tubes and from this point on you must not leave unattended. It is important to remove the tubes when the volumes get just below the expected final volumes. The majority of these final volumes is 1ml and methylene chloride will evaporate rapidly in the TurboVap below this level. This may cause extract to go dry or extremely low, which will result in low analyte recoveries.

12.6.9. Using a 9" disposable pipette, add enough fresh solvent to bring the sample to the 1.0 mL mark by rinsing down the side walls of the TurboVap tube in a swirling motion at the point just above where the tube narrows.

12.6.10. Take the entire 1.0 mL sample into the pipette and rinse the same lower portion of the TurboVap tube (see diagram below).



12.6.11. Repeat the above technique two more times. By the time you are done, the 1.0 mL extract will have evaporated to about 0.5 mL.

12.6.12. Transfer the extract into the appropriate vial. Take small volume of solvent and rinse bottom of TurboVap tube and put this into vial (try to keep final volume at or below required amount). Adjust final extract volume to the appropriate volume by either adding more solvent or using N-EVAP to blow down to final volume is you over shot the true final volume. (It is critical that this volume is precise)

12.6.13. Securely tighten the sample extract cap and store all extracts according to the determinative method.

12.7. **TurboVap Maintenance**

12.7.1. TurboVap Sensors

12.7.1.1 The sensors in the TurboVap are optical sensors and have a life expectancy of about one year with average use and six to nine months for labs that may be operating two shifts daily.

12.7.1.2 To prolong the life of the sensors, keep the water bath clean (see below).

12.7.1.3 If you believe the sensors are failing, follow the sensor diagnostics in your Operator's Manual. As routine maintenance, the sensor diagnostics should be done periodically to confirm proper operation.

12.7.2. TurboVap Water Bath

12.7.2.1 Replace the water in the bath every two months or if it becomes cloudy.

12.7.2.2 Place a TurboVap tube in five positions.

12.7.2.3 Pour about 1 liter of deionized water (do not use tap water) through the empty position.

12.7.2.4 Add 15 drops of Clear Bath

12.7.2.5 Add more deionized water until the water's surface is as high as the usual initial solvent level in the tube.

13. Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Matrix-specific; applicable solvent for concentrated waste sample or clean gauze wipes for wipe samples	One per batch of up to 20 samples	Target analytes must be less than reporting limits If results are reported to MDL, the MB must be evaluated to the MDL.	1) Re-analyze blank to confirm failure. 2) Qualify results and / or reanalyze associated samples. ***Exceptions:*** 1) If sample ND, report sample without qualification 2) If sample result >10x MB report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted of this condition. 4) If sample results are reported to MDL and MB is <RL but >MDL, then corrective action is not necessary other than appropriately qualifying the sample results. Unless the customer's QAPP or technical specification instruct to do otherwise.
Laboratory Control Sample (LCS) **Kansas TPH method requires a Laboratory Control Sample Duplicate (LCSD)**	Matrix-specific; applicable solvent for concentrated waste sample or clean gauze wipes for wipe samples spiked with standard	One per batch of up to 20 samples	See analytical SOPs	1) Reanalyze the LCS to confirm failure 2) Reanalyze associated samples. 3) Perform system maintenance 4) If problem persists, check spike solution ***Exceptions:*** 1) If LCS > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. 2) If LCS < QC limits and sample cannot be reanalyzed report sample with appropriate qualifier to indicate an estimated value. Client should be alerted to this condition.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Spike standard in client sample(s)	One set per batch of up to 20 samples	See analytical SOPs	No corrective actions necessary. If LCS recovery is in range, the system is considered valid and the out-of-control MS/MSDs are footnoted appropriately by the analyst.

Table 13.2 – Sample Quality Control Criteria

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Surrogate Standards	See analytical SOPs	Added to all samples, spikes, control samples and method blanks prior to extraction	See analytical SOPs	1) Assess impact of sample matrix 2) In the absence of obvious matrix interference, reanalyze sample. 3) If reanalysis confirms matrix interference, report most QC compliant data set with appropriate data qualifiers. ***Exceptions:*** 1) Surr. recovery above criteria and target compounds < RL, result may be reported with appropriate footnote. 2) Surr. recovery out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See Tables 13.1 and Table 13.2.

16. Corrective Actions for Out-of-Control Data

16.1. See Tables 13.1 and Table 13.2.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Tables 13.1 and 13.2. If there is no additional sample volume to perform re-analyses, if the analytical results are due to the customer, and/or if there is no more holding time remaining; then data will be reported as final with applicable qualifiers. If necessary, an official case narrative can be prepared by the Quality Manager or Project Manager.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. **Method Detection Limit (MDL) Study and Verification:** An MDL study must be performed annually for each sample preparation and analysis-method pair (e.g. Microwave/Method 8270C) on at least one instrument.

18.2.1. The MDL study must meet the criteria defined in ENV-SOP-LENE-0117, Limit of Detection and Limit of Quantitation (or its equivalent revision or replacement).

18.2.2. The calculated MDL must then be verified on every instrument that is to be used for analysis of samples and reporting of data.

18.2.2.1 Analyze a QC sample containing analytes at no more than 2-3X the MDL for single-analyte tests and 1-4X the MDL for multiple-analyte tests.

18.2.2.2 The QC sample must undergo the applicable sample preparation (e.g., silica gel cleanup).

18.2.2.3 All target compounds must be detected (result greater than zero) on all instruments to verify the calculated MDL.

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per ENV-SOP-LENE-0110, Training Procedures.

18.3.1. Extraction of four replicates of reagent water spiked with all analytes of interest at a concentration equivalent to the LCS.

18.3.2. If the average recovery is within the LCS criteria and the RSD of the replicates is <30%, system performance is acceptable and analysis of samples may begin. If, however, RSD >30% or average recovery falls outside LCS criteria, system performance is unacceptable. In this event, correct the problem and repeat the test.

19. Method Modifications

19.1. A salting-out procedure is used to when analyzing for catechols.

20. Instrument/Equipment Maintenance

20.1 Refer to the sections on specific equipment (Turbo Vap and N-Evap).

21. Troubleshooting

21.1 Refer to associated equipment manuals for any troubleshooting.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

23. Waste Management

23.1. Spent Samples

23.1.1. Spent aqueous samples are consolidated and taken to the Waste Disposal Room. In order to minimize methylene chloride vapors, a peristaltic pump is used to transfer to the Neutralization Tank.

23.1.2. Waste Disposal personnel will neutralize and discharge the waste.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (e.g., before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains information on pollution prevention.

25. References

25.1. Pace Quality Assurance Manual - most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. EPA Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Update III, 12/96, Method 3510C.

26. Tables, Diagrams, Flowcharts, and Validation Data

Table 26.1

Extraction Conditions for Various Methods (Regular ≥500mL Volume)

Method	Initial Extraction pH	Secondary Extraction pH	Exchange Solvent	Final Extract Volume (mL)
8015B/C	as received	N/A	N/A	5.0
8082	5-9	N/A	hexane	10.0
8270C	<2	>11	N/A	1.0
8270C (PAH SIM)	as received	N/A	N/A	1.0
OA-2	as received	N/A	N/A	5.0
Oklahoma DRO	as received	N/A	N/A	5.0
TCLP 8270C	<2	>11	N/A	1.0
MO TPH-DRO/ORO	as received	N/A	N/A	10.0
Kansas TPH	< 2	N/A	N/A	5.0
1,4-Dioxane (SIM)	< 2	N/A	N/A	1.0
8121 Chlorinated Hydrocarbons.	as received	N/A	hexane	10.0

Table 26.2

Extraction Conditions for Various Methods (Reduced 100mL Volume)

Method	Initial Extraction pH	Final Extract Volume (mL)
8015B/C	as received	1.0
8270C (PAH SIM)	as received	1.0
MO TPH-DRO/ORO	as received	1.0
OA-2	as received	1.0

27. Revisions

Document Number	Reason for Change	Date
S-KS-O-029-rev.0	New	October 8, 2007
S-KS-O-029-rev.1	Grammatical/Removal of outdated information.	September 18, 2009
S-KS-O-029-rev.2	Section 7 – Revised Distribution Section 10 - Removed spike and surrogate preparation. Section 12 - Removed reference to Method 8081. Samples to be spiked before addition of bottle rinsates.	January 26, 2011
S-KS-O-029-rev.3	Section 9 – Added TurboVap Section 12 – Added the TurboVap® II Extract concentration procedure Section 12.10 - removed 10 min. time limit, allow to separate before proceeding.	September 28, 2011
S-KS-O-029-rev.4	SOP – Deleted Responsibilities and Distribution section. Section 6 – Substituted reference to Quality Manual. Section 11 – Added spent sample disposal. Section 13 – Added LOD language.	November 4, 2011
S-KS-O-029-rev.5	General – Updated to latest prescribed format and combined reduced volume and regular volume extraction procedures into one SOP Section 7 – Removed analytical holding time. Section 12 – Revised criteria for sample volume adjustments. Added salting out procedure for catechols. Moved solvent exchange procedure to S-EVAP. Revised glassware rinsing procedure to match lab practice. Biphasic samples transferred to separatory funnels before surrogate spiking. Revised TurboVap instructions. 12.3.10 – Revised extraction of reduced volume to use table shaker instead of floor shaker and added extra hand shake out step for OA2 reduced volume 12.3.12 – Revised KD use for reduced volume SIM only. Other reduced volume analyses use TurboVap. Section 13 – Reworded tables for clarity Section 24 – Revised final volume to 1.0mL for reduced volume OA2, 8015, and MODRO	November 15, 2013
S-KS-O-029-rev.6	SOP -- Revised to latest prescribed format. 12.2.12- add floor shake r and make shaker table an option 12.3.10 – add floor shaker and make shaker table an option 12.4.2 – change K-D water batch to set 70 degrees 19.2 – add method modification to spike surrogates and spikes into separatory funnel and not container or grad cylinder.	March 2, 2015
S-KS-O-029-rev.7	Section 2.0 – Inserted "500ml for Kansas TPH" Sections 12.1.5 and 12.1.6 – Kansas TPH 500 mL volume added. Section 12.1.10 – Added rpm specifications. Added Headers of Table 26.1 and Table 26.2 Table 26.1 – Added Kansas TPH Method	April 15, 2016
S-KS-O-029-rev.8	Table 26.1 – Added 1,4-Dioxane (SIM)	November 08,2016
S-KS-O-029-rev.9	SOP – Cover page changed to Pace LLC. Section : 3.2 Added Chlorinated Hydrocarbons Table 26.1 – Added 8121, Chlorinated Hydrocarbons	April 16, 2018
ENV-SOP-LENE-0039-01	SOP – Removed Cover page, Table of Contents and headers Sections 12.1, 12.2 and 12.3 – Revised instruction for methanol rinse Section 18.2 – Revised SOP reference Section 18.3 – Revised SOP reference	November 2, 2018
ENV-SOP-LENE-0039-02	Section 12.1.5.2 – Revised to spike into the sample bottle. Section 12.1.6.4 – Revised to spike into the sample bottle Section 12.1.6.7 – Removed original section (transferring sediment into different container). Section 12.2.3 and 12.2.5 – Revised to add additional information Section 12.3.5 – Revised to spike into the sample bottle Section 12.3.6.5 – Removed original section (transferring sediment into different container). Section 19.2 – Removed method modification on spiking in separatory funnel.	January 9, 2019

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Notes

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Pace Analytical™

STANDARD OPERATING PROCEDURE

GASOLINE RANGE ORGANICS BY 8015

Reference Methods: SW-846, Methods 8015B/C

Local SOP Number:	S-KS-O-026-rev.6
Effective Date:	Date of Final Signature
Supersedes:	S-KS-O-026-rev.5

Approvals

Laboratory General Manager — Date: 10/31/17

Laboratory Quality Manager — Date: 10-27-17

Laboratory Organics Manager — Date: 10-27-17

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

S-KS-O-026-rev.6

TABLE OF CONTENTS

1. Purpose/Identification of Method

1.1. This Standard Operating Procedure (SOP) is applicable to the determination purgeable petroleum hydrocarbons in soil and water by Methods 8015B and 8015C.

2. Summary of Method

2.1. Volatile organic compounds are introduced into the gas chromatograph by a purge-and trap method. The analytes are purged from a sample aliquot or extract with helium and collected on a sorbent trap.

2.2. At the completion of the purge time, the trap is rapidly heated and backflushed with helium to drive the trapped analytes into the inlet of a capillary gas chromatography column. The analytes are separated on-column using a programmed temperature ramp.

2.3. All peaks eluting within a defined retention time range are identified as GRO and externally quantitated.

3. Scope and Application

3.1. Personnel: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method or non-analytical process.

3.2. Parameters: This method is designed to measure the concentration of gasoline range organics in water and soil. This corresponds to a hydrocarbon range of C6-C10 and a boiling range between approximately 60°C and 170°C. This range may be expanded when required by state-specific programs.

4. Applicable Matrices

4.1. This method is applicable to most water and solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, and other solid samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix-related modifications must be documented within the analytical data.

5. Limits of Detection and Quantitation

5.1. The reporting limits (LOQ) for gasoline range organics are listed in the table below. All current MDLs (LOD) are listed in the LIMS and are available by request from the Quality Manager.

Table 5.1 Limits of Quantitation (LOQs)

Analyte	Water (mg/L)	Soil (mg/kg)
Gasoline Range Organics	0.5	10.0
GRO (Arkansas)	0.20	0.40

6. Interferences

6.1. Impurities in the purge gas and organic compounds outgassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system should be avoided.

6.2. Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

6.3. Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

7. Sample Collection, Preservation, Shipment and Storage

Table 7.1- Sample Collection, Preservation, Shipment and Storage

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Two 40-mL VOA vials	Acidified w/ 1:1 HCl (1-2 drops) to pH<2, no headspace.	≤6°C	Unpreserved: 7 days pH Preserved: 14 days
Medium Level Aliquot Soil/Solid	One 2-4 oz. wide-mouth jar. *OR* One 5-g aliquot in vial with 5.0 mL purge and trap grade MeOH. *OR* One 5-g aliquot in empty vial.	Samples collected in wide-mouth jar or empty vials must be transferred into 5 mL of purge & trap grade MeOH within 48 hours of collection.	With methanol: ≤6°C	Unpreserved: 48 hours Preserved with methanol: 14 days

Table 7.2 - Trip Blank Requirements

Sample type	Sample Preservation	Trip Blank Type
Aqueous	Acidified w/ 1:1 HCl (1-2 drops) to pH<2, no headspace.	Two 40-mL vials per cooler - DI water acidified w/ 1:1 HCl (1-2 drops), no headspace.
	Unpreserved	Two 40-mL vials per cooler - DI water, no headspace.
Soil/Solid	Methanol Kit	One Methanol Kit per cooler.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

9. Equipment and Supplies

Table 9.1 – Equipment and Supplies

Supply	Vendor	Model / Version	Comments
Gas Chromatograph	Agilent	6890	or equivalent
Flame Ionization Detector	OI Analytical	4410	or equivalent
Data System	Thruput Systems, Inc.	Target, version 3.4	
Concentrator	Tekmar	3000	or equivalent
Autosampler	Archon	5100	or equivalent
Analytical Column	Agilent	DB-624	30m, 0.53mm, 3.0 um df
Sorbent Trap	Supelco	Vocarb 3000	Purge Trap K
Volumetric Flasks	Fisher	Class A	5mL, 10mL, 50mL, 100mL
Gas tight syringes	Hamilton	Series 1700	10-, 25-, 100-, 500-, 1000-uL

10. Reagents and Standards

Table 10.1 – Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date for unopened ampulated standards. ▪ Stock standards must be replaced six months after ampule is opened or on expiration date, whichever is sooner.	▪ Manufacturer's recommended storage conditions ▪ When standard is opened, record all information in the standard logbook.
Intermediate and Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ 1 month from preparation or the expiration date listed for the stock source, whichever is sooner. ▪ Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	▪ Store in amber vials with Teflon lined screw caps ▪ Manufacturer's recommended storage conditions for stock source solution. ▪ If stock source conditions conflict, store according to method requirements.

Table 10.2 – Reagents and Standards

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
4-Bromofluorobenzene	10 mg/mL	Restek / 30082
Air	Breathing grade	Praxair / AI-BR
Antifoam B® Silicone Emulsion	N/A	JT Baker / B531-05
Gasoline – Regular, Unleaded	20.0 mg/mL; Second-Source standard	Accustandard / GA-001-40X
Gasoline Standard	0.5-1.5 mg/mL; RT Marker	Accustandard / GRH-002S
Helium	4.6 Zero-grade	Praxair / HE 4.6Z
Hydrogen	5.0 Ultra-High Purity	Praxair / HY 5.0UH
Methanol	Purge and Trap grade	Fisher / A453
Ottawa sand	N/A	Fisher / S23
Reagent water	ASTM Type II, purged with inert gas	SOP S-KS-Q-011
Unleaded Gasoline Composite Standard	50.0 mg/mL; Primary standard	Restek / 30206
Retention Time Marker	1.0 mg/mL (C5,C6,C8,C10)	SPEX CertiPrep / VO-PCLKS-19

10.1. Surrogate Solution

10.1.1. The Surrogate Solution is added to all samples, quality control samples, and calibration samples. Prepare by adding 750 uL of 4-Bromofluorobenzene to a 10-mL volumetric flask and bringing to volume with P&T methanol. Transfer to the instrument reservoir and assign an expiration date of one month.

10.2. Retention Time Marker Standard (RT Marker)

10.2.1. Add 10 uL of the Retention Time (RT) Stock standard to a 50-mL volumetric flask containing reagent water, dilute to the mark and invert three times to mix. This will yield a final concentration of 200 µg/L n-hexane (C6), nOctane (C8), n-decane (C10)..

10.3. 8015 Stock Standard

10.3.1. Prepare by diluting a 100-uL aliquot of Unleaded Gasoline Composite Standard into 900 uL of P&T methanol. Transfer to a 1.0- or 2.0-mL Mininert valve vial, assign an expiration date of one month and store in freezer.

Table 10.3 – 8015 Stock Standard

Analyte	Standard Concentration (mg/mL)	Standard Amount (uL)	Solvent	Final Volume (uL)	Final Concentration (ug/mL)
Gasoline Range Organics	50.0	100	Methanol	1000	5000

10.4. 8015 Working Standards

10.4.1. The 8015 Working Standards are prepared by adding varied aliquots of the 8015 Stock Standard to aliquots of reagent water, as shown in the table below.

10.4.2. 8015 Working Standards 1-7 are prepared in volumetric flasks and transferred to individual VOA vials. Cap the vials (leaving no headspace) and transfer to the autosampler.

Table 10.4 – 8015 Working Standard Dilutions and Concentrations

Standard	8015 Stock Standard Amount (uL)	Solvent	Final Volume (mL)	GRO Final Concentration (ug/L)
8015-1	1.0	Water	50	100
8015-2	2.0	Water	50	200
8015-3	5.0	Water	50	500
8015-4	10	Water	50	1000
8015-5	20	Water	50	2000
8015-6	40	Water	50	4000
8015-7	80	Water	50	8000

10.5. Second Source Verification (SSV) Stock Standard

10.5.1. The SSV Stock Standard is analyzed once per initial calibration as a check on the calibration standards. It is prepared from a source independent of that of the calibration standards.

10.5.2. Prepare by diluting a 10.0 uL of Gasoline – Regular, Unleaded (Accustandard / GA-001-40X) into 990 uL of P&T methanol. Transfer to a 1.0- or 2.0-mL Mininert valve vial, assign an expiration date of one month and store in freezer.

Table 10.3 – SSV Stock Standard

Analyte	Standard Concentration (mg/mL)	Standard Amount (uL)	Solvent	Final Volume (uL)	Final Concentration (ug/mL)
Gasoline Range Organics	20.0	10	Methanol	1000	200

10.6. Second Source Verification (SSV) Working Standard

10.6.1. Add 50 uL of the SSV Stock Standard to a 50-mL volumetric flask containing reagent water, dilute to the mark and invert three times to mix. Transfer to a VOA vial, cap (leaving no headspace) and place on the autosampler.

Table 10.4 – SSV Working Standard Dilution and Concentrations

Standard	SSV Stock Standard Amount (uL)	Solvent	Final Volume (mL)	GRO/LRH Final Concentration (ug/L)
SSV Working Standard	50	Water	50	200

10.7. Laboratory Control Sample (LCS)

10.7.1. Add 10 uL of the 8015 Stock Standard to a 50-mL volumetric flask containing reagent water, dilute to the mark and invert three times to mix. Transfer to a VOA vial, cap (leaving no headspace) and place on the autosampler.

Table 10.4 – Laboratory Control Sample (LCS)

Standard	GRO/LRH Stock Standard Amount (uL)	Solvent	Final Volume (mL)	GRO/LRH Final Concentration (ug/L)
Laboratory Control Standard	10	Water	50	500

10.8. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

10.8.1. Water: Inject 8 uL of the 8015 Stock Standard through the septum of the sample vial selected for matrix spiking and place on the autosampler.

10.8.2. Soil: Add 10 uL of the GRO Stock Standard and 1.0 mL of a methanolic sample extract to a 50-mL volumetric flask containing reagent water, dilute to the mark and invert three times to mix. Transfer to a VOA vial, cap (leaving no headspace) and place on the autosampler.

11. Calibration and Standardization

11.1. An initial calibration curve using seven points is analyzed prior to analyzing client samples. Refer to Pace SOP S-KS-Q-049, the latest update for general calibration procedures. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values. Refer to Table 11.1 for compound concentrations.

Table 11.1 – Initial Calibration Standard Concentrations

Compound	GRO Std 1 (ug/L)	GRO Std 2 (ug/L)	GRO Std 3 (ug/L)	GRO Std 4 (ug/L)	GRO Std 5 (ug/L)	GRO Std 6 (ug/L)	GRO Std 7 (ug/L)
Gasoline Range Organics	100	200	500	1000	2000	4000	8000

11.2. Calibration Response Factors

11.2.1. Response factors (RF) establish the relationship of the instruments response in comparison with the concentration of any given analyte. To calculate the RF for any given calibration standard (or calibration verification standard), tabulate the area response of the total ion response against concentration for each compound. Response factors are calculated using the following equation.

$$RF = \frac{C_x}{A_x}$$

Where:
A_x = FID area response within the GRO retention time window.
C_x = Concentration GRO being measured (ug/mL).

11.3. Calibration Curve Fit

11.3.1. The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship.

11.3.2. Average Response Factor ($\overline{RF}$): The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. It is in the most basic sense, a linear regression that is forced through zero at the origin. Because of its simplicity and the interception of the y-axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of $\overline{RF}$.

$$\%RSD = \frac{SD \times 100}{\overline{RF}}$$

Where: SD = Standard deviation of the averaged RFs for a given compound

11.4. Calibration Verification

11.4.1. Second Source Verification (SSV)

11.4.1.1. In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria, but not be accurately made in terms of their true value.

11.4.1.2. Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%Difference = \frac{(Result_{SSV} - True\ Value_{SSV})}{True\ Value_{SSV}} \times 100$$

11.4.2. Continuing Calibration Verification (CCV)

11.4.2.1. As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***.

11.4.2.2. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the CCV from the average RF established in the initial calibration. The equations for this calculation are as follows:

$$\%Difference = \frac{(RF_{CCV} - \overline{RF})}{\overline{RF}} \times 100 \text{ (curves based on } \overline{RF})$$

$$\%Drift = \frac{(Result_{CCV} - True\ Value_{CCV})}{True\ Value_{CCV}} \times 100 \text{ (curves based on linear or quadratic regression)}$$

11.5. Calibration Corrective Actions

11.5.1. Reanalyze the original CCV standard to determine instrument consistency.

11.5.2. Perform instrument maintenance, as required.

11.5.2.1. Replace the injection port liner

11.5.2.2. Remove the first 6"-12" of the capillary column.

11.5.3. Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

11.5.4. Complete recalibration of instrument.

11.5.5. If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy. If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis. Spiked Quality Control samples such as the LCS and MS/MSD must be bracketed by acceptable calibration standards.

Table 11.2 – Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Response Factor Linear Regression Non-linear Regression %RSE/RE for Linear or non-Linear Curves	%RSD ≤ 20% r ≥ 0.99 COD ≥ 0.99 %RSE/RE Mid-point ≤ 30% %RSE Low-point ≤ 50%	If not met, try linear regression fit If not met, try non-linear regression fit If not met, remake standards and recalibrate
Second Source Verification Standard (ICV)	Immediately after each initial calibration	%D ± 25% % Drift ± 25%	If not met, repeat only once. If still not met, recalibrate. Remake standards, if necessary.
Continuing Calibration Verification (CCV)	Prior to the analysis of any samples, every 10 injections thereafter, and at the end of the sequence.	%D ± 15% % Drift ± 15%	If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back.
Instrument/Method Blanks	Immediately following any standard that precedes a client or QC sample.	1) Surrogate recoveries should fall within 50-150%. 2) Target analytes must be less than ½ reporting limit. 3) If results are reported to MDL, target analytes in IB should be non-detect.	Corrective action must be taken prior to reanalysis of affected samples.

12. Procedure

Table 12.1 – Instrument and Operating Parameters

Instrument ID	Component	Settings and Consumables	
60GCV2	Gas Chromatograph	Column: Agilent DB-624, 30m, 0.53mm, 3.0 um df Inlet Liner: Restek #22401 Inlet Seal: Restek #21306	Carrier: Helium, 7.0 mL/min (constant pressure) Initial Temperature: 40 ºC Initial Time: 2.5 min. Rate: 12 ºC/min Final Temperature: 60 ºC Final Time: 0 min. Rate A: 12 ºC/min Final Temperature A: 60 ºC Final Time A: 0 min. Rate B: 16 ºC/min Final Temperature B: 240 ºC Final Time B: 0 min. Injector Temperature: 240 ºC Detector Temperature: 280 ºC Split Purge On: 0.1 min.
	Concentrator	Trap: Supelco Type K/Vocarb 3000	Purge Flow: Helium, 35 mL/min Purge Time: 9.0 min. Desorb Temperature: 280 ºC Desorb Time: 1.5 min. Bake Temperature: 280 ºC Bake Time: 4.0 min. Transfer Line Temperature: 150 ºC
	Flame Ionization Detector	OI Analytical 4410	Air: 175 mL/min

12.1. Water analysis

12.1.1. All samples must be allowed to warm to ambient temperature before analysis.

12.1.2. Samples expected to exceed the instrument calibration range are quantitatively diluted with reagent water, poured into a VOA vial, capped (leaving no headspace), and transferred to the autosampler.

12.1.3. Sample pH will be checked post-analysis by pouring an aliquot from the used VOA vial onto the pH strip.

12.1.4. If the pH is less than or equal to 2 for an HCl-preserved sample, no further action is required provided that the sample was analyzed within 14 days.

12.1.5. If the pH is greater than 2 and the sample was analyzed within 7 days, the analysis is within method compliance. If the pH is greater than 2 and the sample was analyzed after 7 days from the collection date, a footnote must be added to the sample results indicating method noncompliance.

12.1.6. Foaming samples: Samples will occasionally foam when purging, which creates the potential for severe instrument contamination if the foaming sample enters the analytical trap, and possibly into the GC column.

12.1.6.1. Take corrective action (i.e. replace trap, rinse or replace concentrator/transfer lines, etc.) to return the instrument to control. Dilute the sample and add Antifoam B® Silicone Emulsion prior to reanalysis.

- Warm antifoam agent to 40ºC (e.g., in GC oven) and shake vigorously for 3 minutes.
- Wet bore of a 10-uL syringe with methanol (draw/dispense 10uL methanol 3 times).

- Very slowly draw 1uL antifoam agent into syringe (should take 10 - 30 seconds).
- Inject antifoam agent into 5-mL water sample.
- Draw/dispense 10uL sample/antifoam mix 3 times, to transfer all antifoam agent to sample.
- Always include an antifoam-treated blank, LCS, MS/MSD with antifoam-treated samples.

12.2. Medium Level Soils in Sampling Kits

12.2.1. Weigh the sample and vial to the nearest 0.01 gram. Subtract the vial tare weight from the weight measured to determine the sample weight.

12.2.2. If the sample contact time with methanol is less than 24 hours, mix the contents of the vial in the sonic bath for 20 minutes. Allow the contents of the vial to settle for several minutes.

12.2.3. Add 1.0 mL of the methanolic sample extract to a 50-mL volumetric flask containing reagent water, dilute to the mark and invert three times to mix. Transfer to a VOA vial, cap (leaving no headspace) and transfer to the autosampler. A smaller aliquot of extract may be used if sample is expected to exceed the instrument calibration range.

12.3. Medium Level Soils Collected in 4 oz. Jars

12.3.1. Weigh 10.0 g ± 0.1 g sample into a 40-mL VOA vial. Record the sample weight to the nearest 0.1 g in the balance logbook.

12.3.2. Using the methanol dispenser, add 10.0 mL of methanol to the contents of the vial.

12.3.3. Mix the contents of the vial in the sonic bath for 20 minutes. Allow the contents of the vial to settle for several minutes.

12.3.4. Add 1.0 mL of the methanolic sample extract to a 50-mL volumetric flask containing reagent water, dilute to the mark and invert three times to mix. Transfer to a VOA vial, cap (leaving no headspace) and transfer to the autosampler. A smaller aliquot of extract may be used if sample is expected to exceed the instrument calibration range.

12.4. Qualitative Analysis:

12.4.1. The retention time range for GRO is defined as 0.1 minute before the retention time of 2-methylpentane and ending 0.1 min after the retention time of 1,2,4-trimethylbenzene in the daily CCV standard (or midpoint calibration standard if an ICAL was analyzed that day).

12.5. Quantitative Analysis

12.5.1. Quantitation is based on the GRO retention time range area response, using "baseline-to-baseline" integration, as opposed to "valley-to-valley" integration.

12.5.2. If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Matrix-specific; reagent water or Ottawa sand.	One per batch of up to 20 samples	a) Target analytes must be less than ½ the reporting limit. b) If results are reported to MDL, target analytes in MB should be non-detect	1) Re-analyze blank to confirm failure. 2) Qualify results and / or re-extract associated samples. ***Exceptions:*** 1) If sample ND, report sample without qualification 2) If sample result >10x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB detects, report sample with appropriate qualifier to indicate an estimated value.
Laboratory Control Sample (LCS)	Matrix-specific; reagent water or Ottawa sand spiked with gasoline.	One per batch of up to 20 samples	Laboratory-generated limits	1) Reanalyze the LCS to verify failure 2) If LCS passes, review samples for potential injection problems 3) If problem persists, check spike solution 4) Re-extract samples where possible ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Client sample spiked with gasoline.	One per batch of up to 20 samples	Laboratory-generated limits	1) If LCS and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One for every 5% of all environmental samples	Laboratory-generated limits	1) Report results with an appropriate footnote.

13.2. Sample Quality Control

Table 13.2 – Sample Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Surrogate	Bromofluorobenzene	Added to all samples, spikes, control samples and method blanks prior to purging.	SS recoveries within laboratory-derived limits	**Recovery Failure:** 1) Check system parameters 2) Identify and correct likely cause 3) Re-run samples ***Exceptions:*** Surr rec above criteria and target compounds < RL, result may be reported with appropriate footnote. Surr rec out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote.

14. Data Analysis and Calculations

14.1. The GC data system will calculate the concentration of each analyte as ug/L. For water samples, no further calculations are necessary unless a dilution of the sample has been performed.

14.2. Aqueous samples

$$\text{Concentration (ug/L)} = \frac{(X_S)(D)}{V_S}$$

14.3. Soil/solid samples

$$\text{Concentration (ug/kg)} = \frac{(X_S)(D)(V_T)}{(V_I)(W)}$$

Where:

X_S = Calculated mass of the analyte (in nanograms) in the sample aliquot introduced into the instrument.
D = Dilution factor
V_I = Volume of the soil extract that is added to the reagent water just prior to purging.
V_S = Volume of the aqueous sample extracted or purged, in milliliters (mL).
V_T = Total volume of soil extract (in uL).
W = Weight of sample extracted or purged (in grams).

14.4 Relative Error (% RE):

$$\% \text{ RE} = [(x'_i - x_i)/x_i] * 100$$

Where x_i = true value for calibration standard
x'_i = measured concentration of calibration standard

14.5 Relative Standard Error (% RSE):

$$\%\text{RSE} = 100 * \text{ the square root of } \sum_{i=1}^{n} [(x'_i - x_i)/x_i]^2 / (n - p)$$

Where x_i = true value of calibration level i
x'_i = measured concentration of calibration level i
p = number of terms in the fitting equation
(average = 1, linear = 2, quadratic = 3)
n = number of calibration points

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See Tables 13.1 and 13.2.

16. Corrective Actions for Out-of-Control Data

16.1. See Tables 11.2, 13.1, and 13.2.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Tables 11.2, 13.1, and 13.2. If there is no additional sample volume to perform re-analyses, if the analytical results are due to the customer, and/or if there is no more holding time remaining; then data will be reported as final with applicable qualifiers. If necessary, an official case narrative can be prepared by the Quality Manager or Project Manager.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. An MDL study must be performed annually for each sample preparation and analysis-method pair (e.g. Medium-level extraction/Method 8015).

18.2.1. The MDL study must meet the criteria defined in S-KS-Q-032, Limit of Detection and Limit of Quantitation (or its equivalent revision or replacement).

18.2.2. The calculated MDL must then be verified on every instrument that is to be used for analysis of samples and reporting of data.

18.2.2.1. Analyze a QC sample containing analytes at no more than 2-3X the MDL for single-analyte tests and 1-4X the MDL for multiple-analyte tests.

18.2.2.2. The QC sample must undergo the applicable sample preparation (e.g., Medium-level extraction).

18.2.2.3. All target compounds must be detected (result > 0) on all instruments to verify the calculated MDL.

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, Training Procedures.

18.3.1. Analysis of four replicates of organic-free water spiked with the 8015 Stock Standard at a concentration of 500 ug/L or equivalent to the LCS.

18.3.2. Analysis of four replicates of Ottawa sand spiked with the 8015 Stock Standard at a concentration of 50 mg/kg.

18.3.3. If the average recoveries are within the matrix-specific recovery limits and the RSDs are <20%, system performance is acceptable and analysis of samples may begin. If, however, either RSD exceeds the precision limit or any recovery falls outside the range, system performance is unacceptable. In this event, correct the problem and repeat the test.

19. Method Modifications

19.1. High level aqueous samples are diluted in reagent water, not methanol.

19.2. Soil samples are extracted in 10-gram aliquots, which exceed the method's limit of 5 grams.

20. Instrument/Equipment Maintenance

20.1 The system is a purge and trap system connected to a GC and FID detector. There is relatively low instrument maintenance. The maintenance that needs to be checked routinely is gas pressures for the FID (Hydrogen and Oxygen) tanks, The other gases pressures that need checked are the purge and column flow, both on the helium tank. These pressures need to be watched and when below 200 PSI need to be changed. Other maintenance to be reviewed on an ongoing bases is the surrogate solution containers to make sure that sufficient surrogate spike solution is in vessel for analyses. This system is equipped with a sample drain container which requires being emptied by hand and therefore must be checked on a daily basis and dumped as needed. All other maintenance required would be as needed, such as changing out column, changing out trap, etc based on instrument issues.

21. Troubleshooting

21.1 This instrument is used for GRO analyses only and therefore is relative low maintenance and usually has few troubleshooting issues.

21.1.1 No detection of peaks:

Check to make sure that all gases are at sufficient levels all tanks above 200 PSI.
Check to make sure that FID is lit.
Check to make sure that purge vessel is getting sample pulled into it.
Check to make sure that you have purge flow (bubbles during purge cycle)
If all of these are OK, then check with supervisor for review of column and trap issues.

21.1.2 Inconsistent recoveries on LCS spike or surrogate spikes on CCV or CCBs.

Check to make sure that surrogate valve is switching and vial has surrogate solution in it.
Check to make sure that purge value is working properly and sample volume is consistent on the delivery into the sparge vessel.
Check for system leaks around column, sparge vessel.
If all of these are OK, then check with supervisor to review of other possible valve issues.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

22.3. **Equipment**

22.3.1. Portions of the analytical instrumentation operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones.

22.3.2. The GC pneumatic system uses gas under high pressure. These high pressures introduce the risk of injury due to flying objects should a vessel or line rupture. Safety glasses are highly recommended at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-ALL-S-002, Waste Handling.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (e.g., before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains information on pollution prevention.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. EPA Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Methods 5030B, 5035, 5035A, 8000D, 8015B, 8015C.

25.5. Procedure for Using Antifoam Agent, Restek Corporation, 400-00 [002].

25.6. Total Petroleum Hydrocarbons (TPH) and Light Non-Aqueous Phase Liquid (LNAPL) Characterization, Remediation and Management, Bureau of Environmental Remediation, Policy # BER-041, September 1, 2015.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: Client-Specific Criteria (Internal Use Only)

26.2. Attachment II: Client-Specific Criteria (Internal Use Only)

27. Revisions

Document Number	Reason for Change	Date
KS-O-026-rev.0	New	March 27, 2006
S-KS-O-026-rev.1	Revised cover page to new corporate template. Section 6-removed unnecessary definitions Section 7.4- revised review frequency from biennial to annual Section 8-added tables 8.1 and 8.2 Section 8-revised 4 C to ≤6 C Section 9 –removed Aquatek and Velocity XPT P&T systems, centrifuge tubes, and drying oven. Section 10 – revised standard table and prep instructions. Section 11- added table 11.1, revised the curve option verbiage, removed RTW study, added BP min RF criteria. Section 12-deleted 10-mL water instrument. Section 13- added tables 13.1, 13.2 Section 14- updated IDOC criteria. Section 17.5-added 40 CFR MUR reference	December 17, 2007
S-KS-O-026-rev.2	Section 7 – Changed SOP review frequency to biennial. Section 9 – Changed column Section 10 – Revised standard prep procedure. Section 12 – Changed column, revised instrument conditions. Section 18 – Revised references. Table 1 – Revised PQLs. Table 2 – Revised troubleshooting.	September 1, 2010
S-KS-O-026-rev.3	SOP – Updated to latest prescribed format. Removed single-component parameters from procedure. Table 10.2 – Changed grade of helium. Table 11.1 – Revised curve concentrations. Section 12 – Added soil dilution procedure. Added single-component retention time window width. Added antifoam procedure. Table 13.1 – Removed WY UST requirements. Section 14 – Revised equations. Section 18.2 – Revised MDL procedure. Section 23 – Revised references. Attachments I-IV: Added client-specific criteria.	January 15, 2012
S-KS-O-026-rev.4	SOP—Revised to latest prescribed format. Table 11.2- Made Instrument and Method Blank equivalent terms Table 13.1 Made Acceptance Criteria Equivalent to Table 11.2 criterion	March 16, 2015
S-KS-O-026-rev .5	SOP – revised to include State of Kansas LRH information	September 20, 2015
S-KS-O-026-rev .6	SOP – Revised cover to Pace LLC Section 2.3 -- revised to remove State of Kansas LRH information. Section 3.2 – revised to remove State of Kansas LRH information. Table 5.1 -- revised to remove State of Kansas LRH information. Section 10.2.1 – removed n-pentane. Section 10.8.2 – removed LRH. Table 11.2 – Added %RSE/RE Section 12.4.1 – Removed last sentence on LRH retention times. Section 14.0 – Added %RSE and %RE calculations Section 12.5.1 – Removed LRH. Section 25.4 – Updated references to include 8000D.	October 27, 2017

Attachment I – BP 8015B/C Criteria (Internal Use Only)

Quality Control Item	Frequency	Criteria	Corrective Action
Initial calibration[1]	Each time the instrument is set up and when CVS acceptance criteria are not met. Initial calibration consists, at a minimum, of five concentration levels (low standard at or below project required quantitation limit [PRQL]).	%RSD ≤ 20% for RFs for each target and surrogate compound. Otherwise, generate a calibration curve for compounds that do not meet these criteria. The calibration curve must have a correlation coefficient (R) ≥0.99 or a coefficient of determination (COD) > 0.99.	%RSDs >20% require quantitation using a calibration curve. If the %RSD > 20%, R < 0.99, and COD < 0.99 for a target compound, a new initial calibration must be performed.
Initial Calibration Verification Standard (ICV)	Must be analyzed after the initial calibration and prior to samples. The ICV must have a concentration at or near the mid-point of the calibration range of the instrument.	• ≤15% D based on "true" concentration when quantitated as a sample. • RT of each target compound must be within RT window (reset daily at the beginning of the sequence for the 24-hour day and recentering the RT window is only permitted once per 24 hours).	If the ICV does not meet criteria, reprepare and reanalyze the ICV once. If the ICV fails a second time a new initial calibration should be rerun. ICV criteria must be met before sample analysis may begin.
Calibration Verification Std. (CVS)	Must bracket each set of 10 sample analyses (inclusive of all laboratory and field QC). The concentration of the CVS must be at or near the mid-point of the calibration range of the instrument.	≤15% D based on "true" concentration when quantitated as a sample. RT of each target compound must be within RT window (reset daily at the beginning of the sequence for the 24-hour day and recentering the RT window is only permitted once per 24 hours).	Correct cause of noncompliant CVS. A compliant initial calibration must then be generated. Reanalyze all samples and QC not bracketed by compliant CVS. (Exception for reanalysis: If the associated samples are < PRQL for the respective target compound, and the noncompliant CVS shows increased sensitivity [i.e., CVS target compound recovery >115% R]. Therefore, if associated samples are < PRQL for the respective target compound, results may be reported with no corrective action for those samples.)
Method Blank	One per batch of ≤20 samples per matrix per concentration level per day. Must undergo all preparative procedures.	Concentration <½ PRQL of the compound. Not applicable if positive results were not reported for any associated samples. Must meet surrogate criteria.	Reanalyze blank. If still out and in hold, reprepare and reanalyze associated samples containing the same contaminant, unless samples contain > 10x amount found in blank. If samples are past hold or if blank is still out after reprepare/reanalysis, report first analysis and notify designated consultant.
Laboratory Control Sample (LCS)	One per batch of ≤ 20 samples per matrix per day. Must undergo all preparative procedures. The LCS must be from a second source (different from the initial calibration standards) and have a concentration at the mid-point of the calibration range.	% recoveries of all compounds within laboratory-generated limits.	Reanalyze LCS. If still out, reprepare and reanalyze all associated samples and a new LCS. Exception: If LCS recovery is high and no associated positives, then address in SDG Narrative and no further action needed.
Matrix Spike/Matrix Spike Duplicate	One per extraction batch per matrix per concentration level ≤ 20 samples per day. Must undergo all sample preparative procedures. Must be spiked with all target analytes at concentrations at or near the mid-point of the calibration range.	% recoveries within laboratory- generated limits. RPDs within laboratory-generated limits.	If LCS is acceptable, then report in the SDG Narrative that there was probable matrix interference.
Retention Time (RT) Windows	Established at ± 3x std. dev. of RT of three standard analyses over 72 hours (use default if window is too narrow). Recentered daily based on RT of each of the compounds in first calibration check standard of day.	RT of sample peak within ± 3x std. dev. per frequency description. RT windows for target compounds must not overlap and recentering the retention time windows is only permitted once per 24 hours.	Adjust system and recalibrate.
Retention Time (RT) Shift	Each CVS analysis: RT of analytes in the CVS are evaluated against the daily ICV.	Column and compound specific, varies with each ICV: compound should be within window established by ICV RT ± the calculated RT window or a default based on the calculated RT window.	• Inspect chromatographic system for malfunctions, if appropriate. • Evaluate data based on a comparison with other standards run during the analytical sequence, consider the RTs for the surrogate and spiked compounds analyzed before and after the sample in question. • Expand the RT windows to encompass the shift in compound location. • If no peaks are found in the expanded window, report the compound as non-detected.

Quality Control Item	Frequency	Criteria	Corrective Action
Surrogate	Added to all standards, blanks, samples, and QC samples. Calibrated and quantitated as target compounds.	% recovery within method limits.	If recovery of any one surrogate is not within limits: • Check to be sure that there are no errors in calculations and surrogate solutions, Also, check instrument performance. • If no problem is found, prepare and analyze the sample a second time. • If the reanalysis is within limits and holding times, then report only the reanalysis. • If the reanalysis is within limits, but out of hold, then report both sets of data. • If the reanalysis is still out of limits, then report both sets of data. • If the sample was chosen for the MS/MSD analysis and the MS and/or MSD are outside limits, then no reanalysis is required.
Qualitative/ Quantitative Issues	If instrument level of any compound in a sample exceeds the instrument level of that compound in the highest level standard, the sample must be diluted to approximately mid-level of the calibration range and reanalyzed. If the concentration of the target analyte that exceeded the calibration range is present in the sample analyzed immediately after the high level sample at a level ≤5x PRQL, then that sample must be reanalyzed to determine if carryover occurred. For each sample, evaluate the chromatographs for potential interferences.	The instrument level of all compounds must be within the calibration range for all samples. The sample analyzed immediately after a high-level sample must display concentrations of the high-level target compounds > 5x PRQL. Sample chromatographs should not display levels of interference in the RT window of any target compound at a level > the PRQL.	• Dilute the sample to bring the level of the highest concentration of target compounds within the calibration range. • A sample displaying concentrations of target compounds ≤ 5x the PRQL which was analyzed immediately after a high-level sample must be reanalyzed. If the results do not agree within the PRQL, report only the second analysis. • If chromatographic interference is observed during the RT window of any target compound, then report in the SDG Narrative that the reported results are quantitatively estimated and are tentative identifications (flag "N"). A discussion regarding the qualitative and quantitative reliability of the analyses must be included in the SDG Narrative.

[1]Heated purge required for calibration standards associated with solid samples for GRO analysis. Forcing a linear regression through zero is not an acceptable curve option for this method.

Attachment II: Canadian National Railway 8015B Criteria (Internal Use Only)

Quality Control Item	Frequency	Criteria	Corrective Action
Initial calibration	Each time the instrument is set up and when calibration verification criteria are not met. A minimum of five calibration standards is required for linear calibration. The low-level standard must be at or below the laboratory's reporting limit.	%RSD must be ≤ 20% for each carbon range.	Compounds with RSD > 20% require the generation of a calibration curve. A linear or nonlinear calibration curve (with r > 0.99) must be generated when the RSD criterion is not met.
Retention Time Range	The retention time range is calculated based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component. Two specific gasoline components should be used to establish the RT range for GRO – 2-methylpentane and 1,2,4-trimethylbenzene. The RT range for DRO is established from the retention times of the C10 and c28 alkanes. RT range standard must be run before the first CCV in the analytical sequence and must be recentered daily based on the RT of each carbon range in the first CCV standard of the day.	Established at ± 3x the standard deviation of the average RT of three standard analyses over a 72-hour period. RTs for carbon ranges must not overlap.	When the observed retention time of a surrogate is outside of the established retention time window, determine the cause and correct the problem before continuing analyses. Sample chromatograms must be evaluated for false positives and false negatives when surrogate retention time shifts are observed,
Instrument Blanks	Analyzed after CCV standards. Instrument blanks are allowable between samples with high concentrations of target compounds, but must not be analyzed strategically before CCV standards.	All target compounds < ½ the RL.	Reanalyze associated samples. If positive results for contaminant compounds are not observed in the associated samples, no action is required.
Initial Calibration Verification (ICV)	A second-source calibration verification standard must be analyzed after every initial calibration.	% Drift or % Difference must be ≤ 20% for each carbon range and all surrogate compounds.	Correct system and reanalyze ICV. If second ICV fails, recalibrate system.
Continuing Calibration Verification (CCV)	Must bracket each set of 10 analyses (including laboratory and QC analyses).	% Drift or % Difference must be ≤ 15% for all carbon ranges.	Correct system and reanalyze CCV. If second CCV fails, recalibrate system and reanalyze all associated project samples.
Method Blank	One per 12-hour analytical shift and per extraction batch of ≤20 samples, whichever is more frequent.	Carbon range results <½ the RL. If samples are reported to the MDL, carbon ranges results must not be above the MDL. Must meet internal standard and surrogate recovery criteria.	Reanalyze associated samples. If positive results for contaminant compounds are not observed in the associated samples, no action is required. Reanalyze blank if surrogate or internal standard criteria are not met.
Surrogate Compounds	Added to all blanks, samples, and QC samples.	All surrogates must meet laboratory-generated acceptance limits.	Check to be sure that there are no errors in the calculations, surrogate solutions, or internal standards. Check instrument performance. Correct the problem and reanalyze the extract if a problem is identified. If no problems are identified, reextract and reanalyze the sample. If surrogate recovery criteria are met upon reextraction/reanalysis, report the reanalysis results. If the surrogate recovery criteria are not met upon reextraction/reanalysis, report both sets of data. If the reextraction/reanalysis is performed outside of holding time, provide both the original and reextraction/reanalysis results.

Quality Control Item	Frequency	Criteria	Corrective Action
Laboratory Control Sample (LCS)	One per analysis batch of up to 20 samples. LCS must undergo all sample preparation procedures and must contain all carbon ranges from a second source at the midpoint of the calibration range.	% Recoveries within laboratory-generated limits.	Reanalyze LCS to confirm results. If LCS results are outside of acceptance criteria upon reanalysis, reextract and reanalyze associated project samples. If high recoveries are observed and "not-detected" results are reported for the associated samples, reanalysis is not required.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	One per matrix per extraction batch of up to 20 samples. All requested carbon ranges must be included in the spiking solution.	% Recoveries and RPDs within laboratory-generated limits.	If LCS results meet acceptance criteria, report probable matrix interference for the MS/MSD outliers in the SDG Narrative. Do not reanalyze the MS/MSD unless laboratory error is confirmed *(e.g.,* non-spiked).
Qualitative/ Quantitative Issues	If the instrument level of any carbon range in a sample exceeds the calibration range, the sample must be diluted and reanalyzed.	The instrument level of all carbon ranges must be within the calibration range. When medium-level extractions are performed for GRO or dilutions are performed for DRO, the solvent lot number must be recorded.	Dilute the sample to bring the carbon range level within the calibration range.
Manual Integrations	Manual integrations may not be performed for the purpose of meeting calibration or QC criteria.	Manual integrations must be performed in accordance with the associated laboratory SOP. Manual integrations must be reviewed and approved by a supervisor.	N/A

Notes:

- For GRO, sample pH must be measured and recorded after sample analysis. If the sample pH does not meet the method acceptance criterion, CN and/or designated consultant must be contacted if the sample is analyzed beyond 7 days from collection.
- The laboratory may be requested to perform state-specific GRO/DRO/hydrocarbon methods. The more stringent of the method requirements and requirements provided herein must be followed.
- The laboratory must identify the carbon ranges of target species in the Case Narrative.
- The calibration of GRO is different from that for single-component analytes in that the response used for calibration must represent the entire area of the chromatogram within the retention time range for each fuel type (excluding surrogate compounds), including the unresolved complex mixture that lies below the individual peaks.
- GRO and DRO are distinguished on the basis of the ranges of retention times for characteristic components in each type of fuel. The RT ranges for DRO and GRO are defined during calibration. Two specific gasoline components are used to establish the RT range for GRO – 2-methylpentane and 1,2,4-trimethylbenzene. The RT range for DRO is established from the retention times of the C10 and C28 alkanes.
- Initial calibration is performed with a minimum of five calibration standards. The low-level calibration standard must be at or below the reporting limit. When the initial calibration RSD criterion is not met, initial calibration standards may be reanalyzed or calibration points may be removed from the extreme ends of the calibration range only in a manner consistent with the analytical method. Reanalysis of calibration points must occur before project samples are analyzed. If a low-level calibration standard is dropped, the reporting limit must be raised to the concentration of the next lowest-level standard. When a linear or nonlinear calibration curve is utilized, the correlation coefficient (r) must be > 0.99.
- RT ranges must be established at ± 3x the standard deviation of the average RT of three standard analyses over a 72-hour period. If the standard deviation of the analyses is zero, a default standard deviation of 0.01 minute is used to generate RT windows. RTs for carbon ranges must not overlap.
- Calibration must be verified at the beginning of each analytical shift and after each 10 analyses (including QC analyses). Instrument blanks must not be preferentially analyzed immediately prior to CCV.
- Surrogate compounds must be added to all initial calibration standards, CCV standards, samples, and QC samples (including instrument blanks).
- One method blank is required per instrument per analytical shift. All method blank runs must be reported.
- MS/MSD samples must be prepared and analyzed concurrently with the project samples.
- LCS and MS/MSD samples must be spiked with all carbon ranges. When the LCS recovery criteria are not met for a carbon range (confirmed by reanalysis), the entire extraction batch must be reextracted and/or reanalyzed. Reextraction and reanalysis are not required when high recoveries are observed for a carbon range and that compound is not detected in the associated project samples. No action is required when MS/MSD recoveries are outside of recovery and/or precision criteria, provided the associated LCS results are within criteria; probable matrix interference must be reported in the Case Narrative.
- All instrument maintenance must be meticulously recorded in the associated instrument logbook.
- Equipment blanks/field blanks must not be reanalyzed when contamination is observed.
- Analysis sequence logs must contain all analyses, not only those reported.

Attachment III: Canadian National Railway 8015C Criteria (Internal Use Only)

Quality Control Item	Frequency	Criteria	Corrective Action
Initial calibration	Each time the instrument is set up and when calibration verification standard acceptance criteria are not met. Initial calibration consists, at a minimum, of five concentration levels (low standard at or below lower limit of quantitation (LLQ)).	%RSD ≤ 20% for RFs for each target and surrogate compound. Otherwise, generate a calibration curve for compounds that do not meet these criteria. The calibration curve must have a correlation coefficient (R) ≥0.99 or a coefficient of determination (COD) > 0.99.	%RSDs >20% require quantitation using a calibration curve. If the %RSD > 20%, R < 0.99, and COD < 0.99 for a target compound, a new initial calibration must be performed.
Calibration Verification Std. (CVS)	Must bracket each set of 10 sample analyses (inclusive of all laboratory and field QC). The concentration of the CVS must be at or near the mid-point of the calibration range of the instrument.	• ≤15% D based on "true" concentration when quantitated as a sample. • RT of each target compound must be within RT window (reset daily at the beginning of the sequence for the 24-hour day and recentering the RT window is only permitted once per 24 hours).	Correct cause of noncompliant CVS. A compliant initial calibration must then be generated. Reanalyze all samples and QC not bracketed by compliant CVS. (Exception for reanalysis: If the associated samples are < PRQL for the respective target compound, and the noncompliant CVS shows increased sensitivity [i.e., CVS target compound recovery >115% R]. Therefore, if associated samples are < PRQL for the respective target compound, results may be reported with no corrective action for those samples.)
Method Blank	One per batch of ≤20 samples per matrix per concentration level per day. Must undergo all preparative procedures.	Concentration may not exceed one-half of the LLQ of the compound. Not applicable if positive results were not reported for any associated samples. Must meet surrogate criteria.	Reanalyze blank once. If still out and in hold, reprepare and reanalyze associated samples containing the same contaminant, unless samples contain > 10x amount found in blank. If samples are past hold or if blank is still out after reprepare/reanalysis, report first analysis and notify designated consultant.
Laboratory Control Sample (LCS)	One per batch of ≤ 20 samples per matrix per day. Must undergo all preparative procedures. The LCS must be from a second source (different from the initial calibration standards) and have a concentration at the mid-point of the calibration range.	% Recoveries of all compounds within in-house calculated or vendor-generated limits.	Reanalyze LCS once. If still out, reprep and reanalyze all associated samples and a new LCS. Exception: If LCS recovery is high and no associated positives, then address in SDG Narrative and no further action needed.
Matrix Spike/Matrix Spike Duplicate	One per extraction batch per matrix per concentration level ≤20 samples per day. Must undergo all sample preparative procedures. Must be spiked with all target analytes at concentrations at or near the mid-point of the calibration range.	% Recoveries within in-house calculated or vendor-generated limits. RPDs within in-house calculated or vendor-generated limits.	If LCS is acceptable, then report in the SDG Narrative that there was probable matrix interference.
Retention Time (RT) Windows	Established at ± 3x std. dev. of RT of three standard analyses over 72 hours (use default if window is too narrow). Recentered daily based on RT of each of the compounds in first calibration check standard of day.	RT of sample peak within ± 3x std. dev. per frequency description. RT windows for target compounds must not overlap and recentering the retention time windows is only permitted once per 24 hours.	Adjust system and recalibrate.
Retention Time (RT) Shift	Each CVS analysis: RT of analytes in the CVS are evaluated against the daily ICV.	Column and compound specific, varies with each ICV: compound should be within window established by ICV RT ± the calculated RT window or a default based on the calculated RT window.	Inspect chromatographic system for malfunctions, if appropriate. Evaluate data based on a comparison with other standards run during the analytical sequence. Expand the RT windows to encompass the shift in compound location. If no peaks are found in the expanded window, report the compound as non-detected.
Surrogate	Added to all standards, blanks, samples, and QC samples.	% Recovery within in-house calculated or vendor-generated limits.	If recovery of any one surrogate is not within limits, check to be sure that there are no errors in calculations and surrogate solutions, Also, check instrument performance. If no problem is found, reprep and reanalyze the sample. If the reanalysis is within limits and holding times, then report only the reanalysis. If the reanalysis is within limits, but out of hold, then report both sets of data. If the reanalysis is still out of limits, then report both sets of data.

Quality Control Item	Frequency	Criteria	Corrective Action
Qualitative/ Quantitative Issues	If instrument level of any compound in a sample exceeds the instrument level of that compound in the highest level standard, the sample must be diluted to approximately mid-level of the calibration range and reanalyzed. If the concentration of the target analyte that exceeded the calibration range is present in the sample analyzed immediately after the high level sample at a level ≤5x LLQ, then that sample must be reanalyzed to determine if carryover occurred. For each sample, evaluate the chromatographs for potential interferences.	The instrument level of all compounds must be within the calibration range for all samples. The sample analyzed immediately after a high-level sample must display concentrations of the high-level target compounds > 5x LLQ. Sample chromatographs should not display levels of interference in the RT window of any target compound at a level greater than the LLQ.	Dilute the sample to bring the level of the highest concentration of target compounds within the calibration range. A sample displaying concentrations of target compounds ≤ 5x the LLQ which was analyzed immediately after a high-level sample must be reanalyzed. If the results do not agree within the LLQ, report only the second analysis. If chromatographic interference is observed during the RT window of any target compound, then report in the SDG Narrative that the reported results are quantitatively estimated and are tentative identifications (flag "N"). A discussion regarding the qualitative and quantitative reliability of the analyses must be included in the SDG Narrative.

Notes:

- Heated purge required for calibration standards associated with solids samples for GRO analysis.
- Forcing a linear regression through zero is not acceptable for this method.

Attachment IV – ConocoPhillips 8015B Criteria (Internal Use Only)

Quality Control Item	Frequency	Criteria	Corrective Action
Initial calibration	Each time the instrument is set up and when calibration verification criteria are not met. A minimum of five calibration standards is required for linear calibration. The low-level standard must be at or below the laboratory's reporting limit.	%RSD must be ≤ 20% for each carbon range.	Compounds with RSD > 20% require the generation of a calibration curve. A linear or nonlinear calibration curve (with r > 0.99) must be generated when the RSD criterion is not met.
Retention Time Range	The retention time range is calculated based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component. Two specific gasoline components should be used to establish the RT range for GRO – 2-methylpentane and 1,2,4-trimethylbenzene. The RT range for DRO is established from the retention times of the C10 and c28 alkanes. RT range standard must be run before the first CCV in the analytical sequence and must be recentered daily based on the RT of each carbon range in the first CCV standard of the day.	Established at ± 3x the standard deviation of the average RT of three standard analyses over a 72-hour period. RTs for carbon ranges must not overlap.	When the observed retention time of a surrogate is outside of the established retention time window, determine the cause and correct the problem before continuing analyses. Sample chromatograms must be evaluated for false positives and false negatives when surrogate retention time shifts are observed,
Instrument Blanks	Analyzed after CCV standards. Instrument blanks are allowable between samples with high concentrations of target compounds, but must not be analyzed strategically before CCV standards.	All target compounds < ½ the RL.	Reanalyze associated samples. If positive results for contaminant compounds are not observed in the associated samples, no action is required.
Initial Calibration Verification (ICV)	A second-source calibration verification standard must be analyzed after every initial calibration.	% Drift or % Difference must be ≤ 20% for each carbon range and all surrogate compounds.	Correct system and reanalyze ICV. If second ICV fails, recalibrate system.
Continuing Calibration Verification (CCV)	Must bracket each set of 10 analyses (including laboratory and QC analyses).	% Drift or % Difference must be ≤ 15% for all carbon ranges.	Correct system and reanalyze CCV. If second CCV fails, recalibrate system and reanalyze all associated project samples.
Method Blank	One per 12-hour analytical shift and per extraction batch of ≤20 samples, whichever is more frequent.	Carbon range results <½ the RL. If samples are reported to the MDL, carbon ranges results must not be above the MDL. Must meet internal standard and surrogate recovery criteria.	Reanalyze associated samples. If positive results for contaminant compounds are not observed in the associated samples, no action is required. Reanalyze blank if surrogate or internal standard criteria are not met.
Surrogate Compounds	Added to all blanks, samples, and QC samples.	All surrogates must meet laboratory-generated acceptance limits.	Check to be sure that there are no errors in the calculations, surrogate solutions, or internal standards. Check instrument performance. Correct the problem and reanalyze the extract if a problem is identified. If no problems are identified, reextract and reanalyze the sample. If surrogate recovery criteria are met upon reextraction/reanalysis, report the reanalysis results. If the surrogate recovery criteria are not met upon reextraction/reanalysis, report both sets of data. If the reextraction/reanalysis is performed outside of holding time, provide both the original and reextraction/reanalysis results.
Laboratory Control Sample (LCS)	One per analysis batch of up to 20 samples. LCS must undergo all sample preparation procedures and must contain all carbon ranges from a second source at the midpoint of the calibration range.	% Recoveries within laboratory-generated limits.	Reanalyze LCS to confirm results. If LCS results are outside of acceptance criteria upon reanalysis, reextract and reanalyze associated project samples. If high recoveries are observed and "not-detected" results are reported for the associated samples, reanalysis is not required.

Quality Control Item	Frequency	Criteria	Corrective Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	One per matrix per extraction batch of up to 20 samples. All requested carbon ranges must be included in the spiking solution.	% Recoveries and RPDs within laboratory-generated limits.	If LCS results meet acceptance criteria, report probable matrix interference for the MS/MSD outliers in the SDG Narrative. Do not reanalyze the MS/MSD unless laboratory error is confirmed *(e.g.*, non-spiked).
Qualitative/ Quantitative Issues	If the instrument level of any carbon range in a sample exceeds the calibration range, the sample must be diluted and reanalyzed.	The instrument level of all carbon ranges must be within the calibration range. When medium-level extractions are performed for GRO or dilutions are performed for DRO, the solvent lot number must be recorded.	Dilute the sample to bring the carbon range level within the calibration range.
Manual Integrations	Manual integrations may not be performed for the purpose of meeting calibration or QC criteria.	Manual integrations must be performed in accordance with the associated laboratory SOP. Manual integrations must be reviewed and approved by a supervisor.	N/A

Notes:

- For GRO, sample pH must be measured and recorded after sample analysis. If the sample pH does not meet the method acceptance criterion, ConocoPhillips and/or designated consultant must be contacted if the sample is analyzed beyond 7 days from collection.
- The laboratory may be requested to perform state-specific GRO/DRO/hydrocarbon methods. The more stringent of the method requirements and requirements provided herein must be followed.
- The laboratory must identify the carbon ranges of target species in the SDG Narrative.
- The calibration of DRO and GRO is different from that for single-component analytes in that the response used for calibration must represent the entire area of the chromatogram within the retention time range for each fuel type (excluding surrogate compounds), including the unresolved complex mixture that lies below the individual peaks.
- GRO and DRO are distinguished on the basis of the ranges of retention times for characteristic components in each type of fuel. The RT ranges for DRO and GRO are defined during calibration. Two specific gasoline components are used to establish the RT range for GRO – 2-methylpentane and 1,2,4-trimethylbenzene. The RT range for DRO is established from the retention times of the C10 and C28 alkanes.
- Initial calibration is performed with a minimum of five calibration standards. The low-level calibration standard must be at or below the reporting limit. When the initial calibration RSD criterion is not met, initial calibration standards may be reanalyzed or calibration points may be removed from the extreme ends of the calibration range only in a manner consistent with the analytical method. Reanalysis of calibration points must occur before project samples are analyzed. If a low-level calibration standard is dropped, the reporting limit must be raised to the concentration of the next lowest-level standard. When a linear or nonlinear calibration curve is utilized, the correlation coefficient (r) must be > 0.99.
- RT ranges must be established at ± 3x the standard deviation of the average RT of three standard analyses over a 72-hour period. If the standard deviation of the analyses is zero, a default standard deviation of 0.01 minute is used to generate RT windows. RTs for carbon ranges must not overlap.
- Calibration must be verified at the beginning of each analytical shift and after each 10 analyses (including QC analyses). Instrument blanks must not be preferentially analyzed immediately prior to CCV.
- Surrogate compounds must be added to all initial calibration standards, CCV standards, samples, and QC samples (including instrument blanks).
- One method blank is required per instrument per analytical shift. All method blank runs must be reported.
- MS/MSD samples must be prepared and analyzed concurrently with the project samples.
- LCS and MS/MSD samples must be spiked with all carbon ranges. When the LCS recovery criteria are not met for a carbon range (confirmed by reanalysis), the entire extraction batch must be reextracted and/or reanalyzed. Reextraction and reanalysis are not required with high recoveries are observed for a carbon range and that compound is not detected in the associated project samples. No action is required when MS/MSD recoveries are outside of recovery and/or precision criteria, provided the associated LCS results are within criteria; probable matrix interference must be reported in the SDG Narrative.
- All instrument maintenance must be meticulously recorded in the associated instrument logbook.
- Equipment blanks/field blanks must not be reanalyzed when contamination is observed.
- Analysis sequence logs must contain all analyses, not only those reported.

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QM Approval

Name/Signature	Title	Date	Meaning/Reason
Gregory Busch (003971)	Quality Manager	13 Dec 2018, 12:08:55 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
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1. Purpose/Identification of Method

1.1. This Standard Operating Procedure (SOP) describes the analysis of extractable petroleum hydrocarbons by GC/MS.

2. Summary of Method

2.1. Samples are extracted with methylene chloride and followed by gas chromatography/mass spectrometry (GC/MS) detection.

2.2. Calibration standards are made from a 1:1 mixture of commercially available unleaded gasoline and #2 diesel fuel. Retention time range boundaries are established with normal-alkane markers (C10, C21, and C35).

2.3. TPH Quantitation is based on external calibration of the Total Ion Chromatogram (TIC); use of individual quantitation ions is not appropriate for TPH quantitation. Surrogates are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using a multi-point calibration curve.

3. Scope and Application

3.1. Personnel: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method or non-analytical process.

3.2. Parameters: This SOP measures extractable petroleum hydrocarbons corresponding to the retention time range established by normal-alkanes from C10 to C35.

4. Applicable Matrices

4.1. This method is applicable to most water, solid or oily samples. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, and other solid samples, neat petroleum product, crude oil, or waste.

4.2. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix-related modifications must be documented within the analytical data.

5. Limits of Detection and Quantitation

5.1. The reporting limit (LOQ) for all analytes is listed in the table below for this method. All current MDLs (LOD) are listed in the LIMS and are available by request from the Quality Manager.

Table 5.1 Limits of Quantitation

Analyte	Water (mg/L)	Soil (mg/kg)
TPH-DRO (>C10-C21)	1.0	15
TPH-ORO (>C21-C35)	1.0	15

5.2. LOQ's are subject to change based on current analytical system performance and actual sample matrices.

6. Interferences

6.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

6.2. Interferences by phthalate esters can pose a major problem in all. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross-contamination of clean glassware occurs when plastics and samples are handled by personnel. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

6.3. Matrix interferences may be caused by high concentration contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the site being sampled. Aliphatic hydrocarbons and sulfur can interfere with achieving acceptable chromatography.

6.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent (methylene chloride) between sample injections. When a concentrated sample is injected, a solvent blank should follow to ensure there is no carryover.

7. Sample Collection, Preservation, Shipment and Storage

Table 7.1 Sample Collection, Preservation, Shipment and Storage

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Amber glass bottle with PTFE-lined cap. Capacity between one liter and 100 mL.	N/A	≤6°C, not frozen.	7 days after collection.
Soil/Solid	Wide mouth glass 2- or 4-oz container.	N/A	≤6°C, not frozen.	14 days after collection.
Extracts	2-5mL glass vials, same as used for standard storage	None	≤6°C, not frozen.	40 days after extraction.

8. Definitions

8.1. Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

Table 9.1 – Equipment and Supplies

Supply	Vendor	Model / Version	Comments
Analytical balance	Ohaus	SP202	Capable of weighing 0.01g
Analytical column	Agilent	DB-5	15m x 0.25mm, 0.25 um df
Autosampler	Hewlett-Packard	7693	Or equivalent
Autosampler Vials	Fisher	03-375-2S	2-mL, amber
Data system	Thruput Systems, Inc.	Target, version 3.4	
Mass spectrometer	Agilent	5972	Or equivalent
Gas chromatograph	Agilent	7890A	Or equivalent
Gas tight syringes	Hamilton	Series 1700	10-, 25-, 100-, 500-, 1000-uL
Glass pipettes	Fisher	13-678-6A	Disposable 5 ¾"
Microdispensers	Fisher	21-176E	100-uL
Replacement bores	Fisher	21-175-25	
Septa	CRS	236115	7/16" diam.
Serological pipettes	Fisher	13-678-31-J	10 mL, 1/10 mL subdivisions
Volumetric Flasks	Fisher	Various	5-, 10-, 50-, 100-mL

10. Reagents and Standards

Table 10.1 – Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date for unopened ampulated standards. ▪ Stock standards must be replaced 1 year after ampule is opened or on expiration date, whichever is sooner.	▪ Manufacturer's recommended storage conditions ▪ When standard is opened, record all information in the standard logbook.
Intermediate and Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ One year from preparation or the expiration date listed for the stock source, whichever is sooner. ▪ Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	▪ Store refrigerated in amber vials with Teflon lined screw caps at ≤ 6°C.

Table 10.2 – Reagents and Stock Standards

Reagent/Standard	Concentration/ Description	Vendor/ Item #
Acetone	Fisher Optima™ grade	Fisher / A929
Hexane	Fisher Optima™ grade	Fisher / H303
Methanol	Fisher Optima™ grade	Fisher / A454
Methylene chloride	Fisher Optima™ grade	Fisher / D151
Base/Neutrals Surrogate Standard	1000 ug/mL in methylene chloride/acetone	SPEX CertiPrep / CLP90-SB5
Carbon Number Distribution Marker Stock Standard	200 ug/mL each in pentane	Restek / 31639
Diesel Fuel #2 Composite Standard	50 mg/mL in methylene chloride	Restek / 32159
EPA 8270 GC-MS Tuning Solution	50 ug/mL in methylene chloride	Supelco / 47387
Stock Gasoline/Diesel Calibration Soln.	20 mg/mL in methylene chloride	Accustandard / DRH-TX-002-D-40X
SV Internal Standard Mix	2000 ug/mL in methylene chloride	Restek / 31206
Unleaded Gasoline Composite Standard	50 mg/mL in methanol	Restek / 30206

10.1. DFTPP Tuning Standard – Use the EPA 8270 GC-MS Tuning Solution undiluted, injecting 1.0 uL into the instrument at the beginning of each 12-hour analytical sequence.

10.2. Internal Standard Solution – Add 1.0 mL of SV Internal Standard Mix to a 10-mL volumetric flask containing approximately 5 mL of methylene chloride, bring to volume and invert three times to mix.

10.3. Retention Time Marker Solution – Add 400 uL of Carbon Number Distribution Marker Stock Standard to a 4-mL volumetric flask containing approximately 2 mL of methylene chloride, bring to volume and invert three times to mix.

10.4. Second Source Verification Standard – Add 400 uL of Stock Gasoline/Diesel Calibration Solution to a 4-mL volumetric flask containing approximately 2 mL of methylene chloride, bring to volume and invert three times to mix.

10.5. TPH Spiking Solution – Add 10 mL of Unleaded Gasoline Composite Standard and 10 mL of Diesel Fuel #2 Composite Standard to a 100-mL volumetric flask containing approximately 50 mL of methanol, bring to volume and invert three times to mix. Verify spike concentration according to SOP S-KS-O-003 prior to initial use.

10.6. TPH Surrogate Solution – Add 5.0 mL of Base/Neutrals Surrogate Standard to a 500-mL volumetric flask containing approximately 250 mL of methanol, bring to volume and invert three times to mix. Verify surrogate concentrations according to SOP S-KS-O-003 prior to initial use.

10.7. Surrogate Stock Solution – Add 4.0 mL of Base/Neutrals Surrogate Standard to a 500-mL volumetric flask containing approximately 250 mL of methylene chloride, bring to volume and invert three times to mix.

10.8. TPH Stock Solution – Add 9.6 mL of Unleaded Gasoline Composite Standard and 9.6 mL of Diesel Fuel #2 Composite Standard to a 20-mL volumetric flask, bring to volume with methylene chloride and invert three times to mix.

10.9. TPH Calibration Standards – Prepare working standards from the TPH and Surrogate Stock Solutions in methylene chloride using Class A volumetric flasks according to the table below:

Table 10.3 – TPH Calibration Standards

Standard	TPH Stock Soln. (mL)	Surrogate Stock Soln. (mL)	Solvent	Final Volume (mL)	Gasoline (ug/mL)	Diesel (ug/mL)	TPH (ug/mL)	Surrogates (ug/mL)
TPH ICAL-1	0.006	0.1	$CHCl_2$	4.0	36	36	72	5.0
TPH ICAL-2	0.02	0.2	$CHCl_2$	4.0	120	120	240	10
TPH ICAL-3	0.1	0.4	$CHCl_2$	4.0	600	600	1200	20
TPH ICAL-4	0.2	0.8	$CHCl_2$	4.0	1200	1200	2400	40
TPH ICAL-5	0.5	1.0	$CHCl_2$	4.0	3000	3000	6000	50
TPH ICAL-6	1.0	1.6	$CHCl_2$	4.0	6000	6000	12000	80
TPH ICAL-7	2.0	2.0	$CHCl_2$	4.0	12000	12000	24000	100

11. Calibration

11.1. Tune Verification

11.1.1. The mass spectrometer tune status must be verified prior to initial calibration and at the beginning of each analytical sequence. If the current tune status does not meet the ion ratio criteria (see Table 12.2) take corrective actions as outlined in the equipment manufacturers' instructions for re-tuning the mass spectrometer. The tune status must be re-verified after the tuning procedures.

11.2. Initial Calibration (ICAL)

11.2.1. An initial calibration curve using a minimum of five points is analyzed prior to analyzing client samples. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values.

11.3. TPH Response Factors

11.3.1. To calculate the RF for TPH in any given calibration standard (or calibration verification standard), tabulate the area response of the defined time range (or total area) against concentration for each compound. It is highly likely that the calibration standards used for this method will have little presence in the C21 to C35 (TPH-DRO) window. The response factor calculated for the C10 to C21 window must be used for the C21 to C35 (TPH-ORO) window.

$$RF = \frac{C_X}{A_X}$$

Where:

Cx = Concentration of the compound being measured (ug/mL).
Ax = Area of the peak for the compound being measured.

11.4. Surrogate Response Factors

11.4.1. To calculate the surrogate RF for any given calibration standard (or calibration verification standard), tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation.

$$RF = \frac{A_X C_{IS}}{A_{IS} C_X}$$

Where:

A_X = Area of the characteristic ion for the compound being measured.
C_X = Concentration of the compound being measured (ug/mL).
A_{IS} = Area of the characteristic ion for the specific internal standard.
C_{IS} = Concentration of the specific internal standard (ug/mL).

11.5. Calibration Curve Fit

11.5.1. The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. The curve is produced in several ways depending on the nature of the "goodness of fit".

11.5.2. **Average Response Factor ($\overline{RF}$):** The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. Because of its simplicity and the interception of the y-axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of the $\overline{RF}$ (see Table 11.1). The % RSD is calculated as follows:

$$\%RSD = \frac{SD \times 100}{\overline{RF}}$$

Where:

SD = Standard deviation of the averaged RFs for a given compound

11.5.3. The average response factor is also used to diagnose the integrity of the chromatography system as it relates to calibration linearity. The %RSD for each analyte is compared to the method criteria. If any %RSD exceeds the criteria, the system needs to be inspected for potential sources of errors and recalibrated.

Second Source Verification (SSV)

11.5.4. In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

11.5.5. Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%Diff = \frac{(RF_{SSV} - \overline{RF})}{\overline{RF}} \times 100$$

11.6. Continuing Calibration Verification (CCV)

11.6.1. As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***. The validity of the initial calibration is checked at the beginning of every 12-hour analytical sequence. This is accomplished by analyzing the Continuing Calibration Verification Standard (CCV). The accuracy of the standard is assessed as a percent difference or percent drift from the true value according to the following equations:

$$\%Diff = \frac{(RF_{CCV} - \overline{RF})}{\overline{RF}} \times 100$$

11.7. Calibration Corrective Actions

11.7.1. Reanalyze the original CCV standard to determine instrument consistency.

11.7.2. Perform instrument maintenance, as required.

11.7.2.1 Replace the injection port liner

11.7.2.2 Remove the first 6"-12" of the capillary column.

11.7.2.3 Clean the MS ion source. Any maintenance performed on the physical mass spec components requires recalibration.

11.7.3. Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

11.7.4. Complete recalibration of instrument.

11.7.5. If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

11.7.6. *Exceptions:* If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis. Spiked Quality Control samples such as the LCS and MS/MSD must be bracketed by acceptable calibration standards.

Table 11.1 – Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Response Factor	%RSD ≤ 20%	If not met, take corrective action to include instrument maintenance. Remake standards if necessary.
Second Source Verification Standard	Immediately after each initial calibration.	%Diff ±30%	Only two injections of the same standard are permitted back to back before corrective action is required. Remake standards if necessary.
Continuing Calibration Verification	Prior to the analysis of any samples and every 12 hours thereafter.	%Diff ±20%	If the requirements for continuing calibration are not met, corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back before another initial calibration must be analyzed.
Retention Time Marker	Prior to the analysis of any samples and every 12 hours thereafter.	RT ± 30 seconds	Compare to corresponding midpoint standard in the initial calibration.

12. Procedure

12.1. Sample Preparation

12.1.1. Water Samples

12.1.1.1 Aqueous samples are prepared according to EPA 3510C. Refer to SOP ENV-SOP-LENE-0039 for details on the preparation of 1-liter and 100-mL aqueous samples.

12.1.2. Soil Samples

12.1.2.1 Soil samples are prepared according to EPA 3546. Refer to SOP ENV-SOP-LENE-0005 for details on the preparation of soil or solid samples.

12.2. GC/MS System Preparation

12.2.1. Configure the GC/MS system to match the following operating parameters based on instrument configuration. The parameters themselves are saved as a method on the chromatography data system. By loading the last method used, the instrument will auto-configure to match the parameters from the last time the system was operated under that method. Verify that the settings in the software match the appropriate configuration.

Table 12.1 –Instruments and Operating Parameters

Instrument IDs	Component	Settings and Consumables	
60MSS3 Backup: 60MSS6	Gas Chromatograph	Column: Supelco SLB-5ms, 30m x 0.25mm, 0.25 µm df Inlet Liner: Restek #22401 Inlet Seal: Restek #21306 Column Ferrules: Agilent #5062-3508. (Equivalent items from other manufacturers may also be used.)	Flow: Helium, 2.5 mL/min (constant) Initial Temperature: 45 ºC Initial Time: 2 min. Rate: 35 ºC/min Final Temperature: 320 ºC Final Time: 4.0 min. Injector Temperature: 255 ºC Transfer Line Temperature: 305 ºC MS Source Temperature: 230 ºC MS Quad Temperature: 150 ºC Split Purge On: 0.1 min.
	Mass Spectrometer	Tune File: dftpp.u	Mass range must be set to 35-550 amu.
	Autosampler	Sample Washes: 0 Sample Pump: 2 Injection Volume 1.0 uL Syringe Size: 10 uL	PostInj Solvent A Washes: 3 PostInj Solvent B Washes: 2 Viscosity Delay: 0 sec. Plunger Speed: Fast PreInjection Dwell: 0 min PostInjection Dwell: 0 min

12.3. Tune Verification

12.3.1. Prior to analysis of samples (and every 12 hours of analysis thereafter), inject 1.0 uL of the DFTPP Tuning Standard and verify that the system meets the tuning acceptance critera as listed in Table 12.2.

12.3.2. The analyst may evaluate instrument tune using a single scan at the apex of the DFTPP peak or the average of three scans (the peak apex and the scans immediately before and after).

12.3.3. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed to only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

Table 12.2 - DFTPP Key Ions and Abundance Criteria

Mass	Abundance Criteria
51	30.0-80.0% of mass 198
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	25-75% of mass 198
197	Less than 1.0% of mass 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of mass 198
275	10.0-30.0% of mass 198
365	Greater than 0.75% of mass 198
441	Present, but less than mass 443
442	40.0-110.0% of mass 198
443	15.0-24.0% of mass 442

12.3.4. If the ratios do not meet the criteria, refer to the corrective actions in Section 10.4 address the problem. Any changes made to the system must be followed with the reanalysis of a DFTPP Tuning Standard. Any maintenance performed on the physical mass spec components requires recalibration. “Autotunes” may be performed as long as the following CCV meets all criteria for response, retention time and sensitivity.

12.4. Initial Calibration

12.4.1. After a successful DFTPP analysis, inject the Retention Time Marker Solution.

12.4.1.1 The retention time window for TPH-DRO is defined as beginning 0.1 minutes after C10 to 0.1 minutes after C21.

12.4.1.2 The retention time window for TPH-ORO is defined as beginning 0.1 minutes after C21 to 0.1 minutes after C35.

12.4.2. Inject the TPH calibration standards (withdraw 100 uL of standard and add to a low-volume insert that has been placed in an autosampler vial. Add 10 uL of Internal Standard Solution to the low-volume insert, cap and crimp.)

12.4.3. Calculate the responses for the surrogates and TPH-DRO (C10-C21). The surrogate responses will be calculated using the internal standard approach. This requires a separate processing method and therefore your standards will need to be processed twice (Once for the surrogates and once for the TPH-DRO/ORO). Note: It is highly likely that the calibration standards used for this method will have little presence in the C21 to C35 (TPH-DRO) window. The response factor calculated for the C10 to C21 window must be used for the C21 to C35 (TPH-ORO) window.

12.4.4. Calculate the Percent Relative Standard Deviation (%RSD) of each compound. The RSD of all compounds must be 20% or less to proceed with sample analysis, otherwise take corrective action in the form of instrument maintenance and repeat the Initial Calibration beginning with injection of the DFTPP Tuning Standard.

12.4.5. Inject the Second Source Verification Standard. This standard is an independent check on the TPH Initial Calibration. The acceptance criterion is 70-130% from the amount injected. If the recoveries are not within those limits see the Supervisor immediately for further action.

12.5. Continuing Calibration Verification (CCV) - The CCV consists of three steps that are performed at the beginning of each 12-hour analytical shift, in the following order:

12.5.1. Inject 1.0 uL of the DFTPP tuning standard and verify that the system meets the tuning acceptance criteria as listed in Table 12.2.

12.5.1.1 The analyst may evaluate instrument tune using a single scan at the apex of the DFTPP peak or the average of three scans (the peak apex and the scans immediately before and after).

12.5.1.2 Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed to only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak.

12.5.2. Inject the Retention Time Marker solution to verify the retention time windows have not varied by more than 30 sec. from those of the corresponding standard in the last acceptable initial calibration.

12.5.3. Inject a midpoint calibration standard (withdraw 100 uL of standard and add to a low-volume insert that has been placed in an autosampler vial. Add 10 uL of Internal Standard Solution to the low-volume insert, cap and crimp.)

12.5.4. Verify that the response of all compounds have not varied from those in the initial calibration by more than 20% difference. The standard concentration should be at the midpoint of the calibration curve.

12.5.5. If the CCV meets control criteria, the system is deemed to be in control and analysis of samples may commence. If the CCV does not meet control criteria, follow the corrective action procedures listed Section 11.8

12.5.6. *Note:* In situations where the instrument will run unattended (i.e. overnight), the analyst may load sequential (back-to-back) CCVs in anticipation of that the first in the series may fail due to carry over from a previous sample. If so, both CCVs must be evaluated according to the protocol set forth in the Quality Assurance Manual within Section 6 – Equipment and Measurement Traceability.

12.6. Sample Analysis

12.6.1. Withdraw 100 uL of sample extract and add to a low-volume vial insert that has been placed in an autosampler vial.

12.6.2. Add 10 uL of Internal Standard Solution to the low-volume insert, cap and crimp.

12.6.3. Place on autosampler tray, load ChemStation method '8270', and start instrument.

12.6.4. Process all runs with Target software.

12.6.5. Post data to EPIC Pro.

12.6.6. Sample analysis may begin and continue for 12 hours after the DFTPP Tuning Standard was injected.

12.7. Dilutions

12.7.1. Dilutions on sample extracts must be prepared in a volumetric fashion. Sample aliquots should be taken in volumetric syringes and brought to volume by the addition of solvent via an appropriate syringe.

12.7.2. In the event a dilution is made to bring a target analyte into calibration range, the analyst should make a dilution such that the target analyte is roughly the equivalent of the mid-calibration point whenever possible.

12.7.3. If dilutions are made on extracts that already contain internal standards, a proportional aliquot of internal standard solution must be added to the diluted extract based on the volume of diluent used.

13. Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Matrix-specific; Reagent water or Ottawa sand	One per batch of up to 20 samples.	1) Target analytes must be less than ½ reporting limit. 2) If results are reported to MDL, target analytes in MB should be non-detect	1) Re-analyze blank to confirm failure. 2) Qualify results and / or re-extract associated samples. ***Exceptions:*** 1) If sample ND, report sample without qualification 2) If sample result >10x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB detects, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	Matrix-specific; Gasoline and Diesel fuel mixture spiked into reagent water or Ottawa sand.	One per batch of up to 20 samples.	Laboratory-derived limits	Reanalyze the LCS to verify failure: 1) If LCS passes, review samples for potential injection problems 2) If problem persists, check spike solution 3) Re-extract samples where possible ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Gasoline and Diesel fuel mixture spiked into client sample.	One per batch of up to 20 samples.	Laboratory-derived limits	If LCS and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences.
Matrix Spike Duplicate (MSD)	MS Duplicate	One per batch of up to 20 samples	Laboratory-derived limits	Report results with an appropriate footnote.

Table 13.2 – Sample Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Surrogate Standards	Nitrobenzene-d_5, Terphenyl-d_{14} and 2-Fluorobiphenyl	Added to all samples, spikes, control samples and method blanks prior to extraction.	Laboratory-derived limits.	**Recovery Failure:** 1) Re-analyze extract to confirm failure. 2) Assess impact of sample matrix 3) In the absence of obvious matrix interference (high background, extremely dark extract), re-extract sample. ***Exceptions:*** 1) Surr rec above criteria and target compounds < RL, result may be reported with appropriate footnote. 2) Surr rec out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote.
Internal Standard	Naphthalene-d8 Acenaphthene-d10 Phenanthrene-d10 Chrysene-d12 Perylene-d12	Added to all samples, spikes, control samples and method blanks prior to analysis.	IS peak area within 50-200% of the associated CCV standard. IS retention time within ±30 seconds of the associated CCV standard.	**Recovery Failure:** 1) Re-analyze sample to confirm failure 2) Assess impact of sample matrix 3) In the absence of obvious matrix interference, reanalyze sample. **Retention Time Failure:** 1) If matrix interference is NOT probable, the analytical system must be checked for source of retention time shifting. 2) Affected samples should be reanalyzed in the absence of an obvious instrument or matrix related interference.

14. Data Analysis and Calculations

14.1. Qualitative Analysis – Identification is based upon the retention times of compounds in the Retention Time Marker standard.

14.1.1. The retention time window for TPH-DRO is defined as beginning 0.1 minutes after C10 to 0.1 minutes after C21.

14.1.2. The retention time window for TPH-ORO is defined as beginning 0.1 minutes after C21 to 0.1 minutes after C35.

14.1.3. Visually examine the computer-generated baseline for every analytical run, and manually adjust the baseline when needed. A properly drawn baseline must extend over the entire retention time window and include the area under the entire TPH-DRO or TPH-ORO series of peaks. It is not appropriate to draw the baseline "peak to peak".

14.2. Quantitative Analysis

14.2.1. Quantitation is based on the integrated peak area within a retention time range.

14.2.2. The data system will calculate the concentration of each analyte in the sample extract. The LIMS will be able to calculate the results back to the original matrix. The calculation for the concentration of the target analyte in the original matrix is listed below and is based on the calibration table in units of ppm (ug/mL).

14.3. Aqueous samples:

$$\text{TPH Concentration (mg/L)} = \frac{(C_X)(V_X)(DF)}{V_S}$$

Where:
C_X = Concentration of TPH in extract (µg/mL).
V_X = Volume of final extract (mL).
DF= Dilution factor.
V_S = Volume of sample extracted (mL).

14.4. Solid samples

$$\text{TPH Concentration (mg/kg)} = \frac{(C_X)(V_X)(DF)}{W_S}$$

Where:
C_X = Concentration of TPH in extract (µg/mL).
V_X = Volume of final extract (mL).
DF= Dilution factor.
W_S = Weight of sample extracted (g).

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See Tables 13.1 and 13.2.

16. Corrective Actions for Out-of-Control Data

16.1. See Tables 11.1, 13.1, and 13.2.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Tables 11.1, 13.1, and 13.2. If there is no additional sample volume to perform re-analyses, if the analytical results are due to the customer, and/or if there is no more holding time remaining; then data will be reported as final with applicable qualifiers. If necessary, an official case narrative can be prepared by the Quality Manager or Project Manager.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. **Method Detection Limit (MDL) Study and Verification:** An MDL study must be performed annually for each sample preparation and analysis-method pair (e.g. Microwave/Method 8270C) on at least one instrument.

18.2.1. The MDL study must meet the criteria defined in ENV-LENE-SOP-0117, *Limit of Detection*, or its equivalent revision or replacement.

18.2.2. The calculated MDL must then be verified on every instrument that is to be used for analysis of samples and reporting of data.

18.2.2.1 Analyze a QC sample containing analytes at no more than 2-3X the MDL for single-analyte tests and 1-4X the MDL for multiple-analyte tests.

18.2.2.2 The QC sample must undergo the applicable sample preparation (e.g., extraction).

18.2.2.3 All target compounds must be detected (result greater than zero) on all instruments to verify the calculated MDL.

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per ENV-SOP-LENE-0110, Training Procedures.

18.3.1. Analysis of four replicates of reagent water spiked with the TPH Spiking Solution at a concentration equivalent to the LCS.

18.3.2. Analysis of four replicates of Ottawa sand spiked with the TPH Spiking Solution at a concentration equivalent to the LCS.

18.3.3. If the average recovery is within the matrix-specific LCS acceptance criteria and the RSD of the replicates is ≤30%, system performance is acceptable and analysis of samples may begin. If, however, RSD >30% or average recovery falls outside the LCS criteria, system performance is unacceptable. In this event, correct the problem and repeat the test.

19. Method Modifications

19.1. Area counts for the internal standards and surrogates are subtracted from the total area count for TPH-DRO and TPH-ORO by the chromatography software.

20. Instrument/Equipment Maintenance

20.1 On an as needed basis, change injection port liner, trim column, change septa and gold seal, change out column and clean MS source. Please inform supervisor of issues and your plans for repairing these issues.

21. Troubleshooting

21.1 No detection of peaks:

21.1.1 Check to make sure that the gases are at sufficient levels above 200 PSI.

21.1.2 Check to make sure that MS is seeing PFTBA (tuning solution), if not switch filaments and try again.

21.1.3 Check to make sure that autosampler is pulling up sample into the needle.

If all of these are OK, then check with supervisor for review of column issues.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

22.3. **Equipment**

22.3.1. Portions of the analytical instrumentation operate at high temperature. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones.

22.3.2. The instrument also uses gas under high pressure. These high pressures introduce the risk of injury due to flying objects should a vessel or line rupture. Safety glasses are mandatory at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in ENV-SOP-LENE-0127, Waste Handling.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (e.g., before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains information on pollution prevention.

25. References

25.1. Pace Quality Assurance Manual - most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. EPA Test Methods for Evaluating Solid Waste, SW-846, Update III (12/1996), Methods 8000D and 8270C.

25.5. USEPA CLP Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration OLM04.2, 5/1999.

25.6. Missouri Risk-Based Corrective Action (MRBCA) Process for Petroleum Storage Tanks, Missouri Department of Natural Resources, Jan. 2004.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment 1: Characteristic Ions of Surrogates and Internal Standards

26.2. Attachment 2: Client-Specific Criteria (Internal Use Only)

26.3. Attachment 3: Client-Specific Criteria (Internal Use Only)

26.4. Attachment 4: Client-Specific Criteria (Internal Use Only)

27. Revisions

Document Number	Reason for Change	Date
KS-O-024-rev.0	New	March 30, 2006
KS-O-024-rev.1	Title – Added ORO Section 7.4 – Changed biennial to annual. Section 9 – Deleted extraction equipment. Section 9.1.2 – Changed column. Section 10.8 – Changed standard stability period. Section 11.1 – Changed final temperature Section 11.3 – Added table of initial calibration requirements. Section 11.3.1 - Added retention time window definitions. Section 11.3.2 – Added TPH-ORO RF statement. Section 11.3.4 – Changed SSV criteria. Section 12 - Deleted extraction procedure. Sections 13.2-4 – Removed references to WY STR program. Section 13.3.3 – Modified guidance for non-detects with high LCS bias. Section 17.1 – Deleted references for 8015C and extraction methods.	October 16, 2007
S-KS-O-024-rev.2	SOP – Updated to corporate template format. Section 8 – Added extract criteria. Section 11 – Added corrective actions. Section 14 -Added DOC procedure.	September 21, 2009
S-KS-O-024-rev.3	SOP – Deleted Responsibilities and Distribution section. Section 6 – Substituted reference to Quality Manual. Section 11 – Removed reference to Method 3520C. Table 11.1 - Revised operating parameters. Section 13 – Added LOD reference. Deleted Method Modifications. Section 14 – Revised SOP reference.	December 24, 2011
S-KS-O-024-rev.4	Section 2 – Added reduced-volume sample option. Table 7.1 – Added 100-mL bottle. Section 9 – Revised spike and surrogate concentrations. Section 11 – Revised aqueous sample preparation SOP reference.	March 5, 2012
S-KS-O-024-rev.5	SOP – Updated to latest prescribed format. Section 10 – Revised standards to combine TPH and surrogates. Added internal standard solution prep. Section 11 – Removed linear regression section. Added internal standard surrogate calibration. Section 12 – Internal standard addition for samples QC and standards. Table 12.1 – Mass range must be set to 35-550 amu. Attachment 1-4: Added	January 22, 2014
S-KS-O-024-rev.6	SOP _ Revised to latest format	October 11, 2016
ENV-SOP-LENE-0031-01	SOP—Removed cover page, Table of Contents and Headers. Section 12.1 -- updated SOP references Table 12.1 – Revised backup instruments Section 18.2 – updated SOP references Section 18.3 – updated SOP references Section 23.1 – updated SOP references Section 25.4 – updated to 8000D	December 13, 2018

Attachment 1: Characteristic Ions of Surrogates and Internal Standards

Compounds	Primary Ion	Secondary Ion(s)	Internal Standard
Surrogates			
Nitrobenzene-d5	82	128,54	1
2-Fluorobiphenyl	172	171	2
Terphenyl-d14	244	122,212	4
Internal Standards			
Naphthalene-d6	136	68	1
Acenaphthene-d10	164	162,160	2
Phenanthrene-d10	188	94,80	3
Chrysene-d12	240	120,236	4
Perylene-d12	264	260,265	5

Attachment 2– BP-Specific 8270 Criteria (Internal Use Only)

Calibration Metric	Frequency	Criteria	Corrective Action
Tune Check (50-ng DFTPP)	Every 12 hours.	Ensure correct mass assignment. DFTPP % relative abundance criteria as specified in method.	Retune. Do not proceed with analysis until tune meets criteria.
Initial calibration	Each time the instrument is set up and when CCCs and SPCCs in the calibration do not meet criteria. Established initially at five concentration levels - low standard at or below project-required quantitation limit (PRQL).	Ave RRF for each SPCC and surrogate compound ≥0.050. %RSD for each CCC and surrogate compound ≤20%.	If a target compound does not meet the acceptance criteria, a new initial calibration must be performed. If SPCC or CCC criteria are not met, a new initial calibration must be performed.
Initial Calibration Verification	Immediately following the initial calibration and prior to sample analyses. Must be at or near the mid-point calibration range for all target compounds, SPCCs, CCCs, and surrogates.	RRF for each SPCC and surrogate compound ≥0.050. %D for RRFs of all target analytes and surrogates ≤20%.	Reprepare and reanalyze the ICV once. If it fails a second time a new initial calibration should be rerun.
Continuing Calibration Verification	Every 12 hours. Must be at or near the mid-point calibration range for all target compounds, SPCCs, CCCs, and surrogates.	RRF for each SPCC and, surrogate compound ≥0.050. %D for RRFs of all target analytes and surrogates ≤20%.	Correct system, if necessary, and recalibrate. Criteria must be met before sample analysis may begin.
Internal standards	Added to all blanks, standards, QC samples, and samples.	Peak area within -50% to +100% of area in associated continuing calibration standard. Retention time (RT) within 30 sec of RT for associated continuing calibration standard.	Inspect instrument for malfunctions; correct identified malfunctions, then reanalyze samples. If no instrument malfunction is identified, proceed as follows: Reanalyze sample. If reanalysis is out, report both sets of data. If in, report only second set.
Surrogate Compounds	Calibrated and quantitated as target compounds. Added to all standards, blanks, samples, and QC samples.	All recoveries must be within acceptance limits.	If recovery acceptance criteria are not within limits: Check to be sure that there are no errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance. If no problem is found, prepare and analyze the sample a second time. If the reanalysis is within limits and holding times, then report only the reanalysis. If the reanalysis is within limits, but out of hold, then report both sets of data. If the reanalysis is still out of limits, then report both sets of data. If the sample was chosen for the MS/MSD analysis, and the MS and/or MSD are outside limits, then no reanalysisis required.

Calibration Metric	Frequency	Criteria	Corrective Action
Method Blank	One per extraction batch of 20 or fewer samples per matrix per day. Must undergo all sample preparative procedures. Must be run on each instrument used for sample analysis.	Target compounds <½ PRQL. Must meet surrogate and internal standard criteria.	Reanalyze to determine if instrument contamination was the cause. If the method blank is still noncompliant, reextract and reanalyze all samples unless >10x the blank, or there are no positive results.
Laboratory Control Sample (LCS)	One per matrix per extraction batch (if applicable) per set of 20 samples per day. Must undergo all sample preparative procedures. Must contain all target compounds at concentrations at the mid-point of the calibration range.	% Recoveries (and RPDs, if applicable) within laboratory-generated limits.	Reanalyze the LCS to determine if instrumental conditions or analytical preparation was the cause. If still out reprepare and reanalyze associated samples and LCS. Exception: If LCS recovery is high and no associated positive results are reported, then address the issue in the SDG Narrative and no further action is needed.
Matrix Spike/Matrix Spike Duplicate	One per matrix per extraction batch (if applicable) per set of 20 samples per day. Must undergo all sample preparative procedures. Must be spiked with all target compounds at concentrations at or near the midpoint of the calibration range.	% Recoveries within laboratory-generated limits. RPDs within laboratory-generated limits.	If LCS is acceptable, then report in the SDG Narrative that there was probable matrix interference.
Qualitative/ Quantitative Issues	If instrument level of any compound in a sample exceeds the instrument level of that compound in the highest level standard, the sample must be diluted to approximately mid-level of the calibration range and reanalyzed. If the concentration of the target analyte that exceeded the calibration range is present in the high-level sample and in the sample analyzed immediately after at a level greater than the PRQL, but ≤5x PRQL, then that second sample must be reanalyzed to determine if carryover occurred.	The instrument level of all compounds must be within the calibration range for all samples. The sample analyzed immediately after a high-level sample must display concentrations of the high-level target compounds < the PRQL or greater than 5x PRQL.	Dilute the sample to bring the level of the highest concentration of target compounds within the calibration range. A sample displaying concentrations of target compounds between the PRQL and 5x the PRQL which was analyzed immediately after a high-level sample must be reanalyzed. If the results do not agree within the PRQL, report only the second analysis.

Attachment 3: Canadian National Railway 8270C Criteria (Internal Use Only)

Calibration Metric	Frequency	Criteria	Corrective Action
GC/MS Tuning (50-ng DFTPP)	Every 12 hours.	Ensure correct mass assignment. Ion abundances must meet the method acceptance criteria.	Retune instrument. Do not proceed with calibration until tune criteria are met.
Initial Calibration	Each time the instrument is set up and when calibration verification criteria are not met. A minimum of five calibration standards is required. The low-level calibration standard must be at or below the reporting limit.	%RSD must be ≤20% for target analytes and surrogates All target analytes and surrogate compounds are considered CCCs and SPCCs and must meet method criteria.	When the minimum RRF is not met, a new calibration must be performed. A new calibration must be performed when SPCC and CCC criteria are not met.
Initial Calibration Verification (ICV)	Second-source calibration verification standard must be analyzed after every initial calibration.	% Difference must be ≤ 20% for target analytes and surrogates.	Correct system and reanalyze ICV. If second ICV fails, recalibrate system.
Continuing Calibration Verification (CCV)	At the beginning of each 12-hour shift (following the DFTPP tune check).	% Difference must be ≤ 20% for target analytes and surrogates.	Correct system and reanalyze CCV. If second CCV fails, recalibrate system and reanalyze all associated project samples.
Internal Standards	Added to every standard, sample, and QC sample. Sample internal standard area counts and RTs must be compared to the internal standard area counts and RTs of the associated CCV standard. CCV internal standard area counts and RTs must be compared to the area counts and RTs of the ICV standard.	Area counts of the internal standard peaks must be 50-200% of the internal standard area observed in the reference. Retention time (RT) of the internal standard must not vary more than ± 30 seconds from the RT of the internal standards observed in associated CCV standard.	Correct system, if necessary; reanalyze sample.
Instrument Blanks	Analyzed after CCV standards. Instrument blanks are allowable between samples with high concentrations of target compounds, but must not be analyzed strategically before CCV standards.	Target compound results < %the RL. If samples are reported to the MDL, target compounds must not be present above the MDL.	For results >½ the RL, reextract and reanalyze associated samples. For results > the MDL but <½ the RL where samples are reported to the MDL, reextract and reanalyze associated samples or qualify associated sample data in the Case Narrative. If positive results for the contaminant compounds are not observed in the associated project samples, corrective action is not required.

Calibration Metric	Frequency	Criteria	Corrective Action
Method Blank	One per extraction batch of 20 or fewer samples analyzed on each instrument used for analysis of CN samples. A method blank is required for each extraction method.	Target compound results <1/2 the RL. If samples are reported to the MDL, target compounds must not be present above the MDL. Must meet internal standard and surrogate recovery criteria.	Reextract and reanalyze associated samples. If positive results for the contaminant compounds are not observed in the associated project samples, corrective action is not required. Reanalyze blank if surrogate or internal standard acceptance criteria are not met.
Surrogate Recovery	Calibrated as target compounds. Added to all blanks, samples, and QC samples.	All surrogates must meet laboratory-generated acceptance limits.	Check to be sure that there are no errors in the calculations, surrogate solutions, or internal standards. Check instrument performance. Correct the problem and reanalyze the extract if a problem is identified. If no problems are identified, reextract and reanalyze sample. If surrogate recovery criteria are met upon reextraction/reanalysis, report the reanalysis results. If surrogate recovery criteria are not met upon reextraction/reanalysis, report both sets of data. If the reextraction/reanalysis is performed outside of holding time, provide both the original and reanalysis results to the data user.
Laboratory Control Sample (LCS)	One per extraction batch of up to 20 samples. LCS must undergo all sample preparation procedures and must contain all target compounds at the midpoint of the calibration range.	% Recoveries within laboratory-generated limits.	Reanalyze LCS to confirm results. If LCS results are outside acceptance criteria upon reanalysis, reextract and reanalyze associated project samples. If high recoveries are observed and "not-detected" results are reported for the associated samples, reanalysis is not necessary.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	One per matrix per extraction batch of up to 20 samples.	% Recoveries and RPDs within laboratory-generated limits.	If LCS results meet acceptance criteria, report probable matrix interference in the Case Narrative. Do not reanalyze the MS/MSD samples unless laboratory error is confirmed (e.g., non-spiked).
Qualitative/Quantitative Issues	If the instrument level of any target compound in a sample exceeds the calibration range, the sample must be diluted and reanalyzed.	The instrument level of all target compounds must be within the calibration range. Solvent lot numbers must be recorded for all samples reanalyzed at dilutions.	Dilute the sample to bring the target compound level within the calibration range.

Calibration Metric	Frequency	Criteria	Corrective Action
Manual Integrations	Manual integrations may not be performed for the purpose of meeting calibration or QC criteria.	Manual integrations must be performed in accordance with the associated laboratory SOP. Manual integrations must be reviewed and approved by a supervisor.	N/A

Notes:

- Initial calibration is performed with a minimum of five calibration standards. The low-level calibration standard must be at or below the reporting limit. When the initial calibration RSD criterion is not met, initial calibration standards may be reanalyzed or calibration points may be removed from the extreme ends of the calibration range only in a manner consistent with the analytical method. Reanalysis of calibration points must occur before project samples are analyzed. If a low-level calibration standard is dropped, the reporting limit must be raised to the concentration of the next lowest-level standard.
- Calibration must be verified at the beginning of each 12-hour analytical shift, immediately following the DFTPP tune check. Surrogate compounds must be calibrated as target compounds (i.e., with a minimum of five concentration levels).
- Surrogate compounds must be added to all initial calibration standards, CCV standards, samples, and QC samples (including instrument blanks).
- Internal standard compounds must be added to all calibration standards, samples, and QC samples. Sample internal standard area counts and retention times must be compared to the area counts and retention times of the associated CCV standard. Internal standard area counts and retention times for CCV standards must be compared to the ICV standard, which must be compared to the mid-level calibration standard. Sample and QC sample internal standard area counts and retention times must be compared to the associated CCV standard. Internal standard area counts and retention times must meet the criteria specified on the table.
- When an extraction batch is analyzed using more than one instrument, the method blank must be analyzed on at least one instrument used for sample analysis.
- MS/MSD samples must be extracted with the project samples but may be analyzed at any time in the sample batch.
- LCS and MS/MSD samples must be spiked with all target compounds. When the LCS target compound recovery criteria are not met (confirmed by reanalysis), the entire extraction batch must be reextracted and reanalyzed. Reextraction and reanalysis are not required when high recoveries are observed for a target compound and that compound is not detected in the associated project samples. No action is required when MS/MSD analyses are outside of recovery and/or precision criteria, provided the associated LCS results are within criteria; probable matrix interference must be reported in the Case Narrative.
- All instrument maintenance must be meticulously recorded in the associated instrument logbook. Equipment blanks/field blanks must not be reanalyzed when contamination is observed.
- Analysis sequence logs must contain all injections, not only those reported.

Attachment 4 – ConocoPhillips 8270C Criteria (Internal Use Only)

Calibration Metric	Frequency	Criteria	Corrective Action
GC/MS Tuning (50-ng DFTPP)	Every 12 hours.	Ensure correct mass assignment. Ion abundances must meet the method acceptance criteria.	Retune instrument. Do not proceed with calibration until tune criteria are met.
Initial calibration	Each time the instrument is set up and when calibration verification criteria are not met. The low-level calibration standard must be at or below the reporting limit.	Surrogate compounds are considered CCCs and SPCCs and must meet method criteria.	When the minimum RRF is not met, a new calibration must be performed. A new calibration must be performed when SPCC and CCC criteria are not met.
Initial Calibration Verification	Second-source calibration verification standard must be analyzed after every initial calibration.	% Difference must be ≤20% for all target compounds and surrogates.	Correct system and reanalyze ICV. If second ICV fails, recalibrate system.
Continuing Calibration Verification	At the beginning of each 12-hour shift (following the DFTPP tune check).	% Difference must be ≤20% for all target compounds and surrogates.	Correct system and reanalyze CCV. If second CCV fails, recalibrate system and reanalyze all associated project samples.
Internal standards	Added to every standard, sample, and QC sample. Sample internal standard area counts and RTs must be compared to the internal standard area counts and RTs of the associated CCV standard. CCV internal standard area counts and RTs must be compared to the area counts and RTs of the ICV standard.	Area counts of the internal standard peaks must be 50-200% of the internal standard area observed in the reference. Retention time (RT) of the internal standard must not vary more than ± 30 seconds from the RT of the internal standards observed in associated CCV standard.	Correct system, if necessary; reanalyze sample.
Surrogate Recovery	Calibrated as target compounds. Added to blanks, samples, and QC samples.	All recoveries meet laboratory-generated acceptance limits.	Check to be sure that there are no errors in the calculations, surrogate solutions, or internal standards. Check instrument performance. Correct the problem and reanalyze the extract if a problem is identified. If no problems are identified, reextract and reanalyze sample. If surrogate recovery criteria are met upon reextraction/reanalysis, report the reanalysis results. If surrogate recovery criteria are not met upon reextraction/reanalysis, report both sets of data. If the reextraction/reanalysis is performed outside of holding time, provide both the original and reanalysis results to the data user.

Calibration Metric	Frequency	Criteria	Corrective Action
Method Blank	One per extraction batch of 20 or fewer samples analyzed on each instrument used for analysis of ConocoPhillips samples. A method blank is required for each extraction method.	Target compound results <½ the RL. If samples are reported to the MDL, target compounds must not be present above the MDL.	Reanalyze to determine if instrument contamination was the cause. If the method blank is still noncompliant, reextract and reanalyze all samples unless >10x the blank, or there are no positive results.
Laboratory Control Sample (LCS)	One per extraction batch of up to 20 samples. LCS must undergo all sample preparation procedures and must contain all target compounds at the midpoint of the calibration range.	% Recoveries within laboratory-generated limits.	Reanalyze LCS to confirm results. If LCS results are outside acceptance criteria upon reanalysis, reextract and reanalyze associated project samples. If high recoveries are observed and "not-detected" results are reported for the associated samples, reanalysis is not necessary.
Matrix Spike/Matrix Spike Duplicate	One per matrix per extraction batch of up to 20 samples.	% Recoveries and RPDs within laboratory-generated limits.	If LCS results meet acceptance criteria, report probable matrix interference in the SDG Narrative. Do not reanalyze the MS/MSD samples unless laboratory error is confirmed (e.g., non-spiked).
Qualitative/ Quantitative Issues	If the instrument level of any target compound in a sample exceeds the calibration range, the sample must be diluted and reanalyzed.	The instrument level of all target compounds must be within the calibration range. Solvent lot numbers must be recorded for all samples reanalyzed at dilutions.	Dilute the sample to bring the target compound level within the calibration range.
Manual Integrations	Manual integrations may not be performed for the purpose of meeting calibration or QC criteria.	Manual integrations must be performed in accordance with the associated laboratory SOP. Manual integrations must be reviewed and approved by a supervisor.	N/A

Notes:

- Initial calibration is performed with a minimum of five calibration standards. The low-level calibration standard must be at or below the reporting limit. When the initial calibration RSD criterion is not met, initial calibration standards may be reanalyzed or calibration points may be removed from the extreme ends of the calibration range only in a manner consistent with the analytical method. Reanalysis of calibration points must occur before project samples are analyzed. If a low-level calibration standard is dropped, the reporting limit must be raised to the concentration of the next lowest-level standard.
- Calibration must be verified at the beginning of each 12-hour analytical shift, immediately following the DFTPP tune check.
- Surrogate compounds must be calibrated as target compounds (i.e., with a minimum of five concentration levels).
- Surrogate compounds must be added to all initial calibration standards, CCV standards, samples, and QC samples (including instrument blanks).
- Internal standard compounds must be added to all calibration standards, samples, and QC samples. Sample internal standard area counts and retention times must be compared to the area counts and retention times of the associated CCV standard. Internal standard area counts and retention times for CCV standards must be compared to the ICV standard, which must be compared to the mid-level calibration standard. Sample and QC sample internal standard area counts and retention times must be compared to the associated CCV standard. Internal standard area counts and retention times must meet the criteria specified on the table.

- When an extraction batch is analyzed using more than one instrument, the method blank must be analyzed on at least one instrument used for sample analysis.
- MS/MSD samples must be extracted with the project samples but may be analyzed at any time in the sample batch.
- LCS and MS/MSD samples must be spiked with all target compounds. When the LCS target compound recovery criteria are not met (confirmed by reanalysis), the entire extraction batch must be reextracted and reanalyzed. Reextraction and reanalysis are not required when high recoveries are observed for a target compound and that compound is not detected in the associated project samples. No action is required when MS/MSD analyses are outside of recovery and/or precision criteria, provided the associated LCS results are within criteria; probable matrix interference must be reported in the SDG Narrative.
- All instrument maintenance must be meticulously recorded in the associated instrument logbook. Equipment blanks/field blanks must not be reanalyzed when contamination is observed.
- Analysis sequence logs must contain all injections, not only those reported.

Document Information

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Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Pace Analytical™

STANDARD OPERATING PROCEDURE

CATION EXCHANGE CAPACITY OF SOILS

Reference Methods: SW-846, Method 9081

Local SOP Number:	S-KS-M-007-rev.7
Effective Date:	Date of Final Signature
Supersedes:	S-KS-M-007-rev.6

Approvals

Laboratory General Manager — Date: 9/8/17

Laboratory Quality Manager — Date: 9-8-17

Department Manager — Date: 9/8/17

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

S-KS-M-007-rev.7

TABLE OF CONTENTS

1. Purpose/Identification of Method

1.1. The purpose of this method is to provide a laboratory-specific procedure meeting the requirements in Method 9081 for the determination of the cation exchange capacity of soil samples.

2. Summary of Method

2.1. A soil sample is mixed with an excess of sodium acetate solution, resulting in an exchange of the added sodium cations for the matrix cations. Subsequently, the sample is washed with isopropyl alcohol. An ammonium acetate solution is then added, which replaces the absorbed sodium with ammonium. The concentration of the displaced sodium is then determined by emission spectroscopy (ICP).

3. Scope and Application

3.1. Personnel: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method or non-analytical process.

3.2. Parameters: This SOP measures the degree to which a soil can adsorb and exchange cations.

4. Applicable Matrices

4.1. This method is applicable to most soils, including calcareous and noncalcareous soils.

5. Limits of Detection and Quantitation

5.1. This method's reporting limit (LOQ) for cation exchange capacity (CEC) is 0.1 meq/100g. MDLs (LODs) are not applicable to this procedure.

6. Interferences

6.1. Method interferences may be caused by contamination in reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

7. Sample Collection, Preservation, Shipment and Storage

Table 7.1 Sample Collection, Preservation, and Storage

Sample type	Collection per sample	Preservation	Storage	Hold time
Soil	Glass jar, 4-ounce.	N/A	N/A	180 days

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

9. Equipment and Supplies

Table 9.1 Equipment and Supplies

Supply	Vendor	Model / Version	Comments
Analytical balance	Mettler-Toledo	PB3002-S	or equivalent
Centrifuge	International Equipment Company	Clinical	rotor with 50-mL slots
Centrifuge tubes	Fisher	06-443-19	50-mL
Filter paper	Fisher	09-850-D	Whatman Grade 41, 12.5 cm dia.
Oblong bottles	Fisher	02-911-953	125-mL, HDPE
Shaker table	Eberbach	6010	reciprocating shaker
Volumetric flasks	Fisher	100-mL, 1- , 2-L	Class A

10. Reagents and Standards

Table 10.1 Reagents and Standards

Reagent/Standard	Concentration/ Description	Vendor/ Item #
Acetic acid, glacial	ACS Reagent Grade	Fisher / A38
Ammonium hydroxide	~14.8N, ACS Reagent Grade	Fisher / A669
Glass beads	KIMAX KG-33 glass	Environmental Express / GL13500
Isopropanol	HPLC Grade	Fisher / A451
Reagent water	ASTM Type II	SOP S-KS-Q-011 (latest revision)
Reference Soil	North American Proficiency Testing Program	Soil Science Society of America
Sodium acetate trihydrate	Crystalline, ACS Reagent Grade	Fisher / S209
Sodium hydroxide pellets	ACS Reagent Grade	Fisher / S318

10.1. Sodium acetate solution, 1.0N: Dissolve 136 g of sodium acetate in reagent water and dilute it to 1 liter. The pH of this solution should be 8.2. If needed, add a few drops of acetic acid or NaOH solution to bring the pH of the solution to 8.2.

10.2. Ammonium acetate solution, 1.0N: In a 2 liter vessel, dilute 114 mL of glacial acetic acid with reagent water to a volume of approximately 1 liter. Add 138 mL of concentrated ammonium hydroxide and add reagent water to obtain a volume of about 1,980 mL. Check the pH of the resulting solution. Add more NH_4OH, as needed, to obtain a pH of 7. Dilute the solution to a volume of 2 liters with reagent water.

11. Calibration and Standardization

11.1. Calibrate the analytical balance as per SOP S-KS-Q-036, *Support Equipment* each day of use.

12. Procedure

12.1. Method Blank (MB): Weigh five grams of glass beads into a labeled, 50-mL centrifuge tube.

12.2. Laboratory Control Sample (LCS): Weigh five grams of Reference Soil into a labeled, 50-mL centrifuge tube.

12.3. Client Samples and Sample Duplicate: Weigh 5 grams of soil and transfer to the appropriately labeled, 50-mL centrifuge tube.

12.4. Add 33 mL of sodium acetate solution to each tube, cap. Place on a mechanical shaker for 5 minutes. Centrifuge the solution until the supernatant liquid is clear.

12.5. Decant and dispose of the liquid. Loosen compacted soil from bottom of centrifuge tube.

12.6. Repeat the process of adding solution, shaking and centrifuging two more times.

12.7. Add 33 mL of isopropanol to each tube, cap. Place on a mechanical shaker for 5 minutes. Centrifuge the solution until the supernatant liquid is clear.

12.8. Decant and dispose the liquid. Loosen compacted soil from bottom of centrifuge tube.

12.9. Repeat the process of adding isopropanol, shaking and centrifuging two more times.

12.10. Add 33 mL of ammonium acetate solution and screw the cap on the tube. Place on a mechanical shaker for 5 minutes. Centrifuge the solution until the supernatant liquid is clear.

12.11. Filter the decanted washing into a 100-mL volumetric flask. Loosen compacted soil from bottom of centrifuge tube.

12.12. Repeat the process of adding solution, shaking and centrifuging two more times.

12.13. Dilute the combined washings to the 100-mL mark with the ammonium acetate solution and transfer to labeled, 125-mL HDPE oblong bottles.

12.14. Analyze washings for sodium by SOP S-KS-M-005, *Inductively Coupled Plasma Atomic Emission Spectroscopy*. Samples are to be run at a ten-fold dilution by ICP.

13. Quality Control

Table 13.1 Batch Quality Control

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Glass beads	One per batch of up to 20 samples	Target analytes must be less than the reporting limit.	1) Re-analyze blank to confirm failure. (Repeat only once) 2) Qualify results and / or reprep associated samples. ***Exceptions:*** 1) If sample ND, report sample without qualification 2) If sample result >10x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination. 3) If sample result <10x MB detects, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	Reference Soil	One per batch of up to 20 samples	60-140%	1) Analyze another LCS to confirm failure (Repeat only once) 2) If failure confirms, qualify results and / or reprep associated samples. 3) If failure confirms, perform system maintenance and/or recalibrate system ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Duplicate	Sample Dup	One per batch of up to 20 samples.	Max RPD: 30%	1) Report results with an appropriate footnote.

14. Data Analysis and Calculations

$$\text{CEC (meq/100g)} = \frac{([\text{Na}])(V)(100)}{(22.9)(W)(1000)}$$

Where:

[Na] = Sodium concentration in washings, mg/mL
V = Volume of the washings, mL
W = Weight of sample, g.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See Table 13.1.

16. Corrective Actions for Out-of-Control Data

16.1. See Table 13.1.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. See Table 13.1.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files

18.2. **Demonstration of Capability (DOC):** Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, Training Procedures.

18.2.1. Analyze of four replicates of Reference Soil.

18.2.2. If the average recovery meets the matrix-specific LCS criteria and the RSD of the replicates is <20%, system performance is acceptable and analysis of samples may begin. If, however, RSD >20% or average recovery falls outside LCS criteria, system performance is unacceptable. In this event, correct the problem and repeat the test.

19. Method Modifications

19.1. Not applicable.

20. Instrument/Equipment maintenance

20.1. Not applicable.

21. Troubleshooting

21.1. Check reagents and replace as needed.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

22.3. **Mercury**: Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analyses should be conducted in a laboratory exhaust hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-KS-S-002, Waste Handling.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (e.g., before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains information on pollution prevention.

25. References

25.1. Pace Quality Assurance Manual - most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. EPA Test Methods for Evaluating Solid Waste. SW-846, Third Edition, 9/1986, Method 9081.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Not applicable.

27. Revisions

Document Number	Reason for Change	Date
KS-I-4340-A	New	July 11, 2001
KS-I-4340-B	Grammatical. Removal of outdated information	June 3, 2004
KS-M-007-rev.2	Grammatical. Removal of outdated information	September 12, 2006
S-KS-M-007-rev.3	Overall conversion to template format. Changes required based on conversion are not explicitly noted unless change represents a significant policy change. Section 10 – Added reference sample. Section 13 – Added DOC procedure and control limit generation.	May 8, 2008
S-KS-M-007-rev.4	Section 7 – Revised Dir QST and Distribution. Table 9.1 – Revised instrument. Section 12 – Use boiling stones for blank. Section 15 – Changed Waste SOP reference. Section 16 – Revised references.	January 31, 2011
S-KS-M-007-rev.5	SOP – Updated to latest prescribed format. Table 7.1 – Changed storage temperature. Table 10.1 – Replaced boiling stones with glass beads. Section 12 – Replaced boiling stones with glass beads. Added "loosen soil after decanting". Table 13.1 – Revised acceptance criteria and corrective actions	June 13, 2013
S-KS-M-007-rev.6	SOP – Updated to latest prescribed format. Section 12.14 – Revised to add a 10 fold dilution.	September 21, 2015
S-KS-M-007-rev.7	SOP – Updated Cover to Pace LLC.	September 8, 2017

APPENDIX D-6

PACE GREEN BAY SOPS

Document Information

Document Number: ENV-SOP-GBAY-0006 **Revision:** 01

Document Title: Sample Management

Department(s): Client Services

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All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-GBAY-0006 **Revision:** 01
Title: Sample Management

All dates and times are in Central Time Zone.

ENV-SOP-GBAY-0006 -Rev.01 Sample Management

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Kate Verbeten (007119)	Quality Manager	07 May 2019, 02:17:33 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Nils Melberg (007142)	General Manager	07 May 2019, 04:04:18 PM	Approved
Alee Her (007671)	Working Supervisor	14 May 2019, 08:43:21 AM	Approved

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to outline the procedures involved with the receipt, login, storage, and disposal of samples received by Pace Analytical Services, LLC.

2. Summary of Method

2.1. Samples are delivered to the laboratory via several delivery mechanisms. Samples received are checked for adherence to the Sample Acceptance Policy (see Attachment I) with any discrepancies noted. Discrepancies are communicated to the client if necessary for their acknowledgement and decision making.

2.2. The Laboratory Information Management System (LIMS) assigns all samples with a unique sample number and manages the analyses assigned to each sample.

2.3. Samples are labeled with the appropriate information and staged in refrigerated sample storage coolers if temperature preservation is required or possibly stored on open shelves for samples not requiring sub-ambient temperature preservation. Samples will remain under these conditions until prepared and/or analyzed. Samples received under United States Department of Agriculture (USDA) protocols need to be stored separately (please refer to the lab's Regulated Soils SOP, if applicable).

2.4. Samples and associated sub-samples (digestates, extracts, etc.), are maintained for a minimum of 45 days from receipt of samples unless otherwise requested by the client or other regulatory agency.

2.5. Samples are disposed of in accordance with local laboratory regulatory requirements, waste handling procedures, and any USDA regulated soil requirements.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP apply to all personnel involved in the receipt, login, storage, and disposal of samples.

3.2. The Sample Acceptance Policy (Attachment I) contains the guidelines for acceptable sample conditions. Any deviation from these guidelines requires detailed documentation within the report, usually as a footnote, or on the chain-of-custody (COC), or Sample Condition Upon Receipt (SCUR) form and may require client contact.

3.3. **Parameters**: Not applicable to this SOP.

4. Applicable Matrices

4.1. Refer to Table 8.1 in this SOP for the applicable matrices.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Samples may be prone to cross contamination from others within the same delivery group or from other client projects. The sample receiving personnel must make every effort to minimize cross-contamination.

6.2. Preservation checks are one of the most likely situations where cross-contamination may occur. Materials used in the process must be specific to each sample and may not used for multiple samples or multiple containers of the same sample.

6.3. Samples are stored under specific conditions and in specific locations, typically per the requirements of the analytical method. However, consideration must be given to samples that are uniquely different from others. Samples that are anticipated to be severely contaminated must be segregated from others in anticipation that the high levels of contaminants may cross-contaminate others in close proximity. USDA samples must also be distinctly segregated for storage.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Acceptable sample preservation, containers, and hold times can be referenced in the Bottle and Preservation Table, available within the Pace Quality Assurance Manual, or as a separate document. Samples are stored separately from all standards and reagents and any known highly contaminated samples.

7.2. NOTE: To avoid contamination, no food or drink products can be located near the areas where samples are unpacked, labeled, or staged.

7.3. Sample Storage – See Section 12.3 for general storage guidelines.

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

8.2. **Chain-of-Custody (COC):** a form used to record the field identification of samples collected, analyses requested, date and time of collection, sample preservation used, and traceability of samples from time of collection until delivery to the laboratory. This is a legal document.

8.3. **Laboratory Information Management System (LIMS):** a computer system used to manage the flow and traceability of environmental samples and associated data within the laboratory.

8.4. **Matrix:** the bulk characteristics of a sample. See Table 8.1 below.

8.5. **Safety Data Sheet (SDS):** contains information on chemicals used in the laboratory.

8.6. **Sample Custody:** a sample is considered to be in someone's custody if:

8.6.1. It is in one's physical possession;

8.6.2. It is in someone's view, after being in someone's physical possession;

8.6.3. It is kept in a secured area, restricted to authorized personnel only.

8.7. **Sample Condition Upon Receipt (SCUR) form:** a form used to record the condition of samples received in the laboratory.

8.8. **Sample Receipt Form (SRF):** form generated by LIMS system after a project is logged in. Contains sample and project information.

8.9. **UN Number:** identification numbers preceded by the letters UN are associated with proper shipping names considered appropriate for international and domestic transportation. These shipping names along with the identification numbers are located in the Federal Register (49CFR172.101).

Table 8.1

NELAC/TNI defined matrix	Corresponding EPIC Pro matrices
Air and Emissions: Whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbant tube, impinger solution, filter, or other device.	Air (AR)
Aqueous: any aqueous sample excluded from the definition of Drinking Water or Saline/Estuarine. Includes surface water, ground water effluents, and TCLP or other extracts.	Water (WT)
Biological tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.	Tissue (TS) or Tissue Dry (TD)
Chemical Waste: a product or by-product of an industrial process that results in a matrix not previously defined.	Oil (OL) or Other (OT)
Drinking Water: any aqueous sample that has been designated a potable or potentially potable water source.	Drinking Water (DW)
Non-aqueous liquid: any organic liquid with < 15% settleable solids.	Other (OT)
Saline/Estuarine: any aqueous sample from an ocean or estuary, or other salt water source such as the Great Salt Lake.	Water (WT)- not assigned as a separate matrix.
Solids: includes soils, sediments, sludges and other matrices with > 15% settleable solids.	Solid (SL)
(No corresponding matrix to wipes; wipes would be included in with solids)	Wipe (WP) or Swab (SW)

9. Equipment and Supplies (Including Computer Hardware and Software)

Table 9.1

Equipment/Supplies	Description	Vendor/Item #
Sample Labels	Adhesive	
Thermometers	Jacketed, Digital, NIST traceable	
Sample storage cooling units	Capable of holding required storage temperatures	NA
COC forms	Chain of Custody Forms	N/A
SCUR forms	Sample Condition Upon Receipt	N/A
pH paper	Wide Range 0-14	CTL 921-10
Label Printer	Thermal Printer	NA
LIMS computer system	EPIC Pro	NA
Disposable pipettes	Plastic	Baxter Scientific, P200-1
Sample containers	Glass or Plastic	C&G, QEC, Fisher
Temperature blank	Plastic	NA

10. Reagents and Standards

10.1. All reagents used in this procedure must be labeled with:

10.1.1. Laboratory reagent identification number;

10.1.2. Unless otherwise noted, the name and concentration of the reagent;

10.1.3. Date the reagent was received, opened and, as needed, prepared;

10.1.4. Person preparing reagent;

10.1.5. Expiration date.

10.2. **Reagents: Table 10.1**

Reagent	Formula	Concentration
Sulfuric Acid	H_2SO_4	1:1
Nitric Acid	HNO_3	1:1
Hydrochloric Acid	HCl	1:1
Sodium Hydroxide	NaOH	50% or Pellets
Sodium Thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	As provided by vendor
Zinc Acetate Solution (for sulfide)	$Zn(CH_3CO_2)_2 \cdot 2H_2O$	As provided by vendor
Methanol	MeOH	Purge and Trap Grade
Ascorbic Acid (for cyanide)	$C_6H_8O_6$	As provided by vendor
Sodium Bisulfate	$NaHSO_4$	5mL:40mL vial
Ammonium sulfate/ ammonium hydroxide (for hexavalent chromium)	$(NH_4)_2SO_4$/ NH_4OH	Provided by sub-lab as necessary

10.3. For acids, bases and other reagents obtained from other laboratory departments, this information is located in the appropriate hardcopy or electronic standards/reagent preparation log. In the event that these reagents are managed within the Sample Receiving group, the department must maintain its own reagent preparation log.

10.4. Some Pace labs use preserved sample containers. In this case, documentation must be maintained for bottleware and preservation traceability.

11. Calibration and Standardization

11.1. Thermometers, IR-Guns, and other equipment used for measuring temperatures must be calibrated according to SOP ENV-SOP-GBAY-0115 *Support Equipment*, or its equivalent revision or replacement.

12. Procedure

12.1. **Sample Receipt**

12.1.1. The laboratory receives client samples via three major methods: mail/commercial delivery service, Pace Analytical courier/field services and hand delivery.

12.1.2. Courier COC Procedures: Pace labs use courier services that pick up client samples on either a regular schedule or on an as-needed basis as communicated by Project Managers (PMs) or by the client.

12.1.2.1. When the client is present during courier pick-up, the client signs the COC relinquishing custody to the courier. The courier signs the COC as accepting the samples and provides the client with a copy of the COC. When the courier returns to the lab with the client samples, the courier signs the COC as relinquishing the samples to the lab.

12.1.2.2. If the client is not present during courier pick-up, the courier signs the COC as accepting the samples and leaves a copy of the COC for the client. If a client also has a sample log in use, the courier must sign and date the log when the samples are picked up. When the courier returns to the lab with the client samples, the courier signs the COC as relinquishing the samples to the lab. The date/time of delivery to the lab by the courier is the official date/time received by the lab (analogous to the official date/time of receipt by an outside commercial carrier or courier).

12.1.2.3. To ensure the sample security, the Pace courier vehicle is locked at each client pick-up location. IMPORTANT: Pace Analytical courier/field services personnel must open the sample coolers and verify there is adequate ice in the coolers before transporting or shipping to the laboratory. An exception to this policy would be for coolers already custody-sealed by the client. These coolers are not to be opened except by the receiving lab personnel.

12.1.3. **Lab COC Procedures**: The COC (see example Attachment II) is signed immediately upon receipt of the samples from the client. If the client drops off the samples, a copy of the signed COC is given to the client at that time. If samples are received via commercial carrier or mail delivery, the COC should be signed immediately when the cooler or package is opened and ultimately placed in the project file. The delivery date and time is considered the date/time received.

12.1.3.1. **Samples Dropped Off:** Sample receiving personnel must review the COC for any evidence of rush turnaround requests, analyses with short hold times, or samples with very little hold time remaining. Projects that fall under these conditions must be given immediate attention. The PM responsible for that client must be alerted in the event that they have not already alerted the laboratory to the project as it may be possible that the client did not pre-schedule the project. Once the samples are received and logged into the LIMS, the sample technician and project manager will coordinate the notification and delivery of samples to the laboratory.

12.1.4. **Sample Acceptance Policy -** Copies of the Sample Acceptance Policy must be provided, in the form of a letter, fax, or e-mail to each client or sampler, as necessary. Samples are considered acceptable if they meet the criteria listed in the Sample Acceptance Policy (see Attachment I)

12.1.4.1. For WI drinking water samples: Samples that do not meet the criteria in the Sample Acceptance Policy will be rejected by sample custody. Sample custody will notify the PM and the client will be notified before proceeding with login. If the client wishes to proceed with analysis, the project manager will retain documentation of the request to proceed.

12.1.5. **Measuring temperature when temperature blank present:** Open the cooler and verify the temperature of the samples by taking the temperature of the temperature blank. The temperature of the cooler must be taken using a NIST-traceable thermometer. The thermometer is placed into the temperature blank. After 5 minutes, the thermometer is read to the nearest 0.5°C increment and recorded.

12.1.6. **Measuring temperature when NO temperature blank present:** If there is no temperature blank in the cooler, measure the temperature of a representative sample bottle or cooler melt water. A representative sample will reflect an "average" condition of the samples in the cooler and, depending on the manner in which they are packed, may not necessarily be in direct contact with the cooling material.

12.1.6.1. Procedure using a stick thermometer: If an IR gun is not used, the temperature of the cooler must be taken using a NIST-traceable thermometer. If there is no temperature blank, the thermometer is placed into the melt water of the cooler for approximately 5 minutes. After 5 minutes, the thermometer is read to the nearest 0.5°C increment and recorded. If no ice is present, a sample aliquot (non-volatile) is poured into a small container and the temperature of the sample is taken.

12.1.6.2. Procedure using an IR gun: If an IR gun is used, the temperature must be taken from an opaque surface such as the bottle label. Measurements taken through a transparent surface (clear or amber glass) may not be reliable and must incorporate a specific temperature correction factor for that surface reading.

12.1.7. Record the uncorrected and corrected cooler temperatures on the COC (example in Attachment II) and/or SCUR form (example in Attachment III). In addition, record the type of "ice" used for packing the cooler (e.g., wet ice, "blue ice", gel packs, etc.).

12.1.8. If samples within a project are spread over multiple coolers and one or more of the coolers are outside of the temperature criteria, then the contents of the cooler must be itemized and the samples and sample containers affected by the out-of-control temperature must be listed on the SCUR form for qualification in the final report. This itemization must be retained in the project file for future reference.

12.1.9. Unpack the cooler and COC. Organize the samples, grouped by client sample ID, according to the order on the COC. Review COC against samples to make sure the bottles received match the analysis requested. All anomalies must be recorded on the SCUR form.

12.1.9.1. If the lab receives coolers late or cannot unpack a cooler until the following day the following is performed:

12.1.9.1.1. The cooler is visually inspected and opened.

12.1.9.1.2. The COC is removed and signed.

12.1.9.1.3. The temperature of the cooler is taken and recorded on COC.

12.1.9.1.4. The COC is checked for short hold time samples. If short hold time samples are present, the cooler is processed immediately.

12.1.9.1.5. If short hold time samples are not present, the cooler and contents are placed into the designated Walk-in Cooler to be processed the following day.

12.1.10. For USDA samples, the cooler and all contents must be decontaminated (refer to Regulated Soil SOP for procedure). For non-USDA samples, discard any ice or water that remains in the cooler and the packing material used to secure the samples. Water or ice should be discarded down a drain that connects to the local sewer. Packing materials should be placed in the garbage. If a sample container was broken, the contents remaining in the cooler MUST be discarded in a manner consistent with the hazardous waste handling standard operating procedure.

12.1.11. **pH Verification Instructions:**

12.1.11.1. The pH of the sample must be verified on all preserved sample bottles requiring pH preservation (see exceptions below).

12.1.11.2. Open each preserved bottle (except as noted below). Use a new disposable pipette, a stirring rod or another inert utensil to withdraw a small portion of the sample. Dispense the aliquot on a sample specific pH strip and check the pH.

12.1.11.3. NOTE: Do not check the pH of samples for coliform, volatiles, Total Organic Carbon (TOC), Wisconsin Diesel Range Organics (WI-DRO), oil and grease, or hexane extractable materials (HEM). These analyses will be checked by the analyst at the bench and must not be opened by sample management personnel.

Table 12.1 – General pH Preservation Requirements by Preservative

Sample Preservatives	Sample pH Requirement
Hydrochloric Acid (HCl)	must be less than 2
Nitric Acid (HNO_3)	must be less than 2
Sulfuric Acid (H_2SO_4)	must be less than 2
Sodium Hydroxide (NaOH)	must be greater than 12
Zinc Acetate and Sodium Hydroxide (NaOH)	must be greater than 9

12.1.11.4. If the pH for a sample container that is supposed to be preserved is not within the required range, indicate the anomaly on the SCUR form or on the COC. If a sample does not require preservation, write N/A in the applicable section of the SCUR form.

12.1.12. **pH Preservation Adjustments:**

12.1.12.1. If a sample container does not meet the pH preservation required, the pH of the sample must be recorded on the COC or SCUR. Additional preservative is added so that the preservative content is < 1% of the sample container volume. For example:

12.1.12.1.1. For a 100mL container, a maximum of 1mL of preservative may be added;

12.1.12.1.2. For a 250mL container, a maximum of 2.5mL of preservative may be added;

12.1.12.1.3. For a 500mL container, a maximum of 5mL of preservative may be added;

12.1.12.1.4. For a 1L container, a maximum of 10mL of preservative may be added.

12.1.12.2. The appropriate preservative is added to the sample container, the sample is mixed and the pH is taken again. The new pH reading is also recorded on the COC or SCUR along with the amount, type and lot number of the preservative added. In addition, the sample container is marked with the preservative added, volume added, date, time and initials of the technician. For Metals analyses specifically, the lab must wait 24 hours after pH adjustment to pH < 2 before sample preparation can begin.

12.1.12.3. If unpreserved sample is received by lab and requires preservation, a clean container is used with appropriate preservation. An aliquot of unpreserved sample is poured out into preserved containers. Sample container is marked with a yellow sticker to notify lab that preservation was done in-house.

12.1.13. **Checking for Sulfide in Cyanide analyses:** Test for sulfide by placing a drop of sample onto a piece of lead acetate paper. Darkening of the paper indicates the presence of sulfide. Follow specific method instructions for removing sulfide from samples.

12.1.14. Note any discrepancies pertaining to samples as defined by the sample acceptance policy detailed above on the COC or SCUR. Any discrepancies involving temperature, preservation, hold time, collection dates and times, sample volume, sample containers, and unclear analysis, must be reported to project management as soon as possible.

12.1.15. For short hold samples, the laboratory is notified and the samples are staged per section 12.2.

Table 12.3 – Analyses with Hold Times Less Than 72 Hours

Short Hold Time	Analyses	Details
15 minutes	Field Parameters	pH, Dissolved Oxygen, Residual Chlorine
8 Hours	Total/Fecal Coliform (MPN, MF), Enterococci, Fecal Streptococci MPN	Non-potable water only
8 Hours	Heterotrophic Plate Count (HPC)	
24 Hours	Hexavalent Chromium	
24 Hours	Fecal Sludge MPN	
24 Hours	Odor	
30 Hours	Total Coliform (Presence / Absence)	
48 Hours	Color	
48 Hours	MBAS	
48 Hours	Nitrate (unpreserved)	If Preserved, reported as NO_3+NO_2
48 Hours	Nitrite (unpreserved)	If Preserved, reported as NO_3+NO_2
48 Hours	Ortho –phosphate	
48 Hours	Settable Solids	
48 Hours	Turbidity	
48 Hours	VOA - Soils by Unpreserved EPA5035	Jars, Encores, Sleeves
48 Hours	Gross Alpha (NJ 48hr method)-waters	EPA NJAC 7:18-6
48 Hours	UV254	
48 Hours	Asbestos	
48 Hours	Chlorophyll A	48 hours to filtration
72 Hours	3030C Metals	
72 Hours	Volatiles – Air TO-18	Tedlar bag or equivalent

12.2. **Sample Login**

12.2.1. All samples received by the laboratory must be logged into the LIMS. Rush projects and/or projects with short holds should be prioritized. After these projects have been addressed, projects should be addressed on a first in, first out basis.

12.2.1.1. Samples are transferred to the Project Coordinator and must be logged into the LIMS so the samples can be uniquely identified (lab sample identification numbers). These lab sample ID numbers are used to track the prep and analysis activities of the samples, as well as identify the sub-samples, digestates, extracts, and other sample byproducts. This laboratory code maintains an unequivocal link with the unique client field sample ID code assigned to each sample.

12.2.1.2. Clients and Project Profiles are created in EPIC Pro as per Training Document *Epic Pro 02: Client Setup*. Projects are logged as per Section 1 of Training Document *Epic Pro: Login* (most current revisions or replacements).

12.2.1.3. Tests are assigned as per Training Document *Epic Pro 02: Client Setup,* and as per Section 1 of Training Document *Epic Pro: Login*.

12.2.2. Project Coordinator generates sample labels and returns folder to Sample Management.

12.2.2.1. Local SRF generation is as per Section 3 of Training Document *Epic Pro: Login*.

12.2.2.2. Local sample label generation is as per Section 2 of Training Document *Epic Pro: Login*.

12.2.3. Sample Management attaches the sample labels to the appropriate sample bottles.

12.2.3.1. Sample Management must make sure all sample IDs match COC, Samples are staged on the counter in rows by Sample ID. All sample containers are recorded on COC.

12.2.3.2. If sample labels do not match then Sample Management can reprint labels. One label is printed per sample container.

12.2.3.3. The label is placed onto the side of the container

12.2.4. If any samples require analyses performed outside of the laboratory, prepare the samples for subcontracting according to the procedures listed in the SOP describing the subcontracting of analytical services, ENV-SOP-GBAY-0005 *Subcontracting Samples*, or equivalent revision or replacement.

12.2.5. The Project Manager, Project Coordinator, or designated Client Services personnel must review and verify the following information by comparing the COC to SRF. Some of this information may not be provided by the client and those fields should be left blank:

12.2.7.1. Report Recipient;

12.2.7.2. Invoice Recipient;

12.2.7.3. Additional Report Recipient;

12.2.7.4. PO#;

12.2.7.5. Project Name;

12.2.7.6. Project Number;

12.2.7.7. Requested Due Date;

12.2.7.8. Sample ID;

12.2.7.9. Matrix;

12.2.7.10. Collection Date & Time;

12.2.7.11. Received Date & Time;

12.2.7.12. Analysis: Double check compound lists;

12.2.7.13. Price;

12.2.7.14. Region Codes;

12.2.7.15. Work Region % Split (for Pace internal subcontracted work).

12.3. **Sample Storage**

12.3.1. Once unpacked, samples will be logged into the LIMS in a timely manner and returned to appropriate storage conditions as soon as possible. Labs must make every effort to keep samples under the required thermal conditions during the login process. For the exceptional case where samples are not logged in the day they were received, they must be stored under appropriate temperature-controlled conditions until login takes place. In all cases, the sample temperatures must be taken as soon after receipt as possible (before samples are placed into storage) and the samples stored so as to maintain the required storage conditions while awaiting log-in.

12.3.2. Once logged into the LIMS and labeled, samples are placed in the appropriate storage areas. Specific temperature requirements are outlined in the analytical methods, but general guidelines are outlined below:

12.3.2.1. Short hold samples are placed in the short hold storage area or delivered directly to the laboratory.

12.3.2.2. Biological tissue samples are staged by receiving date or project number on shelves in a freezer for all types of analyses.

12.3.2.3. Summa canisters and Tedlar bags are stored on designated shelving at ambient temperature.

12.3.2.4. Volatiles- Aqueous samples are stored by receiving date or by project number in a segregated volatiles cooler. Associated trip blanks are stored with the samples.

12.3.2.5. Volatiles- Soil and other solid samples received preserved in methanol are stored by receiving date or by project number in a segregated volatile cooler. Associated trip blanks are stored with the samples.

12.3.2.6. Volatiles- Soil and other solid samples received preserved with a stir bar, or deionized water and a stir bar, are stored by receiving date or by project number in a segregated volatiles freezer. Associated trip blanks are stored with samples.

12.3.2.7. Volatiles- Soil and other solid samples received in 4oz containers or similar bottleware must be preserved within 48 hours. In order to preserve these samples, it is necessary to collect a 5g aliquot of the sample and transfer it to a 40mL vial. One of the following preservation options must be utilized:

12.3.2.7.1. The 5g aliquot is preserved with a stir bar, 5mL of deionized water and a stir bar, or 5mL of sodium bisulfate and a stir bar and stored in a freezer until analysis, or;

12.3.2.7.2. Within 48 hours of collection in the field, the 5g aliquot must be immediately extracted with 5mL of methanol and stored in a segregated volatiles cooler until analysis, or;

12.3.2.7.3. Within 48 hours of collection in the field, the 5g aliquot can be preserved with 10mL of deionized water and a stir bar, stored in a segregated volatile cooler and analyzed within 48 hours of collection.

12.3.2.8. Volatiles- Soil and other solid samples received in Encore samplers must be managed within 48 hours of collection by freezing the Encore or extruding it.

12.3.2.8.1. If extruding the sample into a 40mL vial containing a stir bar or a stir bar and 10mL of deionized water, then the sample is stored in the segregated volatile freezer until analysis.

12.3.2.8.2. If extruding the sample into methanol, then the sample is extracted within 48 hours of collection and the sample is stored in a segregated volatile cooler until analysis.

12.3.2.8.3. NOTE: if samples are not received within 48 hours of collection or are not received with enough time to process the samples correctly within 48 hours of collection, this must be noted in a way that will be visible on the final report (e.g., footnote in LIMS).

12.3.2.9. General Chemistry/Semi-volatiles- Waters and other liquid samples are staged by receiving date or by project number on the shelves in the appropriate sample storage cooler.

12.3.2.10. General Chemistry/Semi-volatiles- Soils and other solid samples are staged by receiving date or by project number on the shelves in the appropriate sample storage cooler.

12.3.2.11. Metals Solids and Liquids: These samples are staged by receiving date or by project number on designated shelving in the laboratory or appropriate designated area. These samples may be stored at ambient temperature unless Mercury or Hexavalent Chromium analysis is needed. If Mercury or Hexavalent Chromium analysis will be performed, the samples are staged by receiving date or by project number in the appropriate sample storage cooler. Samples requiring low level mercury analysis by Method 1631 are taken to the clean room for preservation and ambient storage.

12.4. **Sample Retention and Disposal**

12.4.1. If samples must be returned to customers, the lab must take special care to ensure that the samples are not damaged during any handling, testing, storing, or transporting processes.

12.4.2. Samples may need to be retained longer than the normal sample retention time (45 days from sample receipt). Reasons for this extended sample retention include: customer, program, or contract requirements so that samples can be retained in a secure location for the customers that is designated as a long-term storage area.

12.4.3. Disposal of unconsumed samples: Refer to the laboratory SOPs regarding waste handling and disposal: ENV-SOP-GBAY-0125 *Waste Handling and Management.* and ENV-SOP-GBAY-0121 *Regulated Soil Handling*, (most current revisions or replacements).

13. Quality Control

13.1. For any sample received at the laboratory that does not meet the sample acceptance, hold time or preservation criteria, the client must be contacted by project management and advised of the situation.

13.1.1. If the client instructs the laboratory to proceed with the analysis, all appropriate personnel/departments must be informed and the client approval must be documented on the SCUR or COC. Data will be appropriately qualified.

13.1.2. The client may also instruct the laboratory to preserve the samples at the laboratory prior to proceeding with analysis. This must be documented on the COC or the SCUR, and must be noted in the final laboratory report.

13.2. All supporting documentation related to sample custody must be retained by the laboratory. This includes: memorandums, fax transmissions, the original COC, all paperwork received with the COC, the completed SCUR form and copies of email transmissions. Please contact the laboratory QM/SQM for documentation retention time frames required.

13.3. Documenting discrepancies during receipt of samples:

13.3.1. The following are examples of client discrepancies that need to be documented on the appropriate paperwork (e.g., SCUR form):

13.3.1.1. Lost samples/insufficient sample volume;

13.3.1.2. Broken or missing bottles;

13.3.1.3. Missing COC;

13.3.1.4. Mislabeled bottles;

13.3.1.5. Preservation error;

13.3.1.6. Missing sample related details (date, time, sample type).

13.3.2. Pace sample management discrepancies will be documented on the SCUR form, COC or within the project files. Discrepancies attributable to errors and omissions on the part of the laboratory will be addressed and resolved through the formal corrective action process.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Not applicable to this SOP.

21. Troubleshooting

21.1. Not applicable to this SOP.

22. Safety

22.1. Hazards and Precautions - Use extreme caution in handling samples and wastes as they may be hazardous. Each reagent and chemical used in this method should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats, safety glasses, and ventilation hoods. SDS are on file and available to all personnel.

22.2. All personnel involved in sample management are responsible for complying with OSHA and DOT regulations. These regulations pertain to the safe handling and/or shipping of the chemicals specified in this procedure. Refer to the Sample Control Supervisor for any questions or concerns related to the safe handling and shipment of hazardous materials.

22.3. Other laboratory safety requirements are contained in the Chemical Hygiene Plan/Safety Manual. Immediate questions can also be addressed with the local Safety Officer.

23. Waste Management

23.1. Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ENV-SOP-GBAY-0125, *Waste Handling and Management*.

24. Pollution Prevention

24.1. Pollution prevention encompasses any technique or procedure that reduces or eliminates the quantity or toxicity of waste at the point of generation.

24.2. The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. TNI Standard, Management and Technical Requirements for Laboratories Performing Environmental Analyses, EL-V1-2009.

25.3. TNI Standard, Management and Technical Requirements for Laboratories Performing Environmental Analyses, EL-VI-2016-Rev.2.1.

25.4. SW-846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA, current revision.

25.5. American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1995, Standard Methods for the Examination of Water and Wastewater, A.E. Greenberg, L.W. Clesceri, A.D. Eaton and M.A.H. Franson, eds., 19th ed., American Public Health Association, Washington D.C.

25.6. U.S. Environmental Protection Agency, 1983, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

25.7. U.S. Environmental Protection Agency, 1988, Methods for Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039, Environmental Monitoring Systems Laboratory, Cincinnati, Ohio.

25.8. Code of Federal Regulations- most recent version.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: Sample Acceptance Policy, from form F-ALL-C-006 (most recent revision or replacement).

26.2. Attachment II – Example Chain of Custody, F-ALL-Q-020 (most recent revision or replacement).

26.3. Attachment III – Example Sample Condition Upon Receipt form, F-ALL-C-003 (most recent revision or replacement).

26.4. Attachment IV – Example Sample Preservation Receipt Form, F-GB-C-046 (most recent revision or replacement).

27. Revisions

Document Number	Reason for Change	Date
SOT-ALL-C-001-rev.06	Cover page: revised the footer language and removed the uncontrolled document numbering line. General: made administrative edits that do not affect the policies or procedures within the document. Table 8.1: updated to match 2016 TNI Standard. Section 12.1.2.3: removed language regarding custody seals. Section 12.1.4: removed all Sample Acceptance Policy language in lieu of Attachment I. Sections 12.1.5, 12.1.6: reworded for clarity. Section 12.1.11, 12.1.13, 12.1.14: changed some text from red to black. Section 12.2.5: new section added requiring the state of origin to be documented. New Attachment I: Added Sample Acceptance Policy from form F-ALL-C-006. Old Attachment III: removed example SRF. Old Attachment IV: removed bottle/preservation table and all references to it within the SOP.	03Apr2017
S-GB-C-010-Rev.08	General: Added Pace-GB specific information which was in previous version of local SOP.	03Apr2017
ENV-SOP-GBAY-0006-Rev.01	Document Number: Changed from S-GB-C-010-Rev.08 to ENV-SOP-GBAY-0006-Rev.00 to Rev.01. Cover page: Changed to Master Control layout. Table of Contents: Removed. Throughout Document: Updated from Inc to LLC and to current SOP numbers from MC. Corrected formatting errors. Table 10.2: Provided Formula/concentration for reagents that were blank. Added attachment IV, Sample Preservation Receipt Form.	07May2019

Attachment I – Sample Acceptance Policy (from F-ALL-C-006)

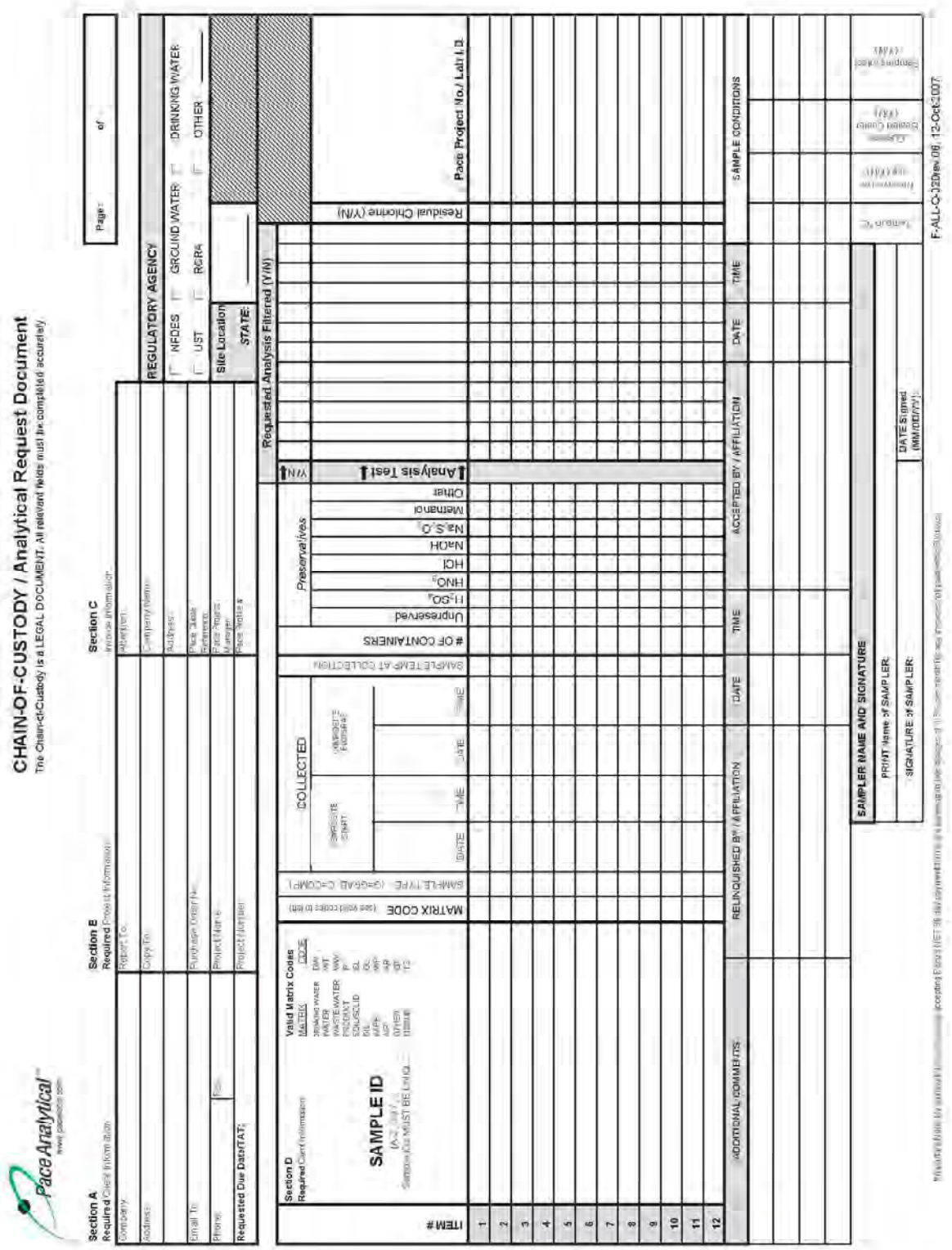
In accordance with regulatory guidelines, Pace Analytical facilities comply with the following sample acceptance policy for all samples received.

If the samples do not meet the sample receipt acceptance criteria outlined below, the Pace facility is required to document all non-compliances, contact the client, and either reject the samples or fully document any decisions to proceed with analyses of samples that do not meet these criteria. Any results reported from samples not meeting these criteria are appropriately qualified on the final report.

Sample Acceptance Policy requirements**:**

1. Sample containers must have unique client identification designations, and dates and times of collection, that are clearly marked with indelible ink on durable, water-resistant labels. The client identifications must match those on the chain-of-custody (COC);
2. There must be clear documentation on the COC, or related documents such as the Sample Condition Upon Receipt (SCUR) form, that lists the unique sample identification, sampling site location (including state; some regulations may require city, county, etc.), date and time of sample collection, and name and signature of the sample collector;
3. There must be clear documentation on the COC, or related documents, that lists the requested analyses, the preservatives used, sample matrix, and any special remarks concerning the samples (i.e., data deliverables, samples are for evidentiary purposes, field filtration, etc.);
4. Samples must be in appropriate sample containers. If the sample containers show signs of damage (i.e., broken or leaking) or if the samples show signs of contamination, the samples will not be processed without prior client approval;
5. Samples must be correctly preserved upon receipt, unless the method requested allows for laboratory preservation. If the samples are received with inadequate preservation, and the samples cannot be preserved by the lab appropriately, the samples will not be processed without prior client approval;
6. Samples must be received within required holding time. Any samples with hold times that are exceeded will not be processed without prior client approval;
7. Samples must be received with sufficient sample volume or weight to proceed with the analytical testing. If insufficient sample volume or weight is received, analysis will not proceed without client approval;
8. All samples that require thermal preservation are considered acceptable if they are received at a temperature within 2°C of the required temperature, or within the method-specified range. For samples with a required temperature of 4°C, samples with a temperature ranging from just above freezing to 6°C are acceptable. Samples that are delivered to the lab on the same day they are collected are considered acceptable if the samples are received on ice. Any samples that are not received at the required temperature will not be processed without prior client approval.
9. For all compliance **drinking water** samples, analyses will be <u>rejected at the time of receipt</u> if they are not received in a secure manner, are received in inappropriate containers, are received outside the required temperature range, are received outside the recognized holding time, are received with inadequate identification on sample containers or COC, or are improperly preserved (with the exception of VOA samples- tested for pH at time of analysis and TOC- tested for pH in the field).
10. Some specific clients may require custody seals. **For these clients**, samples or coolers that are not received with the proper custody seals will not be processed without prior client approval.

Attachment II – Example Chain-of-Custody Form



Attachment III – Example Sample Condition Upon Receipt Form

Pace Analytical 1241 Bellevue Street, Green Bay, WI 54302	Document Name: **Sample Condition Upon Receipt (SCUR)** Document No.: **F-GB-C-031-Rev.07**	Document Revised: 25Apr2018 Issuing Authority: Pace Green Bay Quality Office

Sample Condition Upon Receipt Form (SCUR)

Project #:

AFFIX WORKORDER LABEL HERE

Client Name: _____

Courier: ☐ CS Logistics ☐ Fed Ex ☐ Speedee ☐ UPS ☐ Waltco
☐ Client ☐ Pace Other: _____

Tracking #: _____

Custody Seal on Cooler/Box Present: ☐ yes ☐ no Seals intact: ☐ yes ☐ no

Custody Seal on Samples Present: ☐ yes ☐ no Seals intact: ☐ yes ☐ no

Packing Material: ☐ Bubble Wrap ☐ Bubble Bags ☐ None ☐ Other _____

Thermometer Used SR - _____ **Type of Ice:** Wet Blue Dry None ☐ Samples on ice, cooling process has begun

Cooler Temperature Uncorr: _____ /Corr: _____

Temp Blank Present: ☐ yes ☐ no **Biological Tissue is Frozen:** ☐ yes ☐ no

Temp should be above freezing to 6°C.
Biota Samples may be received at ≤ 0°C.

Person examining contents:
Date: _____
Initials: _____

Chain of Custody Present:	☐Yes ☐No ☐N/A	1.
Chain of Custody Filled Out:	☐Yes ☐No ☐N/A	2.
Chain of Custody Relinquished:	☐Yes ☐No ☐N/A	3.
Sampler Name & Signature on COC:	☐Yes ☐No ☐N/A	4.
Samples Arrived within Hold Time:	☐Yes ☐No	5.
- VOA Samples frozen upon receipt	☐Yes ☐No	Date/Time:
Short Hold Time Analysis (<72hr):	☐Yes ☐No	6.
Rush Turn Around Time Requested:	☐Yes ☐No	7.
Sufficient Volume:		8.
For Analysis: ☐Yes ☐No MS/MSD:	☐Yes ☐No ☐N/A	
Correct Containers Used:	☐Yes ☐No	9.
-Pace Containers Used:	☐Yes ☐No ☐N/A	
-Pace IR Containers Used:	☐Yes ☐No ☐N/A	
Containers Intact:	☐Yes ☐No	10.
Filtered volume received for Dissolved tests	☐Yes ☐No ☐N/A	11.
Sample Labels match COC:	☐Yes ☐No ☐N/A	12.
-Includes date/time/ID/Analysis Matrix: _____		
Trip Blank Present:	☐Yes ☐No ☐N/A	13.
Trip Blank Custody Seals Present	☐Yes ☐No ☐N/A	
Pace Trip Blank Lot # (if purchased): _____		

Client Notification/ Resolution: If checked, see attached form for additional comments ☐

Person Contacted: _____ Date/Time: _____

Comments/ Resolution: _____

Project Manager Review: _____ **Date:** _____

Page____ of ____

Pace Analytical 1241 Bellevue Street, Green Bay, WI 54302	Document Name: **Sample Condition Upon Receipt (SCUR)**	Document Revised: 25Apr2018
	Document No.: **F-GB-C-031-Rev.07**	Issuing Authority: Pace Green Bay Quality Office

Sample Condition Upon Receipt Form (SCUR)

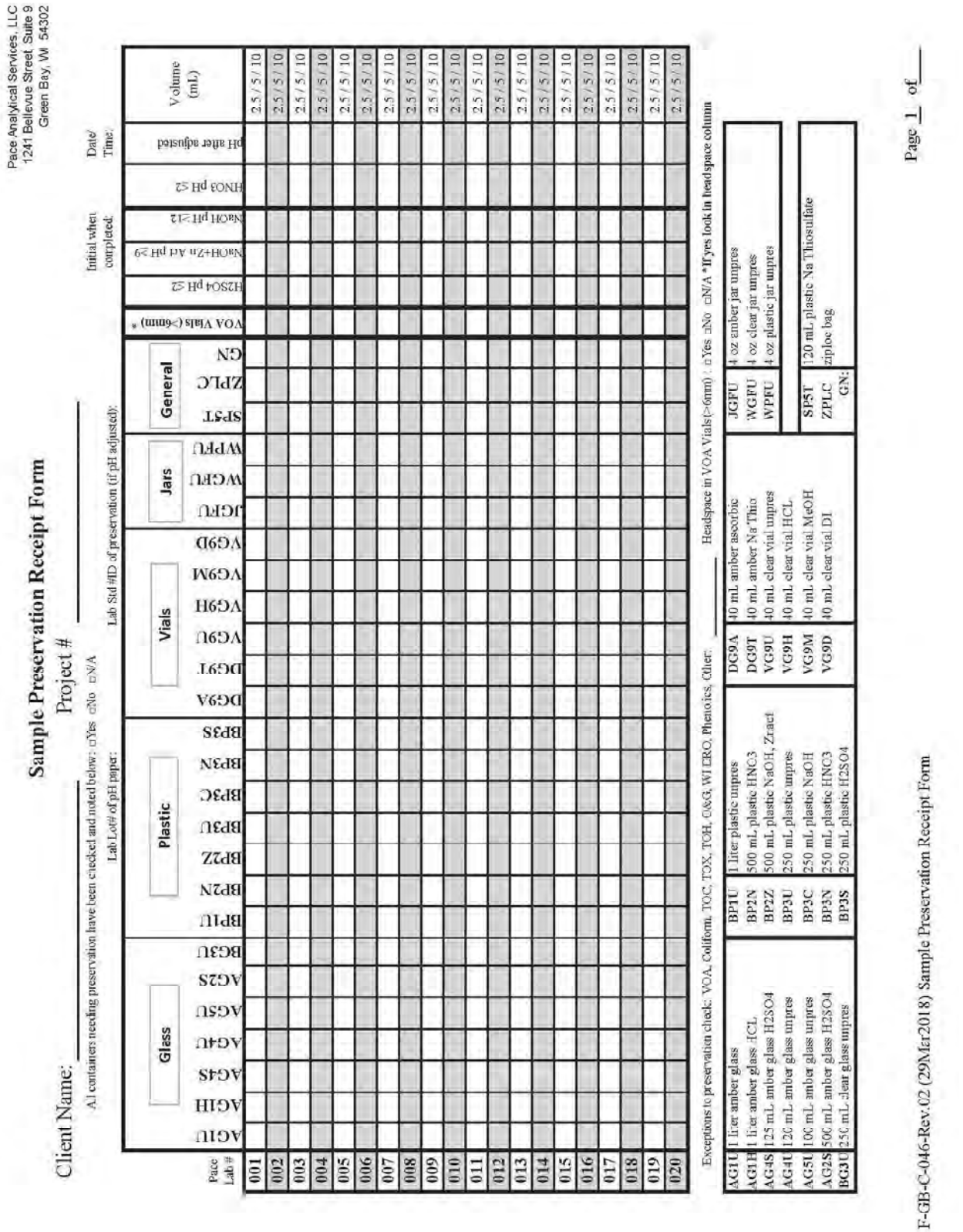
Client Name: _____ Project # _____

Additional Comments/Resolution: _____

Project Manager Review: _____ **Date:** _____

Page____ of ____

Attachment IV – Sample Preservation Receipt Form



END OF DOCUMENT

Document Information

Document Number: ENV-SOP-GBAY-0004 **Revision:** 00

Document Title: Measurement of Percent Moisture in Soils and Solids

Department(s): Client Services

Previous Document Number: S-GB-C-008-rev.05

Date Information

Effective Date: 20 Dec 2016

Next Review Date: 31 Oct 2020 **Last Review Date:** 31 Oct 2018

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-GBAY-0004 **Revision:** 00

Title: Measurement of Percent Moisture in Soils and Solids

All dates and times are in Central Time Zone.

Review: ENV-SOP-GBAY-0004 00 Measurement of Percent Moisture in Soils and Solids

Review

Name/Signature	Title	Date	Meaning/Reason
Kate Verbeten (007119)	Quality Manager	31 Oct 2018, 03:40:22 PM	Reviewed

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STANDARD OPERATING PROCEDURE

MEASUREMENT OF PERCENT MOISTURE IN SOILS AND SOLIDS

Reference Methods: ASTM D 2974-87

LOCAL SOP NUMBER:	S-GB-C-008-Rev.05
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-C-008-Rev.04
SOP TEMPLATE NUMBER:	SOT-ALL-L-004-rev.00

LOCAL APPROVAL

Nils Melberg, Laboratory General Manager — Date: 12/20/16

Kate Verbeten, Laboratory Quality Manager — Date: 12/19/16

Alee Her, Department Manager — Date: 12/19/16

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

This is **COPY#** 1 Distributed on **12/27/16** by JLS and is **X** **CONTROLLED**

S-GB-C-008-Rev.05

Table of Contents

1. Purpose/Identification of Method

1.1 This is Standard Operating Procedure (SOP) describes procedures used to measure percent moisture of soils and solid samples based on ASTM D 2974-87 Standard Test Methods.

2. Summary of Methods

2.1 A sample aliquot is weighed before and after heating to dryness at 103-105° C. The weight loss is calculated as % Moisture.

3. Scope and Application

3.1 **Personnel**: The policies and procedures contained in this SOP are applicable to all analysts experienced with the used of laboratory balances, desiccators, and ovens. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.2 **Parameters:** This SOP applies to percent moisture typically used to correct results of inorganic and organic parameter analysis to dry weight basis.

4. Applicable Matrices

4.1 This SOP is applicable to soil and solid samples (including sludges) containing at least 0.1% moisture.

5. Limits of Detection and Quantitation

5.1 Not applicable to this SOP.

6. Interferences

6.1 Non-representative materials, e.g., leaves and sticks should be removed from the sample prior to measurement.

6.2 Measurements are subject to negative bias for samples containing significant quantities of ammonium carbonate, volatile organics, or other volatile materials that could be lost during drying.

7. Sample Collection, Preservation and Handling

Sample type	Collection per sample	Preservation	Storage	Hold time
Soil/ solid	Wide mouth glass or plastic 4-oz container	N/A	≤6°C	30 Days. Note: Analyze as soon as possible to minimize microbiological decomposition of organic solids.

8. Definitions

8.1 Refer to Glossary section of the Pace Quality Manual.

9. Equipment and Supplies

9.1 Instrumentation:

Equipment	Vendor	Model / Version	Laboratory Identification	Description / Comments
Analytical Balance	Mettler Toledo	PB602-S	40BAL9	Electronic with RS-232 output, capable of weighing 0.01g
Analytical Balance	A&D	EK200I	40BALN/ 40BALQ	Electronic with RS-232 output, capable of weighing 0.01g
Drying Oven	VWR	1370 FM	40OVN7	Capable of maintaining temperature at 103-105°C
Drying Oven	VWR	1370 GM	40OVNH	Capable of maintaining temperature at 103-105°C
Computer for Electronic Prep Log				Automated sample weight upload into LIMS

9.2 Supplies

Supplies	Vendor	Model / Version	Description / Comments
Desiccators	Fisher	Fisher p/n 08-644	Labconco Model
Indicating Desiccant	Fisher	Fisher p/n 07-578-4B	
Non-indicating Desiccant	Fisher	Fisher p/n 07-577-3B	
Disposable Aluminum Weighing Dishes	Fisher	Fisher p/n 08-732	
Spoonula Lab Spoons	Fisher	Fisher p/n 14-375-10	
Trays, plastic or metal	NA	NA	

10. Reagents and Standards

10.1 Not applicable to this SOP.

11. Calibration and Standardization

11.1 Analytical Balance Calibration

11.1.1 Annual Calibration - The balance must be calibrated at least annually by an outside agency and checked daily before each use using Class 1 or 2 weights. Refer to Pace SOP, S-GB-Q-030 *Support Equipment* (most current revision or replacement).

11.2 Daily Calibration Check

11.2.1 Clean the balance and surrounding area prior to starting the daily calibration check.

11.2.2 Check the sight level on the balance. If it needs adjusting, level the balance.

11.2.3 The weight set ID indicated in the logbook is used as the primary set. If an alternate weight set ID is used, that ID must be recorded in the comment section of the balance calibration logbook for that day.

11.2.4 Tare the balance before weighing the NIST certified weights.

11.2.5 Use forceps or other means to lift each weight (Do not touch the weights with fingertips as the residue may artificially adjust the true value of the weights). Record the date of the calibration check, the true value of the weight, and the actual measured weight in the logbook. Repeat this procedure for the other certified weights. If calibration weights differ from the certified weights by more than specified in the balance calibration logbook, corrective action must be taken (see 11.3).

11.3 Corrective Action

11.3.1 Clean the balance and balance pan. Check the sight level on the balance and adjust if necessary. Re-tare and re-weigh all the certified weights.

11.3.2 The internal calibration function (if available) of the balance may be used as a means of corrective action.

11.3.3 Utilize the internal calibration function and diagnostics. Refer to instrument manual.

11.3.4 Contact the QA office for assistance if the balance does not meet the calibration tolerances.

11.3.5 If the above action does not correct the problem, the balance should be taken out of service and appropriately labeled to avoid improper usage. A service technician should be contacted.

11.3.6 Record any corrective action. Initial and date all entries in the logbook.

12. Procedure

12.1 Locate the samples to be analyzed, place on a cart and allow samples to warm to ambient temperature prior to processing.

12.2 Review location of samples. Soil samples that are collected in regulated domestic areas or that are of foreign origin must be handled in accordance with the Pace SOP: S-GB-S-001, *Regulated Soil Handling* (most current revision or replacement).

12.3 Determine the number of aluminum weighing pans required for the number of samples to be analyzed plus one for a duplicate.

12.4 The samples scheduled for analysis are batched in the PMST QUEUE in groups of 20. The QC batch will also include a duplicate for one of the project soil samples.

12.5 After batching samples in EPIC Pro print the work list.

12.6 Open the Electronic Prep Log. To start a new worksheet, select the template from the list of active templates. You may also search for them by clicking the triangle expanded button and entering in criteria for your search. Then press enter (or click the search button) to perform the search. Once you have the needed template, double click on it.

12.7 Now that the template is loaded you need to enter the Batch for your test. You can either drag over the Batch Samples in the order you need them, or you can drag them over and then reorder them using the drag and drop method. Once you have them in the order you need them click the arrows to the right of "Search by Batch" to minimize the space the "Search Samples" section takes up.

12.8 Save your data by pressing the disc icon next to the search template button. If this is your first time saving it will request you to enter a prep group description. This is used by your group to find the Electronic Log you are making. Enter the name of the queue, batch number and lab group (example for Sample Receiving enter "SR").

12.9 Verify balance calibration - refer to section 11 for balance check procedures and corrective actions. Refer to the balance logbook for the acceptance criteria for the designated balance.

12.10 Not that you have your run set-up, you can start entering results.

12.11 To use the balance, verify the balance matches the instrument ID and click the balance icon in between the search button and the Autopost button.

12.12 For each sample, label and record the tare weight (to the nearest 0.01 g) for an aluminum weighing dish by placing your curser in the field you wish to put the weight in and press the print button on the balance.

12.13 Using a clean spoonula lab spoon, stir the material in the sample container. Transfer at least 10g of the remaining sample to the tared weighing dish

12.14 Weigh the sample and dish, recording to the nearest 0.01g.

12.15 Place the samples to **dry in the** oven overnight at 103-105°C. Check that the oven temperature **is recorded on the** Electronic Prep Log benchsheet and is within required specifications before placing samples into oven as per Pace SOP S-GB-Q-030 *Support Equipment* (most current revision or replacement).

12.16 Overnight is a period of time ≥ 8 hours.

12.17 Record the oven temperature prior to removal of the samples and verify it is still within the required specifications of 103-105 °C. Remove the sample from the oven place in a desiccator to cool. The desiccator should contain mostly non-indicating desiccant with enough indicating desiccant to demonstrate that the desiccant is still active.

12.18 After the sample has cooled, weigh the dried residue to the nearest 0.01g. If the sample has been oven dried for at least 8 hours, proceed to section 12.20. If dried less than 8 hours, proceed to the next section.

12.19 Return the samples to the oven for one additional hour. At the end of the hour, **remove the** samples once again; allow them to cool to room temperature and reweigh. If the weight is within 0.01g or 0.1% of the previous weight, record the weight and proceed to 12.20. If the weight has changed by more than 0.01g or 0.1%, repeat step 12.15 until a constant weight (<0.01g or 0.1% change) is achieved.

12.20 As weights are entered Percent Difference and Weight Differences will be calculated when using multiple weighings.

12.21 You can manually select a weight to use by entering an "M" in the Use test box to override the automatic weight chosen. If you want to manually de-select a weight, enter an "m". The weights are chosen using weight differences being less than 5mg.

12.22 Once all of your weights have been taken and additional information has been entered your results will be calculated and you will be ready to autopost the data into EpicPro.

12.23 Save your data by pressing the disk icon next to the search template button.

12.24 If required you may print or create a PDF of your data by selecting Menu -> Print Landscape.

12.25 Verify all of the samples you wish to autopost have a Y for select, then press the AutoPost Button.

12.26 Select a few samples randomly and verify that the % Moisture final result is being calculated correctly following Section 14 for the calculation.

12.27 Once data is autoposted, review for precision. See Section 14 for the RPD Calculation.

13. Quality Control

13.1 **Duplicate Sample** – Measure one duplicate sample with each batch of 20 samples. The Relative Percent Difference (RPD) for duplicate results must be ≤ 10%. If this is not met the entire batch must be re-analyzed.

13.2 Documentation of Equipment Operation and Calibration – The balance calibration check and oven temperature should be recorded on the lab datasheet for each sample batch. In addition, the oven temperature should be read each day it contains active samples and the temperature recorded in the oven log. If balance checks and oven temperatures are not within acceptable limits, all effected samples must be re-analyzed.

14. Data Analysis and Calculations

14.1 % Moisture is calculated and in the Electronic Prep Log worksheet using the following equation.

$$\% \text{ Moisture} = (W_w - W_d) * 100\% / W_w$$

Where:

W_w = Wet weight of the sample (Dish + sample weight before drying – dish tare weight)
W_d = Dry weight of the sample (Dish + sample weight after drying – dish tare weight)

14.2 Relative Percent Difference (RPD) is calculated as follows:

$$\%RPD = (S1 - S2) * 100\% / ((S1 + S2)/2)$$

Where: S1 = %Moisture for Sample
S2 = %Moisture for Sample Duplicate

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1 See Section(s) 11.3 and 13.

16. Corrective Actions for Out-of-Control or Unacceptable Data

16.1 See Section 13.

17. Contingencies for Handling Out-of-Control Data

17.1 See Section 13.

18. Method Performance

18.1 All applicable personnel must read and understand this SOP with documentation of SOP reviewed maintained in their training files. Additionally, staff must read and understand the Pace SOP: S-GB-S-001 *Regulated Soil Handling* (most current revision) in addition to receiving Regulated Soil Training upon hire and annually thereafter.

18.2 **Demonstration of Capability (DOC)** – Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) described in S-ALL-Q-020, *Orientation and Training Procedures* (most current revision or replacement). All results must be ± 10% of the mean to qualify the analyst for reporting sample results. Results of DOC studies for each analyst shall be retained in the lab quality assurance office. Each analyst must successfully repeat this study annually to maintain qualification.

19. Method Modifications

19.1 Method modifications for ASTM D2974-87 are as follows:

19.1.1 Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.

19.1.2 All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.

19.1.3 Procedures identified as "Best Practices" by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace Laboratories.

19.1.4 ASTM D2974-87 states to use 50 g of the test specimen; Pace Analytical Services, Inc – Green Bay uses a 10 g aliquot.

19.1.5 ASTM D2974-87 states to dry the sample for 16 hours, Pace Analytical Services, Inc. – Green Bay defines the drying time as overnight, which is a drying time of ≥8 hours.

20. Instrument/Equipment Maintenance

20.1 Maintain the analytical balance, ovens, and furnaces according to the most current revision of SOP S-GB-Q-030, *Support Equipment.*

21. Troubleshooting

21.1 Refer to Section 11.3. If additional assistance is required refer to the operations manual for the oven or balance as needed.

22. Safety

22.1 **Standards and Reagents**: Not applicable to this SOP.

22.2 **Samples** - Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

22.2.1 Regulated soil samples are to be handled in accordance with Pace SOP: S-GB-S-001, *Regulated Soil Handling* (most current revision or replacement).

22.3 **DO NOT WEAR LATEX OR NITRILE GLOVES WHILE HANDLING HOT TRAYS.**

23. Waste Management

23.1 Procedures for handling waste generated during this analysis are addressed in S-GB-W-001, *Waste Handling and Management* (most current revision or replacement).

24. Pollution Prevention

24.1 The Pace Chemical Hygiene Plan/Safety Manual contains additional information on pollution prevention.

25. References

25.1 Pace Quality Assurance manual (most current revision or replacement.

25.2 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems" (most current revision or replacement).

25.3 ASTM D 2974-87 Test Method A "Standard Test Methods for moisture, Ash and Organic Matter of Peat and Other Organic Soils", American Society of Testing and Materials, Reapproved 1995.

25.4 EPA Contract Laboratory Program SOW for Inorganic Analysis Doc. ILM 1.03 March 1990.

25.5 ASTM D 2216-98 "Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass", American Society of Testing and Materials, 1998.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1 Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-GB-C-008-Rev.04	Throughout Document: Updated SOP to new format following SOP: S-GB-Q-017 *Preparation of SOPs* (most current revision or replacement). Updated SOP references throughout document. Section 7: Added 30 day hold time. Section 9.1: Updated to current oven and balance equipment listings. Section(s) 12.2, 18.1, and 22.2.1: Added pertinent information on the requirements for Regulated Soil Handling Procedures. .	19Dec2014
S-GB-C-008-Rev.05	Cover Page: Updated QM name, name change.	12Dec2016

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Notes

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All Dates and Times are listed in: Central Time Zone

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STANDARD OPERATING PROCEDURE

The Determination of Total Organic Carbon Using the Walkley-Black Procedure

Reference Methods: Methods of Soil Analysis, Walkley-Black

SOP NUMBER:	S-GB-I-037-Rev.06
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-I-037-Rev.05

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 01/15/18

Kate Verbeten, Laboratory Quality Manager — Date: 1/12/18

Chad Rusch, Department Manager — Date: 1/12/18

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL

Signature	Title	Date

This is **COPY#** ____ Distributed on _____ by _____ and is ___ **CONTROLLED**

S-GB-I-037-REV.06

Table of Contents

1 Purpose

1.1 The purpose of this Standard Operating Procedure (SOP) is to describe the method used to determine the concentration of Total Organic Carbon (TOC) in soil samples compliant with the Walkley-Black procedure.

2 Summary of Method

2.1 An aliquot of a dried and homogenized solid sample is put into a COD vial and caped. The sealed tubes are heated in a hot block at 150°C. After two hours, the tubes are removed, cooled and measured spectrophotometrically at 620 nm.

3 Scope and Application

3.1 **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method or non-analytical process.

3.2 **Parameters**: This SOP applies to Total Organic Carbon (TOC).

4 Applicable Matrices

4.1 This SOP is applicable to sediments, soils and sludges.

5 Limits of Detection and Quantitation

5.1 Current LOD and LOQ can be found in the Laboratory Information Management System (LIMS) - EpicPro.

5.2 Level of Detection (LOD): The LOD is determined by the 40CFR Part 136B MDL study. Once the 40CFR Part 136B MDL is determined it may be elevated, if deemed unrealistic as demonstrated using method blank evaluations.

5.3 Level of Quantitation (LOQ): The LOQ is calculated as 3 times the LOD. A realistic LOQ is typically near the lowest non-zero calibration point and higher than typical blank measurements. If 3 times the LOD is less than the low standard, the LOQ is set as the low standard.

6 Interferences

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

6.2 For the Walkley Black method, organic carbon that is not easily oxidizable results in a low bias. As described in the 1933 Walkley Black paper, this incomplete oxidation results in a recovery of organic carbon in the range of 60 to 86 percent. A correction factor was determined from their studies to be a multiplier of 1.32. This is solely based on the 20 soils in their study. Additional papers have demonstrated recoveries to be in the range of 59 to 94%. As a result, by applying the 1.32 multiplier the TOC result may be biased low or high. This procedure follows the modification to the Walkley Black method and heats the sample in the presence of the dichromate and H2SO4 at 150°C for two hours. This modification results in the oxidation of difficult to oxidize organic carbon and provides a more accurate result.

6.3 Chloride results in a positive interference. Chlorides are oxidized to free chlorine by chromic acid. Where consumption of dichromate is used to determine organic carbon, the presence of Cl can result in erroneously high organic carbon. Mercuric sulfate in the digestion tubes complexes the chlorides and minimizes the interference from chlorides.

6.4 The presence of ferrous iron (Fe^{2+}) consumes the dichromate and results in a positive interference. Drying of the sample during preparation for analysis oxidizes Fe^{2+} to Fe^{3+}, minimizing the amount of Fe^{2+}.

7 Sample Collection, Preservation, Shipment and Storage

7.1 The lab provides appropriate bottle ware, including preservative, for requested testing. Where applicable, the bottle ware is demonstrated to be free of target analytes. When bottle ware not originating from the lab is used, the data may be qualified with either one or both of the following data qualifiers:

7.1.1 Sample field preservation does not meet EPA or method recommendations for this analysis.

7.1.2 Sample container did not meet EPA or method requirements.

7.2 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

Matrix	Method	Container(s)	Preservation	Hold	Shipment Conditions	Lab Storage Conditions
Solid	Walkley Black	Clean 4oz glass containers	Thermal to ≤6°C	28 days	On ice ≤6° Celsius	≤6°C

8 Definitions

8.1 Total Carbon (TC): TC includes both the Inorganic and Organic constituents of a sample.

8.2 Total Organic Carbon (TOC): All carbon atoms covalently bonded in organic molecules. TOC is the carbon stored in the soil organic matter.

8.3 Total Inorganic Carbon (TIC): TIC is the sum of the inorganic carbon species in a sample. These can include bicarbonate, carbonate, and other carbonate minerals.

8.4 Soil Organic Matter (SOM): Organic matter is the organic component of soil. It consists of varying proportions of plant and other organisms, both living and decomposing as well as stable organic matter known as humus. SOM is estimated to be 58% soil organic carbon (OM = TOC x 1.72). This assumption can vary with the type of organic matter, soil type, and soil depth.

8.5 Fractional Organic Carbon (f_{OC}, FOC): The FOC of soil is the fraction of the organic matter that is carbon. It can be simply defined as the TOC content and can be expressed as a decimal fraction (i.e. 2.5% TOC = 0.025 FOC).

8.6 Additional definitions can be found in Definitions Section of the Pace Analytical Services Quality Manual.

9 Equipment and Supplies

9.1 Equipment

Equipment	Manufacturer	Model(s) /Catalog Number
Top loading Balance	Mettler Toledo	AE160
Spectrophotometer	Hach	DR2000
COD reactor block	Hach	45600
Adjustable pipettor (0.5-5.0mL)	Eppendorf / Fisher	3123000071 / 13-690-033
Drying Oven (74-76°C)	Curtin Matheson	213-454
Mortar and Pestle	Coors	60316, 60317
Vented Hood	Hamilton or Equivalent	

Or equivalent

9.2 Supplies

Supplies	Manufacturer	Catalog #
COD digestion vials	Columbia Analytical Instruments / Fisher	COD15000
Thermal gloves	Fisher	19-013-541
5000 µL Pipette tips	Unifit National Scientific / MG Scientific	NUN05ME-BP
Mortar	CoorsTek / Fisher	60316 / 12-961A
Pestle	CoorsTek / Fisher	60317 12-961-5A
10 mL volumetric flasks	Kimble / Fisher	92812G10 / 10-310-235
50 mL volumetric flasks	Pyrex / Fisher	564050 / S14290
100 mL volumetric flasks	Pyrex / Fisher	5660100 / S14291
1000 mL volumetric flask	Pyrex / Fisher	56401L / S14295
Wire racks	Fisher	Cat# 14802

Or Equivalent

10 Reagents and Standards

10.1 Stock Standards and Reagents

Standard/Reagent	Alias	Purchased From	Catalog Number	Concentration / Purity	Expiration	Storage
Nanopure® Water	Water	In House	NA	≥18 Mega ohm	6 months	Room Temp
Primary Source	5310C-STK	SCP Science	250-250-051	1,000 mg/L	Manufacturer's	Room Temp
Secondary Source	TOC-SPK1000	Ultra Scientific	IQC-106-5	1,000 mg/L	Manufacturer's	Room Temp

10.2 Working Standards and Reagents

Standard / Reagent	Alias	Stock or Intermediate	Amount Used	Final Volume (W/Diluent)	Diluent	Final Concentration	Expiration	Storage
Calibration Standard 0	CAL0, MB, ICB, CCB	Water	2.0 mL	50 mL	Water	0 mg/L	made daily	NA
Calibration Standard 3	CAL3	5310C-STK	2.5 mL	50 mL	Water	50 mg/L	made daily	NA
Calibration Standard 1	CAL1, CRDL	CAL3	2.0 mL	10 mL	Water	10 mg/L	3 Months	≤6°C
Calibration Standard 2	CAL2	CAL3	4.0 mL	10 mL	Water	20 mg/L	made daily	NA
Calibration Standard 4	CAL4	5310C-STK	2.0 mL	10 mL	Water	200 mg/L	made daily	NA
Calibration Standard 5	CAL5, CCV	5310C-STK	20 mL	50 mL	Water	400 mg/L	3 Months	≤6°C
Calibration Standard 6	CAL6	5310C-STK	8.0 mL	10 mL	Water	800 mg/L	made daily	NA
Initial Calibration Verification	ICV	TOC-SPK1000	4.0 mL	10 mL	Water	400 mg/L	made daily	NA
Secondary Spike	5310C-SPK	TOC-SPK1000	32 mL	40 mL	Water	800 mg/L	3 Months	≤6°C
Laboratory Control Spike/Laboratory Control Spike Duplicate	LCS/ LCSD	5310C-SPK	1 mL	2 mL	Water	400 mg/L	made daily	NA
Matrix Spike/Matrix Spike Duplicate	MS/ MSD	5310C-SPK	1 mL	2 mL	Water	400 mg/L	made daily	NA

11 Calibration and Standardization

11.1 A new calibration curve should be prepared yearly at minimum or whenever the continuing calibration standard does not pass control criteria.

11.2 Prepare a calibration curve using calibration standards and a blank. Add 2.0 mL of each curve standard to a digestion tube and digest per Section 12.

11.3 Turn on Spectrophotometer and set to 620 nm and allow it to warm up for at least 20 minutes.

11.4 Wipe the outside of each vial with tissue paper to remove any fingerprints. Place Level 0 calibration standard into the spectrophotometer and zero the instrument.

11.5 Place the standard cells into the spectrophotometer and record standard absorbance at 620 nm into the electronic prep log. Calculate and lock curve to set as the new curve.

11.6 The data is saved within the program and can be referenced when needed. Note: Record the HBN# associated to the curve as it needs to be entered for each new preplog worksheet created.

11.7 In order for the calibration to be acceptable a linear regression analysis of the absorbance values against the corresponding concentrations must yield a correlation coefficient of >0.995. The y-intercept must be less than the Pace Reporting Limit and the analysis of an ICV, ICB, and CRDL must be within acceptance criteria prior to analyzing samples.

11.8 If the calibration does not pass acceptance criteria, correct the problem and recalibrate.

12 Procedure

12.1 Soil samples that are collected in regulated domestic areas or that are of foreign origin must be handled in accordance with the Pace SOP: S-GB-S-001, *Regulated Soil Handling* (most current revision or replacement).

12.2 Sample Preparation.

12.2.1 Oven-dry overnight and grind to a size that the sample will pass through a 0.5-mm sieve.

12.2.2 Mix the sample thoroughly before selecting a portion for analysis.

12.2.3 Discard any foreign objects such as sticks, leaves, and rocks.

NOTE: Document all sample sizes, standards and reagents used in the digestion in the electronic Preplog.

12.3 Analytical

12.3.1 Samples are batched in Horizon/Epic Pro (the LIMS) with the appropriate batch QC.

12.3.2 The electronic Prep Log is used to document the Prep and Analytical steps and to post the data to the LIMS. Use the TOC Walkley Black Prep and WB TOC Walkley Black Analytical templates.

12.3.3 Label COD digestion vials

12.3.4 Unseal the vials and carefully weigh out 0.05 g using a calibrated balance. Place the 0.05 g of soil into a vial. Pipette 1.95 mL of water into a vial such that it forms a layer on top of the reagents contained in the vial.

12.3.5 Prepare CCV, CCB, MB, LCS, MS, and MSD.

12.3.6 Carefully seal the vial. During digestion, the reagents and sample are raised to a point just below boiling. Improperly sealed vials may leak or break.

12.3.7 Thoroughly mix the contents of the sealed vial by shaking. CAUTION: The vial will get very hot during mixing. It is recommended that vials be mixed

either in racks or with the use of insulated gloves. Eye protection MUST be worn.

12.3.8 Place the digestion vials in the reactor block at 150°C ± 5°C for 2 hours.

12.3.9 Cool about ½ hours. Then invert vials to mix.

12.3.10 Cool to room temperature. Allow any suspended precipitate to settle.

12.3.11 Turn on Spectrophotometer and set to 620 nm. Let warm up at least 20 minutes.

12.4 Wipe the outside of each vial with tissue paper to remove any fingerprints. Place ICB/CCB into the spectrophotometer and zero the instrument. Then, place the sample vials into the spectrophotometer and record sample and QC absorbance at 620 nm into the prep log.

12.4.1 The prep log will calculate the sample results in mg/L TOC, upload from the prep log, and report the final results in LIMS.

13 Quality Control:

13.1 Refer to the most current version of the Pace Quality Manual Appendix I *Quality Control Calculations* and SOP S-GB-Q-009 *Common Laboratory Calculations and Statistical Evaluation of Data* for equations and calculation details.

13.2 Initial Calibration Verification (ICV):

13.2.1 The ICV must be analyzed immediately after calibration, prior to samples.

13.2.2 The recovery must be within ±10% of the true value.

13.2.3 When measurements are outside the control limits, reanalyze once. If the measurement is still outside of the control limits, the analysis must be terminated, the problem corrected, and the calibration re-verified.

13.2.4 The source of the purchased 1,000mg/L TOC standard used to make the ICV must be different from that of the calibration curve standards and CCV.

13.3 Continuing Calibration Verification (CCV):

13.3.1 The CCV is analyzed after every 10 samples.

13.3.2 Concentration must be within ±10% of the true value.

13.3.3 When measurements are outside the control limits, reanalyze once. If the measurement is still outside of the control limits, the analysis must be terminated, the problem corrected, and the calibration re-verified. If the reset CCV fails recalibrate and reanalyze all samples back to the last acceptable CCV.

13.4 **Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB):**

13.4.1 The ICB must be analyzed after the ICV and before samples. The CCB must be analyzed after each CCV and before samples.

13.4.2 The absolute value must be <LOQ.

13.4.3 When the absolute value of the measurements, are greater than the LOQ, the blank may be immediately reanalyzed. If the reanalyzed blank passes, continue with analysis. If the reanalyzed blank fails, recalibrate and reanalyze all samples back to the last acceptable instrument blank.

13.4.4 No samples may be reported if bracketed by an ICB or CCB that is outside of the control limits, with the following exceptions:

13.4.4.1 If the sample concentration is greater than ten times the absolute measurement in the ICB or CCB, the samples do not need to be reanalyzed and can be reported without qualification.

13.4.4.2 For positive blank failures, with a sample that is a non-detect, the sample does not need to be reanalyzed and can be reported without qualification.

13.5 **Reporting Limit Verification Standard (CRDL)** – A standard prepared at the concentration of the Pace Reporting Limit.

13.5.1 It is analyzed after the calibration and also before each new batch,

13.5.2 Concentration must be within ±40% of the true value.

13.5.3 If outside the limits, reanalyze once. If still outside the limits, recalibrate.

13.6 **Method Blank (MB)**

13.6.1 The MB is laboratory grade water analyzed exactly like a sample. The MB is used to verify that interferences caused by contaminants in the solvents, reagents, glassware, etc. are known and minimized.

13.6.2 A MB must be analyzed with each batch of samples or every 20 samples, whichever is more frequent.

13.6.3 Acceptance Criteria: The MB is evaluated for both positive and negative bias and must have an absolute value less than the LOQ. For samples reporting down to the LOD, the MB measurements are evaluated to the LOD. In these cases qualify applicable samples for MB measurements from >LOD to <LOQ.

13.6.4 If the MB is greater than the LOQ, perform the following:

13.6.4.1 Check for errors in calculations. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.6.4.2 If there is sufficient sample available and hold time remaining, re-prepare the MB and all associated. If the MB is less than the LOQ in this analysis, accept the second set of data. If the MB is still outside the RL after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant MB.

13.6.4.3 If sufficient sample volume is not available, report the sample data with a qualifier flag on each of the samples associated with the non-compliant MB. Contact the project manager regarding the occurrence.

13.6.5 MB data qualifying

13.6.5.1 In the absence of project specific requirements, samples with concentrations greater than 10 times the absolute blank measurement may be reported unqualified.

13.6.5.2 In the absence of project specific requirements, samples that are non-detect may be reported unqualified if the blank measurement demonstrates a positive bias.

13.6.5.3 In the absence of project specific requirements, samples that are non-detect must be qualified if the blank measurement demonstrates a negative bias between and including the LOD and LOQ. Non-detect samples may not be reported with a blank negative bias greater than the LOQ.

13.6.5.4 For samples that need qualification resulting from MB measurements that are positive, apply a B data qualifier to the analyte. B = "Analyte was detected in the associated method blank."

13.6.5.5 For samples that need qualification resulting from MB measurements that are negative, apply a hand entered qualifier with the measurement and the units. "Analyte was measured in the associated method blank at a concentration of -#.# units."

13.7 **Laboratory Control Sample (LCS):**

13.7.1 The LCS is carried through all preparation procedures with frequency of 5% or one per batch of up to 20 environmental samples. A Laboratory Control Spike Duplicate (LCSD) must be analyzed if there is insufficient sample volume to perform a matrix spike/matrix spike duplicate or if the client requests one.

13.7.2 The recovered concentration must be within default limits of ± 20%.

13.7.3 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a data qualifier.

13.7.4 If no errors are found reanalyze once. If the measurement is still outside of the control limits and sufficient sample is available, re-prepare the LCS (and/or LCSD) and all associated samples. If the recovery is within the limits in the analysis, accept the second set of data. If the recovery is still outside the limits after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant LCS.

13.7.5 If sufficient sample volume is not available, report the sample data with appropriate data qualifier on each of the samples associated with the non-compliant LCS (and/or LCSD). Contact the project manager regarding the occurrence.

13.7.6 The precision between the LCS and LCSD must be ≤ 20% RPD.

13.7.6.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

13.7.6.2 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with appropriate data qualifier.

13.7.7 The source of the 1,000mg/L TOC standard used to make the CCV is not the same for the LCS.

13.8 **Matrix Spike (MS) and Matrix Spike Duplicate (MSD):**

13.8.1 MS/MSD pairs are analyzed in each batch at a 10% frequency or one pair per 10 environmental samples. Both the MS and MSD are evaluated for accuracy and precision.

13.8.2 The recovered concentration must be within default limits of ±20%.

13.8.2.1 If four times the concentration of the spike is less than the analyte concentration of the parent, accuracy need not be calculated.

13.8.2.2 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a data qualifier.

13.8.2.3 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with appropriate data qualifier.

13.8.3 The precision between the MS and MSD must be ≤ 20% RPD.

13.8.3.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

13.8.3.2 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with appropriate data qualifier.

13.8.4 The sample used for MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows. Avoid the use of field, filter, trip or equipment blanks for MS/MSD parent samples.

13.8.5 The source of the 1,000mg/L TOC standard used to make the CCV is not the same for the MS and MSD.

13.9 Duplicate sample (D) –A duplicate aliquot of a sample to be analyzed along with the original sample. Duplicate analysis indicates the precision associated with the sample collection, preservation and storage, as well as, laboratory procedures. An MSD is normally performed instead of a Duplicate Sample.

13.9.1 Duplicate sample analysis will be performed if requested by the client.

13.9.2 Acceptance limits: The RPD must be within 0-20% between the original sample and the duplicate.

13.9.3 If the RPD is exceeded, then:

13.9.3.1 Check for errors in calculations and sample preparation. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.9.3.2 If no errors are found in calculations report the parent sample with the appropriate data qualifier.

13.10 **Hold:** When preparation of a sample exceeds 28 days past the time of collection, notify the project manager before proceeding. If a sample is run past 28 days after collection, flag the result with appropriate data qualifier.

13.11 If a sample was diluted due to matrix effects and the result is a non-detect, the result must be qualified with appropriate data qualifier.

14 Data Analysis and Calculations

14.1 $$\frac{\text{(mg/L TOC from the curve) X (Final Volume (mL))}}{\text{(Weight in (g))}} = \text{TOC (mg/Kg)}$$

14.2 TOC (%) = (concentration in mg/kg / 10,000)

14.3 Accuracy:

A laboratory control spike / laboratory control spike duplicate is analyzed for each analytical batch of 20 or fewer samples.

$$\text{LCS, \% Recovery} = \frac{\text{TOC, mg/kg}}{\text{True Value mg/Kg}} \times 100$$

14.4 Precision:

The precision is calculated based on the recovery of the sample / sample duplicate result. A sample duplicate is performed at a frequency of 10% or one per batch whichever is more frequent and must meet laboratory specific limits for precision.

Relative percent difference (RPD) calculation:

$$\%\ RPD = \frac{|\ S-SD\ |}{(S+SD)/2} \times 100$$

S = Sample Value
SD = Sample Duplicate Value

15 Data Assessment and Acceptance Criteria for Quality Control Measures

Table A. QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	**Walkley Black**	**Acceptance Criteria**
Method Blank (MB)	One per batch of samples, up to 20 environmental samples.	<LOQ. Detections ≥ LOD but < LOQ must be evaluated for data qualification.
Laboratory Control Spike and Duplicate (LCS/LCSD)	One per batch of samples, up to 20 environmental samples. A LCSD is required if MS/MSD is not performed.	Recovery must be within ± 20% of the true value. If LCSD is run RPD <20%
Matrix Spike / Matrix Spike Duplicate (MS/MSD)	One pair per batch of samples, up to 10 environmental samples.	Recovery must be within ± 20% of the true value. RPD <20%
Sample Duplicate (DUP)	Upon client request	Project Specific or RPD <20%
Initial Calibration	Minimum of 5 standards plus blank. Performed once a year at a minimum.	Correlation coefficient ≥0.995
CRDL	After the calibration and following the initial CCV/CCB in each batch.	Recovery must be within ± 40% of the true value.
Calibration Verification (ICV/CCV)	ICV – analyzed after calibration but before samples. CCV – analyzed after every 10 samples.	Recovery must be within ± 10% of the true value.
Calibration Blank (ICB/CCB)	ICB – analyzed after ICV. CCB – analyzed after every CCV pair.	Project Specific or <LOQ

16 Corrective Actions for Out-of-Control Data

Table B. ANALYST/TECHNICIAN DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**Walkley Black If these conditions are not achieved ⇒**
Method Blank	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Sample Duplicate	• 4
Initial Calibration	• 5
CRDL standard	• 6
Initial / Continuing Calibration Verification	• 7
Initial / Continuing Calibration Blank	• 8

1. If not <LOQ, verify by second analysis. If second analysis confirms contamination for target analyte at or greater than the LOQ, re-digest sample batch and batch QC provided sufficient sample volume remains. If insufficient sample volume remains, consult with project manager and client on how to proceed. For MB detections greater than or equal to the LOD, but less than the LOQ; qualify applicable sample results. For negative measurements more negative than the LOD, applicable data is given the following data qualifier: "Analyte was measured in the associated method blank at a concentration of -#.# units."
   * For positive MB failures, samples that are non-detection need not be qualified. In addition, samples that are greater than 10 times the MB detection need not be qualified.
   * For negative MB failures samples that are greater than 10 times the MB detection need not be qualified.

2. If the parent, MS, or MSD is greater than the reportable linear dynamic range, dilute and reanalyze the parent, MS, and MSD. If the concentration of the spike is less than 25% of the concentration of the parent the MS and MSD recoveries are not evaluated. Any failures resulting from this are qualified appropriately. If the concentration of the spike is greater than 25% of the concentration of the parent, appropriately qualify the parent sample if either the MS and/or MSD fail accuracy. If the MS and MSD fail precision control limits flag the parent with the appropriate precision data qualifier.

3. Verify failure by second analysis. If second analysis confirms LCS (LCSD) failure, re-digest sample batch and batch QC provided sufficient sample volume remains. If insufficient sample volume remains, consult with project manager and client on how to proceed.

4. If no errors are found in calculations report the parent sample with the appropriate data qualifier.

5. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.

6. It is analyzed after the calibration and following the initial CCV/CCB in each batch, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

7. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.

8. If ICB/CCB is outside the control limits reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.

17 Contingencies for Handling Out-of-Control or Unacceptable Data

17.1 See Section 16.

18 Method Performance

18.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

18.2 The analyst must read and understand this procedure with written documentation maintained in his/her training file. Additionally, staff must read and understand the Pace SOP: S-GB-S-001 *Regulated Soil Handling* (most current revision) in addition to receiving Regulated Soil Training upon hire and annually thereafter.

18.3 An initial demonstration of capability (IDOC) must be performed per the most recent version of S-ALL-Q-020, *Orientation and Training Procedures* (most current revision or replacement). A continuing demonstration of capability (CDOC) must be performed annually. A record of the DOCs will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

18.4 At a minimum, the 40CFR part 136 appendix b study must be performed every year, per the most recent version of S-GB-Q-020, *Determination of the LOD and LOQ* (most current revision or replacement). Additional studies may be performed to achieve a realistic LOD and LOQ. This is to be done for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

18.5 Periodic performance evaluation (PE) samples are analyzed per the most recent version of S-GB-Q-021 *PE/PT Program* (most current revision or replacement), to demonstrate continuing competence. All results are stored in the QA office. These are performed twice a year per matrix.

18.6 A linear dynamic range study must be conducted at least once. The study is conducted for each analyte by analyzing increasing concentrations (at least 3 levels) until the results generated exceed ±10% difference from the true value. The highest concentration within the 10% criteria is the maximum of the linear range for that analyte. Once the linear dynamic range study determination is performed, keep the data, and then quarterly at a minimum verify with a single high point. Pace Analytical Services, LLC – Green Bay Laboratory will not use any data over the highest calibration standard used. All samples will be diluted and reanalyzed that are over the calibration range.

19 Method Modifications

19.1 The Walkley Black (WB) method uses an acidic dichromate solution to react with a soil sample to oxidize the organic matter. It is then titrated with ferrous sulfate to a color change endpoint from a green to reddish brown color. The endpoint can be difficult to determine in the stirred up sample during titration. This procedure utilizes COD vials with the same acidic dichromate solution to oxidize the organic matter. This reduces the hazardous waste volume produced by the test and allows for a quicker, more accurate spectrophotometric analysis of the sample.

19.2 If a client fails to provide sufficient volume for the method required Matrix Spike/Matrix Spike Duplicate (MS/MSD), the laboratory will analyze a Laboratory Control Spike Duplicate to demonstrate precision. The analytical batch will be qualified with the "M5" data qualifier.

19.3 The 0.68 correction factor also does not need to be used, as the COD vials are heated with the sample in them at 150±5°C for 2 hours. This completes the oxidation process and eliminates the need for the correction factor.

19.4 The Walkley Black method describes samples as "Finely divided soil, passing a 100-mesh sieve, taken in amounts between 10 and 25 mgm of carbon". This procedure does not pass the sample through a 100 mesh sieve, but does pulverize the samples by mortar and pestle after drying and prior to subsampling for analysis.

20 Instrument/Equipment Maintenance

20.1 See the Hach DR200 instrument Maintenance and Operator's Manual.

21 Troubleshooting

21.1 See the Hach DR200 instrument Maintenance and Operator's Manual.

22 Safety

22.1 All samples, standards, and reagents should be treated as hazardous. Safety glasses, gloves, and lab coats are to be worn. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by a safe technique. Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion.

22.2 A reference file of Safety Data Sheets (SDS) is made available to all personnel involved in the chemical analysis, and is located at the following link: https://msdsmanagement.msdsonline.com/e0ce0b0a-17d3-4f3c-afc6-25352729b299/ebinder/?nas=True. A formal safety plan has been prepared and is distributed to all personnel with documented training.

22.3 Regulated soil samples are to be handled in accordance with Pace SOP: S-GB-S-001, *Regulated Soil Handling* (most current revision or replacement).

23 Waste Management

23.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

23.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of S-GB-W-001, *Waste Handling and Management*.

24 Pollution Prevention

24.1 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

25 References

25.1 Pace Quality Assurance Manual (most current revision or replacement).

25.2 The NEALC Institute (TNI): Volume 1, Module 2, "Quality Systems" (most current revision or replacement).

25.3 Walkley, A.; Black, I.A. 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Science 37:29-38.

25.4 Recommended Soil Testing Procedures for the Northeastern United States, 2nd Edition, Northeastern Regional Publication No. 493, Revised December 15, 1995.

25.5 Methods of Soil Analysis, 1982 Second Edition, Method 29-3.5.2.1 Walkley-Black Procedure.

25.6 Nelson D W, Sommers L E. A Rapid and Accurate Method for Proceedings of the. Indiana Academy of Science, 1975, 84: 456-462.

25.7 EPA Manual 600 4-79-020, March 1983, Method 410.4, 40CFR Part 136

26 Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

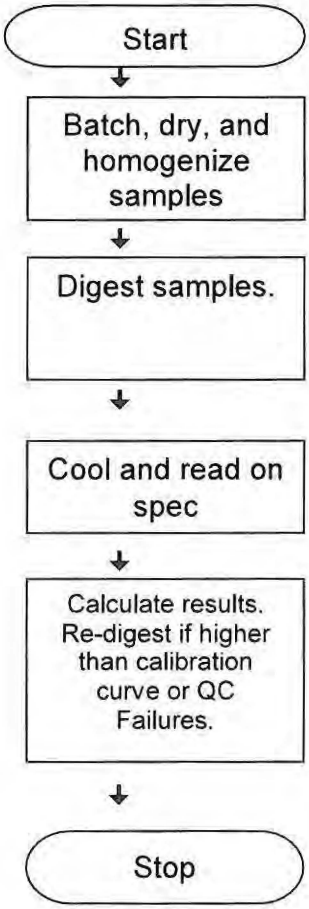
26.1 Attachment I: Flowchart

27 Revisions

Revision Number	Reason for Change	Date
S-GB-I-037-Rev.04	Updated SOP references throughout document. Section 2—Added reference to the LOD and LOQ Throughout document: Incorporated electronic preplog. Section 8, 10 and 11: Updated to pre-made standards.	15Aug2012
S-GB-I-037-Rev.04	Throughout document: Removed Method References for SW846 7196. Updated formatting following current revision of SOP: S-GB-Q-017 *Preparation of SOPs*. Section 7.2: Changed temperature to ≤6°C. Moved Attachments I & II into sections 15 &16	19Nov2014
S-GB-I-037-Rev.05	Signature Page: Updated from Inc to LLC, updated QM name. General: made administrative edits that do not affect the policies or procedures within the document. Throughout Document: Added information on Regulated Soils. Section 6: Addressed additional interferences. Section 8: Added definitions for TC, TIC. SOM and FOC. Section(s) 9 and 10: Updated to Table Format. Section 13: Added QC not previously listed. Section 19: Added 19.4. Section 22.2: Added SDS link. Section 25: Added Pace and TNI references. Section 27: Removed previous revision information that can be found in prior version of SOP	12Jan2018

Attachment I:

FLOWCHART



APPENDIX D-7

MATERIALS AND CHEMISTRY LABORATORY, INC SOPS

MATERIALS AND CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE	
Operator Aids: Materials and Chemistry Laboratory, Inc.	Approved: _____ _____ MCLinc President Date _____ _____ Quality Assurance Officer Date

1.0 PURPOSE

As a reminder to the analyst, "operator aids" are used in the laboratory to assist the user on specific instrumentation operation. All operator aids are considered controlled documents.

2.0 SCOPE AND APPLICATION

The need for operator aids is up to the analyst or operator of a particular instrument and, if prepared and used, must become a part of this SOP.

3.0 RESPONSIBILITIES

Analyst/Instrument Operator - must follow the operator aids and as necessary recommend changes or additions.

Quality Assurance Manager - responsible for proper use and maintenance of the SOP.

4.0 PROCEDURE-AIDS AVAILABLE

4.1 Appendix 1 – List of Operator Aids

4.2 Individual Operator Aids Beginning with Appendix A

Appendix 1

List of Operator Aids

APPENDIX A

Beckman ϕ 50 pH Meter

PROCEDURE:

1. Press “ON”.
2. Press “CLEAR”.
3. Rinse electrode and blot dry.
4. Immerse electrode in pH 4.00 buffer.
5. Stir briefly.
6. Press “pH”, then “STD”.
7. After flashing stops, remove electrode, rinse and blot dry.
8. Immerse electrode in pH 7.00 buffer.
9. Stir briefly.
10. Press “STD”.
11. After flashing stops, remove electrode, rinse and blot dry.
12. Immerse electrode in sample.
13. Stir briefly.
14. Press “pH”.
15. After flashing stops, display will show pH of sample.

REFERENCES:
“Standard Methods for the Examination of Water and Wastewater”, 18th Ed., 1992, Section 4-65.

Owner’s manual

Note: For all pH Operator Aids: After calibration with the 4.00 and 7.00 buffers, check unit with 10.0 buffer solution. Limits for 4.00 and 7.00 are $\pm$ 0.05 pH units and for the pH 10.0 buffer is $\pm$ 0.2 pH units.

APPENDIX B

Orion 701A and Orion 611 pH Meter

PROCEDURE:

1. Immerse electrode in pH 7.00 buffer.
2. Turn “FUNCTION” switch to “pH”.
3. Stir briefly.
4. Turn “CALIB” switch until display reads “7.00”.
5. Remove electrode, rinse and blot dry.
6. Immerse electrode in pH 4.00 buffer.
7. Stir briefly.
8. Adjust “SLOPE” switch until display reads “4.00”.
9. Remove electrode, rinse and blot dry.
10. Immerse electrode in sample.
11. Stir briefly.
12. Record pH of sample.

REFERENCES:

“Standard Methods for the Examination of Water and Wastewater”, 18th Ed., 1992, Section 4-65.

Owner’s manual

Note: For all pH Operator Aids: After calibration with the 4.00 and 7.00 buffers, check unit with 10.0 buffer solution. Limits for 4.00 and 7.00 are $\pm$ 0.05 pH units and for the pH 10.0 buffer is $\pm$ 0.2 pH units.

APPENDIX C

Orion SA520 pH Meter

PROCEDURE:

1. Switch “ON”.
2. Press “CAL”.
3. Display asks for buffer “1”.
4. Immerse electrode in pH 4.00 buffer.
5. Stir briefly.
6. Press “UP” or “DOWN” arrows until display indicates “4.00”.
7. Press “ENTER”
8. Display asks for buffer “2”.
9. Remove electrode from pH 4.00 buffer rinse and blot dry,
10. Immerse electrode in pH 7.00 buffer.
11. Stir briefly.
12. Press “UP” or “DOWN” arrow until display indicates “7.00”.
13. Press enter.
14. Remove electrode from pH 7.00 buffer rinse and blot dry,
15. Immerse electrode in sample.
16. Stir briefly.
17. Press “SAMPLE”.
18. Record pH of sample.

REFERENCES:
“Standard Methods for the Examination of Water and Wastewater”, 18th Ed., 1992, Section 4-65.

Owner’s manual

Note: For all pH Operator Aids: After calibration with the 4.00 and 7.00 buffers, check unit with 10.0 buffer solution. Limits for 4.00 and 7.00 are $\pm$ 0.05 pH units and for the pH 10.0 buffer is $\pm$ 0.2 pH units.

APPENDIX D

Orion PerpHecT 350 pH Meter

1. Attach the pH electrode to the meter.

2. Press the CAL key to initiate calibration sequence. CAL is displayed for 2 seconds. Press the SCROLL (▲,▼) keys until 3PT is displayed. Press the YES key to accept. The 4 annunciator will be displayed. Place electrode in pH 4.01 buffer. Reading will be displayed and updated as calibration continues. When the READY light comes on, indicating electrode stability, press the YES key.

3. The 7 annunciator will be displayed. Rinse electrode with deionized water and place into pH 7.00 buffer. Reading will be displayed and updated as calibration continues. When the READY light comes on, indicating electrode stability, press the YES key to accept.

4. The 10 annunciator will be displayed. Rinse electrode with deionized water and place into pH 10.01 buffer. When the READY light comes on, press the YES key to accept.

5. SLP will be displayed in the upper field while the calculated slope is displayed. Meter will automatically proceed to measure mode.

6. The annunciators for the type of calibration performed will remain lit until another calibration is performed. Remove electrode from third buffer, rinse with deionized water and place into sample.

1.1. 7. If operating in the LogR mode or using an ATC probe, the temperature-corrected pH reading is displayed.

8. Record pH directly from the main meter display and temperature from upper field when the READY light is displayed or when electrode signal is stable.

Note: For all pH Operator Aids: After calibration with the 4.00 and 7.00 buffers, check unit with 10.0 buffer solution. Limits for 4.00 and 7.00 are $\pm$ 0.05 pH units and for the pH 10.0 buffer is $\pm$ 0.2 pH units.

APPENDIX E

Orion 901 pH Meter

Switches

1. Set up the 901.
2. Turn STD thumbwheel switches to read the pH of the higher pH buffer.
3. If SET BLANK light is on, press to turn off.
4. Set mode switch to pH.

Calibration

1. Set slope thumbwheel switches to read electrode slope from table 3. Turn sign switch to plus.
2. Place electrodes in the buffer whose value is displayed on STD VALUE switches. Press CLEAR/READ MV.
3. Allow time for reading to stabilize. Press SET CONCN button.
4. If ±0.05pH unit or better accuracy is required, rinse electrodes and place in pH buffer of lower pH. Slowly adjust slope thumbwheel switch so that exact buffer pH is displayed.*

Table 3

Temperature ^{o}C	Slope
0	54.2
10	56.2
20	58.2
25	59.2
30	60.2
40	62.1
50	64.1

*Do not reset concentration. SET CONCN will clear previous memory.

PH Measurements

1. Rinse electrode and place in sample.
2. Allow time for reading to stabilize. Record the sample pH from the display. Repeat steps 1 and 2 for subsequent pH measurements.

Note: For all pH Operator Aids: After calibration with the 4.00 and 7.00 buffers, check unit with 10.0 buffer solution. Limits for 4.00 and 7.00 are $\pm$ 0.05 pH units and for the pH 10.0 buffer is $\pm$ 0.2 pH units.

APPENDIX F

Electrodes: Filing and Storage Solutions

ELECTRODE NAME	FILLING SOLUTION	STORAGE SOLUTION
Orion Reference |Ag|AgCl # 90-01-00	Orion 90-00-01	DI H2O
Schott-Gerate Redox PT65	Beckman Sat. KCl # 566468	DI H2O
Corning Combination pH # 476531	Beckman Sat. KCl # 566468	Beckman Sat. KCl # 566468
Orion Ross Combination 3104	Orion 81-00-0 3M KCl	pH 7.00 buffer

APPENDIX G

Corning Electrodes

pH Combination Electrodes

This instruction sheet provides information for the following electrodes:

Catalog Number	Description	Connector
476530	General Purpose Combination	BNC
476531	General Purpose Combination	US STD
476540	Semi-Micro Combination	BNC
476541	Semi-Micro Combination	US STD
476550	Flat Surface Combination	BNC
476551	Flat Surface Combination	US STD
476560	Rugged Bulb Combination	BNC
476561	Rugged Bulb Combination	US STD
476570	Deep Vessel Combination	BNC
476580	Spear Tip Combination	BNC

Intended Use and Principles

1.2. Corning's unique technology has combined the pH electrode and the Ag/AgCl reference electrode into a superior range of pH combination electrodes. These combination pH electrodes are designed to provide rapid and reliable pH results over a wide range of ionic strength (concentration) and temperature with negligible sodium and acid error. Corning's combination electrodes range from all glass to those with rugged polypropylene outer bodies. The latter offer the additional feature of replaceable junctions. Replaceable junctions are useful in applications that the junctions are prone to clogging, such as semisolids, oil based solutions, and suspensions. The reference element in each electrode incorporates a unique silver ion barrier that prevents clogging due to AgCl precipitation. The specially formulated glass membrane responds to hydrogen ion activity by developing an electrical potential across the membrane. The electrical potential follows the Nernstian principle, and varies linearly with the pH of the solution being measured.

1.3.

1.4. Operating Instructions

1.5. For optimum performance, use the following operating procedures:

1. Prior to use, unplug the fill hole cover at the cable connector end of the electrode. Remove the wetting cap from the tip of the electrode.
2. Verify that the fill solution is not more than one inch (2.5cm) below the fill hole. If necessary, add saturated KCl with a transfer pipet until the level is within one inch of the fill hole.
3. Inspect the ceramic junction for air bubbles. Remove any air bubbles by gently tapping the electrode until bubbles are expelled.
4. Condition the new electrode by soaking it in 7.0 buffer for a minimum of two hours.
5. Plug the electrode connectors into the appropriate inputs on the pH meter. Refer to the pH meter instruction manual for detailed directions.
6. Calibrate and proceed with sample measurements according to the instructions given in the pH meter instruction manual.

1.6. Notes: For best results, rinse the electrode with deionized water between measurements. The electrode and samples should be at room temperature prior to measurement. If not, refer to the pH meter instruction manual for temperature compensation procedures.

1.7.

7. When calibration and sample measurements are complete, check the fill solution level and fill with saturated KCl as needed. Plug in the fill hole cover and place the electrode in 7.0 buffer until the next use.

1.8.

1.9. For storage longer than one week, fill the wetting cap with saturated KCl and place the cap on the electrode tip.

Reagents

1.10. For optimum performance of the pH combination electrodes, the correct solutions must be used. The following solutions are available from Corning:

4.00 Buffer, Cat. No. 478540
7.00 Buffer, Cat. No. 478570
10.01 Buffer, Cat. No. 478510
Saturated KCl Fill Solution, Cat. No. 477000
Ammonium Bifluoride (electrode activator solution), Cat. No. 478353

Precautions and Limitations

1. **Do not** allow the electrode to run dry. Always maintain the fill solution level within one inch (2.5cm) of the fill hole.
2. **Do not** wipe the electrode tip. Blot dry with a lint-free tissue.
3. **Do not** use a KCL solution saturated wit AgCl as the fill solution, as it could permanently damage the reference element.
4. **Do not** leave the electrode in organic solvents or strongly basic solutions, for extended periods. If measurements are made in these solutions, readings should be taken quickly and the electrode rinsed immediately with deionized water. After rinsing the electrode, soak it in 7.0 buffer for two hours before using.
5. **Do not** use the electrodes in solutions that exceed a temperature range of 0-100°C.
6. **Do not** use the non-replaceable junction electrodes to measure the pH of semi-solids, oils and suspended solids. These solutions are best measured with the replaceable junction electrodes.
7. **Do not** use the electrode in fluoride solutions or hydrofluoric acid.

Maintenance and Troubleshooting

1.11. Electrode performance can be reduced as a result of prolonged use and aging of the glass membrane. If your pH electrodes are exhibiting slow response, low slope values, continuous drift, or erratic readings, follow the procedures listed below.

1. **Slow or drifty response**
   Usually caused by a reduction in the strength of the Saturated KCl fill solution. Remove all KCl and refill with fresh.

2. **Blocked junction**
   Some samples can cause the junction to become blocked. To test for this, blot the tip dry using a lint-free tissue, and let the electrode air dry for 15 minutes. If the junction is functioning properly, KCl crystals will appear on the tip of the electrode. A failure to observe crystals indicates a blocked junction.

   If the junction is blocked, place the electrode in warm (50°C) deionized water for 1 hour. Repeat the preceding test and treatment until the junction flows freely. If necessary, replace the junction if you have a replaceable junction electrode. To replace the junction use the Replaceable Junction Kit (containing three junctions), Cat. No. 477269.

3. **Excess KCl crystals**
   After prolonged use KCl crystals may build up inside the electrode and settle on the electrode tip, of the KCl may become discolored. Remove the old fill solution with a transfer pipet and replace it with warm deionized water to dissolve the crystals. Remove the water and fill the electrode with fresh saturated KCl solution.

   Note: To avoid excess build up of KCl crystals, Corning recommends the fill solution be changed weekly.

4. **Cleaning the pH bulb**
   Protein contamination: Soak the electrode bulb for 30 minutes in a 10% solution of pepsin. Rinse with deionized water and soak the electrode in 7.0 buffer for two hours before using.

   Oil contamination: Wash the electrode with a 50% water-acetone solution. **Do not** soak he electrode in the acetone solution, as it will deteriorate the bottom seals of the plastic electrodes. Rinse with deionized water and soak the electrode in 7.0 buffer for two hours before using.

5. **Reconditioning the pH Bulb**
   If the preceding maintenance and cleaning procedures fail to restore electrode performance, you need to recondition the pH bulb. Soak the electrode in a 0.1M ammonium bifluoride solution for two minutes. Rinse immediately with deionized water and soak overnight in 7.0 buffer before using.

   Warning: Do not exceed the two minutes in the ammonium bifluoride solution. Excess time in this solution will permanently damage the electrode.

Performance Specifications

The Corning combination pH electrodes meet the following specifications:

pH range	0-14
Temperature Range	0-100°C
Zero Point	pH = 7.0 $\pm$ 0.5

For technical application assistance call toll-free, 1-800-222-7740.

APPENDIX H

Milli-Q Plus Water System Operation (*B108*)

1. Turn on distilled H_2O valve.

1.12. 2. Press “OPERATE/STANDBY” button.

3. Wait until readout indicates *>1* MΩ cm.

4. Switch dial from “RECIRCULATION” to “PRODUCTION.”

5. Allow H_2O to go to drain for *1-2 minutes*, then begin collecting.

6. When finished collecting, switch dial back to “RECIRCULATION.”

7. Press “OPERATE/STANDBY” button.

8. Close distilled H_2O valve.

9. If the H_2O does not meet the specifications of >1 MΩ cm, check with external meter. *If it is still non-compliant, follow Operator Aid MCL-7775, Appendix 21.*

10. Routine external meter checks monthly by QA.

APPENDIX I

Water Treatment System Operation Using Ion Exchange Resins in Lab 107 & Lab 101

1. Open main distilled water supply valve

2. *Make sure the "ON/OFF" switch is "ON".*

3. *Leave treated water running in sink until meter reads >1.0 MΩ-cm (ASTM Type II level). If the water doesn't meet that level, request QA to run a conductivity and evaluate systems per MCL-7775 Appendix 21*

4. *When acceptable level is reached, move outlet hose to container to fill.*

5. *After filling container, turn off water supply valves and switch to off.*

6. *For the resin water treatment system in Lab 101, the system is not metered but used for radiological analyses. It is monitored monthly for conductivity, and blanks are run in any radiological analyses. Operate by turning on the distilled feed water supply and allow to run into sing for five minutes to flus columns, then collect in a column for use.*

7. Allow the system pressure to drop to <1.0 and put the recalculating valve in the recirculation position.

8. If the system pressure is <40 during collection, then look at changing the final polish filter.

9. If the H_2O does not meet the specifications of >1.0MΩ-cm, evaluate for end use (i.e. metals) as determined by running method blanks. Troubleshoot as defined in "Operator Aid," MCL-7775, Appendix 21.

10. If system pressure exceeds 30 psi, perform system maintenance.

APPENDIX J

X-ray Diffraction

Name of Instrument

1. These instructions are for the Rigaku Mini-Flex Instrument in *Lab 110.*

Instrument Start-up

1.0. Turn on main switch.

Sample Exchange

2.0. Open door.
3.0. Exchange sample.
4.0. Close door.

Instrument Operation

1. Operation of the XRD is covered in the Rigaku manual and SOP MCL-7712, "X-Ray Diffraction Operation Guide."

Instrument Shut-down

.

1. Press the X-RAY OFF button.
2. Allow the system to cool for ~2 minutes.
3. Turn off main switch.

Reference

4. The Rigaku manual is kept with the XRD unit in *Lab 110*.

APPENDIX K

LSC Protocol ID's

Protocol Number	Description
1	^{99}TC Windows
2	
3	
4	Total Activity Screen (Energy) (Equivalent to #4 on 2550)
5	General Energy Windows
6	QIP ^{14}C Efficiency
7	QIP ^{3}H Efficiency
8	QIP Background
9	
10	
SNC	Self-normalization and calibration With ^{14}C

APPENDIX L

Carbon Coater Use

Stand-By Position

Cage and Bell Jar:	Replace
Nitrogen Tank:	Closed
Vent:	Closed
Backing/Roughing Valve:	Backing
Baffle Valve:	Closed to Bell Jar

Insert Sample

Backing/Roughing Valve:	Backing
Baffle Valve:	Closed to Bell Jar
Nitrogen Tank:	Open
Vent:	Open

Remove Bell Jar when vacuum is released

Nitrogen Tank:	Closed
Vent:	Closed

Prepare carbon rod

Sample:	Insert
Cage and Bell Jar:	Replace

Pump Down

Nitrogen Tank:	Closed
Vent:	Closed
Backing/Roughing Valve:	Roughing

Wait until Pirani Gauge reads lower than $2x10^{-1}$ mbar (midway on a gauge)

Backing/Roughing Valve:	Backing
Baffle Valve:	Open to Bell Jar

Wait until Pirani Gauge reads lower than $8x10^{-2}$ mbar (midway on a gauge)

Turn on Penning gauge briefly to read value

Wait until Penning Gauge reads lower than $6x10^{-4}$ mbar (~10 minutes), then continue

Coat

Electrode Power:	On
Check Electrode Position:	3 for Carbon
Electrode Voltage:	~4.1 (just as electrode barely sparks)
Electrode Control:	Toggle to Pulse
Spin Motor:	On slow speed

Push and hold pulse button several times until thinned portion of carbon rod is used

Spin Motor:	Off
Electrode Power:	Off
Electrode Voltage:	0
Electrode Control:	Toggle to Off

Follow **Vent to Air** instructions

Vent to Air

Backing/Roughing Valve:	Backing
Baffle Valve:	Closed to Bell Jar
Nitrogen Tank:	Open
Vent:	Open
Cage and Bell Jar:	Remove
Nitrogen Tank:	Closed
Sample:	Remove

If done coating, go to **Stand-By Position**
If not done coating, go to **Insert Sample**

APPENDIX M

Gold Coater Use

1. Turn on N_2 tank
2. Close 2-way valve
3. Set selector switch to COAT
4. Remove top and insert sample
5. Adjust substrate platform such that the sample is about 1 inch above the baseplate
6. Replace top
7. Close VENT valve
8. Turn on GAUGE
9. Close the BLEED valve
10. Turn PUMP on
    a. Turn CURRENT completely counter clockwise
11. Wait for gauge to read less than 150 microns
12. Open the BLEED valve and until pressure is >500 microns
13. Close the BLEED valve
14. Wait for gauge to read less than 100 microns
15. Open the BLEED valve and until pressure is >500 microns
16. Close the BLEED valve
17. Wait for gauge to read less than 40 microns
18. Open the BLEED valve and adjust pressure to ~75 microns
19. Set the timer for 2 ½ minutes (setting 3)
20. Turn on the OUTPUT switch
    a. Increase the CURRENT to 15 ma and maintain current at this level
22. When cycle has stopped, turn off the OUTPUT switch
23. Turn the PUMP off
    a. Open the VENT valve
    b. Close the BLEED valve
    c. Turn GAUGE off
    d. Turn CURRENT fully counter clockwise
24. Remove top and remove sample
    a. Close N_2 tank
    b. Open 2-way valve

APPENDIX N

Fluorescence Measurements Using A Fluorometer

Apparatus

1. Picofluor dual-channel Fluorometer with Turner Designs Software package
2. 5 cc methacrylate or polystyrene cuvettes
3. 3 cc syringes
4. 0.45 um syringe filters - Gelman 4487T or equivalent
5. Volumetric flasks or poly bottles for standard solution makeup

Scope

The Picofluor can be used to measure low parts per billion concentrations of fluorescein and rhodamine dye tracers in groundwater samples.

Reagents

Standard solutions of fluorescein and rhodamine prepared to cover the anticipated concentration range of the dye test samples to be analyzed.

Fluorescein: Disodium salt, 98% - Stock # A11659 - Lot # A2850A

Rhodamine B: Stock # A13572 - Lot # 16961A

Calibration

1. Before start of calibration, assign numeric values for the standard solutions to be used for calibration.

- To calibrate to analyze for Rhodamine, use a 0.10 ppm Rhodamine standard solution and assign a numeric value of 100.

- To calibrate to analyze for Fluorescein, use a 1.0 ppm Fluoroscein standard solution and assign a numeric value of 999.

> NOTE: THESE NUMERIC VALUES AND STANDARD SOLUTION CONCENTRATIONS ARE SELECTED BECAUSE, AFTER CALIBRATION WITH THESE NUMERIC VALUES AND STANDARD SOLUTION CONCENTRATIONS, FLUORESCENCE MEASUREMENTS WILL APPEAR ON THE SCREEN, AND MAY BE READ DIRECTLY AS PARTS PER BILLION (PPB).

Detailed Steps Required by Procedure to Calibrate the Picofluor

1. Turn the Picofluor on by pressing the <ON/OFF> button.

2. Choose the appropriate channel for analysis and calibration. To do this, press the <A/B> button to toggle between the 2 channels. The activated channel will be shown in the left corner of the screen. It will show "RHOD" for rhodamine and "Blue" for fluorescein.

3. <STD VAL> button and use the arrows to adjust to the standard value. When finished, press <ENT> to accept the value.

4. Press the <CAL> button, then the <ENT> button to start calibration.

5. Insert a blank (3 ml of DI water) and press <ENT>. The Picifluor will average the standard fluorescence for 10 seconds.

6. Insert the calibration standard and press <ENT>. The Picofluor will average the standard fluorescence for 10 seconds.

7. Press <ENT> when calibration is complete to accept the calibration. If <ENT> is not pressed within 10 seconds, you will be asked to accept or abort the calibration. Press the up or down arrow to accept or abort the calibration.

8. After calibration, measure fluorescence on 2 standard solutions of known concentration. Make 3 measurements each, for both of the standard solutions. Record and average the measured fluorescence value for each of the standard solutions tested.

9. Measure fluorescence of the solid standard provided by Picofluor. Take 3-5 readings of the standard, with the standard being removed and reinserted between each use. Record and average these replicate readings and keep for future comparisons.

> NOTE: DURING CALIBRATION, PROMPTS WILL BE SHOWN ON THE SCREEN THAT WILL LEAD YOU THROUGH THE CALIBRATION.

Detailed Steps Required for Sample Analysis

1. Attach a 0.45 um syringe filter to a 3 cc syringe and withdraw 3 cc of solution from the sample bottle for analysis.

2. Transfer the 3 cc of sample to a cuvette.

3. Verify that the Picofluor is on the appropriate channel and has been calibrated using a standard solution for the dye to be analyzed for.

The word "logging" should appear in the lower right hand corner of the Home screen. This indicates that the Picofluor is ready to accept, log, and store data. Up to 1000 data points may be logged. If "logging" is not on the Home screen, refer to the section on Internal Data Logging to activate data logging.

4. Insert the sample cuvette into the Picofluor.

5. Press either of the <READ> buttons. The instrument will autorange and average the fluorescence signal over a 5-second interval.

6. The result will be displayed at the top and center of the screen.

7. Record in a laboratory notebook the sample results displayed on the screen for each sample analyzed. Even though the results are logged and stored in the Picofluor, record the readings in a laboratory notebook.

8. The top left corner will display WAIT for 5 seconds. Once WAIT disappears, another sample measurement may be started.

> NOTE: IF THE APPROPRIATE NUMERIC VALUE AND CALIBRATION STANDARD IS USED, SAMPLE ANALYSIS RESULTS SHOULD APPEAR ON THE SCREEN AND BE READ DIRECTLY AS PPBs.

Internal Data Logging (IDL)

The Picofluor DATA screens control logging, downloading, and erasing of data. The Picofluor can log up to 1000 data points. Before start of sample analysis, activate Data Logging.

To Activate Data Logging

1. Press the <DATA> button 2 times.

2. Press <ENT> to toggle between logging and stop.

3. Press <ESC> when finished to return to Home screen.

The word "logging" should appear in the lower right hand portion of the Home screen. This indicates the Picofluor is ready to log data.

To Download Data

WHEN READY TO DOWNLOAD DATA, TAKE THE PICOFLUOR TO BOB JARABEK IN *L-107* FOR DOWNLOADING BY THE FOLLOWING STEPS:

1. Connect the Picofluor to the serial port of the selected PC using the provided interface cable.

2. Open the Turner Designs Interface Software.

3. Press the <DATA> button 3 times.

4. Press <ENTER> 5 times to start the data download.

5. Press <ESC> when finished to return to the Home screen.

TO ERASE DATA LOGGED INTO THE PICOFLUOR

1. Press the <DATA> button 4 times.

2. Press <ENT> 5 times to erase all logged data.

3. Press <ESC> when finished to return to the Home screen.

APPENDIX O

Sample Receiving Based on MCL-7704

1. MCLinc may receive samples in the following manner:

    a. Common carrier delivery to the laboratory
    b. Hand Delivered by Customer*
    c. Collected and delivered by MCLinc personnel

2. In the case of "a" above where no other instructions were received (i.e. – unknown client shipment or client samples are hazardous) the sample package should be taken to *Sample Receiving 102 Hood* for opening and radiation scan. This should be performed within 3 hours of receipt or if received late or after working hours within 3 hours of the start of the next business day.
3. In the case of "b" above where no other instructions were received the sample package will be brought to the sample cart in A-corridor and the sample custodian (SC) notified. The package, prior to opening, will then be scanned for radioactivity. If there is any indication of radioactivity or package is so labeled, then move the package immediately upon arrival to *Lab 101*. Have the sample deliverer open package and hand over the paperwork where possible. In the case of "c" above the MCLinc person delivering the samples is required to make sure samples are handled as defined herein and that the SC gets the paper work ASAP. The SC is responsible for all other duties as specified in MCL-7704.

4. Scan and open the package (any work in *Lab 101* will be done by Rad Worker II trained individual** who will scan samples for radioactivity, check contents and verify sample types, numbers and condition and communicate the information, sign chain of custody and pass paperwork on to the SC). Otherwise the SC will open package in A corridor, and scan for radioactivity***, verify contents, complete chain of custody (COC), and perform other duties of SC as specified in MCL-7704. If necessary, (COC not received with the samples) create one using MCLinc COC form.

5. SC will log samples into data base and notify project manager or if unknown notify Jack Hall. If Rush or Priority samples notify them immediately.

6. SC prints sample labels and places with the samples along with a copy of the paperwork.
   The project manager has the responsibility if known ahead of time to notify the SC and project team of any special hazards or concerns with a sample. Also MCLinc may define certain client samples be handled in a certain way. For example, all samples from a D & D operation should be treated as suspected high radioactive samples and taken immediately into *Lab 101* and placed in an appropriate hood.

7. Sample preservation and storage of samples received that require preservation are checked and if not preserved, noted on the chain of custody and then preserved. Temperature levels are noted on the COC also. Samples requiring thermal preservation are stored in refrigerators which are monitored for temperature daily. (<6ºC). If the samples are not analyzed and reported to assure thermal preservation over the weekend, the samples are placed in a large cooler with at least 2- 10lb bags of ice. The analyst will notify QA or the Lab Manager if needed. The ice has been shown to last at least four (4) days.

.

* Classified samples will be prearranged and handle per Security Plan requirements with all issues directed to the Security Officer Earl Munday.

**If you are asked to open a package by the SC, please do so as soon as possible and make sure it is completed within 3 hours of receipt.

***Any indication of radioactivity above background, immediately request a staff member with Rad Worker II training to move samples, container and related packing materials to *Lab 101*. The radioactivity level must be evaluated against the criteria in the Radiation Protection Plan (Radioactive Material License R-73025-K25) and the Nuclear Materials Control and Accountability Plan (MCL-7705) to determine proper handling and inventory information for the sample(s). (Questions see the RSO)

Anyone handling the primary sample container i.e. sample bottle should wear surgical gloves as a minimum.

APPENDIX P

Taking PCB Wipe Samples From Pieces of Scrap Metal

Scope

This Operational Aid provides a method for sampling large pieces of scrap metal for PCBs by taking a representative 100 sq cm wipe sample from the piece.

Equipment and Apparatus

1. Pieces of sterile cotton gauze (approximately 3" x 3").

2. Wide mouth, low form 125 cc glass sample jars with teflon lid inserts.

3. Tweezers or forceps for handling the gauze pads.

4. A large (500 cc) wide mouth glass jar to hold the hexane soaked gauze pads.

5. Latex gloves.

Reagents

1. Hexane, Pesticide Grade.

Detailed Steps Required by Procedure

1. Select a representative spot on the piece of scrap metal to be sampled. Place the 10 x 10 cm template over this spot.

2. Using forceps, remove one of the hexane soaked gauze pads from the jar. With the forceps, roll the gauze against the inside wall of the jar to squeeze out excess hexane.

3. While wearing gloves, take the gauze pad in hand and wipe first in one direction and then in the other direction the entire 10 cm x 10 cm sample area within the template. Finally wipe the outside area within the template.

   NOTE: IF THE PAD BECOMES EXTREMELY DIRTY, AFTER THE FIRST DIRECTION WIPE USE A SECOND PAD TO WIPE THE OTHER DIRECTION.

4. Place the wipe in a 125 cc wide mouth jar.

5. With a second hexane soaked wipe repeat the above procedure.

6. Turn the piece of scrap metal over, select a sample location, place the template on this spot, wipe this 100 sq cm sample area with a hexane soaked wipe, followed by a second wipe, and place these 2 wipes in the 125 cc jar with the wipes from the other side.

7. These 4 wipes are the sample for PCB analysis.

8. Label sample jar with both the customer sample number and the MCLinc sample number.

APPENDIX Q

Core Sampling Large Pieces of Scrap Metal

Scope

This Operational Aid describes a method for sampling large pieces of scrap metal by core drilling the sample with a drill press and collecting the drillings as a sample for analysis.

Equipment and Apparatus

1. Drill press with stand capable of handling pieces of scrap metal up to 36 inches in diameter.

2. Case hardened drill bits (1/4 inch to 1/2 inch).

3. 50 cc sample vials or equivalent.

Cleaning drill bits

1. After use, wash drill bits in warm soapy water with a stiff brush.

2. Rinse with isopropyl alcohol and allow to dry.

3. Before use, always inspect drill bits to make sure they are clean and free of loose particles.

Detailed Steps Required by Procedure

1. Place piece of scrap metal to be sampled on drill press stand.

2. Determine approximate diameter of piece to be sampled.

3. If diameter is 3/8 inch or less, select 3 equidistant representative points on the piece to be sampled and drill core holes completely through the metal at these 3 points.

4. Collect drillings. If less than 20g, drill additional holes until 20g of drillings have been collected.

5. Put core drillings in sample vial. This is the sample for analysis. Blend by shaking vigorously for 3 minutes.

6. If the diameter of the piece of metal to be sampled is greater than 3/8 inch, sample from both sides by drilling holes partially through the piece of metal on both sides.

7. Select 3 equidistant representative sample points on the metal and drill core holes at each point. Collect drillings and place in sample vial.

8. Turn the piece of scrap metal over, select 3 points on this side, drill core holes at each point, collect drillings, and combine these drillings with drillings from other side. This is the sample for analysis.

9. Sample weight should be at least 20 g. If not, drill additional holes. Blend sample by vigorously shaking the vial for 3 minutes.

10. Label vial with both the customer sample number and the MCLinc sample number.

APPENDIX R

Colormetric Determination of Hexavalent Chromium

Method Reference

ASTM-7196A "Standard Test Method to Determine the Concentration of Dissolved Hexavalent Chromium in EP/TCLP Characteristic Extracts and Ground Waters."

Scope

This method may be used to determine the concentration of chromium Cr(VI) in TCLP characteristic extracts and ground waters. It may also be used for Cr(VI) determination for certain industrial wastes and even sludges by extracting the chromium into a sulfuric acid solution.

Equipment and Apparatus

1. A Spectrophotometer, for use at a wavelength of 540 nm providing a light path of 1 cm or longer.

2. 1-cm Absorbance cells

3. Volumetric flasks (25, 50, and 100 ml).

4. Various sizes of pipettes (1 to 10 ml).

Reagents

1. Demineralized water

2. Potassium dichromate stock solutions:

Stock solution A: Prepare by dissolving 141.4 mg of reagent grade potassium dichromate, 2Cr2O7, in DI water and dilute to 1 Liter (concentration = 50 mg Cr/L or 1 ml of solution = 50 ug Cr).

Stock solution B: Prepare by diluting 10 ml of stock solution A to 100 ml with DI water. (concentration = 5.0 mg Cr/L or 1ml = 50 ug Cr.

3. Potassium dichromate standard solutions required to develop a calibration curve: Prepare by diluting aliquots of stock solution B (concentration = 5.0 mg Cr/L) to 100 ml standard solutions in the following manner:

5.0 mg/L Cr Stock Solution, ml	Concentration, mg Cr/L
40	2.0
20	1.0
15	0.75
10	0.50
8	0.40
3	0.30
4	0.20
2	0.10
1	0.05
0.5	0.025

4. Sulfuric Acid, 10% v/v: Dilute 10 ml of reagent grade H_2SO_4 to 100ml with DI water.
5. Diphenylcarbazide Solution: Dissolve 250 mg of 1,5-diphenylcarbazidein 50 ml of acetone, Store in brown bottle.
6. Acetone (reagent grade).

Detailed Steps Required by Procedure

1. Transfer 95 ml of the sample to a 100-ml volumetric flask. Add 2.0 ml of diphenylcarbazide solution and mix. Add H_2SO_4 dropwise to pH = 2 +0.5. Dilute to 100 ml with DI water and let stand for 5 to 10 minutes for full color development. Transfer an appropriate amount to the 1-cm absorbance cell and measure absorbance at 540 nm.

NOTE: IF THE SAMPLE IS TURBID AFTER DILUTION TO 100 ML, A TURBIDITY BLANK SHOULD BE RUN. TO DO THIS, PREPARE A SAMPLE AS ABOVE EXCEPT DO NOT ADD THE DIPHENYLCARBAZIDE. MEASURE ABSORBANCE AND SUBTRACT THIS VALUE TO GIVE THE CORRECT ABSORBANCE VALUE.

2. The sequence for sample measurement with the Spectronic 20D is:

   a. Set wavelength at 540 nm by using the wavelength control knob.

   b. Set mode to TRANSMITTANCE (press the MODE select button until the TRANSMITTANCE" LED on the right of the display is lit).

   c. With sample compartment empty and door closed, adjust Zero Control knob so that meter reads 0% T.

   d. Insert DI water reference blank into the instrument sample compartment and set transmittance at 100% T.

   e. Set MODE to ABSORBANCE by pressing the MODE select button until the "ABSORBANCE" LED on the display is lit.

   f. With DI water sample in sample compartment, adjust absorbance to read 0.0%.

   g. Insert sample and read measurement from display in per cent absorbance.

3. Develop a calibration curve by plotting the measured absorbance value for each of the calibration standard solutions against the concentration of Cr(VI) in each of the calibration standards. The calibration curve range should be 0.025 mg/L to 2.0 mg/L Cr(VI).
4. For absorbance measurements and development of a calibration curve, prepare the calibration standard solutions for analysis by the same procedure as used for samples.

Quality Control

1. Dilute, with DI water, any sample that is more concentrated than the highest standard solution on the calibration curve.
2. Run a minimum of one DI water blank per sample batch to determine if contamination or memory effects are occurring in the instrument.
3. Run one duplicate sample through the entire sample preparation and analytical process.

APPENDIX S

Determination of Persulfate by Titration with Sodium Thiosulfate

Method reference

Standard Method 4500-Cl B. Iodometric Method I - Modified

Discussion

It is known that chlorine liberates free iodine from potassium iodide (KI) solutions at pH 8 or less and this liberated iodine may be titrated with standard solutions of sodium thiosulfate ($Na_2S_2O_3$), using starch as an indicator. Since persulfate (S_2O_8) also liberates free iodine from potassium iodide solutions, concentrations of persulfate may also be determined by similar iodometric titrations with sodium thiosulfate, using starch as an indicator.

Equipment and Apparatus

1. Volumetric flasks, 1000 ml.
2. Burettes, 50 ml.
3. Pipettes, 50, 25, 5, 2, and 1 ml.
4. Mag-mix stir plate.
5. Erlemeyer flasks, 250 ml.
6. Balance, top loading capable of weighing accurately to +0.10 g.

Reagents

1. Acetic acid, conc glacial
2. Patassium iodide, KI, crystals
3. Sulfuric acid, conc
4. Sodium bicarbonate
5. Standard sodium thiosulfate solution, 0.10N: Dissolve 24.83 g $Na_2S_2O_3 \cdot 5H_2O$) in 1000 ml freshly boiled DI water and standardize against the potassium iodate standard solution.

$Na_2S_2O_3 \cdot 5H_2O = 248.3$ g $S_2O_3 = 112$ g

$$\frac{112}{248.3} \times 24.83 \text{ g} = 11.2 \text{ g } S_2O_3 \text{ /L or } 11.2 \text{ mg } S_2O_3 \text{ /ml}$$

6. Standard potassium iodate solution, 0.10N: Disolve 3.567 g KIO3 (dried at 103 degrees centigrade for 1 h) in sufficient DI water to make 1000 ml.

7. Standard sodium persulfate solution, 1000 mg persulfate (S2O8) per liter or 1.0 mg S2O8/ ml: Dissolve 1.2349 g Na2S2O8 in enough DI water to make 1000 ml.

8. Starch indicator solution: With constant stirring, add 1 g of dry starch to 200 ml of boiling DI water. Let settle overnight. Use only the clear supernate.

Procedure to Standardize the 0.10N Sodium Thiosulfate Solution

a. Add 1 ml of concentrated sulfuric acid to 80 ml of DI water in a 250 ml Erlemeyer flask and stir.

b. Add 10 ml of the 0.10N potassium iodate solution.

c. Add 1 g KI.

d. Titrate with the 0.10N sodium thiosulfate solution until the yellow color of the iodine is discharged (yellow to clear).

e. Add approximately 1 ml of starch indicator and titrate until blue color is gone (blue to clear).

$$\text{Normality of } Na_2S_2O_3 = \frac{\text{ml } Na_2S_2O_3 \times \text{normality}}{\text{ml } KIO_3 \text{ sample}}$$

Detailed Steps Required by Procedure for Persulfate Titration

1. Add 50 ml of persulfate sample to a 250 ml Erlemeyer flask.

2. Add 1 g of sodium bicarbonate. Swirl to remove air.

3. Add 4 g of potassium iodide (KI). Swirl to dissolve.

4. Let stand for 15 minutes.

5. After 15 minutes, acidify by adding 1 to 2 ml of acetic acid.

6. Add 1 ml of starch indicator.

7. Titrate with sodium thiosulfate until blue color changes to clear. Wait 10 minutes and check to see that the blue color has not returned.

Calculation

$$\text{Concentration } S_2O_8, \text{ mg/ml} = \frac{A \times B}{\text{ml(Sample)}}$$

Where

A: ml of sodium thiosulfate used

B: concentration of thiosulfate (mg/ml)

Quality Control

For each batch of samples, Run:

a. 1 DI water blank (same volume of water as samples).

b. 1 duplicate sample.

c. 1 Control sample (a persulfate sample of known concentration).

Appendix T

Sample Preparation Outline for PCB's in Soil

Purpose: Prepare PCB Extracts of Soil/Solid Samples for Analysis

This procedure is to prepare PCB extracts of soil/solid samples expected to be greater than 20ppm and is also especially useful for samples with short turnaround times (TAT's).

Preparation

1. To a 40 ml sample vial add to the nearest 0.01g, 2 grams of soil. Record sample weight using PCB prep sheet.
2. Add 25 microliters of TCMX surrogate to each sample.
3. Add 5 ml, 80:20 methanol/water solution *and shake.*
4. *Add 10mL hexane*.
5. Position vial on sonication platform.
6. Sonicate for 2 minutes – output-2, pulser-40%.
7. Allow water and hexane to separate – if emulsion is noted, set aside for centrifugation or if hexane layer is not clear, set aside for acid cleanup.
8. Using a glass transfer pipette, transfer the hexane layer to a 7 ml vial containing one-eighth inch of sodium sulfate.
   NOTE: If sulfuric acid cleanup is required, "DO NOT" add the sodium sulfate.
9. Label vial and place in tray for analysis.
10. For each batch of samples prepare one blank and one LCS – for LCS, add 25 microliters of PCB standard and 25 microliters of TCMX surrogate to 5 ml of methanol/water. Add 5 ml of hexane. Blank is 25 microliters of TCMX surrogate added to 5 ml of 80:20 methanol/water. Add 5 ml of hexane.
11. Record all information on prep sheet. (See Attached)

Acid Cleanup (If needed – See Step 6 above)

1. Using a glass transfer pipette, transfer the hexane layer to a 7 ml vial.
2. Using a glass transfer pipette, transfer concentrated sulfuric acid to the vial containing the colored hexane layer. Add ~one-fourth inch (~3ml) of sulfuric acid.
3. Cap the vial and shake by hand for 10 seconds.
4. Allow hexane and acid to separate. If hexane is clear, (acid may be slightly discolored) transfer hexane to labeled vial for analysis. If hexane shows discoloration, pipet out the dirty acid, add clean acid to repeat the cleanup step until the hexane layer is clear or until there is no further reduction in color in the hexane layer. When a clear hexane layer is accomplished, transfer to a labeled vial for analysis. If a clear hexane layer can't be accomplished, contact your supervisor who will determine if further cleanup is needed.

5.

PCB SAMPLE PREPARATION
LOG SHEET

Date Received:_____ Prepared By:_____ Project ID:_____

Date Prepared:_____ Surr. ID:_____

Sample ID	Sample Wt. (g)	Surr. ul	Acid Cleanup (Y/N)	Comments

BALANCE CALIBRATION				
Balance	Date	Mass	Weight	Weight
		1.0		
		5.0		

QA/QC: Required Blank, Duplicate plus LCS

Prepared By:_____

Appendix U

Analysis of Volatile Halocarbons by GC-FID

Purpose: The purpose of this procedure is to analyze the following volatile halocarbons – trichloroethylene (TCE), trichloroethane (TCA), dichloroethane (DCA), dichoroethene (DCE), and carbon tetrachloride. Other compounds may be analyzed by this procedure as needed.

Instrument Conditions: See attached GC Project/Compound Setup Guidance

Procedure:

4. After set-up of instrument per attached conditions, run a blank water solution.

5. Prepare a standard from stock standards to have 10 ug/mL of each compound.

6. Add 0.1 ml of solution from #2 above with auto-pipet to purge and trap bubbler tube with blank water, and then add 10 uL of toluene. Purge. (See attached chromatogram).

7. Sample prep: Weigh 2 g to the nearest 0.01 g directly in the empty bubbler tube and then cover with ~1" blank water and add 10 uL toluene and purge.

8. Calculate samples using the response as peak area per ug for the standard peak of concern versus the response of the sample at that relative retention time versus the toluene. Peak area of std./ug X peak area of sample = ug per weight of sample in grams = ug/g or mg/Kg for reporting. If dilution is required, multiply by dilution factor.

Run Sequence:

Blank
Standard
Samples
Blank
Standard #2

Quality Control:

Blank must have less that $1/5^{th}$ the reporting limit.
Standard chromatogram must have separation of all compounds.
Standard #2 acts as the CCV or LCS and must be within 50% of original standard.

GAS CHROMATROGRAPHY
PROJECT/COMPOUND SETUP GUIDANCE

Instrument: SRI 8610A

Compounds (Estimated TµG on-column)

Trans 1,2-DCE 0.1	1,1-DCA 0.1	Cis 1,2-DCE 0.1	Chloroform (Tricichloromethane) 0.25
1,1,1-TCA 0.1	Carbon Tetrachloride 0.5	1,2-DCA 0.1	TCE 0.05
1,1,2-TCA 0.1	Perchloroehtane (Perc.) 0.1		

Set UP

Column	Carrier Gas and Flow (ml/min)Flow	Detector	Detector Gas	Detector Gas Flows (ml/min)
J&W Scientific 75mx0.53mmx3µ DB524 cat#1251374	Hydrogen 10	FID	Hydrogen Air	20 60

Temperature Program

Temp ºC	Hold (min)	Ramp ºC/Min	Temp ºC
35	7	5	45
45	3	1	50
50	0	12	135

Purge and Trap

Trap Type	Trap/Purge Temp. (ºC)	Flow (ml/min.)
Tenax	350	45-60

Events

Event	On Time (min.)	Off Time (min.)	Description
Integ. None	0.01		Intergration off
E	0.20		Purge start [1]
E		2.00	Purge off
F	4.00		Trap heat on
F		8.00	Trap heat off
Integ. Auto	10.5		Begin intergration

[1]Trap must be below 20ºC for best efficiency take to and hold at < 5ºC; leave valve closed when purge first starts to check for leaks.

Retention Times

Compound	RT	RT window	REL RT	Comment
Trans 1,2-DCE	11.11	11.0-11.3	0.6041	RRT's are to TCE
1,1-DCA	12.12	12.0-12.3	0.659	RRT's are to TCE
Cis 1,2-DCE	13.5	13.4-13.6	0.7325	RRT's are to TCE
Chloroform	14.5	14.4-14.6	0.7881	RRT's are to TCE
1,1,1-TCA	14.9	14.8-14.5	0.8097	RRT's are to TCE
Carbon Tetrachloride	15.4	15.3-15.5	0.837	RRT's are to TCE
1,2-DCA	16.2	16.1-16.3	0.881	RRT's are to TCE
TCE	18.4	18.3-18.5	1.0	RRT's are to TCE
1,1.2-TCA	21.9	21.8-22.0	1.191	RRT's are to TCE

Intergration/Ops

Sample Rate (Hz)	Port Address	End Time/shot to shot (min)
5	280	24/30
%Peak	**%Base**	**Area Reject**
60	45	25

Lab name : MCLinc
Client : PRISM
Analysis date : ~~01/09/1980 15:40:24~~ 02/25/04
Method : HP 5890 ECD
Description : 0.5ML 50PPM STD
Column : J&W DB624 0.53X30
Carrier : FID HYDROGEN
Data file : PRM1.ASC (c:\psm1348)
Operator : D Peery

03/04/04

Retention	Height	Area
11.336	227.683	1632.83
11.966	21.855	187.89
12.260	175.712	1756.56
13.470	6.935	62.30
13.763	23.534	237.58
14.753	45.348	611.61
15.276	68.381	1230.33
15.820	21.905	345.53
16.840	68.561	943.35
18.860	171.193	1446.21
19.183	58.610	128.54
21.670	156.750	961.08
22.096	21.679	49.10
22.440	111.426	637.87

APPENDIX V

OPERATIONAL AID FOR BALANCE CHECKS

Purpose:

This operator aid provides the procedure to check balances prior to use for any critical measurements like sample weights, reagents, etc. It should be applied to all projects. It does not replace or change the procedure for weighing controlled nuclear material. *Also included is the balance acceptance criteria.*

Procedure:

- Make sure the balance is clean prior to use**.** Turn on and zero out per manufacture or balance instructions. If unit does not zero out (show all zeros) contact QA.
- From the weight set assigned to that lab or area, select a weight below the target weight to be measured. Weigh and record results from duplicate measurements. Then weigh in duplicate a weight above the target and record results. Record the results in a notebook, bench sheet or the balance notebook with the balance. For example for a sample weight of 2g, checking with1g and 5 g weights is proper.
- Check to make sure the weights are within the limits based on type of balance. For a 3 or > decimal place balance(shows 3 or more decimal points right of the decimal) the weight should be within +/- 0.001 times the value of weight, for example a 100g weight should be within +/-0.1g. For a 2- decimal place balance the tolerance factor is +/- 0.01 times the value of the weight and for a 1- decimal place balance it would be +/- 0.1 times value of the weight. A 1-place balance should not be used for critical measurements.
- Any balance, set of weights or any weights out of tolerance should be taken out of service and QA notified.

Notes:

Several of the MCLinc balances are certified by a third party vendor annually and are so marked on the balance and the balance inventory kept *in the QA files*. DOECAP related work must be done on a certified balance. The other balances are checked by MCLinc on an annual basis. The balance sets in the laboratory are checked annually against a certified set of weights maintained by QA for that purpose only.

APPENDIX W

OPERATIONAL AID FOR PREPARATION OF STANDARDS

Purpose:

This operator aid provides procedures and guidance on the preparation of standards for analysis by ICP, GC, IC, SIE, and other applicable procedures, i.e. wet chemistry.

Procedure:

- Where possible the purchase of certified standard solutions from an approved vendor is the MCLinc policy. Any questions of what is appropriate should be directed to QA. These are considered the stock solutions and must only be used within their expiration date. Start to use date and expiration date should be noted on stock solution bottle.

- Each procedure or SOP should define the number and concentration levels to be prepared and run by the procedure. If not, analyst must follow Step 3. Caution: Use only glassware known to be clean.

- Standards should be prepared within the working range of the instrument or method with the lowest standard concentration run as the default MCLinc Method Reporting Limit (RL).

  Example: If an ICP Standard for As is run at 10, 20, 50, 100ug/L the 10-100ug/L defines the working range and the RL is 10ug/L.

1. Original certificates that come with the certified standards must be given to QA and kept in QA files.

2. The certified working stocks must be diluted appropriately, i.e. pipet 5ml into 100ml volumetric flask and dilute to mark or use calibrated auto-pipet to transfer 25ul to 10ml volumetric and make to mark. An inappropriate dilution would be a small volume to a very large volume, i.e. 0.5ml to 2 liters. Instead, dilute in two steps, i.e. 5ml of stock to 100 ml and then 10mls of the new solution to 2 liters.

3. New standards should be checked against prior standards and for ICP and chromatography techniques a second source standard is to be used as the CCV (continuing calibration verification).

4. All standards should reflect date of preparation and expiration date and should be recorded in standard prep log or notebook.

5. If unable to purchase a certified standard solution or time does not permit its purchase, prepare one from a new chemical of known purity and chemical structure (waters of hydration must be considered to calculate weight required to prepare a stock, if appropriate). Again, document source of chemical, formula weight, and final dilution in notebook. Any questions contact Technical Director or QA.

APPENDIX X

Operator Aid for Acid Extraction and TCLP for K-25/27 Project

1. Purpose

1.1 In most cases MCLinc will not be doing any analyses, but the following:

1. A radiochemistry 6M nitric acid extraction to remove the surface contamination of a 4" diameter coupon for analysis by USEC Portsmouth. Procedure outlined below.
2. Perform TCLP metals extract of separate coupon samples as requested, but <100g and able to get in 3.5" extraction vessel
3. Sample load at ~8 samples per day. Each sample will be for one extract only (either radiochemical or TCLP).

1.2 MCLinc will have a 3 day TAT for each of the above and do the following:

- Log-in Samples and assign MCLinc numbers but lab folks will use NFT #'s for all documentation. Submit copy of any documentation with rad. information to Bob Fellows to track in-house Rad.
- Fax completed Field Chain of Custodies (FCOC) to Angelique Jones at MDM within 24 hours of receipt. FAX same information to NFT along with Log-in batch information. Batch designation will be ETTPRAD plus date or ETTPTCLP plus date i.e.ETTPRAD071404
- Take picture of deposit side of coupons with NFT sample# in photo using digital camera. If not sure of deposit side take picture of both sides.
- Use project prep sheets for radiochemical extraction and 2 page TCLP prep sheet for each sample for TCLP extraction. MDM will provide labels for extracts.
- Turn over to MDM for shipping a 250mL plastic bottle (provided by USEC) from the radiochemistry extraction including a blank with each batch.
- Turn over to MDN for shipping up to 2 each 1-L plastic bottle from the TCLP extract and for each batch a blank and MS and MSD (USEC will provide spiking solutions).
- Using a copy of the FCOC, prepare COCs for each batch of samples and Fax to MDM and they will prepare LCOC that will be delivered when MDM picks up the extracts. ALL bench sheets are to be sent to USEC with copy of FCOC and bench sheets and copy of the FCOC to Marie at NFT.
- Run and Spike TCLP sample designated as QC sample using USEC provided spiking solution and instructions for each batch. A measured 250mL of the designated sample extract will be spiked and labeled as sample number-MS and another 250mL aliquot will be spiked and labeled as sample number-MSD. And the remaining sample sent as well for analysis by USEC
- Submit a blank for each batch and extraction type.

2.0 Radiochemical Extraction Procedure

- Samples should arrive in plastic bags and be an ~ 4" diameter coupon of metal or in some cases pieces of metal or component of valve or electrical item.
- Remove all of sample from the bag into a tared Glad Plastic Dish purchased for this project.
- Take digital picture of deposit side of the coupon with the NFT sample # clearly visible in picture. May need to put # on post-it.
- Record weight and other information on bench sheet provided for the project.
- Move dish to shaker platform and add ~200ml of 6M nitric acid to each sample slowly and carefully since metal may react violently.
- Shake gently for 4 hours. Stop and then observe each sample to see if surface is clean, i.e. rust or paint or contamination removed. If it does not appear clean, continue to shake and monitor up to 20 hours then continue to next step.
- Pick up coupon or metal piece and wash with DI water into Glad dish. Any fines should go with liquid.
- Then wash the dish including the fines into a labeled 250mL bottle pre-marked and verified at 250mL level. .[Label should include date, analyst initials, sample # and words "Radiochemical Extract"] MDM should provide labels.
- Place coupon or metal piece(s) on clean towel or surface in hood and allow sample to dry and then reweigh. Record weight and calculate weight loss during extraction on prep sheet.
- Do a Rad scan on surface of coupons and note in notebook.
- For each batch process a blank 200mL 6M acid diluted to 250mL
- Complete COC for the return of coupons using same sample number and calling them "used sample residuals".

3.0 TCLP Procedure

NOTE: This project does not require the following:

- A liquid test for the sample or % moisture
- pH test of sample
- Size reduction of sample

1.0 Separate samples for TCLP Metals extraction should be in a plastic bag with <100gm and < 3.5" in diameter for use with large mouth extraction vessels.
2.0 Remove the entire sample from plastic bag into a tared container.
3.0 Take digital pictures of deposit side of the sample with NFT sample # displayed in the picture. May require writing # on a post-it.
4.0 Record weight and all other required information on the appropriate USEC bench sheets for TCLP.

5.0 Calculate using weight in grams times 20 to determine mLs of Extraction Solution #1 to add.
6.0 Transfer sample to extraction vessel and add the appropriate volume of TCLP extraction solution and turn on rotator. Record start time, date and room temperature.
7.0 Tumble for 18 hours, than stop rotation and record time, date, and room temperature on bench sheet.
8.0 Filter sample through 0.7micron TCLP filter. Measure pH of solution. Transfer filtered extract to one or more 1-L plastic bottles with label containing date, NFT sample #, analyst, and the words "TCLP Metals Extract" MDN to provide labels.
9.0 Add nitric acid preservative to adjust pH to <2. Measure and record pH.
10.0 Each batch should have a blank run through the procedure
11.0 Run and Spike TCLP sample, designated* as QC sample for each batch, using USEC provided spiking solution and instructions for each batch. A measured 250mL of the designated sample extract will be spiked and labeled as sample number-MS and another 250mL aliquot will be spiked and labeled as sample number -MSD. The remaining sample sent as well for analysis by USEC
12.0 Do a Rad scan on surface of coupons and note in notebook and then notify Taryn samples are ready for return.

*** If not designated analyst picks one for spiking based on volume of leachate available.**

4.0 Special Requests under this Statement of Work (SOW)

Under this SOW NFT may require the following:

- Identification of contaminants on paint or surface scrapings by SEM/EDS,XRD and XRF.
- Some cases as requested collect 5-10g by drilling or cutting a coupon or metal piece or apparatus after "cleaning" or extraction by the radiochemical procedure above for submission to USEC for metals. Use current operator aid for this step. Purpose of this analysis is to determine materials of construction only.
- Remove a small 5-10g sample of mercury from a mercury trap.
- Disassemble valves, etc to use internal parts as a sample for one of the above extracts.
- Four samples will require drilling out sub-samples after radiochemical leaching. A portion of the sub-sample will be digested with nitric acid and hydrochloric acid and the digestate and ~30-50g of drillings sent to USEC via MDM.

Note: All samples, and related contact trash that may be contaminated will be returned to the client site. Therefore separate and collect that trash in separate rad bags.

Sample Preparation

Batch # _____ Analyst _____ Date _____

Balance Used No. _____ NB_____ pg_____

Matrix _____

	Sample ID	LIMS ID	Initial Wt. (g)	Final Wt. (g)	Difference (g)	Final Volume (ml)
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						

Comments: _____

TCLP Work Sheet
Method 1311

Customer No. _____ Start Date _____

Computer ID # _____ QA File No. _____

Sample Source _____

Daily Monitoring (if used)

Balance Check: Serial No. _____ NB _____ pg _____

pH Meter Standardization and Check: Serial No. _____ NB _____ pg _____

Reagent Water Resistivity @ 25°C

Weekly Analysis: Conductivity NB _____ pg _____

Rotary Agitator: Serial No. _____ Quarterly RPM's check NB _____ pg _____

Sample Evaluation

Solid with no filterable liquids _____ Multiphase _____ Liquid _____

Particle size reduction required _____ Sample replicate required _____

Agitation Begun: Date _____ Time _____ Room Temp. _____

Agitation Ended: Date _____ Time _____ Room Temp. _____

Comments:_____

_____

_____

_____

_____

Analyst: _____

Metals Procedure

Extraction Fluid No. _____ pH _____ Date/Time _____/_____

Weight of Extraction Fluid = 20 percent solids x weight of waste filtered / 100

Bottle No. _____ Wt. of Solids _____ (grams)

Wt. of Extraction Fluid _____ (grams)

The solids were filtered through a 0.7 micron borosilicate, acid washed, glass fiber filter, with no binder.

Extract pH _____ Preservation pH _____

Preservation Date/Time _____/_____

TCLP Metals: Sample No. _____

Matrix Spike Requested: LSR No. _____

Metal Concentrations (mg/l): Antimony _____ Cadmium _____ Chromium _____

Lead _____ Arsenic _____ Mercury _____ Strontium _____ Nickel _____

Silver _____ Tin _____ Vanadium _____

Matrix Spike

Preservation pH _____

Date/Time _____/_____

Sample No. _____

Matrix Spike Duplicate

Preservation pH _____

Date/Time _____/_____

Sample No. _____

APPENDIX Y
Calibration and Checking Autopipettors

1.0 Purpose

The purpose of this operator aid is to define the procedure for checking the calibration of and calibrating autopipettors.

2.0 Daily Check Procedure – *Prior to Use*

2.1 Inspect and evaluate the autopipettor to ensure that it is functioning properly each day that it is used.

2.2 Tare a clean beaker on an analytical balance. Pipet a known aliquot of deionized water into the tared beaker. Record the data in the Pipet Check Log. The pipettor performance is acceptable if the weight is ±2% of the expected value.

Note: If the pipettor performance is not acceptable, the quarterly calibration procedure shall be performed.

3.0 Quarterly Calibration Procedure

All battery operated autopipettors with a delivery capacity of 0.1mL or more used for quantitative analysis shall be calibrated quarterly.

3.1 Tare a clean beaker. Deliver an aliquot of deionized water at 100% of autopipettor capacity to the tared beaker and record weight. Re-tare the beaker and repeat delivery for a total of 5 replicates.

3.2 Repeat with 5 replicates each for autopipettor capacities of approximately 75%, 50% and 10%.

3.3 Calculate the mean (X) and standard deviation (SD) for each capacity.

3.4 Accuracy is calculated by comparing X to the specific gravity of water times the volume (V) of water. The mean X must be within ± 2%. At 20°C, the specific gravity of water is 0.998 and the range is:

$X \pm 0.998 * V * 0.02$

3.5 Precision should be <1% and is calculated as relative standard deviation (RSD) by the following formula:

$RSD = 100 * SD / X$

SD = standard deviation
V = volume of water

4.0 Procedure for Digital Microdispensor

4.1 Digital microdispensers have digital adjustment and are for microliter deliveries. They are certified by the manufacturer to deliver within 1% of the digital set value. Because of the small volume, there is no way to check the delivery volume without encountering error in the measuring system. The replaceable glass capillaries are calibrated.

4.2 Prior to each use, inspect the glass capillary to verify that it has not cracked or fractured. The 100µL microdispenser capillary is particularly fragile and should be closely visually inspected. If the capillary is damaged, it must be replaced.

4.3 Prior to each use, verify that the zero volume setting has the plunger tip even with the bottom edge of the capillary. Verify that the maximum volume has the plunger tip even with the calibration line printed on the capillary. This serves as the calibration check.

5.0 Manual Calibration

Autopipettor units that have digital adjustment but not a certified delivery system should be manually calibrated.

5.1 Determine the volume to be delivered by the autopipettor, e.g. 5.0 mL.

5.2 Set the autopipettor to deliver 5.0mL. Process the autopipettor as in Section 3.1.

5.3 If the autopipettor fails the accuracy test in Section 3.4, adjust the dial in small increments and repeat Section 3.1 until acceptable accuracy is achieved.

6.0 Corrective Action

If the autopipettor cannot be corrected to meet the defined criteria above, the unit shall be removed from service and returned to the manufacturer for repair and calibration.

APPENDIX Z
OPERATIONAL AID FOR CALIBRATION OF THERMOMETERS

1.0 Scope and Summary of Method

This provides a method for calibration to determine the accuracy of most thermometers and other temperature measuring devices over a temperature range of 0 to 100 degrees centigrade. It is not intended to select thermometers for specific jobs. It is the responsibility of the person performing the work to use this calibration data to select a thermometer that meets the QA requirements for the work being performed. This data should identify in-house thermometers that meet QA requirements for a specific job.

2.0 Equipment and Apparatus

1.0 Hart Scientific (or equivalent) electronic thermometer with thermocouple.

2.0 Water bath capable of maintaining a constant water temperature in the range of 20 to 80 degrees centigrade.

3.0 Reagents

1. Water\ice bath at 0 degrees centigrade
2. Boiling water at 100 degrees centigrade
3. Water bath at selected temperature between 20 and 80 degrees centigrade

4.0 Detailed Steps Required by Procedure

1. Assign the thermometer to be calibrated an identifying number.
2. Measure and record the temperature of the ice/water bath with the thermometer being calibrated. As a control, measure and record the temperature with a previously calibrated digital electronic thermometer.
3. Measure and record temperature of the boiling water bath with both the thermometer being calibrated and the electronic thermometer.
4. Measure and record temperature of the controlled temperature water bath with both the thermometer being calibrated and the electronic thermometer.

5.0 SUMMARY

This method is intended to simply generate calibration data defining the accuracy of a thermometer over a range of temperatures. It is the responsibility of the user to examine this data and select a thermometer that meets the QA requirements of the work being performed. *The thermometer serial number is to be recorded on forms where temperature is recorded, ex: Refrigerator Temperature Log and preparation sheets. The thermometer should be labeled with cal date and next cal date.*

BENCH SHEET FOR CALIBRATION OF THERMOMETERS

Thermometer Checks							
Thermometer ID	Lab	Ice Bath		Water Bath		Boiling Water Bath	
			Ref. Therm.*		Ref. Therm.*		Ref. Therm.*

Reference Thermometer: _____

Notes: _____

_____

Corrective Action: If the above tested thermometer is not within 50% of the limits for the thermometer's use, the unit is not approved for that service and QA should be notified (for example a thermometer used to measure an oven at 105° $\pm$ 2°C must be accurate within 1°C).

APPENDIX AA
OPERATIONAL AID TO PERFORM ANNUAL INSPECTION, INVENTORY, AND FACE VELOCITY CHECK *OF HOODS*

1.0 Purpose

This operational aid provides a method to inspect, inventory, and perform face velocity checks for laboratory hoods *at 161 Mitchell Road*. Inspections are required semi-annually for industrial hygiene hoods internally vented asbestos hoods and annually for other building fume hoods. Face velocity is defined as the airflow required to achieve capture velocity for the hazardous materials being used in the hood.

2.0 Background

OSHA and EPA have set velocity quidelines for laboratory fume hoods in feet per minute (fpm).

The range for hoods that handle normal chemical and environmental samples in 60 – 100 fpm plus or minus 10%.

The range for hoods handling toxic and radiological materials is 100 – 120 fpm plus or minus 10%.

Special – Re-circulating and/or ductless laboratory hoods. These hoods do not have to meet airflow requirements for the above hood classifications. MCLinc's asbestos hoods are examples. These special use hoods simply have to maintain a positive air flow. In fact, high air flow is not desirable since it may disturb the fibers being counted.

3.0 Equipment

- Dwyer Thermal Anemometer
- MCL Inspection Tags
- Sash Position Tags

4.0 Detailed Steps Required by Procedure

a. Inspect all hoods every 12 months and IH hoods every 6 months.

b. Before inspection, calibrate Dwyer Thermal Anemometer by manufacturer's recommended procedure, contained inside the instrument case.

c. For the hood to be inspected, turn switch to "ON" position. Allow 2 to 3 minutes to achieve stable flow.

d. Position hood sash in the normal operating position as indicated by existing hood sash position tags.

e. Remove anemometer probe tip cover and hold the probe in the hood air stream being measured. The flow holes through the probe tip must be parallel to the air flow coming into the hood being inspected.

f. Move the probe tip to several different locations within the working zone of the hood, always keeping the flow holes parallel to the air flow. After a stable flow measurement is achieved, consider this the face velocity of the hood and record.

g. Fill out the "MCLinc Hood Inspection Tag" completely. The information required is:

    a. Hood identification number
    b. Required face velocity for classification
    c. Measured face velocity
    d. Date of next required inspection
    e. Comments to include classification
    f. Inspector's signature.

h. Place hood sash position tags on both sides of hood frame at sash position and height that flow velocity was measured. Initial and date. If the existing sash position tags are at the positions that the flow measurements were performed, simply initial and date the existing tags.

i. For any hood that is inoperable or determined to be unsatisfactory, mark as rejected for use.

j. Enter this inspection and test data into an appropriate database and generate a report that details the findings. Report should be posted, given to QA, and put in Building Inspection notebook. The information included in this report should enable potential hood users to choose a hood for their work that meets hood safety requirements for the planned work and thereby control health hazards while performing the work.

5.0 References

OSHA Laboratory Standard 29CFR 1910.1450, Section C.

EPA Performance Requirements for Laboratory Fume Hoods.

APPENDIX BB
OPERATOR AID FOR CHECKING AND CLEANING SAMPLE RECEIPT CONTAINERS INCLUDING COOLERS

a. Purpose

a. The purpose of this operator aid is to define the MCLinc procedure for identifying and cleaning a radiochemical contaminated sample shipping container received by MCLinc. The procedure also defines actions to be taken if any contaminants are suspected (i.e. sample spilled in cooler).

Note: Our operational procedure on hand delivered samples in secondary containers is to empty the container and return the container where possible to the submitter.

b. This procedure covers, therefore, containers not immediately returned to clients.

b. Procedure

a. All sample containers (including coolers) received by the laboratory via common carrier shall be opened in a hood, inspected, and checked inside and outside with a pancake rad survey meter (i.e. Ludlum Meter) in search of any potential contamination.

b. If a reading above the range of normal background is noted on the meter the empty cooler must be sprayed with a cleaning solution and wiped and dried with paper towels and spent towels placed in a rad waste container. (Wear normal rad lab PPE for this process) The cooler should be then rechecked for rad contamination. If it fails again, then contact the Project Manager to notify the client and arrange for pickup or return to client.

c. Any coolers to be returned to Bechtel Jacobs, LLC or it's subcontract laboratories must be returned per the attached MCLinc Cooler Survey Form using the Tennelec to determine transferable (wipe sample) and a mR/hr. meter for fixed contamination. A copy of the completed form must go with the cooler(s). If above criteria is not met, clean as described in Section 2.2. If still contaminated discuss with appropriate BJC Project Manager (see attached form).

d. If a container has a broken or leaking sample. The sample either liquid or solid shall be containerized for return to the client and the cooler cleaned per Section 2.2 and then checked for contamination. If still contaminated return to client.

e. Any other problems encountered relating to potential contamination of sample receiving containers shall be brought to the attention of the Operations Manager immediately for evaluation of corrective action.

f. Any sample container received that is broken or non-reusable and not contaminated shall be disposed of properly to avoid further use. If contaminated arrange through the PM for pickup or return to the client.

MATERIALS & CHEMISTRY LABORATORY, INC.

"Linking Technology to Solutions"

MCLinc Cooler Survey Form

Responsible: Quality Assurance

Materials & Chemistry Laboratory, Inc. (MCLinc)
161 Mitchell Road
Oak Ridge, TN 37830-7919
Contact: Preston Spires
(865) 276-6910

This object has been released for unrestricted use. It has been surveyed for both transferrable and fixed radiological contamination. All surface areas were less than the release criteria for radioactive material.

Date/Time Surveyed/Inspected:_____/_____

Personnel Name/Title: _____/_____

Personnel Signature: _____

MCLinc Release Criteria*
Transferrable: (e.g. 20 dpm/100cm2 alpha, 200 dpm/100cm2 beta/gamma)
Fixed: <0.5 mr/hr

*49CFR173.421 for Radioactive Material Excepted Package – Limited Quantity of Material, C/N 2915

APPENDIX CC
OPERATOR AID FOR TITRATION OF HYDROGEN PEROXIDE SOLUTIONS WITH SODIUM THIOSULFATE SOLUTION

Scope

This method is designed for the determination of levels of hydrogen peroxide (0.1% to 10.0%) in aqueous solutions.

Principle

Hydrogen peroxide in the titrated sample reacts with excess potassium iodide in the presence of an ammonium molydate catalyst to produce triiodide ions, which are subsequently titrated with a standard thiosulfate solution.

Equipment and Apparatus

1. Volumetric flasks, 1000ml
2. Burettes, 50ml
3. Pipettes, 50, 25, 15, 5, 2, and 1ml
4. Mag-mix stir plate
5. Erlenmeyer flasks, 250ml
6. Balance, top loading, capable of weighing accurately to 0.10g

Reagents

All reagents should be ACS analytical grade and only DI water should be used.

A. Potassium iodide, KI crystals

B. Standard sodium thiosulfate solution, 0.10N: Dissolve 24.83g $Na_2S_2O_3.H_2O$ in 1000ml freshly boiled DI water and standardize with the 0.10N potassium iodate standard solution.

$Na_2S_2O_3.H_2O$ = 248.3g S_2O_3 = 112g

112/248.3 x 24.83g = 11.2g S_2O_3/L or 11.2mg S_2O_3/ml

C. Standard potassium iodate solution, 0.10N: Dissolve 3.567g KIO_3 (dried at 103° C for 1hour in sufficient water to make 1000ml.

D. Ammonium molydate solution, 3.0 wt%: Dissolve 3.0g of ammonium molydate in enough DI water to make 100ml.

E. Sulfuric acid, 4N: Mix 196ml of concentrated sulfuric acid with enough DI water to make 500ml.

F. Starch indicator solution: With constant stirring, add 1g of dry starch to 200ml of boiling DI water. Let settle overnight. Use only clear supernate.

Procedure to Standardize the 0.1N Sodium Thiosulfate Solution

1. Add 1ml of concentrated sulfuric acid to 80ml of DI water in a 250 ml Erlenmeyer flask and stir.

2. Add 10ml of the 0.10N potassium iodate solution.

3. Add 1g KI

4. Titrate with the 0.10N sodium thiosulfate solution until the yellow color of the iodine is discharged (yellow to clear).

5. Add 1ml of the starch indicator solution and titrate until the blue color is gone (blue to clear).

Normality of the $Na_2S_2O_3$ = ml $Na_2S_2O_3$ x normality/ml of KIO_3

Detailed Steps Required by Procedure to Titrate for Hydrogen Peroxide

1. Pipette an aliquot of the hydrogen peroxide sample (1ml for 10% hydrogen peroxide – 50ml for 0.10% hydrogen peroxide)

2. Add enough DI water to make approximately 100ml of sample in the 250ml Erlenmeyer flask.

3. Add 10ml of the 4N sulfuric acid solution.

4. Add 1g of potassium iodide Swirl to dissolve.

5. Add 3 drops of the 3% ammonium molydate solution. Swirl to mix.

6. Add 1ml of starch indicator solution.

7. Titrate to starch end point (blue to clear) with 0.10N sodium thiosulfate standard solution.

8. Wait 10 minutes and check to see that the blue color has not returned.

Calculation for wt% Hydrogen Peroxide

$$\text{Hydrogen peroxide, wt\%} = \frac{A \times N \times 1.7007}{\text{Sample Volume (ml)}}$$

Where: A = titration volume for sample
N = normality of $Na_2S_2O_3$
1.7007 is conversion factor

Calculation (Concentration: in mg H_2O_2 per ml of sample)

$$\text{Concentration } H_2O_2\text{, mg/ml} = \frac{A \times B}{\text{Sample Volume (ml)}} \times \frac{1.7007}{11.2}$$

Where: A = ml of sodium thiosulfate used
B = concentration of thiosulfate mg/ml
11.2mg S_2O_3/ml in the 0.10N $Na_2S_2O_3.5H_2O$ standard solution
1.7007 is conversion factor

Quality Control

For each batch of samples, run:

A. 1 DI water blank (same volume as samples)

B. 1 duplicate sample.

C. 1 Control sample (a hydrogen peroxide sample of known concentration).

APPENDIX DD
FIRE EXTINGUISHER INSPECTION, MAINTENANCE, AND TESTING OPERATOR AID

Scope: Define a procedure for facility personnel from *within MCLinc* to inspect, perform maintenance, and oversee hydrostatic testing of all in house fire extinguishers.

3.0 INSPECTION

3.2 Frequency. Fire extinguishers shall be inspected when initially placed in service and there after at approximately 30-day intervals. Fire extinguishers shall be inspected, annually and at more frequent intervals when circumstances require.

3.3 Procedure: Periodic inspection of fire extinguishers shall include a check of at least the following items:

1.0 Located in designated place
2.0 No obstruction to access or visibility
3.0 Operating instructions on nameplate legible and facing outward
4.0 Safety seals and tamper indicators not broken or missing
5.0 Fullness determined by weighting or “hefting”
6.0 Examination for obvious physical damage, corrosion, leaking, or clogged nozzle
7.0 Pressure gauge reading or indicator in the operable range or position

3.4 Inspection Record keeping

3.4.1 Personnel making inspections shall keep records of all fire extinguishers inspection, including those found to require corrective actions.

3.4.2 At least monthly, the date the inspection was performed and the initials of the person performing the inspection shall be recorded.

3.4.3 Records for current calendar year shall be kept on a tag or label attached to the fire extinguisher.

3.4.4 Permanent records on an annual inspection shall be maintained on file, or in a electronic method that shows:

3 Serial number and type of extinguisher
4 Location of Extinguisher
5 Inspection date
6 Description of maintenance work or hydrostatic tests carried out.
7 Date of next inspection

8 Date of scheduled annual servicing
9 Inspector's comments
10 Inspector's signature

2.0 MAINTENANCE

2.1 Frequency. Fire extinguishers shall be subjected to maintenance at intervals of not more than 1 year, at the time of hydrostatic test, or when specifically indicated by an inspection notification.

2.2 Procedures. Maintenance procedures shall include a thorough examination of the three basis elements of a fire extinguisher:

a. Mechanical parts
b. Extinguisher agent
c. Expelling means

2.3 Seals or Tamper Indicators. At the time of the maintenance, the tamper seal of rechargeable fire extinguishers shall be removed by operating the pull pin or locking device. After the applicable maintenance procedure is completed, a new tamper seal shall be installed.

2.4 Maintenance Recording. Each fire extinguisher shall have a tag or label securely attached that indicates the month and year the maintenance was performed and that identifies the person performing the service.

3.0 TESTING

3.1 Six Year Maintenance. Every 6 years, stored-pressure fire extinguisher requires a hydrostatic test. They shall be emptied and subjected to the applicable maintenance procedures.

3.2 Hydrostatic testing shall be performed by persons trained in pressure testing procedures and safeguards who have suitable testing equipment, facilities, and a appropriate servicing manual(s) available.

4.0 CORRECTIVE ACTION

Any Fire extinguisher not meeting the criteria defined in the sections above shall be immediately removed for maintenance or replacement.

APPENDIX EE
ANALYSIS OF LEAD INGOTS FOR LEAD CONTENT USING XRF

Instrument for procedure no longer available.

APPENDIX FF
IGNITABILITY BY PENSKY-MARTIN CLOSED CUP

1.0 PURPOSE AND SCOPE

The purpose of this procedure is to accomplish one of three objectives, these being:

2.0 Characterize a sample as possibly being a defined compound/analyte by determining if the ignitability occurs within the same temperature range as is documented for the compound/analyte.

3.0 If an unknown is defined a RCRA flammable in having a flash point of <140^{o}F or 60^{o}C or inflammable in having a flash point of >140^{o}F or 60^{o}C.

4.0 Define an approximate flash point/ignitability temperature.

1. INSTRUMENT SET UP (Pensky-Martens Closed Cup Apparatus)

1. Set the flashpoint tester up in an operational fume hood with the sash adjusted to where the air movement will not extinguish the flash test . Note: because of the low volume of sample and being in a sealed container, the operator may opt to turn the hood blower off just prior to testing (i.e. rotating the test knob) to assure a good quality test flame being used.

2. Check to be sure all connections are secure and tight and that there is ample gas in the supply bottle.

3. Insert the thermocouple probe through the septa and adjust to where the tip will be just below the sample surface (i.e. Reference the engraved sample volume line on the side of the sample cup) but not far enough to be hitting or interfering with the rotation of the propellers.

4. Remove the cup closure/sealer by rotating it (counter clockwise) until the lockdown hook is clear of the fixed hold down screws (Note: The hold-down screws are pre-adjusted to give a consistent tight fit. Do not change).

4.0 PROCEDURE

1.1 Remove the sample cup, inspect for cleanliness. Fill with the thoroughly mixed sample to the etched line on the inside of the cup.

1.2 Replace the cup and attach the closure rotating it clockwise until it is locked in place.

1.3 Ignite both the test flame nozzle and its support nozzle. Adjust the flame on both using a combination of the two gas valves to give a flame of about ¼ inch on both nozzles and move the support nozzle into position over the ignition nozzle. (Note: The test flame must be sufficient to remain ignited as it moves into position inside the test cup).

1.4 Connect the drive motor to the propeller shaft and allow to stir for at least 30 seconds (90-120rpm in downward direction).

1.5 Turn off the drive motor (fume hood if necessary) and turn the testing knob on top of the closure clockwise until it stops; thus opening the test shutter and allowing the test flame to be introduced into the sample cup. (Note: The flame should be strong enough to stay lit during the movement).

1.6 Observe the flame behavior if it is sucked down into the sample cup and a flash flame is prorogated across the surface of the sample within the cup or flames flash out of the test port you have achieved the flash point.

1.7 Look at and record the sample temperature as given by the thermocouple read out; using attached bench sheet.

1.8 If there is not a flash at ambient temperature, turn the drive motor back on and adjust the temperature control knob to the 50-70 range and watch for the temperature of the sample to increase. The moment there is any indication that the sample is starting to warm, turn the temperature control back to 10-20.

1.9 When there has been a 2-3^{o}F turn off the motor and turn the testing knob introducing the flame and look for a flash as described in Section 3.6.

1.10 If there is no flash, turn the drive motor back on and monitor the rate of sample temperature increases and adjust the heater control as needed to where the sample temp is increasing at a rate of about 2-3^{o}F every min.

1.11 Test for flash about every 2-3^{o}F by turning the drive motor off and turning the testing knob.

1.12 Continue testing until

- Flask point occurs and recording the appropriate temperature
- The sample begins to boil with no flash and the resulting off-gassing extinguishes flame
- The temperature with no flash exceeds 65^{o}C (150^{o}F)
- The temperature with no flash is 2X the expected value

- QUALITY CONTROL

a. Before testing an actual sample, it is best to demonstrate and document the system operation by testing a material with a known flash point. Materials that may be used may include but not limited to are: Kerosene (100 -120º F), Xylenes (85$_o$F 29^{o}C), (1.2.4-Trimethylbenzene 118^{o}F 48^{o}C) or other known liquid.

b. Between samples, allow the unit to cool to at least 32^{o}C/ 90^{o}F or half the known flash point of the sample.

c. All samples are run in duplicate with closer attention paid to the second for more precise defining of the flash temperature.

d. Record all data on attached bench sheet.

5.0 METHOD REFERENCE

SW846 – Method 1010 “Pensky-Martens Closed Cup Method for Determining Ignitability”.

BENCH LOG FOR IGNITABILITY DETERMINATION

Date: _____ Project #: _____

Analyst _____

IGNITION SOURCE APPLICATION TEMPERATURE

MCL ID	Final Temp (°F)		Flash (Y/N)		Sample Discription
	Run 1	Run 2	Run 1	Run 2	

Results
:

MCL ID	Reported Temp (°C/°F)	Flamable/Combustiable (Y/N)

_____ _____
Analyst Date

QC Required: Duplicate and standard material of known flashpoint.

QC Test Material _____

Expected Flash Temp. (°F) _____ Measured Flash Temp. _(°F) _____

APPENDIX GG
ACCEPTABLE MANUAL INTEGRATION PRACTICES

3.1. SCOPE AND APPLICATION

This operator aid outlines the procedures required in performing and documenting proper manual peak integration. Manual peak integration is a necessary analytical process when the data system for the analysis does not perform a proper integration of the peak of concern. This procedure applies to any analytical procedure involving quantitation based on peak analysis (e.g. GC, HPLC, IC).

3.2. RESPONSIBLE PERSONS

a. The **analysts** have the responsibility to execute this properly and to seek help as needed to perform proper manual integrations and report any improper manual integrations or calculations to management or QA.

b. The **Quality Assurance Manager** has the responsibility to train analysts on this operator aid and spot check the implementation of this procedure.

c. **Management at all levels** must investigate any improper manual integration reported to them or discovered during the data review process. The results of investigation must be documented.

3.3. DEFINITIONS

Integration is the determination of the area under a curve or peak used to quantitate a result.

Manual Integration includes any adjustments to measurements of the analytical peak initiated by the analysts that was not applied to all samples and QC samples in a batch. These include baseline changes, retention time window adjustments, manual peak height measurements, change in integration slope, or changes to the formula used to model analytical peak areas. Manual integrations, however, are sometimes necessary to accurately analyze samples of peaks that are poorly resolved, exhibit tailing, overlapping, or where the baseline drifts, is noisy, or similar situations.

3.4. SUMMARY OF THE PROCEDURE

a. Analysts and data reviewers must be trained on this operator aid by the QA Manager and understand acceptable peak integration techniques in the analytical area in which they work. This is to ensure that integration parameters are used in a manner that minimizes the need for manual integration and that circumstances requiring manual integrations are performed in accordance with acceptable practices.

b. In some situations manual integrations are necessary to produce good data, but manual integrations must only be performed ONLY when deemed technically necessary by the analyst after review of the data.

c. Upon completion of the sample analytical run the analyst in reviewing the data would then ascertain if the need for manual integration is necessary to assure the quality of the data. The analyst then determines what samples are to be so processed and what changes in the integration process must be changed. Any questions or doubts must be brought to the supervisor's or QA Manager's attention for clarification of the procedure.

d. Manual integrations shall not be performed to manipulate the analytical results (commonly known as peak shaving or peak clipping) in order that the data meet method or project specific quality control (QC) criteria. Willful failure to follow this procedure shall result in disciplinary action up to and including termination.

e. If the software indicates whether manual integration has occurred, no attempt shall be made by anyone to obscure or turn off this function.

f. The same manual integration procedures must be applied consistently in all analyses. Manual integrations of any QC sample that moves the results from unacceptable to acceptable must be documented by including in the raw data an example of the peak before and after integration with accompanying data and integration points, and signed and dated by the analyst. In this case the peak must clearly require manual integration. The second level reviewer must evaluate the integration for applicability. Any questions on this review shall be brought to the QA Manager for final approval.

g. If integration indicates problems with the instrumentation, investigate the problem and take action to correct.

h. Any concerns about violation of this SOP must be brought to the attention of the Technical Manager, QA Manager, or Laboratory Manager

3.5. DOCUMENTATION

The analyst is required to make sure the data reflects the changes made in the record of the manual integration. Documentation of any QC sample that goes from unacceptable (outside criteria limits) to acceptable in the manual integration process must be documented with a copy of the peak before and after manual integration and signed and dated by the analyst. This data must go with the data for second level review and retained with the raw data.

APPENDIX HH
OPERATOR AID FOR SAMPLING SURFACES USING A BULK COLLECTION TECHNIQUE

Scope

The purpose of this operator aid is to describe a procedure of sampling a surface using a bulk collection technique that removes the materials of interest from a defined surface area to allow further analysis.

Equipment Required

At a minimum, a Bulk Sampling Kit consisting of the following in a plastic bag is required:

4.1. Pre-cut 2"X 2" cotton sampling wipe or gauze pad.
4.2. Pre-cleaned Sample Scraper (metal spatula, wood or plastic)
4.3. Clean glass jar with lid, pre-labeled
4.4. Disposable gloves
4.5. Kim-wipes
4.6. Disposable 100cm^2 template form

Procedure

a. At the selected sampling location to sample, open sampling kit and don the gloves.
b. Hold template in place and collect sample by scraping, scooping, and wiping up any noticeable solids within the template area.- 100cm^2
c. Place all of the collected material and the gauze wipe into the glass sample bottle and seal.
d. Identify sample on the bottle label.
e. Clean the outside of the bottle with the Kim-Wipe.
f. Place used gloves and Kim-wipes in plastic bag for proper disposal.

Documentation

a. Document any required field information along with location and time of sampling in a field notebook or sampling sheet.
b. Complete chain of custody for all samples collected and sign.
c. Send or take samples to the laboratory in a cooler, properly packaged with the COC.

APPENDIX II
OPERATOR AID FOR SAMPLING SURFACES USING A WIPE PROCEDURE

Scope

The purpose of this operator aid is to describe a procedure of sampling a surface using a wipe technique to allow further analysis.

Equipment Required

At a minimum, a Wipe Sampling Kit consisting of the following in a plastic bag is required:

4.7. Pre-cut 2"X 2" cotton sampling wipe or gauze pad.
4.8. Clean glass jar with lid, pre-labeled
4.9. Disposable gloves
4.10. Kim-wipes
4.11. Disposable 100cm^2 template form

Procedure

i. At the selected sampling location, to sample, open sampling kit and don the gloves.
ii. Hold template in place and collect sample by wiping with the gauze wipe in two directions over the area within the template.- 100cm^2
iii. After sample is collected, place the sample wipe in the glass bottle and seal.
iv. Identify sample on the bottle label.
v. Clean the outside of the bottle with the Kim-Wipe.
vi. Place used gloves and Kim-wipes in plastic bag for proper disposal.

Documentation

1. Document any required field information along with location and time of sampling in a field notebook or sampling sheet.
2. Complete chain of custody for all samples collected and sign.
3. Send or take samples to the laboratory in a cooler, properly packaged with the COC.

APPENDIX JJ
OPERATIONAL AID FOR WRIGHT INDUSTRIES PROJECT

A. Procedure to Evaluate the Settling Rate of Mixed Isopar L / Aqueous Solutions

A.1 Scope

The scope of this procedure is to provide a simple test to evaluate the separation of Isopar L from salt or nitric acid aqueous solutions with time.

A.2 Equipment

A.2.1 250mL Sample Bottle, clean with Teflon lined Cap
A.2.2 100mL graduated cylinder with 1mL graduations.

A.3 Procedure

A.3.1 Collect a sample of interest (~ 250mL) using a 250mL sample bottle from the contactor sampling port. Quickly add to the graduated cylinder to 100ml and record time and sample appearance.
A.3.2 Record point in time when two layers start to form and then record volume of the top layer(IsoparL) at 1, 3, 5, 10, 20, 40, 60, and 120 minutes after that point. Use attached Worksheet #1 to record data and calculate percent Isopar.

B. Estimation of Maximum Volume of IsoparL Separated by Centrifuging

B.1 Scope

The scope of this procedure is to provide a quick estimate of the total amount of IsoparL that is separable from the aqueous solution from the contactor samples.

B.2 Equipment

B.2.1 Laboratory Bench Centrifuge capable of Operating at 2-3,000 rpm Damon IEC Model HN-S
B.2.2 50mL graduated plastic centrifuge tube

B.3 Procedure

B.3.1 Immediately after transferring the sample in to graduated cylinder in Step 1 above, add 50mL to a graduated centrifuge tube. Continue with Step 2 above until time is available.
B.3.2 Then place centrifuge tube with sample into centrifuge tube holder in centrifuge with counter-balanced blank tube with just water.
B.3.3 Centrifuge at ~3,000 rpm for 5 minutes.
B.3.4 Record volume of Isopar L – top layer on Worksheet #1 and calculate percent Isopar.
B.3.5 This percentage of Isopar L should represent the maximum amount that would settle out in the graduated cylinder and thus can be used to judge the progress of that procedure.

C. Estimation of Maximum Volume of Water Entrained in IsoparL by Centrifuging

C.1 Scope

The purpose of this procedure is to provide a quick estimate of the total amount of water entrained in the Isopar L.

C.2 Equipment

C.2.1 Same centrifuge as above
C.2.2 15mL graduated plastic centrifuge tube
C.2.3 4oz glass bottle(~120mL) with Teflon lined cap

C.3 Procedure

C.3.1 Collect a sample of the Isopar L to be tested in a ~120mL bottle.
C.3.2 Pour into a 15mL centrifuge tube and make to 15mL mark.
C.3.3 Centrifuge at ~3,000 rpm for 5 minutes.
C.3.4 Record if any water noted as bottom layer and an estimate of volume on Worksheet #1 and calculate percent water.

Worksheet # 1

Date_____ Sample#_____ Analyst_____

A. Record of the Settling Rate of Mixed IsoparL/ Aqueous Solution

Total Volume of Sample:_____mL

Observation Interval Min.	Isopar Top Layer Volume mL	Percent IsoparL*	Observation Interval Min.	Isopar Top Layer Volume mL	Percent IsoparL*
1			40		
3			60		
5			120		
10					
20					

***IsoparL volume/ Total Sample Volume X 100 = % Isopar L**

B. Estimation of Maximum Volume of Isopar Separated by Centrifuging

Total Volume of Sample: _____ mL

Volume of Isopar L Top Layer after Centrifuging: _____mL

Percent Isopar L* _____%

C. Estimation of Maximum Volume of Water Entrained in IsoparL by Centrifuging

Total Volume of Sample: _____mL

Volume of Water Lower Layer after Centrifuging: _____mL

Percent Water _____%**
**** Total Volume of Water Layer/ Total Sample Volume X 100 = % water**

APPENDIX KK

Sample Preparation Outline for PCB's in Wipe Samples

1.0 Purpose

Prepare Wipe Samples for PCB Analysis by GC-EC by hexane extraction and extract clean-up as required.

2.0 Preparation

1. The wipe sample(s) are typically left in and prepared as received in wide mouth glass jar(s) (typically125mL) with Teflon-lined lid.
2. Initially determine the amount of hexane necessary to:
   a) fill the jar to the point where at a minimum 50% of the contained gauze are covered with hexane
   b) the volume is not excessive resulting in extended contact with the jar lid resulting in leakage during shaking
   c) The volume doesn't make it prohibitive to report non-detects at concentrations less than the action limit without a concentration step

   Note: typical volumes for 125ml jar containing 1-4 gauze would be 50-75ml
   Record all information required on the attached PCB wipe worksheet.
3. Using good laboratory technique (i.e. graduated cylinder, volumetric flask or calibrated re-pipettor) transfer the same volume of hexane to all samples including batch QA/QC
4. Spike each sample with TCMX/DCBP surrogate to give a concentration of 0.05-0.08µg/mL of each based on the amount of hexane added to the jar. (typically 0.07ug/ml TCMX)
5. Securely cap each jar and shake to wet, to point of saturation, all the gauze in the jars
6. Position all samples/QC samples on table shaker and secure in place and shake for a minimum of 30min (typically 1 hour).
7. Using a clean un-used glass transfer pipet, transfer about 5-7mL hexane extract from each sample to a clean labeled 10mL vial.
8. If the hexane is not clear, set sample aside for acid cleanup (instructions at end). Otherwise; add enough Florisil to the hexane extract to be equivalent to ¼ - ⅓ of the hexane volume. Shake and allow to stand 10-20 minutes.
9. For each batch of 20 or fewer samples prepare one Method Blank (MB) and one laboratory Control Sample (LCS). The MB and LCS are prepared with the same volumes of hexanes and surrogates as the samples. The LCS is prepared by spiking with a known amount of a PCB standard to typically give a concentration of 0.5-1.5µg/mL. If acid cleanup is used for samples, use same cleanup procedure for all QA/QC.
10. Record all information on prep sheet (see attached)

3.0 Acid Cleanup (if needed – see Step 8 above)

1. Using a glass transfer pipet, add about 3mL (1/4th inch) of concentrated sulfuric acid to the vial containing the colored hexane layer.
2. Cap the vial and shake vigorously by hand assuring full contact/mixing of the acid and hexane (typically 10 seconds or so).
3. Allow hexane and acid to separate.
4. The exposed sulfuric acid is removed using a clean glass transfer pipette and steps 1&2 are repeated until the hexane is clear or there is no alteration in the color of the sulfuric acid
5. Once it is determined that the addition of sulfuric acid will not remove any more material (i.e. clear hexane or acid) and all the acid has been removed neutralize the hexane by adding deionized water to the hexane ≈3ml. Cap the vial and shake vigorously by hand till there is complete contact of the hexane and water typically ≈10 seconds. Allow the hexane and water to separate. Pipet out the water with a clean glass transfer pipet, removing as much water as possible. If a clear hexane layer can't be accomplished, contact your supervisor who will determine if further cleanup is needed.
6. Dry the solvent by adding about ¼ inch of cleaned, dried sodium sulfate to the vial. Shake the vial about 10 seconds by hand allowing ample contact of the sodium sulfate and hexane.
7. Add a little activated Florisil to all samples and QA/QC samples and shake. Allow the samples to stand 10-20 minutes.
8. The samples are ready to be analyzed by GC-EC per MCLinc SOP MCL-7740, Determination of PCBs.

PCB WIPE SAMPLE
Work Up Sheet

Date: _____ Prepared By:_____

MCL Sample No.	Extrac. Vol. (ml)	MCL Sample No.	Extrac. Vol. (ml)

Shaker Time

Date _____ Time On _____ Time Off _____

QA/QC

Hexane Lot # _____ Ml's Added _____

Surrogate Source _____ Surr. Conc (ug/ml) _____

Surr Spike Vol.. _____ Calculated Surr Conc. (ug/ml) _____

LCS Source _____ Spike Conc. _____

LCS Spike Vol. (ml) _____ Calculated LCS Conc. (ug/ml) _____

Dup. Sample Number _____ Orig Conc. (ug/ml) _____ Dup. Conc. (ug/ml) _____

RPD _____

APPENDIX LL
OPERATOR AID FOR PREPARATION OF SOILS AND SOLID SAMPLES FOR VOLATILES BY METHANOL EXTRACTION

1.0 Purpose

This procedure is based on USEPA SW-846 Method 5035A July 2002 Revision 1 for extraction of soils and solids for subsequent volatiles analysis.

2.0 Procedure

1.0 Tare a 12mL glass vial with PTFE lined cap.

2.0 Weigh into the vial 5g of sample +/- 0.01g. Record weight.

3.0 Immediately add 5mL of volatiles free Purge and Trap grade methanol to the vial.

4.0 Recap and shake by hand several times to assure contact but avoiding emulsions.

5.0 Allow phases to separate for at least 30 minutes.

6.0 If methanol doesn't separate out add another 5mL methanol and extract again.

7.0 Once methanol is separated decant off into a small sample vial provided.

8.0 Mark with indelible pen the level of solvent in the vial.

9.0 With each batch of 20 field samples or less, the QC samples required are blank.

2.10 Refrigerate prior to shipment or analysis.

2.11 All of the information shall be recorded on the attached Bench sheet.

BENCH SHEET FOR PREPARATION OF SOILS AND SOLID SAMPLES FOR VOLATILES BY METHANOL EXTRACTION

Batch # _____ Date _____ Analyst _____

BALANCE CALIBRATION

Balance	Date	Mass, g	Weight, g	Weight, g

	Sample ID #	MCLinc ID #	Sample wt, g	Methanol, ml	Mark level (Y/N)
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

QA/QC Required: Blank
Prepared By: _____

APPENDIX MM
OPERATOR AID FOR DETERMINATION OF WATER CONTENT BY MASS

1.0 Scope

This test method covers the determination of moisture content of soil, rock, and similar materials where reduction in mass by drying is due to loss of water.

2.0 Summary of Method

A test sample is dried in an oven at 110 ±2 degrees C to a constant mass. The loss of mass is considered to be water.

3.0 Equipment and Apparatus

a. Drying oven, capable of controlling temperature at 110 ± 2 degrees C.

b. Analytical balance, capable of weighing to the nearest 0.1g.

c. Specimen containers to hold samples of 25 and 200 g.

d. Dessicator

e. Hot sample handling equipment: gloves, tongs, or holder, etc.

4.0 Detailed Steps by Procedure

a. Weigh and record weight of clean specimen container (use attached bench log for recording information).

b. For soil samples, weigh 25 ± 0.1g of sample into a tared container. Weigh and record weight of sample plus container.

For rock or aggregate material, weigh 200 ± 0.5g of sample into a tared container. Weigh and record weight of sample plus container.

c. Place container with sample in oven at 110 ± 2 degrees C. Drying time may vary according to type of sample material, but drying overnight (12 to 16 hrs) is adequate.

d. After drying overnight, remove from oven and cool to room temperature in a dessicator.

e. Weigh and record the weight of the dry sample plus container.

f. Calculate weight % water of the sample as follows:

$$\% W = \frac{(Mcws - Mcs) \times 100}{Mcws - Mc}$$

Where

Mc = weight of empty sample container
Mcws = weight of container and wet sample, g
Mcs = weight of container and oven dry sample, g

5.0 Reporting of Results

These results are reported to the nearest 0.1 % as water content (wt % water) of the wet as received sample.

NOTE: FOR GEOTECHNICAL SAMPLES, RESULTS ARE REPORTED BASED ON DRY SAMPLE MASS.

6.0 Method Reference

ASTM-D2216-90 “Standard Test Method for Laboratory Determination of Water Content (% Moisture) of Soil and Rock by Mass.

BENCH LOG FOR DETERMINATION OF WATER CONTENT BY MASS

Method Reference: ASTM-D2216-90, "Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass"

Date:_____

Project#:_____

Customer Sample #:_____ MCLinc Sample #:_____

Sample Description:_____

BALANCE CALIBRATION

Balance	Date	Mass (g)	Weight (g)	Weight (g)

WEIGHTS REQUIRED FOR ANALYSIS

Mc – Mass of Empty Sample Container, g:_____

Mcws – Mass of Container and Wet Sample, g:_____

Mcs – Mass of Container and Oven Dry Sample, g:_____

Temperature:_____ Start Drying: _____ Stop Drying: _____

CALCULATION OF WATER CONTENT

$$\text{CALCUATION OF WATER CONTENT (W)} = \frac{\text{Mcws - Mcs}}{\text{Mcs - Mc}} \times 100$$

$$\text{WATER CONTENT (W)} = \frac{(\_\_\_\_\_) - (\_\_\_\_\_)}{(\_\_\_\_\_) - (\_\_\_\_\_)} \times 100$$

_____ _____
Analyst Date

QC Required: Duplicate Per Batch

BENCH SHEET FOR DETERMINATION OF WATER CONTENT BY MASS

Method Reference: ASTM-D2216-90, "Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass"

Batch #:_____ Project Number:_____

Sample Matrix:_____

	Sample Number	MCL ID#	Mc (g)	Mcws (g)	Mcs (g)	Water Content wt%
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						

BALANCE CALIBRATION

Balance	Date	Mass (g)	Weight (g)	Weight (g)

Analyst_____ Date_____

QC Required: One Duplicate per Batch

APPENDIX NN
OPERATOR AID FOR RADIOCHEMISTRY EXTRACTION USING NITRIC ACID

5.0. SAMPLE RECEIPT AND REQUESTED ANALYSIS

5.1. Preparation to remove and/or dissolve sample material for subsequent analysis for radioactive contamination by leaching with nitric acid. The leachate will be sent to a customer designated laboratory for radiochemicals analysis.

6.0. DETAILED STEPS REQUIRED BY PROCEDURE

1. Weigh 50±0.5g of sample into a tared 400ml beaker. Record weights on Bench Sheet.

2. Add 200ml of 6N HNO3 or other concentration (as defined in project SOW).

3. Place beaker on platform shaker and shake gently for 4hrs.

4. Decant liquid into a labeled 250ml bottle (pre-marked and verified at the 250ml level).

5. Wash sample with DI water and collect washings in the 250ml bottle. Fill to mark (this is sample for analysis).

6. Complete bench sheets and submit with prep sample for analysis.

NOTE: Dispose of sample residue properly.

7.0. REQUIRED QA/QC

7. Duplicate: Randomly select and run one duplicate sample per batch, *if sufficient sample*.

8. Blank: For each batch process one blank (200ml of nitric acid leach solution).

8.0. ATTACHED PREPARATION WORKSHEETS

9. Attached Nitric Acid Preparation Worksheet

10. Attached Sodium Hydroxide Preparation Worksheet (For extraction of alumina material if defined in project SOW).

BENCH SHEET FOR NITRIC ACID *RADIOCHEMICAL EXTRACTION* PROCEDURE

Batch # _____ Project Number: _____

HNO_3 Normality _____ Start Leaching: _____ Stop Leaching: _____

	Client Sample Number	MCLinc Sample	HNO_3 Added (mL)	Sample Weight (g)	Dry Weight (g)	Weight Loss (g)	Final Volume (mL)
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							

BALANCE CALIBRATION

Balance ID	Date	Mass (g)	Weight (g)	Weight (g)

Analyst:: _____ Date: _____

BENCH SHEET FOR SODIUM HYDROXIDE RADIOCHEMICAL *EXTRACTION* PROCEDURE FOR ALUMINA TRAPPING MATERIAL

Batch # _____ Project Number: _____

NaOH Normality _____ Start Leaching: _____ Stop Leaching: _____

	Client Sample Number	MCLinc Sample	NaOH Added (mL)	Sample Weight (g)	Final Volume (mL)
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					

BALANCE CALIBRATION

Balance ID	Date	Mass (g)	Weight (g)	Weight (g)

Analyst:: _____ Date: _____

APPENDIX OO
OPERATOR AID FOR THE SAFE STORAGE, HANDLING AND USE OF COMPRESSED GAS CYLINDERS

This operator aid documents the MCLinc requirements of the safe storage, handling and use of compressed gas cylinders. The requirements include:

1. Compressed gas cylinders shall be kept away from excessive heat, chained up to avoid being knocked over, and stored away from highly combustible materials.

2. Oxidizers (oxygen, fluorine) must be separated from flammable gases.

3. Empty cylinders must be labeled.

4. Store and transport cylinders with valve caps.

5. In moving cylinders, use a cylinder cart with chain in place.

6. When placed in position for use, make sure cylinder is restrained.

7. Inspect cylinder prior to use to make sure there is no damage to valve or threads. DO NOT force a stuck valve.

8. Use proper regulator for each cylinder. DO NOT modify regulator to fit another type of cylinder.

9. Notify R. Jarabek of any problem cylinders so the vendor can be notified.

Reference:
"Compressed Gas Safety", General Safety Guidelines, Montana Department of Labor and Industry, Helena, Montana 59624-1728.

APPENDIX PP
EYEWASH AND SAFETY SHOWER INSPECTION AND TESTING

Scope: This operator aid is a guide for periodic inspection and testing of eyewash stations (fountains) and safety showers.

1.0 Inspection

1.1 Frequency: Both eyewash stations and safety showers are to be inspected monthly. ANSI recommends monthly inspection frequency for eyewash stations. MCLinc also elects to perform monthly inspections on safety showers.

1.2 Procedure for Eyewash Station Testing:

1. Ensure access to eyewash stations are unobstructed.
2. Verify protective eyewash covers are properly positioned, clean, and intact.
3. Check that the bowl is clean and free of trash.
4. Place a dishpan or bucket under the drain to collect the water.
5. Check that the flow is effective and continuous by pressing the hand paddle.
   – Verify the eyewash covers come off when activated.
   – Check that water flows from both eye pieces.
   – Evaluate adequate flow. The streams should cross.
   – Verify water continues to flow for 90 seconds.
   – Check that the water drains from the bowl.
6. Document the inspection date and initial on the form attached on the eyewash bath and the inspection log.
7. Improperly functioning eyewash station will be tagged “Out-of-Service” and the facility operator will be notified for corrective action as well as all employees working in the immediate area.

1.3 Procedure for Safety Shower Testing:

- Ensure access to safety showers are unobstructed.
- Place a portable 55 gallon drum with shower curtain shroud under the safety shower head.
- Activate the safety shower for 30 seconds. Observe that the shower head is not partially stopped and delivers a deluge of water.
- Observe that the safety shower ceases water deluge after pushing up the activation rod.
- Record the date and inspector’s initials on the inspection tag attached to the safety shower and also record the inspection in the safety shower inspection log.
- Improperly functioning safety showers will be tagged “Out-of-Service” and the facility’s operator will be notified for corrective action as well as all employees working in the immediate area.

Reference:
29CFR1910.151 (c), American National Standards Institute (ANSI) Emergency Eyewash Standard.

APPENDIX QQ
PERFORMING INVENTORY ON NUCLEAR MATERIAL

1.0 Scope

This Operational Aid defines guidelines to conduct physical inventories, validate measurement methods, establish and implement training and qualification for performing measurements and maintain measurement methods for all nuclear material on inventory at MCLinc.

2.0 Physical Inventory

NOTE

If an error is made in completion of any documentation supplied to NMC&A, the proper method of correction is for the person making the correction to draw a line through the error and write their initials next to the line. Write the correct information next to the error, or preferably, in the next corresponding space.

A physical inventory of accountable nuclear material (up to Category IV-***B***) that is contained in the MCLinc Material MBA shall be conducted at a minimum frequency of every two years. Inventories are reconciled with the book inventories by using Attachment I per the guidelines described in Section 3.0

The acceptance or rejection criteria for the measurement value between book value and observed measurement shall be no greater than ±5% of the book value.
Validation of measurement methods shall be conducted per Section 3.0 "Guidelines for Scale Operation and Weighing of Nuclear Material."

Training and checking of the test weights that are used for weighing Nuclear Material shall be updated as necessary prior to each weighing of nuclear material as described in Attachment II.

3.0 Guidelines for Scale Operation and Weighing of Nuclear Material

NOTE
Weighing conducted as part of the Verification/Confirmation Program must be observed by either the NMC&A Manager or the NMC&A Manager designee.

3.1 Preparation

3.1.1 If necessary, obtain forms for recording the check weight weights and item weights from the NMC&A Manager.

3.1.2. Ensure appropriate scales are present.

A. The item being weighed should be within the range of accuracy of the scale being used. For example, do not weigh material reportable in grams on a scale that indicates only to the nearest pound.

B. The scales should be in good condition. The scales should not exhibit signs of excessive rust or corrosion. There should not be signs of abuse (severe dents, bent frames, bent arms or indicators, etc).

C. If the scales are electronic, confirm that the power to the scales has been on at least 3 hours. (The time limit for scale electronics to "warm up" varies according to type of scales and manufacturer. For most scales used to weigh NM at this site, 3 hours is adequate but the time should be checked and confirmed according to the manufacturer's specifications).

D. The scales should not be located in an area where they could be affected by vibration or any other detrimental environmental factors. Vibrations and air currents affect the scales' ability to provide accurate readings. Extreme temperature variations are detrimental to operation of the scales.

3.1.3. Ensure appropriate check weights are present.

A. The weight of the check weight and ID number of the scales will be recorded on the Nuclear Material Control and Accountability Observation of Weighing of Check Weights (Attachment III).

B. The check weights should be appropriate for the scales to be used and cover the desired weight range. That is, one check weight should be lighter than the object to be weighed and one check weight should be heavier than the object to be weighed. (Example, If a cylinder of UF_6 has a gross weight of ~ 35 kg, a check weight of 20 kg and a check weight of 40 kg would be good choices to use to check the scales prior to weighing the cylinder.)

C. More than one check weight may be used to obtain the required total check weight, i.e. one 20 kg weight plus two 10 kg weights to obtain a total weight of 40 kg.

D. The check weights should be in good condition. The weights should not exhibit signs of severe corrosion. There should be no signs of abuse (scrapes, dents, gouges, etc.).

3.2 Scale Operation

3.2.1. Assure that the scales will "zero" when required.

With no weights on the scales, the scales' indicator should show only zeros (Ex. – 0.000) on the meter or indicate zero if using a pointer. If the scales indicate other than zero, take the appropriate action to accomplish this. (Ex. – Touch reset bar.) If the scales cannot be set to indicate zero, do not continue. Maintenance may be required and appropriate notification should be made to the NMC&A manager.

3.2.2. Exercise the scales.

A. This action is accomplished by placing a check weight on the scale properly, waiting for the indicated value to stabilize, and removing the check weight properly.

B. Repeat the previous action at least one more time for a minimum of two (2) times. This action is taken to ensure the scale mechanism is operating freely.

3.3 Check Weight Linearity Check

3.3.1. Properly place and remove the check weights from the scales.

NOTE
If the scale is equipped with a locking mechanism, lock the weighing mechanism of the scale when placing weights on the scale or during removal of weights.

A. Extremely small weights (0.1 gram, 1 gram, 5 grams, etc.) are placed on the scales using forceps or other tools to allow gentle placement of the weights. Heavier weights may require other tools or equipment and multiple individuals to accomplish this.

B. Place the check weight(s), as nearly as possible, in the center of the weighing platform.

C. Once the check weight is placed on the scale, unlock the weighing mechanism (if so equipped), allow the mechanism to stabilize, and record the indicated weight on the appropriate documentation. A minimum wait of 20 seconds is recommended for the scales to stabilize.

D. If so equipped, lock the scale mechanism and gently remove the check weight from the scale by lifting. **DO NOT** remove the check weight by sliding it off the scale.

3.3.2. At least two check weights must be used to conduct the check (one lighter and one heavier than the anticipated weight of the item to be weighed). Follow the previous steps for each weight check.

3.3.3. Complete the documentation of Attachment III "Nuclear Materials Control and Accountability Observation of Weighing of Check Weights". Copies of Attachment III may be made and used if extra check weights are used.

3.3.4. Ensure the indicated weight readings fall within ± 1 % of the previously recorded weight reading. If a weight does not fall within limits, check it a second time. If the weight still indicates outside the limits notify the NMC&A manager. The scales may require maintenance and/or repair before proceeding.

3.4 Weighing of Item

3.4.1. Using the same techniques (locking mechanism if so equipped, gentle placement, pause for stabilizing, etc.) practiced in conducting the linearity checks, place the item to be weighed on the scales.

3.4.2. Document the indicated weight using Attachment I "Nuclear Materials Control and Accountability Observation of Weighing of Accountable Nuclear Materials". Other forms or documents may also be used for comparison to book values if the item is already recorded on the other forms.

3.4.3. Using the same precautions and techniques for removing check weights, remove the weighed and documented item.

3.4.4. Check and ensure scales indicate zero weight between each item weighed.

3.4.5. Continue operations until all necessary items have been weighed and documented.

3.4.6. Ensure the observed weights of the items lie in the range of the check weights used. If any of the item weights are not between the lowest and highest check weight values, choose an appropriate check weight to extend the range. Weigh the chosen check weight and document as part of the linearity check. This must be accomplished the same day of the weighing.

NOTE
In unusual cases and with the approval of the NMC&A Manager, the scale zero reading may be used as the lowest check weight reading. Any problems in performing the above instructions shall be reported to the NMC&A manager and the QA representative.

3.5 Documentation

3.5.1. It is recommended that copies of the check weight and item weighing documentation be made and retained by the responsible MBA Custodian.

3.5.2. The documentation of the weighed item(s) is provided to the NMC&A manager and other designated individuals as necessary.

3.5.3. The NMC&A Manager is notified by the MBA Custodian or area representative of the weighing actions within three (3) working days or less. Preferably, notification should be made before the weighing action. This action is taken so the manager may ensure the scales, check weights, and weighing actions meet the required criteria.

3.5.4. The operation is complete once the NMC&A manger has verified the weightings and documentation.

ATTACHMENT I
Nuclear Materials Control and Accountability
Observation of Weighing of Accountable Nuclear Materials

Sheet ____ of ____

Date of Observation: _____

Material Balance Area: **FCC**

NMC&A Representative: _____
(Signature & Badge no.)

Item Identification	Observed Measurement Gross Wt. g/kg	Tare Wt. g/kg	Net Wt. g/kg	Book Value g/kg	% Diff. to Book Value

COMMENTS:

ATTACHMENT II

MEASUREMENT CONTROL
OPERATOR WEIGHING CERTIFICATION CHECKLIST

CHECK WEIGHTS

_____ 1. Confirm scales and check weights are within limits.

_____ 2. Confirm satisfactory condition of scales and check weights. (No damage to scales or check weights, etc.)

_____ 3. Confirm scales' power has been on at least 3 hours if scales are electronic.

_____ 4. Check for vibration or any other detrimental environmental factors.

_____ 5. Assure that scales will "zero" when required.

_____ 6. Exercise the scales.

_____ 7. Check for proper placement of check weights on scales. (Tweezers or other tools used if necessary, check weights centered, gentle placement and removal, no dropping, etc.)

_____ 8. Check for operator pause for scales to stabilize.

_____ 9. Check for proper removal of check weights.

_____ 10. Check for proper documentation use and completion pertaining to check weight test.

_____ 11. Operator checks to assure recorded weights are within limits.

TEST WEIGHT

_____ 12. Check proper placement of test weight on scales.

_____ 13. Check for operator pause for scales to stabilize.

_____ 14. Check for proper removal of test weight.

_____ 15. Check for proper documentation completion.

MBA Custodian _____ Date _____

MBA Custodian _____

Comments:

ATTACHMENT III

Nuclear Material Control and Accountability
Observation of Weighing of Check Weights

Sheet _____ of _____

Date of Observation: _____

Material Balance Area: **FCC**

Location: _____

NMC&A Manager or
MBA Custodian: _____
(Signature & Badge No.)

Second MBA Custodian: _____

Identification of Scale: _____

Weight ID Number	Date Weight Checked	Check Weight Value	Current Scale/Balance Value

COMMENTS:

APPENDIX RR
DETERMINATION OF INSOLUBLE Cr(VI) BY VISIBLE ABSORPTION SPECTROPHOTOMETRY TECHNIQUE

Method Reference: NIOSH Method 7600, Issue 2, 15 August 1994

Applicability:

This method may be used for determination of insoluble Cr(VI) for air filter samples, using 2% NaOH and 3% Na_2CO_3 as the extraction fluid. The working range is 0.2 to 5 micrograms total per air filter. The reporting limit for a 200L air volume would be 1.0 ug/m^3

Reagents:

1. Sodium hydroxide, ACS grade
2. Sodium carbonate, anhydrous
3. Potassium chromate, Reagent Standard Grade
4. Diphenylcarbazide solution. Dissolve 500 mg sym-diphenylcarbazide in 100 ml acetone and 100 ml deionized water.
5. Cr(VI) standard, 1000 ug/ml. Dissolve 3.735 g K_2CrO_4 in deionized water to make 1L.
6. Cr(VI) calibration stock solution, 1.0 ug/ml. Dilute the 1000 ug/ml standard solution 1:1000 with deionized water.
7. Filter extraction solution, 2% NaOH – 3% Na_2CO_3. Dissolve 20 g NaOH and 30 g Na_2CO_3 in deionized water to make I L of solution.
8. Sulfuric acid, 6.0N. Add 167 ml conc. H_2SO_4 to deionized water in a 1-L flask. Dilute to mark.
9. Sulfuric acid, 0.5N. Add 14.0 ml conc. H_2SO_4 to deionized water in a 1-L flask. Dilute to mark.

DETAILED STEPS REQUIRED BY PROCEDURE

1. Remove PVC filter disc from air sampler.

2. Place it in a 50-ml glass beaker and add 5.0 ml of the 2% NaOH/3% Na_2CO_3 solution.

3. Cover the beakers with watch glasses and heat to near boiling, with occasional swirling, for 30 to 45 minutes. Do not boil and do not heat longer than 45 minutes.

4. Do not allow the solutions to go to dryness as hexavalent chrome may be lost.

5. Cool to room temperature and quantitatively transfer with deionized water rinses to a 25-ml volumetric flask, keeping total volume to about 20 ml.

6. If the solution is cloudy, vacuum filter through a PVC filter and rinse with deionized water.

7. Add 1.90 ml of 6N sulfuric acid and swirl to mix.[At this point, if the solution has color do not add diphenylcarbazide, instead make to volume and then transfer an aliquot to a 5ml cuvette and absorbance read.] This reference control absorbance would be subtracted from final sample absorbance and final results corrected for the reduced aliquot.

8. Add 0.5 ml of diphenylcarbazide solution and dilute to 25 ml in the volumetric flask. Invert several times to mix thoroughly. Pour out about one-half the contents of the flask, stopper the flask, shake vigorously several times, removing the stopper each time after shaking to relieve pressure.
   NOTE: This step releases bubbles of CO_2 which otherwise could cause high, erratic readings.

9. Transfer an aliquot of the solution to a 5-ml cuvette and analyze for Cr(VI).

CALIBRATION:

a. Calibrate daily with at least six (6) working standards. Transfer 6 to 7 ml of 0.5N H_2SO_4 to each of a series of 25-ml volumetric flasks.

b. Pipet 0, 0.1, 0.25, 0.50, 0.75, 1.0, 1.5, 2.0, 3.0, 4.0, and 5.0 ml of the 1.0 ug/ml calibration stock solution into these 25-ml volumetric flasks. Add 0.5 ml of diphenylcarbazide solution to each and add sufficient 0.5N H_2SO_4 to bring volume to mark on 25-ml flask.
   These working standards contain 0 to 5 ug Cr(VI).

c. Measure absorbance for these working standards, together with blanks and samples, by the Absorption Spectrometry technique explained below.

d. Prepare a calibration graph: absorbance vs. ug Cr(VI).

MEASUREMENT OF Cr(VI) BY VISIBLE ABSORPTION SPECTROMETRY TECHNIQUE

1. Set wavelength at 540 nm by using the wavelength control knob.

2. Set mode to TRANSMITTANCE (press MODE select button until TRANSMITTANCE LED on display is lit).

3. With sample compartment empty and door closed, adjust Zero Control knob so that the meter reads o% T.

4. Insert deionized reference blank into sample compartment and set transmittance at 100% T.

5. Set MODE to ABSORBANCE by pressing MODE select button until the ABSORBANCE LED is lit.

6. With deionized water reference blank in sample compartment adjust absorbance to read 0.0%.

7. Insert sample and read measurement from display in % absorbance.

8. From the calibration curve and the measured % absorbances for the samples, determine the mass of Cr(VI) in each sample.

9. From this mass of insoluble Cr(VI) extracted from the filter, the concentration of Cr(VI) in the air volume sampled may be calculated.

QA/QC REQUIRED

One (1) process blank (5 ml of the 2% NaOH – 3% $CaCO_3$ extraction fluid carried through the process).

One (1) calibration blank: 0.0 ug/ml of the calibration stock solution.

One (1) deionized water calibration blank.

Appendix SS

Operator Aid for Lockout/Tagout Program

1.0 Purpose

The purpose of this procedure is to establish the responsibilities and method for lockout/tagout requirements to protect personnel working within Materials and Chemistry Laboratory.

2.0 Scope

This procedure applies to all Materials and Chemistry Laboratory personnel and, when appropriate, to subcontractors and visitors.

3.0 Responsibilities

Operation Officer
The operation manager represents the first line management responsible for supplying the resources for the intender program. They have the authority to serve in an emergency capacity as an Issuing Authority, Supervisor, or Authorized Employee as necessary.

Responsible Owner/Operator
An employee whose job requires him/her to operate or use equipment on which servicing or maintenance is being preformed under lockout/tagout. They shall not attempt to start, energize, or use equipment that has been locked or tagout out until the authorized employee informs them that all locks and tags have been removed and servicing and maintenance activities have been completed.

The responsible owner/operator must thoroughly know and understand the system/machinery and all isolation points for the service or maintenance activity they are performing

The responsible owner/operator of the equipment must contact the Issuing Authority for any questions having exempt equipment or having a single source lock out or a permitted lockout preformed.

Authorized Employees

The authorized employee is also the alternate Issuing Authority.

Only authorized trained employees may lockout or tag equipment to perform servicing or maintenance activities.
They shall ensure that the responsible owner/operator understands the impact of these activities and are notified when the situation changes.

Issuing Authority An Issuing Authority is an authorized employee who has responsibility for the equipment being worked and controls the lock/tagout permit system.

Exemptions

Cord and plug connected equipment does not fall under the requirements of this procedure if the hazards due to unexpected energization or startup is controlled by the unplugging of the equipment and the plug is under the exclusive control of the employee performing the work.

Minor changes and adjustments and other minor servicing activities that take place during normal operations and can be done safely.

Live parts that operate at less than 50 volts to ground need not be de-energized if there will be no increased exposure to electrical burns or to explosion due to electrical arcs.

Application

Applicability and appropriate procedure for lockout/tagout depend on the nature of the work activities and exposure scenarios

Lockout/Tagout shall be documented unless all of the following conditions exist:

- The equipment can be unplugged and isolated from the energy source and is exempted from lockout/tagout.

- The equipment can be isolated from an energy source by a single lockout.

Single Source Lockout

To perform a single source lockout the following must be preformed. Shutdown and isolate the equipment, verify isolation, assure that no stored energy is present that is accessible, and apply personal lock(s). The work does not extend beyond the work shift. The work does not create hazards for other employees. This applies to instruments directly wired to a single function box. Only a single lock is necessary.

Permitted Lockout/Tagout

Lockout/tagout procedure shall be followed before servicing and maintenance activities are preformed on equipment that could cause injury to personnel from the unexpected energization or start-up of the equipment or unexpected release of stored energy.

The following are a few examples where this procedure should be used: installation of new equipment or modification of existing equipment, when doing major replacement, repair, or renovation.

Lockout/Tagout Sequence

The following sequence is required for a lockout/tagout that requires a permit.

- Notification of responsible owner operator
- Identifying the type and magnitude of all energy sources, the hazards of the energy, and the means of controlling the energy before the equipment is shutdown
- The equipment shall be shut down using the normal procedures.
- All energy isolating devices that control the energy to the equipment shall be physically located and disconnected
- Verification of isolation may be performed before the application of lockout/tagout device where necessary for employee safety or where visual verification is impeded by the lockout device. This shall be accomplished by trying to operate the equipment using normal operating controls
- Apply your personal lockout device and/or tag to each energy source
- Once the lockout device and tags are applied, all potentially hazardous stored or residual energy shall be relieved, disconnected .or restrained.

Lockout/Tagout Devices

Lockout devices and tags shall be the only device used for controlling energy; they shall not be used for other purposes.

Locks shall have a red band around the lock with the following wording LOCKOUT-DEPARTMENT with the DEPT. Name and Number for the purpose of this procedure the Dept. Number will be 0016.

Personal locks shall be identified with the employee’s name and badge number.

The multi-lock or multiple hole lockbox shall be the standard group lockout devices.

Place lockout device, when used, on each energy isolation device in a manner that will hold the energy isolating devices in a safe position. If an isolation device is lockable, it shall be locked.

Each authorized employee performing work on equipment to be locked out shall have a personal lock(s) exclusively for their use. No person shall have a key to another employee's personal lock.

Personal lock(s) shall be applied to the energy isolation device, multi-lock hasp, or lockbox before work begins on the equipment and removed when work is complete on the equipment.

Only the employee who installs the personal lock has authority to remove it.

Place danger tags, except during single source lockout, at each energy isolation device, in a manner that will clearly indicate that the operation or movement of energy isolating device from a safe or off position is prohibited.

Danger tags may be placed on control circuit breakers. However, push buttons, selector switch, interlocks, and other control circuit type device are not energy isolating devices and may not be used as the sole means to de-energize circuits or equipment.

Where a danger tag cannot be placed directly on the energy isolating device, locate the tag as close as safely possible to the device in a position that will be immediately obvious to anyone attempting to operate the device.

If an energy isolating device is not capable of being locked out, the following shall be observed:

Danger tags shall not be removed without authorization. Danger tags are not to be bypassed, ignored, or otherwise defeated.

Supplemental protection measures such as physical separation, removal of a valve handle, blocking, double block and venting, or stationing an attendant by the tagged equipment to prevent unauthorized or inadvertent change may be necessary.

If electrical equipment cannot be locked out, an additional safety measure is required such as removal of fuses, tagging an additional disconnecting device, blocking of a controlling switch, grounding, or removal of a circuit element.

<u>Temporary Suspension</u>

When lockout and/or tagout devices must be temporarily removed from the energy isolating device(s) and equipment placed in service to test or position the equipment the Issuing Authority and Responsible owner/operator shall authorize removal of necessary locks and tags. Also notify the effected employee(s) of the temporary suspension.

Releasing lockout/tagout control

Before lockout devices and tag are removed and energy is restored to the equipment, the work area shall be inspected to ensure that all personnel are in a safe position. Each isolating device must be removed by the authorized employee who applied the device.

Inspection

The operation manager or appointed representative shall conduct an inspection of the lockout/tagout program at least annually to ensure it is being followed. This inspections shall be documented.

Training

- Authorized employees shall receive training in the recognition of hazardous energy source, the type of energy in the workplace, and the method and means necessary for energy isolation and control.
- Responsible owner/ operator shall be instructed in the purpose and use of the energy control procedure
- All training shall be documented to include their name and date of training.

Appendix TT

Operator Aid for Fall Protection Program

- Purpose

This document provides instructions and guidelines for a Fall Protection Program for the effected employees in Materials and Chemistry Laboratory.

- Scope

This procedure applies to the requirements listed in 29 CFR 1926.500 thru 503. and is intended as guidance for the use of a fall protection plan for any employee that performs elevated work. When the danger of falling more than 6 feet exists, workers must be protected from falls using the method that best matches working conditions and fall protection requirements. Refer to MCL Fall Protection Table for more information.

This procedure is only intended for the area controlled by MCL and employees of MCL. All other activities outside of the group will be under the control of the client specific standard operation procedure.

- Responsibilities

Operation Manager The Operation Manager represents the first level of line. Assures that employees covered by the plan receive the necessary training. Assures that all necessary fall protection equipment is provided and maintained in a good state of repair. Enforces the fall protection plan.

Safety Monitor Assigned by Operation manager as needed shall understand the nature of the fall hazards in the work area. Have knowledge for the correct procedure for maintaining and inspecting the fall protection system to be used with an understanding of the personal fall arrest system. The safety monitor shall warm the employee when it appears that the employee is unaware of a fall hazard or is acting in an unsafe manner. He shall be on the same walking/ working surface and within visual sighting distance of the employee being monitored. Also be close enough to communicate orally with the other employee.

Employees Each employee potentially exposed to a fall hazard shall be trained to recognize the hazards and take action to prevent a fall. All effected employees shall abide by all rules and apply to the fullest extent possible the safety and health precautions specified by this procedure. Report any problems that are observed which could compromise the health and safety to the workers. Maintain the fall protection equipment in a safe and sanitary condition. All effected employees who are exposed to a fall hazard as defined by this plan shall follow the program and any safety training requiring fall protection.

4.0 Equipment Standards

There are at least four methods of fall protection available to protect workers from fall hazards. This procedure will apply to only one of the four the Personal fall arrest systems. All connectors shall be drop forged, pressed or formed steel, or made of equivalent materials. Connectors shall have a corrosion-resistant finish, and all surfaces and edges shall be smooth to prevent damage to

interfacing parts of the system. Dee-rings and snap hooks shall meet the requirements of ANSI Standard. Lifelines shall be protected against being cut or abraded. Ropes and straps (webbing) used in lanyards, lifelines, and strength components of body belts and body harnesses shall be made from synthetic fibers. Personal fall arrest systems, when stopping a fall, shall limit maximum arresting force on an employee to 1,800 pounds when used with a body harness ; be rigged such that an employee can neither free fall more than 6 feet nor contact any lower level; bring an employee to a complete stop and limit maximum deceleration distance an employee travels to 3.5 feet; and have sufficient strength to withstand twice the potential impact energy of an employee free falling a distance of 6 feet or the free fall distance permitted by the system, whichever is less.

The attachment point of the body harness shall be located in the center of the wearer's back near shoulder level, or above the wearer's head. Harnesses and components shall be used only for employee protection (as part of a personal fall arrest system or positioning device system) and not to hoist materials.

Personal fall arrest systems and components subjected to impact loading shall be immediately removed from service and shall not be used again for employee protection until inspected and determined by a competent person to be undamaged and suitable for reuse. Personal fall arrest system shall be inspected prior to each use for wear, damage and other deterioration, and defective components shall be removed from service. The following shall be checked in accordance with the manufacturer's guidelines. D-rings- Cracks, distortion, corrosion, pitting or excessive wear. Buckles- distortion, sharp edges or cracks. Body harnesses- burns, damaged due to chemicals, cut abrasion to the material. Broken stitches- One of the best ways to check the material is to hold sections of the material between the hands and bend the material into a U-shape to look for damage. Keepers and snaps locks- make sure they operate correctly. Do not rely on the sound of the latches, they must be connected. Lanyard (rope, webbed or cable) – Look for cuts, frayed parts, damaged fibers, and the condition of connections. There should be no knots in the line. A knot can result in a substantial reduction in strength.

5.0 Requirements for ladders relating to fall protection over six foot.

Inspect each ladder before use. Ladders with loose, broken, or missing rungs, split or bent side rails, or other defects must be removed from service. Ladder tops must rest against a firm structure. Ladders (other than stepladders) must extend approximately 3 feet above a safe landing or parapet wall. They must be set up with a 4 vertical to 1 horizontal slope, and must be tied, blocked, or otherwise secured to prevent them from slipping. The base of a ladder's side rails must rest on a firm, level foundation. Watch for power lines before erecting a ladder

When climbing up or down, workers should always face the ladder use a three-point contact climbing method (two hands and one foot or one hand and two feet). Only one worker at a time is allowed on a single–width ladder. Workers must not work from the top two rungs of a ladder. Heavy, bulky, or hazardous material must not be carried when climbing ladders. Suitable hoisting equipment must be used for this purpose.

6.0 Certification of Training

The employer shall verify compliance to the procedure by preparing a written certification record to be kept in the employees training records.

MCL FALL PROTECTION TABLE

ACTIVITIES WITH FALL POTENTIAL	EQUIPMENT NEEDED	PRECAUTION
Using ladders under six feet high	Normal PPE	Proper ladder placement. Check condition of ladder. Three point contact.
Changing of light bulbs or other activities in lab over 6 feet high	Ladder over six feet, body harness, lanyard, tie-off strap	Proper ladder placement. Check condition of ladder. Three point contact
Using step ladder		Three point contact.
Using extension ladders	Body harness, lanyard, tie-off strap	Top resting on firm structure. Set up four vertical to one horizontal slope, tie off to prevent slipping
Using fixed ladder on building	Body harness, lanyard	Wear gloves. Proper footing. Only one person on the ladder at a time. No carrying of heavy loads.
Using Genie lift	Safety glasses, gloves, safety shoes	Do not sit, stand, or climb on the platform guard rails. Maintain a firm footing on the platform floor at all times. Do not exit the platform while raising. If a power failure occurs, have ground personnel activate the manual lowering valve. Keep the platform floor clear of debris. Lower the platform entry mid-rail gate before opening.

APPENDIX UU

PROCEDURE FOR THE PREPARATION OF BeO SAMPLES FOR BERYLLIUM ANALYSIS

1.0. SCOPE

This operator aid describes the procedure to digest air samples potentially containing beryllium oxide. *These metals may also be analyzed using this method of preparation: cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), vanadium (V), and zinc (Zn).*

2.0. SUMMARY PROCEDURE

The air filter or wipe sample is digested with sulfuric and nitric acids followed by hydrogen peroxide oxidation to dissolve all BeO present. Final digestate is now ready for ICP analyses.

3.0. EQUIPMENT AND REAGENTS

3.1 Hot block digestor at 95 ± 5°C
3.2 Sulfuric Acid, metals grade
3.3 Nitric Acid, metals grade
3.4 Hydrogen Peroxide 30%, ultra grade

4.0. PREPARATION PROCEDURE FOR AIR FILTER SAMPLES (MCE MEMBRANE FILTERS)

CAUTION: ***Beryllium dust is highly toxic. It is an OSHA regulated carcinogen. The TLV is 0.002 mg/m^3. Take necessary precautions to avoid breathing the dust.***

4.1 Using tweezers or forceps, place filters in separate, labeled digestion tubes. Be sure to get the filter all the way to the bottom of the tube to ensure full contact with acid otherwise pieces of the filter may stick to the tube and not digest.

4.2 If the cassette or vial contains loose dust, carefully pour the dust into the digestion tube. Rinse the cassette with DI H_2O, pour the water into the digestion tube and wipe out the cassette with a moistened, clean filter and place this filter into the sample digestion tube.

4.3 Add 4 mL of 1:1 H_2SO_4 followed by 2 mL of concentrated HNO_3 to each digestion tube. Check that the filters have full contact with the acid, and then allow to sit at least 1 hour.

4.4 Add several drops of H_2O_2 to each digestion tube before placing in the hot block for approximately 10-20 minutes or until the solutions turn brown

and the filters have been digested. The solutions will first turn amber but will eventually turn brown.

4.5 Remove from hot block and cool.

4.6 Carefully add H_2O_2 in 2 or 3 drop groups until each solution becomes clear, colorless, or slightly yellow.

4.7 Heat several more minutes until dense, white fumes of SO3 are just evident. Usually, you will see puffs of white from around the watchglass.

4.8 Remove from the hot block and allow to cool to room temperature before adding 4 mL of concentrated HCl. Rinse the sides of the digestion tubes with DI H_2O then return them to the hot block. Heat until near boiling or until you notice some bubbles forming in the solutions.

4.9 Allow solutions to cool then transfer to 50 mL centrifuge tubes using DI H_2O and dilute to 50 mL with DI H_2O.

4.10 Sample digests are then ready for ICP analysis.

5.0. PREPARATION PROCEDURE FOR WIPE OR PVC FILTER SAMPLES

CAUTION: ***Direct all acid addition down the wall of the centrifuge tube, otherwise direct addition will cause reaction and loss of sample***

5.1 Place each wipe or PVC filter *in* a separate 50mL digestion tube. *Tap wipe or filter to bottom of tubes.*

5.2 Add 8mL 1:1 H_2SO_4 to a wipe or 4mL 1:1 H_2SO_4 to a PVC filter.

5.3 Add 5mL conc. HNO_3 to each sample. Be ready to cool any reaction with deionized water.

5.4 When reaction slows down, add 5mL of conc HNO_3. Rinse down solid material on tube walls. Heat on hot block for 15 minutes and cool.

5.5 Add 1mL H_2O_2, return samples to the hot block and heat 10 minutes.

5.6 Remove samples from heat block and allow to cool to room temperature. Carefully add 4mL conc HCl to sample solutions. Rinse down the insides of digestion tubes with deionized water.

5.7 Heat on hot block for at least 10 min until almost boiling.

5.8 Remove tubes from hot block and allow to cool to room temperature. Quantitatively transfer solutions to 50mL centrifuge tubes and dilute to 50mL with deionized water. Thoroughly rinse PVC filter during quantitative transfer of the sample solution.

6.0. QC SAMPLES

A Method Blank, LCS and LRL (lower reporting limit spike) are the minimum QC to be prepped as noted above in Steps 4.2 – 4.8. *Use the designated spiking solution for the ICP-MS.*

7.0. REFERENCES

OSHA Method ID-125G Metal and Metalloid Particulates in Workplace Atmospheres (ICP Analysis)

Procedure: MCL-7746 or Be MCL-7756, App. UU Sample Type: Air Filters, Wipes, Solids, Soils, Oils

Date: _____ Prepared By: _____ Project ID: _____

Spike ID(s):A_____B_____C_____D_____

Used (check one): Class A Glass Pipets? ☐ Autopipet? ☐ Autopipet #: _____Verification Wt. _____ (DI H_2O) (g)

QA/QC Information	QC Sample ID	Matrix (soil, wipe, filter, DI H_2O)	Aliquot (g) or (mL)	Volume (mL) & Spike ID	Final Vol. (mL)	Comments

Sample Information	MCL Sample ID	Matrix (soil, filter, etc.)	Aliquot (g) or (mL)	Final Vol. (mL)	Digestion Temp (°C)	Comments	Chemicals/Reagents Used (include Prep Log Date)

Balance ID		Weight (g)				
Calibration ID		Actual (g)				
Weight Set ID		Actual (g)				
		Avg (g)				

Hot Block Used (circle one): **A** **B** **C** **D** Thermometer ID: _____
Temp. Blank Location:_____ Signature _____

APPENDIX VV

PROCEDURE FOR ESTIMATION OF EXTRACTABLE ACIDITY AND SELECTIONS FROM OIL SAMPLES

1.0 SCOPE

This operator aid describes an operational method to estimate the potential corrosivity of oil.

2.0 SUMMARY PROCEDURE

Equal volumes of "oil" (hydrophobic phase) and de-ionized water (DI H_2O) are contacted by shaking the phases in a sealed vessel. The phases are subsequently separated, and the aqueous phase is analyzed for extracted indicator parameters (pH, alkalinity, select ions, etc.), as required.

As hydraulic fluids age and break down (especially under oxidizing conditions) they generally form acidic byproducts which can be corrosive to metal components. The greater the fluid degradation, the greater will be the level of corrosive acids and correspondingly the greater the danger of component failure. Note that some hydraulic fluids have additives which are by themselves acidic, so the most meaningful measure is the change in acidity from new fluid.

One useful measure of oil degradation is its acidity, often measured as the amount of standard base needed to neutralize a gram of sample (expressed, e.g., as mg-KOH/gm-oil).[1] In new and used oils, the constituents considered to have acidic characteristics include organic and inorganic acids, esters, phenolic compounds, lactones, resins, salts of heavy metals, and addition agents such as inhibitors and detergents. Similarly, constituents considered to have basic properties include organic and inorganic bases, amino compounds, salts of weak acids (soaps), basic salts of polyacidic bases, salts of heavy metals, and addition agents such as inhibitors and detergents.

The chemistry of organic solvents prevents accurate measurements using the 0-14 scale and standard electrodes. A "relative" pH measurement is obtained by mixing the oil with an equal volume of neutral water (preferably purified with no dissolved salts). The pH of the water should be measured before mixing. Mix the water and oil for approximately 5 minutes and then allow the phases to separate. Measure the pH of the water phase again. In principle, the pH of the water is now a reflection of the pH of the oil. This is not a precise value, but can be used as an operational estimate for most applications.

[1] Total acid number (ASTM D974: Standard Test Method for Acid and Base Number by Color-Indicator Titration; ASTM D664-06ae1: Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration).

3.0 EQUIPMENT AND REAGENTS

Centrifuge cones – 50 mL Poly
Transfer pipets
Water bath
Centrifuge
pH meter
pH standard solutions – pH 4,7, and 10
Standard base solution (e.g., 0.001 mol/L NaOH)

4.0 TEST PROCEDURE

4.1 Add equal volumes of hydrophobic phase and DI H_2O.

This is best accomplished by dispensing hydrophobic phase into a tared vessel, such as a separtory funnel or centrifuge cone. Record the volume and net weight of "oil" phase used, to compute a density estimate. A volume of 25-mL of each phase is adequate for most analyses (see Step 4.4). Dispensing and subsequent phase equilibration of very viscous oil or sludge phase may require first warming the test fluid in a vessel placed in a water bath (set at, e.g., 35 ^{o}C), in order to lower the fluid viscosity. Record the ambient temperature, and if required to facilitate phase contact, the water bath temperature.

4.2 Contact the oil and water phases by shaking or tumbling them (manually or mechanically) in a sealed vessel for at least 5-min (longer times may be required if the oil phase is viscous).

4.3 Separate the phases.

Typical hydrocarbon fluids are lighter (less dense) than water, and thus will float on top of the water, whereas halogenated fluids may be heavier than water, and thus will sink below the water. (The density estimate from Step 4.1 can aid in identifying which is the aqueous phase, which has a density ~ 1-g/mL). Note whether there is a persistent emulsion phase between the aqueous and organic layers. It may be necessary to centrifuge the mixture to achieve layer separation.

4.4 Analyze the Aqueous phase.

At a minimum, determine the pH value of the aqueous phase (see the applicable instrument calibration and operation protocol, as described in MCL-7756, "Operator Aids," Appendix A-G).

An aliquot of the aqueous phase may also be titrated vs. standard base to determine the moles of base per unit of oil (g or mL) to achieve neutrality (pH 7), or to compute the alkalinity of the aqueous aliquot.[2]

[2] Standard methods for the Examination of Water and Wastewater, 18th Ed. (1992), Method 2320 B - Titration.

Other parameters for aqueous-extractable components that may be estimated, depending on the client request, are the conductivity of the aqueous phase or selected extractable anions (with use of MCL-7739, "Anions by Ion Chromatography," or MCL-7749, "Determination of Fluoride and chloride in Aqueous Solutions by Specific Ion Electrode"). Readily leachable metal or radioactivity may also be significant to material disposition (total metal or radioactivity should be determined after digestion of the sample, e.g., MCL-7746 ("Acid Digestion for Metals") or MCL-7733 ("Total Activity Screening").

5.0 FIELD TEST

A convenient field test for acidity in oil is to shake equal volumes of oil and water containing trace (0.1-0.5 wt%) methyl orange indicator in a sealed container for ~ 5 minutes or longer. After the phases separate by quiescent sedimentation, any red coloration in the aqueous layer is an indication that the oil has the potential to become corrosive to metals. The methyl orange indicator in the aqueous phase also makes it easy to see the separate phase layers, since otherwise both oil phase and water may be colorless.

The recommended procedure is based on Method 2, but rather than having to separate phases and measure the aqueous phase pH value with an electrode, a small amount of methyl orange indicator is added to the aqueous phase, and acidity is assessed by the color formation in the aqueous phase. The indicator color in the aqueous phase is visually compared to a range of known pH values in aqueous phase with added indicator (color comparison).

Methyl orange is a water-soluble colorimetric indicator chemical that chemists use in the titration of weak bases with strong acids. The dominant color of indicator solution transitions from orange-yellow (at pH > 4.4) to red (at pH < 3.1). The pH range at which methyl orange transitions to red (pH $\leq$ 4.4) also corresponds to the operational pH range at which some solvents (e.g., d-limonene) have been demonstrated to become corrosive to many metals (especially aluminum).

6.0 QUALITY CONTROL

The DI H_2O used for extraction should be analyzed by the same battery of tests used for the aqueous phase after phase contact with the organic material. Note that DI H_2O is poorly buffered and may give an erratic pH value; water that has equilibrated with carbon dioxide from the atmosphere may have a pH value near 5.5 but will have negligible total alkalinity.

Equilibrated aqueous phase with pH value < 4.5 has the potential to be corrosive to metal (especially aluminum), whereas a pH value < 2 is indicative of corrosivity characteristic as defined by RCRA regulations.

Record the estimated density (or specific gravity) for the test fluid, and the pH value for the separated aqueous phase after contact.

If the field test method is used (5.0), the aqueous phase with indicator should be visually compared to the color produced by aqueous samples adjusted to known pH values.

APPENDIX WW

CBD EXTRACTION PROCEDURE (SCALED TO ACCOMMODATE USE OF 50-cc CENTRIFUGE CONE)

1.0 PURPOSE

The purpose of this operators aid is to extract solid samples with CBB to determine extractable metals of interest .

2.0 QUALITY CONTROL

Include one reagent blank (no sample) per batch;
Run 1 sample in duplicate per batch.
There is currently no accepted standard reference material for this method.

3.0 PROCEDURE

1. To a labeled 50-mL centrifuge cone, add dried sample ~ 2.5-g (record exact amount of sample taken & determine dry weight equivalent, if different)

2. Add 25-mL of combined citrate-bicarbonate reagent (see recipe below):

Preparation of 250-mL combined citrate-bicarbonate reagent:
Sodium citrate dihydrate ($Na_3C_6H_5O_7*2H_2O$; FW = 294): 19.6-g
Sodium bicarbonate ($NaHCO_3$; FW = 84): 2.34-g

3. Heat cone and contents to 80 ^oC

4. Add ~ 1-g sodium dithionite ($Na_2S_2O_4$) – caution: this reagent may cause slurry to foam or spew. Mix with glass rod.

5. Heat an additional 15-min, and then remove containers from water bath.

6. Add 5-mL of saturated NaCl solution to flocculate clay.
(If needed to further aid flocculation, add 5-mL of acetone)

7. Centrifuge sealed tubes at ~ 1,500 to 2,000 RPM for $\geq$ 5-min.

8. Decant supernate liquid to a labeled 50-mL volumetric flask.

9. Rinse step: add 5-mL of room-temperature combined citrate-bicarbonate reagent and 1-mL saturated NaCl solution to solid residue; re-suspend slurry; centrifuge; add supernate to labeled 50-mL volumetric flask. Bring final volume to mark using DI-water.

10. Filter extract through a 0.45-um Nalge™ filter flask. Digest filtered sample (MCL-7752), in preparation for ICP analysis (MCL-7751) for total U and total Fe.

4.0 REFERENCE

Mehra, O.P.; Jackson, M.L. (1960), “Iron Oxide Removal from Soils and Clays by a Dithionite-Citrate System Buffered with Sodium Bicarbonate,” *in Proc. Seventh National Conf. Clays and Clay Minerals*, pp. 317-327.

APPENDIX XX

MODIFIED TESSIER SEQUENTIAL EXTRACTION PROCEDURE FOR 2.5-g SOIL OR SEDIMENT SAMPLE

1. PURPOSE

The practical technique of choice for evaluating low-level radionuclide partitioning in soils and sediments is the sequential extraction approach.[3] This methodology applies operationally-defined chemical treatments to selectively dissolve specific classes of macro-scale soil or sediment components. There is no general agreement on the solutions preferred for the extraction of various components in sediment or soils, due mostly to the matrix effects involved in heterogeneous chemical processes. The protocol below is based on the original method of Tessier et al. (1979), with minor modifications reflecting more recent literature evaluations.

2. SAMPLE RECEIPT AND PREPARATION

It is recommended that soil core samples be shipped overnight to MCLinc, packed with water ice to maintain ~ 0-4 ^{o}C (to minimize potential constituent changes due to microbial activity). If analysis cannot be initiated on the day of receipt, core samples will be placed in a deep freeze (maintained at ~ -20 ^{o}C) until testing can be performed (see, e.g., Hlavay et al., 2004). Unless specific contractual arrangements have been negotiated with the client, sample after thawing will not be excluded from exposure to the ambient atmosphere during sample processing; strict air-exclusion may minimize confounding sulfide-bound metals with their oxide-bound counterparts, and may help preserve in-situ redox conditions for anoxic sediments (Rapin et al., 1986; Peltier, 2005). If air-exclusion is specified and commissioned by the client, then sample preparation and extraction must be performed in an oxygen-free environment (e.g., within a specially maintained anoxic glove box).

Sample size is dictated by the apparent sample homogeneity. If relatively large pebbles are first removed (e.g., with use of a #10 mesh standard screen, to remove particles > 2 mm diameter), a sample size of ~ 2.5 g (dry weight equivalent) of blended soil may be used. (Record actual mass taken). If wet soil is used, the moisture content must be estimated with use of a separate sample, to permit interpretation of results expressed on a dry-weight basis.

The lack of suitable certified reference materials for use with this procedure has precluded intra-laboratory comparability of results and hence good quality control. Quality control is thus the usual controls on analytical accuracy.

[3] http://physics.nist.gov/Divisions/Div846/Gp4/Environ/speciation.html

3. FRACTION 1: EXCHANGEABLE CATIONS (MAGNESIUM CHLORIDE, pH ~7)

Short-term (e.g., 1 h) equilibration of soil with a near-neutral solution containing a relatively high concentration (e.g., 1 mol/L) of electrolyte dissolves water-soluble salts and liberates readily exchangeable cations (by ion displacement). For the extraction of trace contaminants, Phillips and Chapple (1995) and also Tessier et al. (1979) favor use of a solution of 1 mol/L $MgCl_2$ (pH 7).

3.1 Extraction:

Reagent #1: For ~ 250-mL lixivant (extraction reagent), add 50.8-g $MgCl_2 \cdot 6H_2O$ (FW = 203.3) to ~ 200-mL de-ionized water; adjust pH value to ~ 7.0 with use of dilute NaOH or HCl solution, then adjust to final volume (~ 250-mL).

2.5 g dry soil is contacted with 20-mL of 1 mol/L $MgCl_2$ (pH 7) in a sealed 50-cc centrifuge cone for 1-h at ambient temperature. (Optimum contact is provided by tumbling the sealed vial on a TCLP rotary extractor unit). Slurry is subsequently centrifuged (4000 RPM for 12-min) and then the supernate is taken to a labeled 50-mL volumetric flask. Solid residue is rinsed in another 10-mL aliquot of lixivant, and then clarified by centrifugation. The supernate is added to the labeled volumetric flask, and the contents diluted to final volume by addition of demineralized (de-ionized) water.

4. FRACTION 2: CARBONATE-BOUND METALS (ACETATE REAGENT, pH ~ 8.2)

Following the extraction of exchangeable cations, many researchers, including Phillips and Chapple (1995), have included an extraction using 6-h contact with slightly acidic 1 mol/L sodium acetate (pH 5). This step is said to liberate the trace metal ions coprecipitated or otherwise occluded in calcite ($CaCO_3$) sediment deposits. Tessier et al (1979) prefer a variant reagent, in which the pH of the acetate solution is adjusted to 8.2; attack on silicate and sulfide minerals is said to be minimal with use of this reagent.

4.1 Extraction:

Reagent #2: For ~ 250-mL reagent, add ~ 15-g reagent grade acetic acid to ~ 200-mL de-mineralized water. Adjust pH value to ~ 8.2 by the gradual addition of sodium hydroxide, then add de-mineralized water to a final volume ~ 250-mL.

To the wet solid residue from Fraction 1, add 20-mL of ~ 1 mol/L sodium acetate (pH adjusted to a value of 8.2). Contact for 6-h at ambient temperature. The supernate is added to the labeled volumetric flask. Sample may be washed by the addition of another 10-mL aliquot of reagent, briefly re-suspending the solids, followed by centrifugation. Supernate is again added to the labeled volumetric flask and contents diluted to final volume by addition of demineralized water.

5. FRACTION 3: METALS ASSOCIATED WITH HYDROUS IRON- AND MANGANESE OXIDES (HYDROXYLAMINE-ACETATE REAGENT)

(Hydroxylamine-Acetate Reagent)

Methods for leaching iron and manganese oxides involve a combination of reagents to reduce these metals to soluble Fe^{+2} and Mn^{+2} forms, respectively, and to keep these forms in solution at relatively high concentrations. The reagent preferred by Tessier et al. (1979) consists of 0.04 mol/L NH_4OH•HCl in 25 % (v/v) acetic acid (pH ~ 2). The extraction of reducible iron and manganese oxides is said to be complete when soil is contacted with the reagent at 96 ± 3 °C for about 6 h with occasional agitation. The hydroxylamine reagent is said to be more effective than citrate-bicarbonate-dithionite (CBD reagent) for the dissolution of metal sulfide phases (Tessier et al., 1979).

5.1 Extraction: To the residue from Fraction 2, add 20-mL of 0.04 mol/L NH_4OH•HCl (FW = 71.5) in 25 % (v/v) acetic acid (pH ~ 2).

Reagent #3: For ~ 250-mL reagent: to ~ 150-mL de-ionized water add ~ 62.5-mL (~ 65.5-g) metals-grade acetic acid, and then 0.715-g NH_4OH•HCl. Mix well and check pH value; adjust to pH ~ 2 (if necessary) with use of dilute NaOH or HCl solution. Dilute to final volume (~ 250-mL) with demineralized water.

To the residue from Fraction 2, add 20-mL of 0.04 mol/L NH_4OH•HCl (FW = 71.5) in 25 % (v/v) acetic acid (pH ~ 2). *Caution*: for samples containing large amounts of carbonate minerals, CO_2 gas evolution may be excessive, causing bubbling and possible spewing (with loss of sample). If vigorous bubbling is observed upon initial addition of reagent, allow several minutes for degassing in an uncapped vessel before applying heat. The centrifuge cone is then capped loosely and the soil is contacted with the reagent by placing the cone and contents in a water bath (or dry heating bock) maintained at 96 ± 3 °C for about 6 h, with occasional agitation of the bottle and contents. After equilibration, the sample is centrifuged and the supernate is added to the labeled volumetric flask. Sample may be washed by the addition of another 10-mL aliquot of reagent, briefly re-suspending the solids, followed by centrifugation. Supernate is again added to the labeled volumetric flask and contents diluted to final volume by addition of demineralized water.

6. FRACTION 4: BOUND TO ORGANIC MATTER

Trace metals may be bound to various forms of organic matter: natural organic matter (notably humic and fulvic acids), microbes, detritus, coatings on mineral particles, etc. (Tessier et al., 1979). Phillips and Chapple (1995) treat the residue from Fraction 3 (above) with dilute (0.02 mol/L) nitric acid with added hydrogen peroxide solution, heating the mixture to ~ 85 C for a total of ~ 6 h.

6.1 Extraction:

Reagent #4A: Approximately 250-mL of lixivant is prepared by the addition of ~ 100-mL of 0.02 mol/L HNO_3 to ~ 150-mL of 30% hydrogen peroxide (H_2O_2). (Add dilute acid to the peroxide until the mixture pH value is adjusted to ~ 2).
Reagent #4B: Acidic ammonium acetate solution is prepared as 3.2 mol/L (247 g/L) ammonium acetate in 20% (v/v) HNO_3.

The solid residue from Fraction 3 is extracted with ~ 20 mL of acid peroxide solution (Reagent #4A). The solids are re-suspended in this solution, and the slurry heated to ~ 85 $\pm$ 2 ^{o}C for 2 h with occasional shaking. Heating is continued for a total of ~ 5-h, with additional increments of reagent added periodically as required to maintain slurry volume. The container and contents are allowed to cool to room temperature. Next, add ~ 20 mL of acidic ammonium acetate solution (Reagent #4B), and shake the bottle and contents continuously for 0.5 h at room temperature. Centrifuge and collect the supernate into a labeled 50 mL volumetric flask. Sample may be washed by the addition of another 10-mL aliquot of ammonium acetate reagent (Reagent #4B), briefly re-suspending the solids, followed by centrifugation. Supernate is again added to the labeled volumetric flask and contents diluted to final volume by addition of demineralized water.

7. RESIDUAL FRACTION

Because the residual fraction is not considered to be available for release to the environment except on a geological time scale, it may not be necessary to quantitate this fraction unless the data is needed for mass balance closure. Total digestion is relatively difficult and expensive, and seldom used in environmental analysis. More commonly used strong acid-based extractions such as EPA methods 3050 and 3051 generally recover most of the available heavy metal content, but they cannot recover metals locked within a refractory silicate matrix. The proportion of residual metal may also be roughly estimated by mass balance, if an estimate of total constituent analysis is available for the original material. Optionally (as a QC check), the residue from Fraction 5 (above) can be extracted by the same methodology used to estimate the original soil constituent or contaminant inventory; this would thus represent a direct estimate of the residual fraction.

7.1 Extraction (As Total Environmentally Available Constituent)

A separate aliquot sample of test material is extracted with use of MCLinc SOP MCL-7746 (based on EPA preparative method 3050B as defined in SW-846). This estimate for each constituent of interest will represent the total environmentally available constituent. The results for metals analysis for each of the previous sequential extractions may be compared to the available inventory, computing a percentage extracted. Mass balance closure (original inventory less constituent extracted by fractions 1 through 4) represents an indirect estimate of the residual fraction.

7. Analytical Procedures

Analysis by inductively coupled plasma spectroscopy (ICP) may require digestion to destroy excess organic reagent (e.g., acetate) and/or substantial dilution of the sample prior to analysis. Analysis will be for select dissolved metals (e.g., U and Fe, etc.) by ICP (with detection by optical emission spectroscopy, ICP-OES, MCL-7751, or mass spectroscopy, ICP-MS, MCL-7768), with appropriate analytical QA (e.g., MCL-7751, based upon NIOSH Method 7300 and USEPA SW-846 Method 6010B). Due to the very high salt and organic acid concentrations in many lixiviates used, sample digestion (MCL-7752, based on USEPA SW-846 Method 3010A) and extensive dilution will be required prior to ICP analysis. This high salt content of the digested spent lixivant limits the sensitivity for trace elements (e.g., for U in soil, the reporting limit by ICP-OES will be ~ 0.4 µg/g for each of the extraction steps).

8. Calculations

The total mass of selected constituent extracted by each sequential leaching procedure is referenced to the original sample mass (Step 1), and is reported in units of mg/kg (or µg/g).

Constituent (µg/g) = (concentration, µg/L)*(V, L)/(original dry sample weight, g)

Concentration (µg/L) in the original extraction lixivant (corrected for any dilution factors required for analysis) is estimated by the ICP instrumentation. By the procedure above, V = 50-mL = 0.05-L.

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MCL-7751, "Inductively Coupled Plasma – Atomic Emission Spectroscopy Metals Analysis."

MCL-7752, "Acid Digestion of Aqueous Samples (EPA Method 3010A)."

MCL-7768, "ICP-MS Element/Metal Sample Preparation and Analysis."

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APPENDIX YY

OPERATIONAL AID FOR LABORATORY COMPACTION OF SOIL USING STANDARD EFFORT (PROCTOR TEST)

Method Reference

ASTM D 698-07 Standard Test Methods for Laboratory C0impaction of Soil Using Standard Effort (12 400 ft-Ib/ft3 (600 kN-m/m3)

Scope

These laboratory compaction methods may be used to determine the relationship between molding water content and dry unit weight of soils (compaction curve) compacted in a 4 or 6 inch diameter mold with a 5.50-lbf (24.5-N) rammer dropped from a height of 12.0 in. (305mm) producing a compactive effort of 12 400 Ibf/ft3 (600 kN-m/m3).

These tests apply only to soils that have 30% or less retained on ¾ in. sieve and have not been previously compacted in the laboratory; that is, do not reuse compacted soil.

Equipment and Apparatus

5.0 Mold Assembly – 4 and 6 inch molds with collar and base plate.

6.0 Rammer – Manually operated with guide sleeve to fall freely a distance of 12 in.

7.0 2-ft. by 2-ft. drying trays.

8.0 Aluminum trays for water content measurement.

9.0 1-gal bottles or buckets for holding screened sample material.

10.0 Straight edge knife for trimming soil in mold.

DETAILED STEPS REQUIRED BY PROCEDURE

8.0. Obtain a 5-gal soil sample and uniformly spread the soil out over one or more large 2-ft by 2-ft trays for air drying. If soil is very wet, some oven drying may be required. Dry the soil until it will pass through a sieve.

9.0. Collect and retain in a plastic bag a small amount of the as received soil for possible moisture content.

10.0. Screen sample using a No. 4 sieve. If less than 25 wt% is retained on sieve, use Method A. Method A will be used over 90% of the time.

11.0. Collect the material that passes through the sieve and place in a closed bucket or plastic bag. This is the soil for compaction. Set aside the oversize retained material.

12.0. Weigh out 2500g of the dried sieved soil and place into a 2-ft by 2-ft tray. Add water from a pre-weighed bottle or graduated cylinder to get optimum water content. Optimum water content for clay soils – when hand molded, the soil will break into several large chunks when turned 90 degrees. Sandy or loamy soils when hand molded will break into multiple chunks when turned 90 degrees.

13.0. Repeat this procedure 4 to 6 times with additional 2500g aliquots of the soil with water contents varying 2% or 50mls. Try to bracket the optimum water content with two (2) samples below optimum and two (2) samples above optimum water content.

14.0. Put each of the wetted soil samples into a 1gal bottle, seal, and let stand overnight to cure.

15.0. Weigh and record weight of mold.

16.0. Assemble the mold with collar and base late. From the bottle of cured soil, first fill the mold to the half-way mark.

17.0. Use 25 blows and follow the blow pattern shown as figure 3.

18.0. Fill the mold to the mold/collar area with soil. Use 25 blows to compact.

19.0. For the third layer, fill mold to 0.5 inches from top of collar. Use 25 blows.

20.0. Uncouple the collar and base plate.

21.0. Use the straight edge to trim extra material from top of mold.

22.0. Weigh mold and compacted soil sample. Calculate weight density.

23.0. Remove compacted sample from mold. Put approximately 500g in a pre-weighed aluminum tray and dry overnight at 110°C.

24.0. Weigh dried material and calculate water content.

25.0. Determine water content of the retained oversize material by drying a portion in an aluminum tray along with the compacted soil samples.

26.0. Record all data on the “PROCTOR TEST DATA SHEET.”

27.0. The raw test data can then be loaded into the Geo-system software for plotting and determining the optimum moisture and maximum dry density. The software is installed on the computer in A-109.

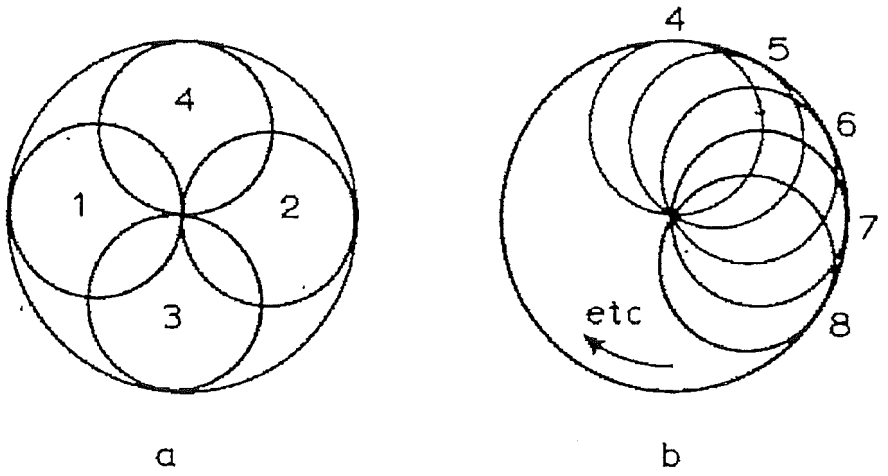

FIG. 3 – Rammer Pattern for Compaction in 4 in. (101.6 mm) Mold

PROCTOR TEST DATA SHEET

Date: _____ Project No.: _____

Project: _____

Sample No.: _____ Elevation/Depth: _____ Sample Length: _____

Location: _____

Description: _____

_____

Testing Remarks: _____

_____

Curve no.: _____ Type of Test: _____

% retained on 2 in. sieve: _____ % retained on # 4 sieve: _____ % passing # 200 sieve: _____

on 3/8": _____ on 3/4": _____

Specific Gravity: _____ Specific Gravity for ZAV Curve: _____ Fig. No.: _____

Specific Gravity of Oversize: _____ Moisture of Oversize: _____

Point No.	1	2	3	4	5	6
Wt.Mold + Soil:						
Wt. Mold:						
Tare No.						
Wt. Wet: #1						
Wt. Dry: #1						
Wt. Tare: #1						
Moisture #1						
Tare No.						
Wt. Wet: #2						
Wt. Dry: #2						
Wt. Tare: #2						
Moisture #2						
Wet Density:						
Avg. % Moisture:						
Dry Density:						

APPENDIX ZZ

VOLUNTARY RESPIRATOR PROTECTION PROGRAM

28.0. PURPOSE

This document provides instruction on and assigns responsibility to create a voluntary respirator protection program for employees of Materials and Chemistry Laboratory, Inc. (MCLinc).

29.0. SCOPE

This procedure applies to requirements listed in Title 29, Code of Federal Regulations (CFR), Section 1910.134 and is intended as guidance for operation in the control of those occupational diseases caused by breathing air contamination. This procedure also applies to control of projects or client specific standard operation procedures (SOP).

This program applies to respirators and does not apply to dust masks which are exempt per 29 CFR 1910.134 (c)(2)(ii).

30.0. RESPONSIBILITIES

Technical Director: The *Technical Director (TD)* represents the first level of line management responsible for supplying the resources for the intended program. The *TD* shall also identify and evaluate the respiratory hazard(s) in the workplace or request the client or Project Manager *(PM)* to provide necessary information, as needed, to the respiratory protection necessary to work on a specific job.

Technical Staff: The staff members using the respirators are responsible for the safe operation and general upkeep which includes cleaning, disinfecting, storage, inspecting, repairing, and otherwise maintaining the respirators. They also must select respirator model and size to ensure the proper fit and use.

Program Administrator: Duties shall include the overseeing of the respiratory protection program and conduct the required evaluations of the program effectiveness. Also ensure that each employee is fit tested prior to initial use of the respirator that is listed on their medical card and all dates are correct.

Medical Department: *CMG HealthWorks will* provide Medical evaluations 1910.134 (e)(5)(i)(A) thru (E) including 1910.134 (e)(5)(ii) and proper fit testing procedures as listed in Appendix A of 29 CFR 1910.134.

31.0. GENERAL GUIDELINES

1. ALL employees using respirators must be fit tested and provided annual training as outlined in Section 8.
2. Note that any modifications to the respirator face piece for the fit testing shall be completely removed and the face piece restored to National Institute for Occupational Safety and Health (NIOSH) approved configuration before that face piece can be used again in the workplace.
3. The employee shall not be permitted to wear a respirator under the following conditions:
    A. Facial hair that comes between the sealing surface of the face piece and the face or that interferes with valve function.

B. Any condition that interferes with the face-to-face piece seal or valve function.

4. Each employee shall wash their face and respirator face piece as necessary to prevent eye or skin irritation associated with respirator use.

5. Each employee shall ensure that each respirator used in routine situations shall be inspected before each use and during cleaning as outlined in Section 6.0.

6. Employees using a respirator shall not work alone.

32.0. STORAGE

All respirators shall be stored to protect them from damage, contamination, dust, sunlight, extreme temperatures, excessive moisture, and damaging chemicals. Respirators shall be packed or stored to prevent deformation of the face piece and exhalation valve.

33.0. INSPECTION

The inspection shall consist of the following: A check of respirator function, tightness of connections, and the condition of the various parts including, but not limited to, the face piece, head straps, valves, connecting tube, and cartridges, canisters or filters; and a check of elastomeric parts for pliability and signs of deterioration.

Certify the respirator by documenting the date the inspection was performed, the name (or signature) of the person who made the inspection, the findings, required remedial action, and serial number or other means of identifying the inspected respirator.

34.0. REPAIRS

Repairs shall be made according to the manufacturer's recommendations and specifications for the type and extent of repairs to be performed.

35.0. TRAINING

Annual *refresher* training shall be provided *for respirator users* to demonstrate knowledge of the following:

1. Why the respirator is necessary and how improper fit, usage, or maintenance can compromise the protective effect of the respirator.
2. The limitations and capabilities of the respirator.
3. How to use the respirator effectively in emergency situations, including situations in which the respirator malfunctions.
4. How to inspect, put on and remove, use, and check the seals of the respirator.
5. What the procedures are for maintaining and storing the respirator.

Training records shall be kept on all affected employees by the Program Administrator in the employee training files.

36.0. PROGRAM ADMINISTRATOR

The Program Administrator of the Respiratory Program is William D. Bostick, Ph.D.

MATERIALS AND CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE	
Waste Management Plan: Materials and Chemistry Laboratory, Inc.	Approved: _____ _____ MCLinc President Date _____ _____ Quality Assurance Officer Date

1.0 INTRODUCTION

All wastes generated in the Materials and Chemistry Laboratory, Inc. (MCLinc) will be managed and disposed in compliance with applicable federal, state, and municipal regulations. The MCLinc facility has an identification code number and is classified as a "conditionally exempt small-quantity generator." MCLinc maintains a Tennessee Radioactive Material License #R-73025-K25.

The objectives of this MCLinc Waste Management Plan are to provide instructions on how to manage these wastes in a manner to: (1) minimize the generation of all wastes; (2) segregate all wastes at the point of origin for compliant accumulation for ultimate disposal; (3) prevent the discharge of hazardous wastes into the sanitary sewage system; and (4) dispose of wastes using permitted Treatment, Storage, and Disposal Facilities (TSDF).

There are four major categories of wastes that are generated at MCLinc: (1) non-hazardous; (2) hazardous; (3) radioactive; and (4) mixed (i.e., both hazardous and radioactive). Hazardous wastes shall **not** be discharged into the sanitary sewer, thrown into the trash, or intentionally evaporated into the air. Laboratory operations should be conducted in such a manner as to minimize the generation of hazardous or mixed wastes.

2.0 DEFINITIONS

Bulk Waste Disposal - The packaging of solid or liquid hazardous waste directly into barrels without intermediate or secondary forms of containment (e.g., glass jars or plastic jugs) for shipment to a disposal facility in accordance with U.S. Department of Transportation (DOT) requirements.

Conditionally Exempt Small Quantity Generator (CESQG) - A generator that generates less than 100 kilogram (kg) of non-acutely hazardous waste per calendar month and accumulates a total on-site inventory of less than 1000 kg of hazardous waste. A CESQG is conditionally exempt from the provisions of 40 (Code of Federal Regulations CFR) Parts 262 through 270.

CFR - Code of Federal Regulations issued by governmental agencies to enforce Acts of Congress.

Disposal Facility - A hazardous waste treatment, storage, or disposal facility permitted under the EPA Resource Conservation and Recovery Act (RCRA).

DOT - The U.S. Department of Transportation; requirements of the DOT are contained in Chapter 49 of the CFR.

EPA - The U.S. Environmental Protection Agency; requirements of the EPA are contained in Chapter 40 of the CFR.

Generator - Any person whose act or process produces a defined RCRA hazardous waste, or whose act first causes a hazardous waste to become subject to regulation. Within the context of this procedure, this is any staff member who creates hazardous waste in the laboratory.

Hazardous Waste Broker - Intermediate party responsible for transportation of hazardous waste from a waste generating facility to an approved waste disposal facility.

Labpack Disposal - The packaging of small containers (e.g., glass jars, plastic jugs, or bags) of solid or liquid hazardous laboratory waste into larger barrels or cans for shipment to a disposal facility in accordance with DOT specifications.

Mixed Waste - As used in this document, mixed waste is waste that satisfies the definition of low-level radioactive waste (LLW) in the Low-Level Radioactive Waste Policy Amendment Act of 1985 and contains hazardous waste in Subpart D of 40 CFR 261 or causes the LLW to exhibit any of the hazardous waste characteristics identified in Subpart C of 40 CFR 261.

Process Waste - Any solid or liquid waste material generated from laboratory operation involving the use and handling of laboratory chemicals.

P-listed Waste - Wastes that contain any chemical listed as acutely hazardous in 40 CFR 261.

Resource Conservation and Recovery Act (RCRA) - The principal federal law enacted in 1976, governing the disposal of solid and hazardous waste.

Sanitary Sewer System - A system of pipes or conduits designed for carrying a combination of aqueous non-hazardous waste from residences and business establishments.

Sanitary Waste - (a) Non-hazardous liquid waste discharges that meet the Waste Acceptance Criteria (WAC) for discharge via a sanitary sewer system to a Publicly Owned Treatment Works or Sewage Treatment Facility; or (b) Non-hazardous solid wastes (debris or trash) that meet the WAC for disposal at a permitted sanitary landfill.

Satellite Accumulation Area (SAA) - Areas at or near the point of generation where waste initially accumulates in compatible containers. Specific accumulation volume limitations apply (55 gallons for hazardous waste or 1 quart for acutely hazardous waste). The area must be under the control of the operator generating the waste (see Section 6.0 for additional detail).

TCLP - Toxicity characteristic leaching procedure (TCLP) is an EPA method used to determine the mobility of select regulated organic and inorganic chemicals present in liquid, solid, and multiphasic wastes. TCLP is used as an indication of waste toxicity.

TDEC - Tennessee Department of Environment and Conservation (TDEC) is the State agency that administers the hazardous waste regulations covered by CFR, Chapter 40, and the radiological material control regulations covered by CFR, Chapter 10. These programs are managed under State Rule 1200-1-11.

Toxic Substance Control Act (TSCA) **-** A law, first enacted in 1976, authorizing the EPA to regulate the production, use, distribution, and disposal of specified toxic substances, including PCBs and asbestos fibers.

Waste Acceptance Criteria (WAC) - Facility-specific, defined compositional restrictions or performance criteria for waste material to be compliantly transferred to a permitted waste treatment, storage, or disposal facility.

Waste Certification Officer (WCO)- An individual, qualified by training and experience, who is assigned by the MCLinc Laboratory Manager to assist laboratory staff in the proper identification of hazardous waste for compliant storage, transportation, and disposal.

Waste Characterization - Determining the physical, chemical, biological, and/or radiological properties of a waste.

3.0 WASTE MINIMIZATION

It is the policy of MCLinc to return all samples and material processing residues to the client, unless other provisions have been specifically contracted; residuals to be returned to the client for disposition are properly segregated but are not declared waste by the MCLinc. This policy minimizes the quantity of material that must be managed as waste by the MCLinc. Benefits to the client for the return of their sample and waste analysis residues include better control of their legal liabilities regarding the disposal of the waste or tracking of radioactive materials. For certain special materials originating from the U.S. Department of Energy (DOE), return of residuals is required by the client (see Section 12.0).

However, it is recognized that some general laboratory operations waste will be generated (i.e., wastes not identified with a specific client); these wastes will be managed at or near the point of generation, in accordance with the provisions of this Waste Management Plan.

Hazardous waste identification and proper waste segregation policies are critical components in compliant, cost-effective waste minimization.

The satellite accumulation containers for aqueous waste should be compatible with acids and covered at all times except when accumulating or transferring waste

4.0 HAZARDOUS WASTE IDENTIFICATION

The first step in the waste management process is to determine if a material is a hazardous waste as defined by the EPA. The following guidelines provide assistance with the identification of hazardous materials; however, when in doubt, provisionally consider the material to be hazardous and contact the Waste Certification Officer to make the final determination. A waste is considered to be hazardous if:

- It exhibits any of the following characteristics of a hazardous waste:

  Toxic - Exceeds the regulatory levels defined by the TCLP found in Title 40 CFR 261, Appendix II.

  Reactive - normally unstable; explosive; reacts violently with water; forms toxic gases, vapors, or fumes when exposed to water; or contains cyanides or sulfides, which are capable of producing toxic gases, vapors, or fumes when exposed to pH conditions between 2.0 and 12.5.

  Ignitable - flash point less that 140 degrees Fahrenheit (^{o}F).

  Corrosive - pH less than 2.0 or greater than 12.5.

- It is specifically listed in Title 40 CFR 261, Subpart D. This Subpart includes the following lists of hazardous wastes:
    - Hazardous wastes from nonspecific sources (F list)
    - Hazardous wastes designated as toxic (D list)
    - Hazardous waste from specific sources (K list)
    - Discarded commercial chemical products designated as acutely hazardous (P list)
    - Discarded commercial chemical products (U List)

During the project planning stage, a determination is made of the categories and disposition of project-related waste.

5.0 SEGREGATION OF HAZARDOUS WASTES

After laboratory wastes have been classified as hazardous and separated from the non-hazardous wastes, the hazardous wastes must be further segregated for packaging and disposal. The segregation procedures are based upon the treatment requirements imposed by the EPA RCRA regulations (as administered by the TDEC) and by MCLinc's hazardous waste brokers. Proper segregation and hazard evaluation are essential to ensure safe handling, as well as economic and timely disposal of hazardous waste. For example, if mercury is added to a waste container, the entire contents of the container must be classified as mercury-bearing waste. The disposal costs for mercury-bearing waste are extremely high on a cost-per-unit basis; therefore, segregating mercury waste from other wastes will reduce overall costs. Waste segregation will be performed by the waste generator in the laboratory at the point of generation.

Every effort must be taken to avoid unnecessary co-mingling of hazardous and radioactive waste streams, which would create a mixed waste. Mixed waste is subject to dual regulation by the radioactive material provisions of CFR Chapter 10 (defined by the Nuclear Regulatory Commission) and the hazardous material provisions of CFR Chapter 40 (defined by the EPA); permitted treatment and disposal capacities for mixed waste are extremely limited, and disposal of mixed waste is correspondingly expensive.

Whenever possible, process procedures and instructions will be written in a manner to avoid the creation of characteristic waste (e.g., the production of corrosive material).

5.1 Segregation Guidelines

The following are basic guidelines for the segregation of hazardous wastes. Deviation from these guidelines may be unavoidable for some laboratory operations; however, such deviations may cause waste disposal costs to be higher.

- **Low Level Dry Radioactive Trash (LLDR).** Examples of dry active waste include paper, wipes, gloves, etc. Avoid mixing dry active waste that is contaminated with D- or P- listed hazardous chemicals with other contaminated dry active waste. Package each separately. Avoid adding contaminated metal scrap to the LLDR trash.

- **Laboratory Operations Wastes.** Examples of laboratory operations waste include waste acid, base, and organic solvents. Be certain not to mix these wastes together at any time. Keep them separated and keep the containers in separate secondary containers.

- **Corrosive Waste.** Avoid adding organic compounds into caustics or acidic waste containers. Do not add reactive organic compounds to strongly oxidizing acid mixtures (e.g., nitric acid at greater than 25%, by volume).

- **Chemical Spill Clean-up Materials.** Keep spent media separated from other wastes.

- **Unused or Discarded Chemicals**. Retain unused laboratory chemicals in their original labeled containers and segregate incompatible chemicals.

- **Unused Sample Disposal.** Upon notification by the Sample Coordinator (SC) that samples are ready for disposal, the Sample Disposition individual will locate the samples and based on information available, sort by waste class for retention or disposal by laboratory. Documentation of the disposed samples is given to the SC to document in the project file and if applicable in tracker. The WCO will be consulted as necessary for proper disposal. The process results in MCLinc tracking samples from receipt to final disposition. All empty sample containers must have labels removed or rendered illegible.

5.2 Hazardous Wastes Requiring Special Treatment

The following categories of hazardous wastes require special treatment and **should be kept separate from other waste streams**. Deviations from these guidelines may be unavoidable for some laboratory operations; however, such deviations may cause waste disposal costs to be higher.

- Radioactive waste.

- Oxidizing solutions containing concentrations greater than two percent of bromates, chlorates, perchlorates, chromates, dichromate’s, periodates, nitrates, nitrites,

persulfates, permanganates, and organic and inorganic peroxides in their original labeled containers.

- Peroxide-forming solvents such as ethyl ether, tetrahydrofuran, and dioxane, at concentrations greater than five percent, unless stabilized.

- Chemicals that cause extreme irritations to the eyes and respiratory system.

- Chemicals that emit a strong odor (e.g., mercaptans, thiols, ethylene diamine, and pyridines).

- Reactive materials, including sulfide or cyanide compounds at levels that may cause the waste mixture to fail the hazardous waste characteristic for reactivity.

- Universal waste such as batteries, thermostats, etc.

- Elemental mercury and inorganic or organic mercury compounds.

- Acutely toxic wastes.

- Polychlorinated biphenyls (PCBs). (This substance is specifically regulated by the special provisions of the Toxic Substances Control Act (TSCA)). PCB wastes should be stored in an area that meets one year storage facility requirements of TSCA (40CFR761.65 (b)). These areas must be monitored monthly to check for leaks. When possible, MCLinc prefers to return PCB Samples to clients.

5.3 Segregation Requirements for Bulking of Liquid Hazardous Waste

Some types of liquid hazardous waste, if properly segregated, may qualify for less costly bulk recycling or disposal options. This waste generally falls into one of the following categories:

- Halogenated solvents - Mixtures of halogenated organic solvents, such as those generated from chemical extraction procedures or glassware cleaning operations.

- Aqueous-based solvents - Aqueous waste contaminated with small amounts of inorganic compounds or contain less than ten percent of organic compounds, such as the aqueous phase from liquid-liquid extractions.

- Non-halogenated solvents - Mixtures of non-halogenated organic solvents.

6.0 REQUIREMENTS FOR A CONDITIONALLY EXEMPT SMALL QUANTITY GENERATOR

The TDEC recognizes MCLinc as a CESQG. To qualify for this status, MCLinc must meet the following requirements:

(1) Comply with 40 CFR 262.11 concerning hazardous waste determination (Section 4.0 of this Standard Operating Procedure [SOP];
(2) Send any hazardous waste to a hazardous waste facility, legitimate recycling facility, or other facility that is authorized by the state to manage industrial or municipal wastes (Sections 8.0 and 15.0 of this SOP);
(3) Never accumulate in a calendar month more than any of the following quantities:
    a. One kg of acutely hazardous waste (as described in Section 4.0);
    b. One hundred kg (220 pounds) of hazardous waste.
(4) Do not accumulate a total hazardous waste inventory of greater than 1000 kg (2,200 pounds).

If a CESQG exceeds any of the threshold values identified above, the CESQC must manage the hazardous waste in accordance with other generator standards, namely those relating to either small or large quantity generators. A qualified CESQG is excluded from 40 CFR Parts 262 through 270 of the RCRA regulations. For example, a CESQG is exempt from the specific requirements for hazardous waste satellite accumulation area record keeping and inspection, and the temporal limits for on-site filled container storage. Wastes generated at MCLinc will be segregated in compatible containers as described in Section 5.0 of this SOP, and hazardous waste will be marked to identify its contents.

MCLinc technical staff may perform elementary neutralization (i.e., adjustment of solution pH to a value between $6 < pH < 9$) to remove the corrosivity characteristic (see Section 4.0 of this SOP). If the conditioned waste meets the requirements for discharge to the sanitary sewer system (see Section 14.0 of this SOP), the waste may be drain disposed (consult with the MCLinc Laboratory Manager for concurrence); otherwise, the waste will be combined with a compatible waste group for permitted off-site disposal. The MCLinc Project Manager (working with the client and the MCLinc Laboratory Manager, as appropriate) is responsible for disposing of samples in a timely manner per Section 5 of this SOP.

7.0 PACKAGING OF PROCESS WASTES FROM LABORATORY OPERATIONS

Hazardous waste must meet minimum packaging standards, defined by the DOT, determined to be acceptable for transport to a hazardous waste facility. Proper packaging reduces the risk to staff, waste transporters, and emergency response personnel of exposure from accidental spills and other physical hazards inherent in handling the waste. Packaging standards are based upon the physical properties of the waste being disposed.

8.0 TRANSFER OF HAZARDOUS WASTES TO AN APPROVED HAZARDOUS WASTE FACILITY

After waste is properly identified, labeled, and packaged, the WCO should arrange for off-site transfer of the material to an approved (permitted) Hazardous Waste Facility. An approved commercial transporter will be contracted for shipment of the waste. The MCLinc WCO has the ultimate responsibility to ensure that the manifesting, bill of lading, and shipment of the waste to a permitted disposal facility are performed in accordance with applicable DOT regulations and requirements.

8.1 An approved waste broker and/or TSDF shall be based upon the results of a site visit to the waste facility or a desktop review that includes information from audits of the facilities conducted by state or federal agencies. The evaluation shall include:

- Liability coverage
- Financial stability
- Notice of violations in last three (3) years
- Relevant permits and licenses to accept waste
- Other relevant information
- State of Tennessee Radiological license that covers the type of waste (including sufficient limits) needing disposal
- DOT Hazardous Materials Certification of Registration for transporting hazardous materials
- State of Tennessee license to ship radioactive materials to disposal sites MCLinc uses within Tennessee
- State of Utah Generator Site Access Permit

8.2 The reviews for approval must be done every three (3) years.

9.0 EVAPORATION OF VOLATILE HAZARDOUS WASTES IN LABORATORY HOODS

The deliberate evaporation of volatile hazardous wastes to avoid responsible disposal of the wastes is prohibited. Volatile hazardous waste must be collected and transferred to the hazardous waste facility for proper disposal. This restriction does not apply to evaporation procedures that are an integral part of a laboratory procedure.

10.0 DILUTION OF THE HAZARDOUS WASTE

The deliberate dilution of hazardous wastes as defined by the RCRA regulations to avoid responsible disposal of the wastes is strictly prohibited.

11.0 RADIOLOGICAL WASTE DETERMINATION

MCLinc has the necessary equipment to evaluate the radioactivity content of solid or liquid materials and wastes that are known or suspected to contain regulated levels of radionuclides, and to perform personnel and work area surveys. The MCLinc Radiation Safety Officer will assist in these determinations. Additional detail on radiation monitoring is provided in the "MCLinc Radiation Protection Plan," MCL-7715.

12.0 DOE SPECIAL MATERIALS

MCLinc has the necessary training and certifications to possess and work with classified and/or special nuclear material, as defined by the DOE. Wastes derived from the analysis or treatment of these special materials will be returned to the DOE for disposition.

13.0 TSCA WASTE

TSCA regulates specific materials, including polychlorinated biphenyls (PCBs) and asbestos.

As defined in 40 CFR 761.3, MCLinc is a laboratory facility that analyzes for PCBs (see MCL-7740, "Determination of Polychlorinated Biphenyls (PCBs) by GC/ECD"), or for other properties of materials that may contain PCBs, but is unaffiliated with any entity whose activities involve the treatment, storage, or disposal of PCBs. MCLinc is not required to notify the EPA or obtain an identification number for its activities involving PCBs, but it must comply with the requirements for PCB waste storage for disposal, as described in 40 CFR 761.65(b)(1)(i) through (b)(1)(iv). The secondary containment vessels used within MCLinc meet the intent of these requirements. As described in Section 5.2, residuals known to contain regulated quantities of PCBs (> 50 parts per million [ppm] should be segregated from other wastes. When the client identifies that submitted samples contain regulated amounts of PCBs, MCLinc contracts specify the return to the client of any unused sample and derivative residuals for their disposition. The PCB waste storage area is in C Corridor and with the waste entered into a PCB log form to record details of the waste as added to the storage area. PCBs will be disposed with each general waste disposal.

MCLinc does create a small amount of derivative waste in its operations, especially in the processing of material for bulk analysis. These wastes are double-bagged for storage, and when possible are returned to the customer for their disposition.

14.0 WASTE DISPOSAL VIA THE SANITARY LANDFILL

MCLinc contracts with a commercial waste handler for the disposal of sanitary solid trash and debris waste, and must meet the terms of the service agreement pertaining to non-conforming wastes.

15.0 NON-REGULATED WASTE

Certain non-hazardous, non-regulated liquid wastes are not eligible for disposal in sanitary sewers or landfills; these will be accumulated for disposal by MCLinc's waste brokers, in accordance with State and local regulations. Notable among these non-regulated wastes are used vacuum pump oils that may be reclaimed or be used for energy recovery (i.e., burned for British Thermal Unit [BTU] content).

16.0 TRAINING

All staff members shall receive this SOP and understand the contents of this document and direct questions to the WCO. In addition, key personnel have attended training for "DOT Hazardous Waste Regulations" and/or "RCRA Hazardous Waste Characterization."

17.0 HAZARD COMMUNICATION, CONTINGENCY PLANNING, AND EMERGENCY RESPONSE

Facility Hazard Communication information is detailed in the "MCLinc Chemical Hygiene Plan," MCL-7702. Contingency planning and emergency response actions (including chemical spill response and cleanup) are detailed in the "MCLinc Health and Safety Plan," MCL-7717. In the event of a spill, laboratory personnel should immediately contact the WCO or other MCLinc management. If the spill is minor and management feel that immediate actions can minimize personnel, facility, and environmental impact without undue risk to the response personnel, staff may take direct action to clean up the spill and containerize the spill clean-up materials. The spill event must be documented, with the estimated quantity of material released and the response activities recorded in a permanent file. If there are any concerns about the hazards generated due to the spill, contact management or actuate a fire alarm within the facility. Management will contact the appropriate emergency response professionals, including firefighters and medical personnel as required.

18.0 RESPONSIBILITIES

Laboratory Staff

The laboratory staff have the largest impact on the success of MCLinc's waste management program because the identification and segregation of hazardous wastes begins in the laboratory. All laboratory staff will:

- Know the physical, chemical, and toxicity characteristics of all hazardous materials that are present in his or her work area. This information is available from several sources, including the manufacturer's Material Safety Data Sheets (MSDSs).

- Know how to handle and dispose of these materials prior to ordering the chemicals and beginning laboratory procedures.

- Dispose of all hazardous wastes in accordance with federal, state, and municipal regulations and Institute requirements.

- Properly label all laboratory chemicals and hazardous waste containers.

- Segregate hazardous waste into proper categories to facilitate economical disposal.

- Package and label hazardous waste containers prior to transfer to an approved hazardous waste facility, under the direction of the WCO.

- Minimize hazardous wastes. It is the responsibility of the laboratory staff to keep the volume of unwanted chemicals at a minimum and to maintain an effective waste minimization program.

Recycle unused materials when possible. Many unused or unopened chemicals can be used by coworkers thereby reducing the cost of disposal as well as the cost of purchasing new material

The WCO will:

- Implement and co-ordinate the provisions of this Waste Management Plan.
- Monitor each waste collection site for proper operation.
- Be available to laboratory personnel to answer questions about proper disposal of any chemical compound or waste material.
- Segregate and package waste containers from the laboratories into DOT-approved containers.
- Oversee the transfer of the hazardous waste to MCLinc's hazardous waste brokers.
- Assures that an evaluation is performed on MCLinc's contracted waste broker every three years.

19.0 REFERENCES

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MCLinc Health and Safety Plan, MCL-7717

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APPENDIX 38
Modified Sequential Extraction Procedure for Characterizing Source Materials from West Lake Landfill (Project Specific)

1.0 Purpose

The purpose of this operator aid is to describe a methodology for the operational assessment of the potential mobility for select potential contaminants of concern (PCOC), principally Ra-226, in submitted soil and debris samples originating from the West Lake Landfill, located in Missouri, USA. The procedure described herein is based on the selective sequential extraction methodology described by Liu and Hendry (2011), incorporating select client-recommended modifications as indicated in Appendix 1.

2.0 Sample Receipt and Preparation

Samples of radiological soil (approximately 250-g) will be shipped to MCLinc within a vacuum bag in frozen condition, in order to minimize potential constituent changes due to microbial activity. If analysis cannot be initiated on the day of receipt, core samples will be placed in a deep freeze (maintained at ~ -20 ^{o}C) until testing can be performed (see, e.g., Hlavay et al., 2004). Sample thawing will be performed within the as-received vacuum bag (e.g., by placement in a nitrogen-purged ambient-temperature storage vessel, such as a glove box), to help preserve in-situ redox conditions for anoxic sediments. It is recommended that testing be performed with aliquots of as-received sample that has experienced only minimal exposure to the ambient atmosphere prior to initiating sample conditioning and testing (Rapin et al., 1986).

Thawed samples will be dried under nitrogen to remove superficial water removed with minimal exposure to oxygen in ambient air. Analytical results are to be reported on “gas-dried” equivalent mass basis.

Sample size is dictated by the apparent sample homogeneity. If relatively large pebbles are first removed (e.g., with use of tweezers to remove particles > 2 mm diameter), a sample size of ~ 1 g (dry weight equivalent) of blended soil may be used. (Record actual mass taken). **If “container dried” soil is used, the moisture content must be estimated with use of a separate sample aliquot, to permit interpretation of results expressed on a dry-weight basis (MCL-7756, Appendix MM).**

Note: in order to yield sufficient volume of lixiviate for the requested battery of analyses, two separate 1-g aliquots of sample solids will be carried through the entire procedure, with lixiviate and water wash for each fraction combined to form a single sample for analysis.

Reagent-grade chemicals and de-ionized water (DIW) will be used for all extraction media preparations.

The lack of suitable certified reference materials for use with this procedure has precluded intra-laboratory comparability of results and hence good quality control. Quality control is thus the usual controls on analytical accuracy.

3. Fraction #1: Soluble and Exchangeable ions (Appendix 1)

Reagent #1: For 500-mL of lixiviate solution #1 (1 *M* $MgCl_2$, pH 7), add 47.6-g magnesium chloride ($MgCl_2$, FW 95.22).[5] De-aerate solution (e.g., bubble with nitrogen gas), and use without pH adjustment **– but record actual pH value**.

Note: In order to yield sufficient volume of lixiviate for the requested battery of analyses, two separate 1-g aliquots of sample solids (labeled (sample ID)-A and -B) will be processed by the procedure, with lixiviate and water wash for each fraction combined to form a single sample for analysis.

Note: Extraction Steps #1 and #2 are to be performed in a manner such as to minimize sample exposure to air. Sample aliquot will be loaded into the labeled centrifuge cone within a nitrogen-purged glove bag. De-gassed lixiviate will be added and then the centrifuge will be sealed tightly for subsequent phase contact and phase separation operations. (Providing the head space in the centrifuge cone has been purged of air, the sealed container may then be transferred out of the glove bag for external processing on a TCLP rotary extractor and for subsequent centrifugation. However, the sealed tube will only be opened within a nitrogen-purged glove bag, to minimize possible air-exposure of the contents).

For each 1.0 ± 0.1 g (dry-weight equivalent) aliquot of soil, use a labeled 50-mL polypropylene centrifuge cone. Next, add 10-mL of Reagent #1 to the sample aliquot. Seal the cone and contact the phases for 4-h at room temperature (optimum phase contact is provided by tumbling the sealed vial on a TCLP rotary extractor unit). This phase contact is to be performed with minimal potential exposure to ambient air. Slurry is subsequently centrifuged (approximately 4000 RPM for about 10-min). **The sealed centrifuge cone after centrifugation is returned to a nitrogen-purged glove bag for exchange of liquid phase**. Supernate phase is removed to a clean, labeled container with use of a transfer pipet.

The solid phase remaining in the centrifuge cone will be washed between extraction steps by phase contact with a 10-mL aliquot of de-gassed de-ionized water (DIW). Slurry in the sealed, air-free container is subsequently centrifuged (approximately 4000 RPM for about 10-min). Supernate phase is combined with the original lixiviate extract in the labeled container with use of a transfer pipet.

Extracts and wash solutions from processing two replicate 1-g sample aliquots are combined to form a single extract phase. **Record the actual pH value for the combined extract.** The combined aqueous phase will be subsequently digested (MCL-7746) and made up to an appropriate known volume (e.g., 50.0-mL, for combined extracts and wash solutions from aliquots A and B). (**Record final volume**).

[5] Bessinger (21 December 2015): Sequential Extraction Step 1: The first extraction step will be changed from 1 M $Mg(NO_3)_2$ (pH 7) to 1 M $MgCl_2$ (no pH adjustment). The objective of running the first two extractions in a glove box is to ensure the introduction of no potential oxidants. $MgCl_2$ is most-commonly used in sequential extractions and contains no potential oxidants.

4. Fraction #2: Acid Soluble and Carbonates (Appendix 1)

Note: Extraction Steps #1 and #2 are to be performed in a manner such as to minimize sample exposure to air.
Reagent #2: For 500-mL of lixiviate solution #2 (1 *M* CH_3CO_2Na, pH 5), add 68.04-g of sodium acetate hydrate ($CH_3CO_2Na•3H_2O$, FW 136.1). Adjust pH with dilute acetic acid or NaOH, as necessary to attain target pH value (5.0 ± 0.05). De-aerate solution (e.g., bubble with nitrogen gas), and record actual pH value.

To the individual solid residues from Extraction Fraction #1, add 25-mL of Reagent #2 to each centrifuge cone. Seal the cone and contact the phases for 6-h at room temperature (optimum phase contact is provided by tumbling the sealed vial on a TCLP rotary extractor unit). Slurry is subsequently centrifuged (approximately 4000 RPM for about 10-min). **The sealed centrifuge cone after centrifugation is returned to a nitrogen-purged glove bag for exchange of liquid phase**. Supernate phase is removed to a clean, labeled container with use of a transfer pipet.

The solid phase remaining in the centrifuge cone will be washed between extraction steps by phase contact with a 10-mL aliquot of de-ionized water (DIW). Slurry is subsequently centrifuged (approximately 4000 RPM for about 10-min). Supernate phase is combined with the original lixiviate extract in the labeled container with use of a transfer pipet.

Extracts and wash solutions from processing two replicate 1-g sample aliquots are combined to form a single extract phase. **Record the pH value for the combined extract**. The combined aqueous phase will be subsequently digested (MCL-7746) and made up to an appropriate known volume (e.g., 100-mL, for combined extracts and wash solutions from aliquots A and B). (**Record the final volume**).

Note: Extraction Steps #1 and #2 are to be performed in a manner such as to minimize sample exposure to air.

5. Fraction #3: Organics/Sulfides (Humic materials and iron-sulfides) (Appendix 1)

Note Extraction Step #3 and subsequent extractions may be performed without the need for air-exclusion.

Reagent #3: For 500-mL of lixiviate solution #3 (0.1 M $Na_4P_2O_7$, pH 10) add 13.3-g sodium pyrophosphate reagent (FW265.9). Adjust pH with dilute HNO_3 or NaOH, as necessary to attain target pH value (10.0 ± 0.05).

To the individual solid residues from Extraction Fraction #2, add 30-mL of Reagent #3 to each centrifuge cone. Seal the cone and contact the phases for (20 ± 1)-h at room temperature (optimum phase contact is provided by tumbling the sealed vial on a TCLP rotary extractor unit). Slurry is subsequently centrifuged (approximately 4000 RPM for about 10-min). Supernate phase is removed to a clean, labeled container with use of a transfer pipet.

The solid phase remaining in the centrifuge cone will be washed between extraction steps by phase contact with a 10-mL aliquot of de-ionized water (DIW). Slurry is subsequently centrifuged (approximately 4000 RPM for about 10-min). Supernate phase is combined with the original lixiviate extract in the labeled container with use of a transfer pipet.

Extracts and wash solutions from processing two replicate 1-g sample aliquots are combined to form a single extract phase. **Record the pH value for the combined extract**. The combined aqueous phase will be subsequently digested (MCL-7746) and made up to an appropriate known volume (e.g., 100-mL, for combined extracts and wash solutions from aliquots A and B). (**Record final volume**).

6. Fraction #4: Amorphous Oxides and Secondary Uranium Compounds (Appendix 1)

Reagent #4: For 500-mL of lixiviate solution #4 (0.2 M $(NH_4)_2C_2O_4$, pH 3), add 14.21-g of ammonium oxalate monohydrate $(NH_4)_2C_2O_4 \bullet H_2O$, FW 142.1). Adjust pH with dilute nitric acid or NaOH, as necessary to attain target pH value (3.0 ± 0.05).

To the individual solid residues from Extraction Fraction #3, add 10-mL of Reagent #4 to each centrifuge cone. Seal the cone and contact the phases for 4-h at room temperature (optimum phase contact is provided by tumbling the sealed vial on a TCLP rotary extractor unit). During the extraction step, avoid exposure of the slurry to direct light. Slurry is subsequently centrifuged (approximately 4000 RPM for about 10-min). Supernate phase is removed to a clean, labeled container with use of a transfer pipet.

Extracts and wash solutions from processing two replicate 1-g sample aliquots are combined to form a single extract phase. Record the pH value for the combined extract. The combined aqueous phase will be subsequently digested (MCL-7746) and made up to an appropriate known volume (e.g., 50-mL, for combined extracts and wash solutions from aliquots A and B). (Record final volume).

7. Fraction #5: Crystalline Oxides (Appendix 1)

Reagent #5: For 500-mL of lixiviate solution #5 (0.2 M $(NH_4)_2C_2O_4$ in 0.1 M ascorbic acid, pH 3), add 14.21-g of ammonium oxalate monohydrate $(NH_4)_2C_2O_4 \bullet H_2O$, FW 142.1) and 8.81-g L-ascorbic acid, FW 176.1). Adjust pH with dilute nitric acid or NaOH, as necessary to attain target pH value (3.0 ± 0.05).

To the individual solid residues from Extraction Fraction #4, add 25-mL of Reagent #5 to each centrifuge cone. Seal the cone and contact the phases for 0.5-h at 95 ^{o}C, with use of a thermostatic hot block. During heating, the tube lids will not be sealed, and polypropylene cover slips (e.g., environmentalexpress.com PN SC505) will be placed at the open end of the tube to minimize evaporative loss while allowing reaction gases to safely escape. Slurry is subsequently centrifuged (approximately 4000 RPM for about 10-min). Supernate phase is removed to a clean, labeled container with use of a transfer pipet. (**Record pH value of cooled extract solution**).

Extracts and wash solutions from processing two replicate 1-g sample aliquots are combined to form a single extract phase. Record the pH value for the combined extract. The combined aqueous phase will be subsequently digested (MCL-7746) and made up to an appropriate known volume (e.g., 100-mL, for combined extracts and wash solutions from aliquots A and B). (**Record final volume**).

8. Fraction #6: Alkaline-earth sulfates (Appendix 1)

Reagent #6: For a volume of 3.0-L of lixiviate solution #6 (0.11 M Na_2EDTA + 1.7 M NH_4OH) add 122.8-g disodium ethylenediamine tetraacetate (Na_2EDTA, FW 372.2) and sufficient ACS grade ammonium hydroxide solution (approximately 333-mL of stock 29 wt% reagent) [6] to yield a final concentration of 1.7 M as NH_4OH. **Caution: the ammonia reagent is toxic and noxious (use within a fume hood**).

The solid residue from Fraction #5 is transferred by rinsing from its original 50-mL container into a 250-mL HDPE bottle with aliquots from a 200-mL aliquot of Reagent #6. The procedure (Appendix 1) requires that the solid sample residue be contacted with reagent #6 at 95 °C for a total of 4-h. Due to the physical size of the 250-mL bottle, this heating step will be performed in a thermostatic water bath placed within a fume hood. The lid to the bottle will be removed and a watch glass will be used to allow venting of ammonia vapor during the reaction.

At the end of the phase contact interval, the cooled slurry will be filtered by aspiration through a mixed cellulose ester (MCE) membrane (~ 0.7-µm pore) to recover the residual refractory solids. The solids will be rinsed with a 10-mL aliquot of DIW; filtered lixiviate and water rinse will be combined and made to a known volume (e.g., 250-mL). (Record final solution pH value).

9. Fraction #7: Residual (Appendix 1)

The MCE filter from fraction #6, with associated solids, is transferred to a suitable vessel and the filter medium and any residual organic matter is first digested with use of nitric acid and peroxide (MCL-7746). This pretreatment step is best performed with use of a hot block within a fume hood, to vent reaction gases (MCL-7746, § 5.2).

Complete digestion of refractory silicate phases requires the addition of hydrofluoric acid and may require microwave-assist (EPA Method 3052; MCL-7775, Appendix 16).

Note that failure to fume off excess HF reagent before preparing solutions for ICP analysis can cause damage to the instrument nebulizer.

10. **Analysis and Data Report**

Select one sample to run in duplicate (The project has designated Sample 15-5041 for the replicate). There is no accepted standard reference material identified for use in this procedure.

A filtered aliquot of the solution phase from each individual extraction step must be analyzed. Include a reagent blank (no sample) and matrix blank spike for each extraction step. Analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) may require digestion to destroy excess organic reagent (e.g., acetate) and/or substantial dilution of the sample prior to analysis (MCL-7752).

[6] Stock ACS grade NH_4OH solution is nominally 28-30 wt% as ammonia (FW 17), or about 15.3 *M* (SG ~ 0.895). (Check lot analysis). For preparation of 3-L of 1.7 *M* dilute NH_4OH reagent, one would need approximately 333-mL (approximately 300-g) of stock ammonia reagent.

Project-specific parameters to be analyzed include U, Ra, Th, Fe, Mn, Ca, Ba, and sulfur (Appendix 1).

Report data results on the basis of the gas-dried weight of soil taken:

Metal extracted (µg/g) = (metal in extract, µg/L) * (volume of extract, L)/ (dry wt. equivalent for the original sample aliquot, g)

References

Bessinger, B. (S.S. Papadopoulos), in electronic memoranda to B. Stephenson and M. Standers (MCLinc), 9/15/2015 *et seq*.

EPA Method 3052 - Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices (1996).

Hlavay, J.; Prohaska, T.; Weisz, M.; Wenzel, W.W.; Stingeder, G.J. (2004). "Determination of Trace Elements Bound to Soils and Sediment Fractions," *Pure Appl. Chem.*, **76**(2), 415-442.

Liu, D.J., and M.J. Hendry (2011), Controls on ^{226}Ra during raffinate neutralization at the Key Lake uranium mill, Saskatchewan, Canada, *Applied Geochemistry* **26** 2113–2120.

MCL-7746, Acid Digestion for Metals (EPA Method 3050B).

MCL-7752, Acid Digestion of Aqueous Samples (EPA Method 3010A).

MCL-7756, Appendix MM, Operator Aid for Determination of Water Content by Mass.

MCL-7775, Appendix 16, Operator Aid for the CEM Discover SP-D Microwave Digestion System.

Rapin, F.; Tessler, A.; Campbell, P.G.C.; Carignan, R. (1986), "Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure," *Environ. Sci. Technol.*; Vol/Issue: 20:8 836-840

Appendix 1

Sequential Extraction Protocols (Original sample mass is assumed to be approximately 1-g, air-dried)

Table A1. Sequential Extraction Procedure for Characterizing Source Materials

Step	Targeted Phases	Reagent
1	Soluble / Exchangeable: Exchangeable ions	10 mL of 1 M $MgCl_2$, pH 7, 4 hr, 25 °C; water wash (10 mL)
2	Acid Soluble: Carbonates	25 mL of 1 M CH_3CO_2Na, pH 5, 6 hr, 25 °C; water wash (10 mL)
3	Organics/Sulfides: Humic materials and Fe-sulfides	30 mL of 0.1 M $Na_4P_2O_7$, pH 10, 20 hr, 25 °C; water wash (10 mL)
4	Amorphous Oxides: Mn-oxides, ferrihydrite, and secondary U minerals	10 mL of 0.2 M $(NH_4)_2C_2O_4$, pH 3, 4 hr, 25 °C (dark); water wash (10 mL)
5	Crystalline Oxides: Goethite and Magnetite	25 mL of 0.2 M $(NH_4)_2C_2O_4$ in 0.1 M ascorbic acid, pH 3, 0.5 hr, 95 °C; water wash (10 mL)
6	Alkaline-earth sulfates: Barite	200 mL of 0.11 M Na_2EDTA + 1.7 M NH_4OH, 4 hr, 95 °C; water wash (10 mL)
7	Residual: Clays, primary U- and Th-oxides	HF-HNO_3 (Complete digestion)

Notes: Method based on Liu et al. (2011). All extractions use 1 gram of solid and all solutions analyzed for U, Ra, Th, pH, Fe, Mn, Ca, Ba, ~~total carbon~~ and sulfur; Procedure includes digestion/centrifugation, wash/centrifugation, and analysis steps. Finally, steps 1 and 2 will be conducted in a glove box or bag.

SSP = Modified protocol, as recommended by B. Bessinger, S.S. Papadopoulos, in electronic memoranda to B. Stephenson, 9/15/2015 *et seq*. (Memorandum of 12/22/2015 dropped the analysis of total carbon in the extracts).
$MgCl_2$ = magnesium chloride (per B. Bessinger, S.S. Papadopoulos, in electronic memoranda to M. Sanders, 12/21/2015
CH_3CO_2Na = sodium acetate
$Na_4P_2O_7 \cdot 10H_2O$ = Sodium pyrophosphate decahydrate
$(NH_4)_2C_2O_4$ = ammonium oxalate
NH_4OH = ammonium hydroxide
$HClO_4$ = perchloric acid
HNO_3 = nitric acid
Na_2EDTA = disodium ethylenediamine tetraacetate (FW 372.2)

MATERIALS AND CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE	
Operation Guidance Electron Microscopy: Materials and Chemistry Laboratory, Inc.	Approved: _____ _____ MCLinc President Date _____ _____ Quality Assurance Officer Date

1.0 INTRODUCTION

This document and the documents referenced herein provide a framework for the safe and consistent operation of electron microscopes. It is accepted that operating personnel have an understanding of the instrumentation and theory of operation. This guideline will identify the hazards associated with the operation and ensure the safe usage along with providing a high level of confidence in the results obtained.

2.0 GENERAL RESPONSIBILITIES

2.1 Principal Operator

The Principal Operator is responsible for the routine operation, upkeep of the instrumentation, documentation, and work area associated with the instrumentation. The appointment of the Principal Operator for each instrument is made by the *Chief Operating Officer*.

2.2 Secondary Operator

The Secondary Operator should be able to assist the Primary Operator in routine operation and maintenance. The Secondary Operator may be able to perform all operations at the same level of expertise as the Primary Operator, but this is not a requirement. Secondary Operators may be certified by either the *Chief Operating Officer* or the Principal Operator.

2.3 *Chief Operating Officer*

The *Chief Operating Officer* represents the first level of line management which is responsible for supplying the resources for proper upkeep of the required instrumentation.

3.0 EQUIPMENT AND MATERIALS

3.1 Major Components

This table lists the major equipment covered by this guideline. The property number is the property number associated with the main instrument component. It is recognized that additional property numbers may exist for accessories and other secondary components.

Manufacture	***Model #***	***Room #***
JEOL	*JXA-840*	*106*
Hitachi	*H-600*	*110*
JEOL	*JSM-5800LV*	*110*
JEOL	*JEM-2010*	*106*

3.2 Basic Process Description

Electron microscopy (EM) impinges a focused electron beam on a solid surface to produce electron images and x-rays which contain information about the sample. The electrons are used to create electron micrographs (images) and the x-rays are used to obtain elemental information about the sample with associated x-ray analyzers. EMs vary by the nature and relative position of their electron optic components with respect to the sample. EMs can optimize various electron-sample interactions (i.e. scanning, transmission, and diffraction) to obtain various types of materials characterization. The "output" is typically an electron micrograph from a secondary electron detector (SEI), backscattered electron detector (BEI), or transmitted onto a fluorescent screen, electron diffractogram, or elemental composition by x-ray spectroscopy (qualitative or quantitative). The following are brief overviews of typical operational aspects of the instrumentation:

The electron guns operate at very high voltage (1,000 to 200,000 volts) but at very low current (nA to pA range). EMs operate in a vacuum with the electron gun typically being at 10^{-6} to 10^{-7} torr and the sample being between 50 and 10^{-5} torr; hence, sample exchange and manipulation are done via sample exchange interlocks and mechanical stages.

Each instrument has associated equipment required for the vacuum system, cooling, and valving (compressors). Operators are required to understand the interaction of each component and perform routine, preventive maintenance on each component according to the vendor operating manual.

Each scope has an associated x-ray analyzer used to determine elemental composition. X-ray emission is shielded by the metal construction of each instrument.

3.3 *Basic Operating Process*

This describes the *general* guidelines for *sample preparation, instrument operation, and collecting & transferring data for interpretation.*

3.3.1 *Sample Preparation*

Sample preparation for SEM and TEM investigation is the key for a successful investigation. The following notes should be considered prior to loading a sample into the electron scopes:

SEM: Loose powders are not acceptable in the SEMs. SEM preparations are typically mounted on adhesive carbon tape on top of graphite planchets (i.e. Ted Pella, Inc.). Because of sample charging, samples are typically carbon coated to reduce the effect of charging on the images. Feature mapping under a stereoscope prior to analysis is strongly recommended to help navigate on the sample at the higher SEM magnifications.

TEM: Loose powders are not acceptable in the TEM. TEM copper grids with a Formvar film layer can be purchased from Ted Pella, Inc. Three micro liter samples can be mounted directly on these grids, dried, and loaded into the TEM. A dispersion in ethanol with gentle sonication works well. The technique for preparing a TEM grid for NIOSH 7402 is outlined in the NIOSH 7402 procedure and MCLinc SOP 7742.

3.3.2 Instrument Operation

Each instrument has a unique start-up/shutdown procedure outlined in each vendor manual. Instruments must be operated according to the vendor operating manual which outlines procedures for loading/unloading samples, operation, data collection, maintenance, and troubleshooting.

Note that the EMs should never be left unattended when the electron source is activated. When not in use, the EMs should be left in the shutdown condition outlined by the principal operator.

3.3.3 SEM Data Collection and Transfer

The SEMs can collect electron images from 20x to 1,000,000x magnification. Both SEI and BEI images can be collected and stored. Images can be transferred for reporting by:

- Polaroid film: Each SEM unit has been set up to collect images by Polaroid type 52 or 57 land film. Film development takes less than 1 minute and has excellent resolution.

- Printer: Each associated x-ray analyzer has the capability to grab the image from the SEM's CRT and print to a printer. The image can then be scanned and converted to a electronic data file.

- Electronic Data File: The Hitachi 4500 has an EDAX x-ray analyzer that is capable of storing and saving images in various formats including bmp, tif, and jpg formats. Data is readily transferred by memory card or CD.

X-ray spectra can be transferred for reporting by:

- Printer: Each associated x-ray analyzer has the capability to print to a printer. The spectra can then be scanned and converted to a electronic data file.

- Electronic Data File: The Hitachi 4500 has an EDAX x-ray analyzer that is capable of storing and saving spectra in various formats including bmp, tif, and jpg formats. Data is readily transferred by memory card or CD.

3.3.4 TEM Data Collection and Transfer

The JEOL 2000FX TEM can collect electron images from 20x to 1,000,000x magnification. Images can be collected and stored only by Kodak film. Follow manufacturer's instructions for using Kodak D-19 Developer and Kodak Rapid Fixer.

X-ray spectra can be transferred for reporting by a printer associated with the x-ray analyzer. The spectra can then be scanned and converted to a electronic data file.

3.4 Laboratory Supplies

This non-inclusive listing provides a baseline for the types of supplies as well as engineering and administrative controls that should be available, as needed, to ensure a safe (personnel and environmental) work place.

Disposable lint-free or powder-free gloves
Lint-free cloths
Disposable laboratory waste bags
Fume hoods equipped to provide a well-ventilated workspace
Protective eyewear
Protective laboratory coat/apron
Spill cleanup material
Emergency eyewash station
Emergency shower station
Fire extinguisher
Access to MSDS sheets for all chemicals used

Ted Pella, Inc and SPI, Inc. are good sources for various EM supplies for sample preparation such as TEM grids and graphite planchets.

3.5 Standards

The following components, or equivalent ones, should be available for quality control and performance evaluation of the various electron microscopes. The selection and use of the particular standard is based upon operator preference. The standard used should be documented in the appropriate logbook and should be used in agreement with the methods outlined in this document.

Magnification standards:

- NIST 484A Specimen ID JY-55-OJ (2 each)
- NIST 484E Specimen ID-SH
- 2160 lines per millimeter cross grating (E. F. Fullam, Inc., Cat. #60021)

Elemental standards:

- C. M. Taylor Corp. #1 Element STD 202-52
- C. M. Taylor Corp. #2 Element STD 202-52
- C. M. Taylor Corp. #4 Element STD 230-27
- C. M. Taylor Corp. #5 Element STD 230-30
- SPI STD 87-103
- Tousimis 8026 103-S

X-ray performance (FWHM) standards:

- X-checker, Small World (#1)
- X-checker, Small World (#2)
- C. M. Taylor Corp. #1 Element STD 202-52

Resolution standards:

- Prickly gold grid Type D

These standards are centrally located, in dry boxes where applicable. Control is maintained through storage in manufacturers labeled containers or in labeled sample storage containers. The standard certification papers are filed with the QA Officer.

4.0 SAFETY PRECAUTIONS

4.1 General Laboratory Safety

Follow guidance outlined in the Chemical Hygiene Plan for the Materials and Chemistry

Laboratory, Inc. (MCL-7702) and the Quality Assurance Plan to the Materials and Chemistry Laboratory, Inc. (MCL-7701).

Develop and encourage safe laboratory habits.
Food will not be stored or consumed in lab areas.
All work areas are to be kept clean and uncluttered.
Safety glasses are required to be worn as posted.
The appropriate personal protective equipment must be worn when required by the job.
Report accidents and near-miss accidents to your supervisor.
On-the-job injuries must be reported immediately.

4.2 Specific Hazards

The electron guns operate at very high voltage (1,000 to 200,000 volts). When changing a filament or performing maintenance, the vendor operating procedure must be followed exactly to prevent high voltage exposure.

For specific hazards of the instruments see the operator's manual and MCL-7717 for Health and Safety approaches to handling the hazards properly. Do not operate unless you understand potential hazards involved with the instrument.

4.3 Emergency Shutdown

The safest, most direct method of shutting the instrument off should be posted in clear plain sight on the front of the instrument. The instructions should be in large print, signed, dated, and laminated.

5.0 ENVIRONMENTAL AND WASTE MANAGEMENT CONCERNS

5.1 Waste Minimization Methods

Kodak Rapid Fixer - Used fixer will be sent out for resource recovery of silver.
Polaroid Film Packs - Digital images will minimize film waste.

Sample Preparation - Use of smallest possible beaker or test tube for cleaning samples or equipment (e.g. tweezers, spatula). Use only a portion of a paper towel or wipe as needed.

Reuse sample planchets by using small amount of double sticky carbon tape. The carbon tape and sample can be peeled off after the analysis and disposed of as solid waste. The planchet can then be reused to mount samples without being added into the waste stream.

5.2 Waste Disposal Methods

All RCRA/TSCA/RAD waste generated by this process shall be disposed of in accordance with the MCLinc Waste Management Plan MCL-7718.

5.3 Environmental Risks

Routine operation of this equipment poses no environmental risks.

6.0 QUALITY AND PERFORMANCE DOCUMENTATION

6.1 Quality Assurance Documentation

The following information should be documented at a minimum of the time period stated and after maintenance activities have been performed. This information will provide direct documentation of the performance (calibration) parameters affecting the quality of the output (results) of the instrumentation. Documentation is the responsibility of the Principal Operator and will be kept with the instrument.

Image magnification (at least semiannually): A determination of the magnification of applicable image source(s) shall be performed.

Energy calibration (at least semiannually): The energy calibration shall be checked. Standards such as Cu and/or Al should be used.

EDS energy resolution - FWHM (at least semiannually): A Mn Ka peak shall be used to measure the full width at half maximum peak intensity (FWHM).

WDS performance (as needed): The position and FWHM of peaks of interest will be documented.

Performance Documentation

The following information shall be documented in the time period stated.

Instrument usage (every time): Logbooks shall be kept for each EM to record instrument usage, operator and project number.

Scheduled instrument maintenance (per event): A copy of the paper work provided by the service provider should be kept in chronological order. Any information or work which has been provided in response to questions or operational abnormalities that is not clearly documented in the paperwork should be documented and attached.

Non-scheduled instrument maintenance (per event): A copy of the paper work provided by the vendor should be kept in chronological order. Any information or system work which is not clearly documented on the vendor's paperwork or work instructions provided over the telephone should be documented.

Instrument calibration non-conformance (per event): The actions required to bring the instrument back into compliance with operating specifications as noted in section 6.1 should be documented.

6.3 Vendor Manuals

Vendor manuals form the basis of documentation for operating information. These manuals in combination with vendor/professional training and on-the-job training should allow the principal operator to safely, properly, and fully operate the instrumentation.

Vendor manuals shall be readily available during instrument operation.

6.4 Data Tracking

Data documentation and archival information is the responsibility of the originator and should be recorded in the laboratory notebook.

7.0 REFERENCES

MCLinc *Chemical Hygiene Plan* (MCL-7702)

MCLinc *Quality Assurance Plan* (MCL-7701)

MCLinc *Waste Management Plan* (MCL-7718)

Materials and Chemistry Laboratory, Inc. Standard Operating Procedure	
Operation Guide X-Ray Diffraction: Materials and Chemistry Laboratory, Inc.	Approved: _____ _____ MCLinc President Date _____ _____ Quality Assurance Officer Date

1.0 PURPOSE

This document and the documents referenced herein provide a framework for the safe and consistent operation of the x-ray diffractometer (XRD). It is accepted that operating personnel have an understanding of the instrumentation and theory of operation. This guideline will identify the hazards associated with the operation and ensure the safe usage of the instrumentation. This guideline will provide a high level of confidence in the results obtained and provide the foundation for quality control and quality assurance. *Details for analyzing samples are presented in Operator Aid 35 in MCL-7775 Standard Operating Procedure.*

2.0 ROLES AND REFERENCES

2.1. Responsibilities

2.1.1. Principle Operator

The principle operator is responsible for the routine operation, upkeep of the instrumentation, and work area associated with the instrumentation. The appointment of the principle operator for each instrument is made by the *Laboratory Manager*.

2.1.2. Secondary Operator

The secondary operator should be able to assist the primary operator in routine operation and maintenance. The secondary operator may be able to perform all operations at the same level of expertise as the primary operator, but this is not a requirement. Secondary operators may be certified by either the *Laboratory Manager* or the principle operator.

2.1.3. Laboratory Manager

The *Laboratory Manager* represents the first level of line management which is responsible for supplying the resources for proper upkeep of the required instrumentation.

3.0 EQUIPMENT AND MATERIALS

3.1. Major Components

This table lists the major equipment covered by this guideline. The property number is the manufacturer's serial number associated with the main instrument component. It is recognized that additional property numbers may exist for accessories and other secondary components.

Manufacture	Model #	Property #	Room #	Principle Operator	Secondary Operator
Rigaku	MiniFlex II	GD40045	*110*	M.R. Colberg	A.B. Dunaway
Rigaku	*Minifelx 6A*	*BD67000282-05*	*110*	*M.R. Colberg*	*A.B. Dunaway*

3.2. Basic Process Description

X-ray diffraction measures the intensity of x-rays (i.e. Cu Kα) that diffract off a powder sample at discrete angles. The relative angle-intensity relationship provides crystallographic information about the sample. The diffraction pattern serves as a "fingerprint" of the phases of crystalline species present. The following is a brief overview of typical operational aspects of the instrumentation:

- The water cooled x-ray tube operates at high power (2000 watts maximum). Typical operating conditions are 30 kV and 15 mA (e.g. 1050 watts).
- XRD operates at atmospheric conditions.
- X-ray yield is contained/shielded by the instrument.

3.3. Laboratory Supplies

This non-inclusive listing provides a baseline for the types of supplies as well as engineering and administrative controls that should be available, as needed, to ensure a safe (personnel and environmental) work place.

- Disposable gloves
- Disposable laboratory waste bags
- Protective eye wear (during maintenance)
- Spill cleanup material
- Emergency eyewash station
- Emergency shower station
- Fire extinguisher
- Access to MSDS sheets for all chemicals used

-

3.4. Standards

The following components should be available for quality control and performance evaluation of XRD. The selection and use of this particular standard is based upon operator preference. The standard used should be documented in the appropriate logbook.

- Position/Intensity/Resolution Standard: Quartz (Novaculite) (Supplied by Rigaku)

4.0 SAFETY PRECAUTIONS

4.1. General Laboratory Safety

- Abide all guidance outlined in the Chemical Hygiene Plan (MCL-770*2*, *current revision*) and the Quality Assurance Plan (MCL-7701, *current revision*).
- Develop and encourage safe laboratory habits.
- Food will not be stored or consumed in lab areas.
- All work areas are to be kept clean and uncluttered.
- Safety glasses are required to be worn as posted.
- The appropriate personal protective equipment must be worn when required by the job.
- Report all accidents and near-miss accidents to your supervisor.
- All on-the-job injuries must be reported immediately.

4.2. Specific Hazards

These hazards have been identified by the MCLinc. The following sections will list the hazard, its description, what the possible consequences are, and what controls are in place to mitigate the hazard. It is believed that the controls in place are adequate for all hazards identified in this section.

4.2.1. High Voltage

High voltage is required for instrument operations. Exposure to a high voltage source could lead to electric shock of personnel, destruction of equipment, and possible fire. This hazard is controlled by engineering and administrative controls. Engineering controls exist since these instruments have been manufactured to meet all safety and electrical codes. These instruments provide various safety interlocks to ensure that all sources of high voltage are properly shielded and that unintentional contact with high voltage sources is not possible. Administrative control exists since maintenance of the equipment is covered by maintenance agreements with the vendor. This provides highly specialized and skilled personnel to perform all necessary maintenance. These maintenance sub-contractors are also monitored and made to comply with all MCLinc safety rules and regulations. It is recognized that the highest risk from the high voltage can occur during non-routine operational conditions. These conditions are when a water leak is present at or near the instrument. Sources of water leaks can be water-cooling lines for the x-ray source or from drainage from the piping located above the ceiling panel in the room. Whenever uncontained water is detected all operations should cease. This off-normal incident should be reported to the MCLinc *Laboratory* Manager.

4.2.2. Off-shift Operations

Laboratory work being performed outside of normal shift may create a situation where backup support or help is not immediately available. This may lead to a lack or delay of emergency notification in case of an accident. This hazard is controlled by engineering controls and administrative controls. Engineering controls such as emergency pull boxes, telephones, fire sprinkler system, fire extinguisher, building public address system can be used to notify others that of an off-normal situation. Administrative controls exist in that personnel are required to *be approved by senior management* if they will be occupying laboratory or office facilities during off-shift hours. This notification will help support the emergency response personnel in the event of an off-normal event. The performance of new (i.e., first time) activities is not permitted during off-shift hours. These controls and the use of training and on-the-job experience mitigate the hazards associated with this scenario.

4.2.3. Radioactive Materials

The possibility exists that the samples that are being analyzed will be radioactive. (See MCL-7710 for guidance on sample preparation.) Handling radioactive materials could lead to personnel exposure and/or contamination of equipment/property. This hazard is controlled by engineering, administrative and PPE controls. The engineering controls are the methods by which the samples are prepared. (All RAD samples are prepared in a radiological area and are surveyed prior to removal from the area.) The sample is firmly secured onto the sample platform. For proper analysis the sample has to be stable and firmly in place. The administrative controls are enacted by the *RSO. Radioactive samples are received and stored in Laboratory 101.*

4.2.4. Ionizing Radiation

This hazard recognizes the fact that x-rays are produced by the x-ray tube. These x-rays could be a potential source for personnel exposure. This hazard is mitigated by engineering controls. The basic requirements for the production of x-rays require the safety interlock system of the instrument to be operational. This instrument is surveyed for x-ray leakage. This means that it is not possible for a person to place their hand in, at, or near the source of x-ray production. It is also recognized that the source of the ionizing radiation can be totally removed by shutting off the x-ray gun.

4.3. Classified Work

Follow all guidance provided in the MCLinc Facility Security Plan (MCL-7706) for performing classified work.

4.4. Emergency Shutdown

The safest, most direct method of shutting the instrument off should be posted in clear plain sight on the front of the instrument. The instructions should be in large print and laminated.

5.0 ENVIRONMENTAL AND WASTE MANAGEMENT CONCERNS

5.1. Waste Minimization Methods

Sample preparation — use of smallest possible beaker or test tube for cleaning samples or equipment (e.g., tweezers, spatula). Use only a portion of a paper towel or wipe as needed.

5.2. Waste Disposal Methods

All RCRA/TSCA/RAD waste generated by this process shall be disposed of in accordance with MCLinc policies (MCLinc Chemical Hygiene Plan, MCL-7702).

5.3. Environmental Risks

No appreciable environmental risks are noted at this time for XRD operation.

6.0 QUALITY AND PERFORMANCE DOCUMENTATION

6.1. Quality Assurance Documentation

The following information shall be documented in the time period stated. This information will provide direct documentation of the performance (calibration) parameters affecting the quality of the output (results) of the instrumentation. The documents resulting from these QA procedures will be kept in Room A108.

Diffraction Calibration (monthly): The three most intense peaks of the quartz (novaculite) standard will be used to track position and linearity of the goniometer. Here, the difference between the measured 2-theta positions for the quartz (novaculite) standard are compared to a standard quartz diffractogram (ICDD 46-1045). The differences are tracked over time. A regression analysis is performed on the resulting data. A more detailed discussion can be found in Appendix A.

Diffraction Resolution (monthly): A plot of the degrees two theta range from 65 to 70 will be observed for the split of the five peaks that make up this region of the quartz standard diffractogram. An example of this region is in Appendix A.

Detector Performance - (monthly): The measured intensities (in counts per second) of the three most intense peaks of the quartz (novaculite) standard are tracked over time. A regression analysis is performed on the resulting data as a monitor of intensity drift. An example of this tracking is in Appendix A.

6.2. Performance Documentation

The following information shall be documented on the time period stated and after shutdown periods and maintenance. This information will document the scheduled maintenance, non-scheduled maintenance, and root cause for the instrumental non-conformance. The documents resulting from these performance procedures will be kept in room A108.

Scheduled instrument maintenance (per event): A copy of the paper work provided by the vendor should be kept in chronological order. Any information or work which has been provided by the vendor in response to questions or operational abnormalities that is not clearly documented in the vendor's paperwork should be documented and attached to the vendor's paperwork.

Non-scheduled instrument maintenance (per event): A copy of the paper work provided by the vendor should be kept in chronological order. Any information or system work which is not clearly documented on the vendor's paperwork or work instructions provided over the telephone should be documented.

Instrument calibration non-conformance (per event): The actions required to bring the instrument back into compliance with operating specifications as noted in Section 6.1 should be documented.

6.3. Vendor Manuals

Vendor manuals form the basis of the documentation for operating information. These manuals in combination with vendor/professional training and on-the-job training should allow the principle operator to safely, properly, and fully operate the instrumentation.

Vendor manuals shall be kept in good condition and be readily available during instrument operation.

6.4. Data Tracking

Diffraction patterns collected should be stored on disk in the raw data format. All diffraction patterns should be given a unique filename. The file name should be logged with information concerning the sample ID number, the operating conditions, the disk storage ID number, and the date.

7.0 REFERENCES

MCLinc *Chemical Hygiene Plan* (MCL-7702)

MCLinc *Quality Assurance* (MCL-7701)

MCLinc *Sample Preparation Guide* (MCL-7710)

MCLinc Operator Aids: SOP#2 (MCL-7775)

Appendix A
Quality Assurance Documentation

Quality assurance documentation for the XRD is obtained on a monthly basis. The quartz (Novaculite) standard from Rigaku should be run at 30 kV and 15 mA. The program used to do the standard run covers the range 5 to 85 degrees two theta in 0.025 degree steps with a scan speed of 1.0º per minute. The resulting diffraction data is converted into an ASCII format and loaded into the XPowder software for analysis. Peak positions and intensities for the three most intense quartz reflections (see below) are measured manually on "zoomed" peaks. Peak positions are compared a standard quartz diffractogram (ICDD 46-1045) from the International Center for Diffraction Data (ICDD) PDF-2 database. The plots of the diffractogram and the computer printout are archived in *Laboratory 110*. Subsequent computer analysis of the data is done using Microsoft Excel and a scientific graphics software package (SciDavis).

There are three areas of calibration interest. The first of these is the two theta position of the diffractometer. To evaluate this parameter of XRD operation, the positions of the three most intense reflections from a standard quartz pattern (ICDD 46-1045) are compared to the corresponding peaks in the diffractogram determined from the Novaculite standard. 2θ, d-spacing, and intensity data for the three peaks from the standard pattern are listed in table 1.

Table 1: Diffraction data for the three most intense reflections in ICDD 46-1045).

Peak	2θ	d-spacing	Relative intensity (I/I_{100})
1	20.86	4.255	16
2	26.64	3.343	100
3	50.14	1.818	13

The differences between the monthly run and the standard peak locations for each of the three peaks are calculated and recorded. A linear regression analysis is performed on the recorded results (Figure 1). Should the regression analysis show an unacceptable amount of drift, the root cause will be determined and actions will be taken to correct the inconsistency.

The second area of interest is the check of x-ray tube and detector performance. Intensities measured using the Novaculite standard are recorded over time. Drift is assessed using linier regression on the dataset recorded over time. A series of low and high angle diffraction peaks is used to tract any variation in peak intensity. An example of this tracking is shown in Figure 2. If

the intensity falls below an acceptable level, the root cause will be determined and actions will be taken to correct the variance from acceptable operating conditions.

The third area of interest is the check of detector performance. A plot of the 65 to 70 degrees two theta region versus intensity will be observed for the split of the five peaks that make up this region of the quartz standard diffractogram. An example of this region is shown in Figure 2. In addition, the Ka1 peak FWHM at 59.2 degrees two theta will be determined and plotted for variation. If the resolution increases to an unacceptable level, the root cause will be determined and actions will be taken to correct the variance from acceptable operating conditions.

Figure 1
Example of a plot tracking drift in the 2θ position of a selected line in measured quartz (Novaculite) diffractograms recorded at different times.

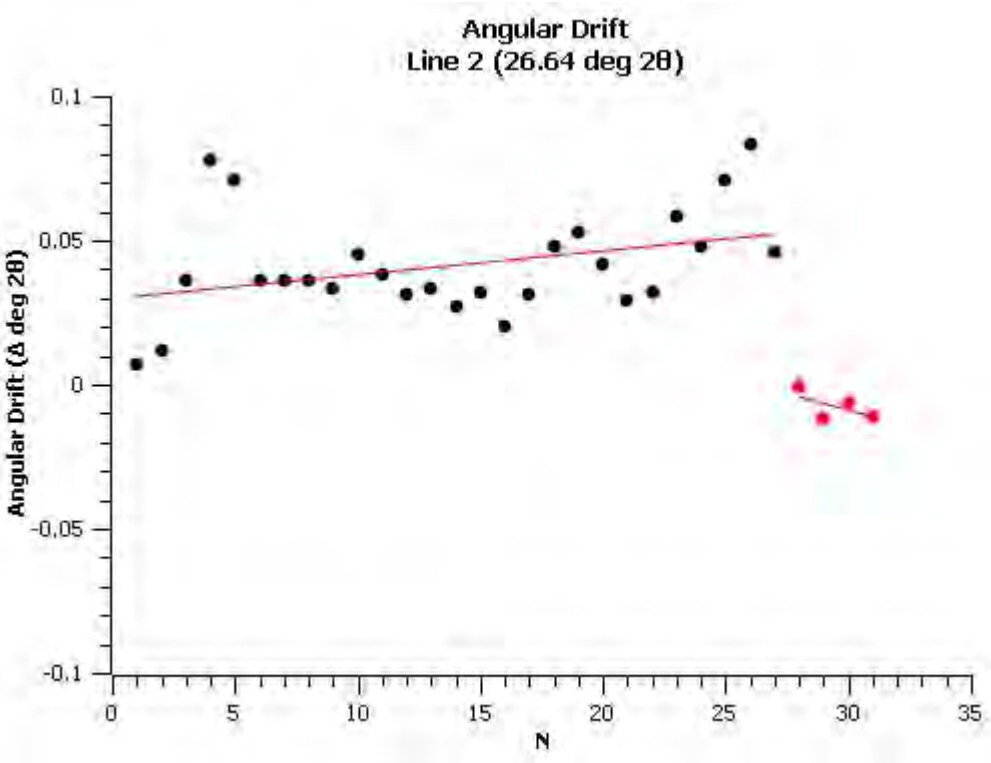


Figure 2
Example of a plot tracking changes in the intensity of a selected line in measured quartz (Novaculite) diffractograms recorded at different times.

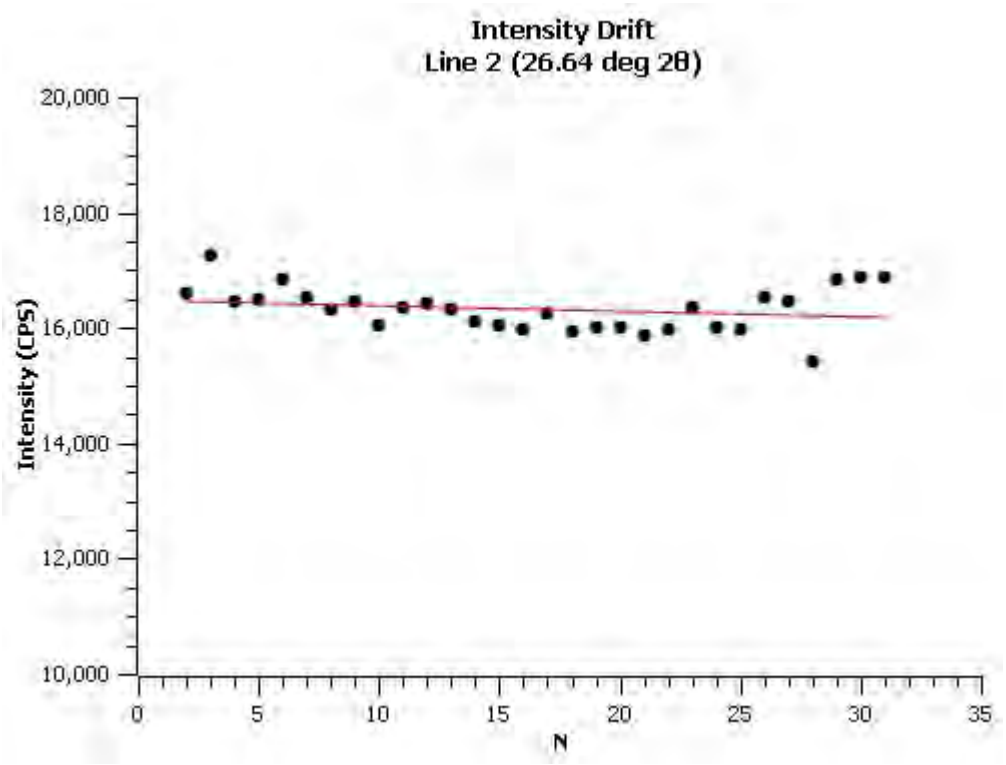
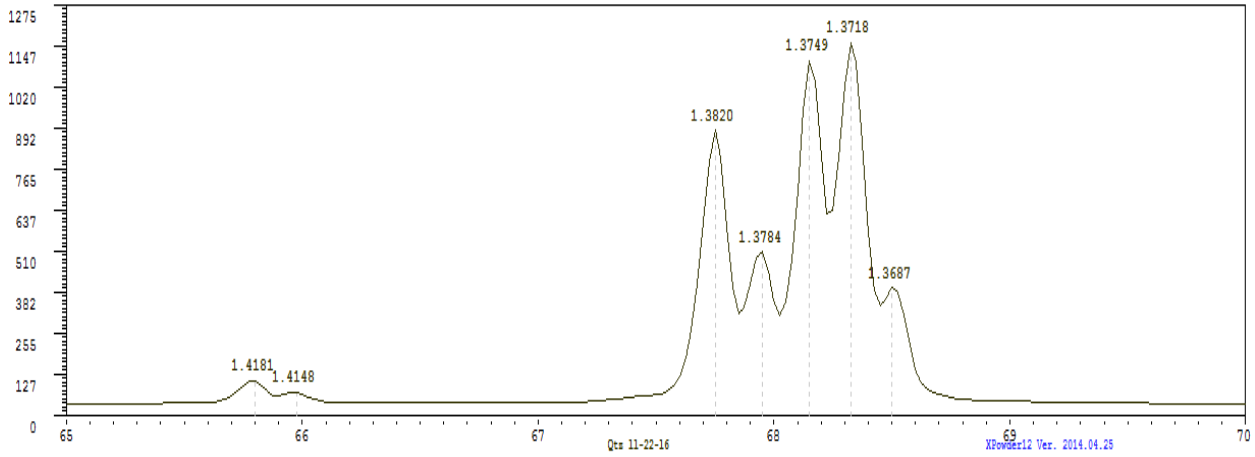


Figure 3
An example of a resolution check.



MATERIALS AND CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE	
Inductively Coupled Plasma-Atomic Emission Spectrometry Metals Analysis: Materials and Chemistry Laboratory, Inc.	Approved: _____ _____ MCLinc President Date _____ _____ Quality Assurance Officer Date

1.0 PURPOSE

This document describes the procedures to determine elements/metals in properly prepared samples based upon NIOSH Method 7300 and USEPA SW-846 Method 6010 Metals using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

2.0 SCOPE AND APPLICATION

2.1 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) determines trace elements/metals, in solution. This method can be used for all elements listed in Table 1. All matrices, excluding filtered acid preserved groundwater samples; other aqueous samples, (i.e. TCLP/EP extracts; unfiltered groundwater), industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Both non-digested and digested samples must be matrix matched with the same type and concentrations of acids as found within the standards.

Table 1 lists the three analytical wavelengths to be measured per element and method detection limits for the elements. Elements other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest is demonstrated.

2.2 Users of this method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using this method for analysis.

2.3 Use of this method is restricted to chemist/qualified operators who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method. They must also have been appropriately trained on the instrumentation and its software, along with use of Attachment 1 for determining results.

3.0 RESPONSIBILITES

MCLinc Project Manager is responsible for seeing that a Total Radiological Activity Screening analysis is performed on radiochemical samples as received in a timely manner prior to ICP analysis. The Project Manager is also responsible for assuring project QA/QC is clearly defined to the ICP operator and sample preparation.

The MCLinc Analyst is responsible for routine operation, inventory of all required materials, upkeep of equipment, reviewing and reporting of results, and the housekeeping of the work area associated with the equipment.

The *Laboratory Manager* represents the first level of management and provides project oversight and is responsible for supplying the resources for proper upkeep of the required instrumentation.

4.0 SUMMARY OF METHOD

4.1 Prior to analysis, samples, except filtered and acid preserved groundwater, must be digested using appropriate sample preparation methods. This includes all total and “acid-leachable" analyses.

4.2 This method describes multi-elemental determinations by ICP-AES using a sequential optical systems and axial/radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry at the defined wavelengths. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required particularly for trace elements. A minimum of one background measurement must be measured at a wavelength adjacent to all analyte wavelengths on all samples and QA/QC during analysis. (Note two point background measurements are the preference and to be done routinely. The selection of one point is for unusual measurements.) The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In the selection of the reported wavelength the analyst should select the best representation of the measured wavelength that is determined to be as free as possible from spectral interference and appropriately compensated for background intensity. Background corrections are made as needed to compensate for excessive interferences if they occur on all three of the calibrated monitored wavelengths.

The logic for the selection of the reporting wavelength and affiliated concentration is shown in Attachment 1.

For each element - two primary and a secondary wavelength are measured. These wavelengths are predetermined (Ref. Table 1) based upon their response and the relative absence of spectral interferences.

5.0 DEFINITIONS

5.1 Applicable definitions are located throughout this SOP.

6.0 INTERFERENCES

6.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra, and instrumental noise (i.e. plasma flutter, pump pressure/nebulizer flutter etc.).

6.2 Background emission and stray light can usually be compensated for by subtracting the background intensity on either side of the analyte wavelength peak. The use of multiple wavelengths for an analyte allows the selection of the wavelengths with the least amount of interference and/or background emission for reporting. The locations selected for the measurement of background intensity are determined by the complexity of the spectrum adjacent to the analyte wavelength peak. The placement of the wavelength peak baseline can be made during method set up before an analysis or during analyst data review after the analysis. The wavelength peak baseline used for routine measurement must be free of off-line spectral interference or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

6.2.1 The analyst in establishing the method and reviewing the resulting spectra will verify presence or absence of spectral interference by:

- Evaluating scanned wavelength on either side of the analyte wavelength peak
- Determining the shape of the analyte wavelength peak of a sample compared to a calibration standard
- Evaluating the analyte wavelength peak integration

6.2.2 Samples that show a elevated background emission/interferences across the range for all three defined wavelengths may be background corrected by applying the instrumental software correction program that uses algorithms to compensate and interpolate contributions from adjoining interfering spectra (i.e. interelement interference etc.). Individual spectra that show interference will be corrected only if deemed necessary due to problems with the other spectra for the affected analyte.

6.2.3 To determine the appropriate location for background correction, the user must scan the area on either side adjacent to the specified wavelength and define these areas appropriately in the establishment of the analytical methods files or during data review.

6.2.4 The potential for spectral overlaps are avoided/greatly reduced by measuring multiple wavelengths for each of the target elements.

6.2.5 Because interelement corrections vary depending upon the choice of background correction points and the complexity of the sample, multiple wavelength measurements are being used in this SOP for routine operation instead of interelement correction factors and corrections. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences that can only be

compensated for by interelement manipulation, use of multiple wavelength, or software algorithms or methods of standard additions.

6.2.6 The interference effects must be evaluated when instrument parameters are changed. Intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). Even though these variables are compensated for by the calibration of each defined wavelength for each target element, the analyst is required to review the results for each wavelength. This review will determine and document per wavelength the effect of the interferences and the selection of the wavelength to be reported.

6.2.7 When the instrumental software interelement correction algorithms are applied, their accuracy should be verified, by analyzing the appropriate spectral interference check solutions.

6.2.8 When interelement corrections are used, verification of absence of interferences is required or proof that the interference is not included in the data. To demonstrate this absence of interference, an Interference Check Solution (ICS) containing similar concentrations of the major components of the interference contributing elements at > 10mg/L must be run with each new project; the resulting data must be kept on file with the sample analysis data and the affected element (those elements with > 20% variability from expected value) flagged appropriately.

6.3 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. A Yttrium internal standard is not used routinely but will be used if the analyst and QC deem necessary to allow for appropriate correction if physical interferences are present.

6.4 Another physical interference that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. Routine maintenance and operational awareness/data review will minimize the occurrence of this interference.

6.5 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample (e.g. the addition of competitive ionization potentional compounds), by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte.

6.6 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and are minimized by high flow flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times.

7.0 SAFETY

7.1 General laboratory protection (safety glasses, lab coat, and disposal latex/nitrile gloves) should be worn at all times when handling standards or samples.

7.2 Stock metal standards and acid solutions may pose potential health risks. Extreme care should be utilized when handling these solutions.

8.0 APPARATUS AND MATERIALS

8.1 Perkin Elmer 2000 Model Inductively Coupled Argon Plasma Atomic-Emission Spectrometer with both axial and radial measurement capability.

8.2 Sequential multiple wavelengths per analyte with affiliated computer-controlled emission spectrometer and background correction.

8.3 Radio-Frequency generator compliant with FCC regulations.

8.4 Mass flow-controller for argon nebulizer gas supply. (Geminheart nebulizer and cyclonic spray chamber)

8.5 Peristaltic pump.

8.6 Perkin Elmer Autosampler.

8.7 Argon gas supply: high-purity grade (99.99%).

8.8 Nitrogen, dry – 99% purity

9.0 REAGENTS

9.1 Acids used in the preparation of standards and for sample processing must be of high purity. Nitric acid (conc), HNO_3, trace metals grade

9.2 Reagent water: All references to water in the method refer to ASTM Type II (>1Mohm-cm) water.

9.3 Standard stock solutions are either purchased commercially as certified standards or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity) within the lab.

Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Standards greater than 100ug/L are stable for one year from preparation date in a 10% acid solution. Standards less than 100ug/L are stable for only 6 months in a 10% acid solution. Stock standards are per manufactures expiration date and in-house at greater than 1,000mg/L are stable for 3yrs in 10% acid.

9.4 Two types of blanks are required for the analysis of samples. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample preparation processing.

9.4.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations. The calibration blank is also analyzed prior to calibration and immediately after all CCV's. The resulting spectral values for each measured wavelength are automatically subtracted from the calibration standards measurements.

9.5 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis. This result is not subtracted from the samples measurements but reported as a separate QC result.

(OPTIONAL) Working ICS Solutions for checking interferences and case-by-case interference correction if required. The stock solutions for the ICS solutions will be procured certified from a commercial source.

9.6 The quality control standard is a second source standard used for Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV).

The second source solution is an independent standard near the midpoint of the calibration linear range at a concentration other than that used for instrument calibration for the majority of the calibration analytes. This standard will contain each analyte found in each of the stock solutions used to prepare the commercial standard. An independent standard is defined as a standard composed of the analytes from either a source different from those used in the standards for instrument calibration or from the same vendor but a different lot.

10.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

10.1 Sample collection procedures should address all considerations described in Quality Assurance Project Plan.

10.2 Plastic or glass containers are acceptable for use in Method 6010B.

10.3 Aqueous samples should be preserved with 1:1 HNO_3 to a pH < 2.

11.0 QUALITY CONTROL

11.1 The type and frequency of the quality control program will be defined by the project. Dependant on the project defined program the following quality control data, and as defined in Table II may be included The resulting data should be maintained and be available for easy reference or inspection.

11.2 Lower Instrument Detection Limits (IDLs) in µg/L can be estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined annually and kept on file. The IDL will be determined by the multiplication of the average standard deviation for each of the three days analysis measurement for each analyte wavelength by 3.14. The IDL will be defined by the least sensitive wavelength as defined in Table 1 for each measured element unless lower limits are required by the specific project.

11.3 The upper detection Limit is defined by the point where data results are not reportable due to either:
1) The calibration line is no longer linear
2) For non linear lines it is the point where the line curvation is lost and the line becomes relatively flat.

11.4 The reporting limits will be defined by the limits of the upper and lower calibration standard. All values outside the calibration range (i.e. the upper and lower reporting limit) will either be diluted to be within the calibration range or reported as estimated values. Table 1 list routine reporting limits based on least sensitive of the three wavelengths except where noted. Lower; lower reporting limits can be achieved on numerous analytes based on one or two lines if need by specific project.

11.5 A minimum three (3) point calibration curve will be developed prior to sample analysis. Two points will be the concentrations defining the upper and lower calibration limit for every wavelength being used in the analytical run (i.e. 3 wave lengths for each target analyte)

11.6 Dilution Test: This test may be applied for unusual matrices. If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the method blank) an analysis of a

fivefold (1+4) dilution must agree within ±15% of the original determination. If not, an interference effect must be suspected. One dilution test, if applicable, would be included for each twenty samples (or less) of each matrix in a batch.

11.7 Post-Digestion Spike Addition: This test may be applied for new or unusual matrices. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within ±25% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect.

11.8 There will be two different Laboratory Control Samples (LCS) analyzed with each batch of samples. These being:

1) LCS shall be prepared and analyzed in duplicate and are solutions spiked to yield concentrations in the lower to mid-range of the calibration curve with all target analytes.
2) LCSL may be requested by the Quality Manage for special projects and are solutions spiked to yield concentrations in the 2-4X the lower calibration standard for each target analyte.

The acceptance criterion for the LCS is the average of the accepted spectral lines 100±30% of the known value or within the laboratory derived acceptance criteria, should that be determined.

11.9 Calibration Verification

11.9.1 Initial Calibration Verification (ICV) verifies the instrument calibration.

The ICV will be prepared from either a second commercial source or a different lot than the primary standard used for calibration from the same commercial supplier.

The ICV will be analyzed immediately after the calibration.

The results of the ICV must agree 100% ± 10% on at least one of the analytical line not exceed 100% ± 20% on the other two analytical lines where there are no known interferences present in the ICV standard solution. The average of the interference lines must not exceed 100 % ± 17%. The 100 % ± 20% is not applicable for the few analytes where a really viable and stable second or third line (noted in Table 1) does not exist.

11.9.2 Continuous Calibration Verification (CCV) solution verifies the calibration during and after sample analysis.

The CCV solution will be analyzed after every ten (10) samples including non-blank QC samples (LCS,MB,MS/MSD samples).CCV results must agree within

100±10%R on at least one elemental line and not exceed 100±20% on the other two (2) elemental lines unless there is interference with one or both lines or if one or two other viable lines do not exist for analyte. Average recovery should not exceed 100±17%R for 3 lines.

11.10 A Matrix Spike (MS) and Matrix Spike Duplicate (MSD) is project specific and is prepared and analyzed at a rate of every batch of 20 or fewer samples of the same matrix.

11.10.1 The Percent (%) Recovery is calculated as follows:
(Acceptance Criteria ± 25%)

$$\%R = \frac{(MS-S)}{TV} \times 100$$

Where:
MS = value of the Matrix Spike
S = value of the sample (unspiked)
TV = Theoretical Value of the Spike (Concentration of spiked solution))

11.10.2 The relative percent difference (RPD) between duplicate determinations must be calculated as follows: (Acceptance Criteria ± 20%)

$$RPD = \frac{|D_1 - D_2|}{\frac{(D_1 + D_2)}{2}} \times 100$$

Where:
RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate)

A control limit of 35% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection reporting limit. If this limit is exceeded, the reason for this situation must be investigated and corrected if appropriate, and if any samples are affected, they should be reanalyzed.

11.11 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line or plasma viewing angle for which quality control data is established.

11.12 MDL's are performed annually; results will be on file in MCLinc's QA/QC files.

12.0 CALIBRATION

12.1 Initiate appropriate operating configuration of the instruments computer according to the instrument manufacturer's instructions.

12.1.1 Turn on the Argon flow (80 PSI minimum)

12.1.2 Turn on the water chiller.

12.1.3 Connect all pump tubing.

12.1.4 Ignite Plasma and allow for warm-up and performance of automated initialization sequence.

12.2 Perform torch alignment.

12.3 Set up the instrument with the proper operating parameters according to the methods development defined parameters.

12.4 During calibration perform a blank and wavelength correction for all of the elements wavelengths in the method preferably using the three lower standards.

12.5 Calibrate the instrument for the analytes of interest using the calibration blank and calibration standards, at the beginning of every run. Flush the system with the rinse blank between each standard solution. Use the average of at least three plasma readings per analyte for both calibration and sample analyses.

13.0 PROCEDURE

13.1 Solubilization and digestion procedures are presented in the sample preparation methods (e.g., EPA Methods 3005 - 3050). See SOP# MCL-7746, MCL-7752, and MCL-7753. For dissolved metals analysis, take an appropriate aliquot of the filtered sample and acidify with concentrated HNO_3 acid so that the final concentration of HNO_3 is 10%.

13.2 Initiate appropriate operating configuration of the instruments method file defining reporting units (ug/L liquid and mg/kg solids) calibration parameters, re-sloping parameters and frequency, CCV frequency, acceptance criteria and corrective actions, LCS Duplicate and matrix spike criteria. In the method file also define by element the 3 wavelengths to be used, axial or radial measurement and the specific plasma operational parameters.

13.2 Set up the Sequence window, which defines the methods to be used, the sample information file to be used, the samples to be analyzed by each method and the Results file name. The Results file is the file in which the data is stored.

13.3 Save the sample and method files, and run the sequence.

13.4 The sample run sequence will have an Instrument Blank (Inst. Blank) Cal Blank immediately following every CCV i.e.:

Calibration Blank
Calibration Standards-Low to High
ICV
Inst. Blank
LRL
LCS
samples including MB, MS, MSD
CCV
Inst. Blank
samples
CCV
Inst. Blank
Etc.

13.6 Flush the system with the rinse blank solution until the signal levels return to the method's levels of quantitation (defined in the established method based on time and flow rate) before the analysis of each sample. Nebulize each sample until a steady-state signal is achieved (defined by the method, depending on flow rate and tubing length etc.) prior to collecting data.

13.7 Dilute and reanalyze samples that have concentrate ions exceeding the linear range for an analyte.

14.0 CALCULATIONS

14.1 Calculations: The quantitative values shall be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and micrograms per gram (ug/g) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values

14.2 For dissolved metals analyses:

$$ug/L = C \times DF$$

Where:
C = Digest concentration (ug/L)
DF = Dilution Factor

14.3 For digested aqueous samples:

$$ug/L = \frac{C \times DF \times V}{W}$$

Where:

C = Digest concentration (ug/L)

DF = Dilution Factor
V = Final volume in L after sample preparation
W = Initial volume in L of sample before sample preparation

14.4 Soil/Solid concentrations may be reported on the basis of the dry weight of the sample (A separate determination of percent solids must be performed):

$$\text{ug/g (dry weight)} = \frac{C \times DF \times V \times S}{W}$$

Where:

C = Digest concentration (ug/L)
DF = Dilution Factor
V = Final volume in L after sample preparation
W = Weight in g of wet sample
S = 100 / % Solids

14.5 Air filter samples may be reported as total microgram or milligrams per filter or if air volume is given as mg/cubic meter

Total micrograms = C x DF x V
Total milligrams = micrograms / 1000
Total mg/cubic meter = $\frac{C \times DF \times V}{\text{Air volume in } M^3}$
Where:

C = Digest concentration (ug/L)
DF = Dilution Factor
V = Final volume in L after sample preparation

14.6 All results should be reported with up to three significant figures.

15.0 METHOD PERFORMANCE

15.1 Refer to Table 1 for Method Detection Limit information.

16.0 POLLUTION PREVENTION

16.1 To minimize hazardous materials generated with this method, minimal quantities of samples are digested (50 mls final volume), and minimal quantities of standards are prepared.

17.0 WASTE MANAGEMENT

17.1 It is the laboratory's responsibility to comply with all applicable federal, state, and local regulations governing waste management.

18.0 REFERENCES

18.1 SW 846 3rd Edition, Method 6010B, Inductively Coupled Plasma – AES

18.2 NIOSH Method 7300, Fourth Edition, Issue 2, August 15, 1994

18.3 EPA SW846, Method 6010C, Inductively Coupled Plasma - AES

Table 1: Wavelength and Reporting Limits

Analyte Element	View	Wave Length #1	Wave Length #2	Wave Length #3	Lower Cal/Reporting Limit (ug/L)[1]	Upper Cal/Reporting Limit (ug/L)[1]
Al	Attn. Axial	396.153	394.401	237.313	100	3000
Ca	Radial	422.673	317.933	315.887	100	3000
Mg	Radial	279.553	280.271	285.213	100	3000
K	Attn. Axial	766.490		769.896	100	3000
K	Axial		404.721		100	3000
Cr	Axial	267.716	205.560	206.158	10	1500
Ni	Axial	227.022	221.648	231.604	10	1500
Ag	Axial	238.068	338.289	233.137[2]	10	1500
Zn	Axial	206.200	213.857	202.548	10	1500
As	Axial	193.696	188.979	197.197	8	4000
Tl	Axial	190.801	276.787	351.924	8	4000
Cd	Axial	214.440	228.802	226.502	4	2000
Se	Axial	196.026	206.279[2]	203.985[2]	25	6000
Pb	Axial	220.353	217.00	283.306	50	6000
Fe	Radial	238.204	239.562	259.939	100	10000
Co	Axial	228.616	238.892	236.380	20	6000
Ba	Axial	455.403	493.408	233.527	4	1000
Mn	Attn. Axial	257.610	259.372	260.568	4	1000
Be	Attn. Axial	313.107	234.861		4	1000
Be	Axial			313.042	4	1000
Cu	Axial	324.752	327.393	224.700	20	5000
V	Axial	292.402	311.071	270.093	20	5000
U	Axial	385.358	367.007	409.014	20	20000
Sb	Axial	206.836	217.582[2]	231.146[2]	50	6000
Ti	Axial	334.940	336.121	337.279	34	8000
Li	Radial	670.784			10	2400
Li	Axial		413.256	610.362[2]	10	2400
Mo	Axial	202.031	203.845	204.597	10	2400
Sr	Radial	407.771	421.552	460.733	7	1600
P	Axial	214.914	177.434	178.221[2]	124	11000
B	Axial	249.677	249.772	208.957	20	8000
Sn	Axial	189.927	235.485[2]	283.998[2]	40	4000
Th	Axial	283.73	401.913	339.204	20	4000
Zr	Axial	343.823	339.197	257.139	10	4000
Si	Axial	251.611	212.412	288.158	50	8000
Cs	Axial	455.531	459.320	None	5000	200000

[1] Based on Standards preparation as of 01/01/05

[2] Line is not strong due to either poor response or strong interference; but best available

Note: these parameters are subject to change based upon further evaluation by the operator

Table 2: Wavelengths and Method Detection Limits

Analyte/ Element	Primary Wave length A (nm)	Primary Wave length B (nm)	Secondary Wave length (nm)	Lower Cal/ Report Limit (ug/L) Single Line	Upper Cal Report Limit (ug/L) Three Line	IDL (ug/L)	MDL Soil (ug/g)	MDL Water (ug/L)
Al								
Ag[2]	328.98	338.289	243.778	10	100	TBD*	TBD*	TBD*
As	228.812	188.979	193.696	10	160	TBD	TBD	TBD
Ba	455.403	493.408	233.527	0.5	2	TBD	TBD	TBD
Be	313.107	234.861	313.042	2	10	TBD	TBD	TBD
Cd	214.440	228.802	226.502	2	5	TBD	TBD	TBD
Cr	267.716	205.560	284.325	1	5	TBD	TBD	TBD
Cu	324.752	327.393	224.700	15	20	TBD	TBD	TBD
Hg	184.886	194.168	253.652	20	75	TBD	TBD	TBD
Mn	257.610	260.568	259.372			TBD	TBD	TBD
Mo	202.031	203.845	204.597	1	5	TBD	TBD	TBD
Ni	231.604	221.648	227.022	4	10	TBD	TBD	TBD
Pb	220.313	217.00	283.306	40	100	TBD	TBD	TBD
Sb	252.851	206.836	217.582	2	20	TBD	TBD	TBD
Se[2]	196.026	206.279	203.985	20	50	TBD	TBD	TBD
Sr	407.771	421.512	460.733	0.1	25	TBD	TBD	TBD
U	385.958	367.007	409.014	20	40	TBD	TBD	TBD
V	292.402	309.310	311.071	1	10	TBD	TBD	TBD
Zn	206.200	213.865	202.548	5	20	TBD	TBD	TBD

Note: The project will define the target concentration and reporting limit; the reporting limit for this SOP will be defined by the least sensitive of the three wavelengths used; unless otherwise noted.

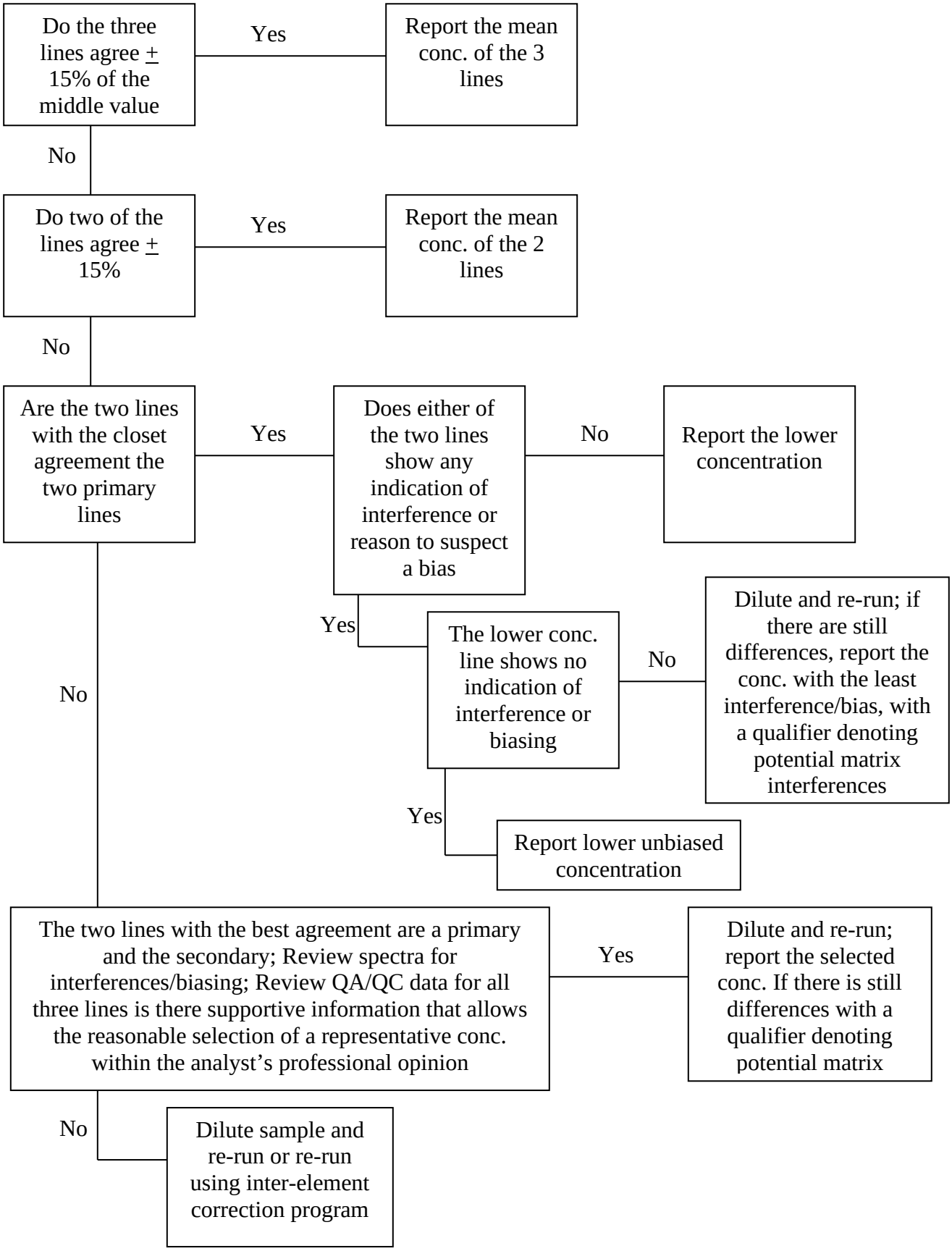
* To be determined and place in instrument log and QA files.

Table 3: QA/QC

Description	Frequency	Acceptance criteria*	Corrective Action
Calibration Curve Defining linear calibration range. 3 points minimum lower and upper defining reporting limits. 3rd point preferably near the lower	Before the analysis of the sample where after instrumental repair or maintenance and when a CCV shows and existing calibration failed	Correlation Coef(R) > 0.99*8*	Check Standards, calibration range, operational parameters ; rerun calibration
Initial Calibration Verification Std. (ICV) Standard containing all target analytes prepared from a second source solution	Immediately after development of calibration curve & before sample analysis	100%R±10% for at least 1 of 3 lines; 100%±20% on other 2 lines except for interference or existence of other viable lines for element.	Reanalyze solution; check solution preparation; recalibrate
Continuing Calibration Verification Std. (CCV) Standard containing all the target analytes prepared from a same source solution	After every 10 samples including non-blank QC's and at the end of analysis sequence	100%R±10% for at least 1 of 3 lines; 100%±20% on other two lines except for interference or existence of other viable lines for element.	Check both CCV and calibration standards preparation; re-calibrate
Calibration Blk.	Immediately following every CCV	Analyte concentration less than half of LRL	Check tubing and acid; remake solution
Laboratory Control Samples Spiked clean material containing all or defined analytes processed through the entire preparation and analysis process according to EPA SW846 6010C	*Two* per batch of sample exceeding no more than 20 samples per batch	%R 100%±30% or as defined by developing recovery studies also is dependent on sample preparation methodology. Criteria according to EPA SW846 6010C	Re-run and if fails again, review all affiliated QA/QC and if deemed necessary by QAM re-prepare and analyze all affiliated samples
Method Blank (MB) Sample composed of all the reagents and process through the entire method	One per batch of sample exceeding no more than 20 samples per batch	No detected compounds exceeding 1/2 the lower reporting limit	Qualify reported data
Lower Reporting Limit (LRL) Reanalyze the lowest concentration calibration standard as a sample	Once per day per metal	100 ± 50%	Internal MCLinc requirement – Review with QAM

*For Air and Wipes, See AIHA Criteria

Attachment 1



ICP Metals
CALIBRATION SOLUTION STANDARD #1
PREPARATION LOG

Prepared By: _____ Date Prepared: 7/17/18 Exp. Date: 1/18/2019

Matrix: 5% HNO3 / 5% HCl

		Standard ID	032218 ICP-STD #5	032218 ICP-STD #1	032218 ICP-STD #2	032218 ICP-STD #3	032218 ICP-STD #4
		Final Vol (ml)	1000	1,000	500	500	50
Analyte	Conc. (ug/ml)		STD 5 Transfer vol.(ml)	4.000	10.000	25.000	25.00
ICP0461 Exp. 10/2018			5.00				
Na*	1,000	ug/L	5,000	20	100	250	2,500
Al	1,000	ug/L	5,000	20	100	250	2,500
Ca	1,000	ug/L	5,000	20	100	250	2,500
Mg	1,000	ug/L	5,000	20	100	250	2,500
K	1,000	ug/L	5,000	20	100	250	2,500
Cr	500	ug/L	2,500	10	50	125	1,250
Ni	500	ug/L	2,500	10	50	125	1,250
Ag	500	ug/L	2,500	10	50	125	1,250
Zn	500	ug/L	2,500	10	50	125	1,250
ICP0427 Exp. Date 6/2019			2.00				
As	1,000	ug/L	2,000	8	40	100	1,000
Tl	1,000	ug/L	2,000	8	40	100	1,000
Cd	500	ug/L	1,000	4	20	50	500
Pb	1000	ug/L	2,000	8	40	100	1,000
Se	500	ug/L	1,000	4	20	50	500
ICP0468 Exp. Date 04/2024			5.250				
Se	1,000	ug/L	5,250	21	105	263	2,625
Total Se	**Total**	**ug/L**	6,250	25	125	313	3,125
ICP0455 Exp. Date 08/2024			10.50				
Pb	1,000	ug/L	10,500	42	210	525	5,250
Total Pb		**ug/L**	12,500	50	250	625	6,250
ICP0443 Exp. Date 08/2019			10.00				
Fe	1,000	ug/L	10,000	40	200	500	5,000
Ba	100	ug/L	1,000	4	20	50	500
Mn	100	ug/L	1,000	4	20	50	500
Be	100	ug/L	1,000	4	20	50	500
Cu	100	ug/L	1,000	4	20	50	500
Co	200	ug/L	2,000	8	40	100	1,000
V	100	ug/L	1,000	4	20	50	500
ICP0420 Exp. Date 07/2021			3.00				
Co	1,000	ug/L	3,000	12	60	150	1,500
Total Co	Total	ug/L	5,000	20	100	250	2,500
ICP0449 Exp. Date 4/2023			9.00				
Cu	1,000	ug/L	9,000	36	180	450	4,500
Total Cu	**Total**	**ug/L**	10,000	40	200	500	5000
ICP0419 Exp. Date 08/2023			4.00				
V	1,000	ug/L	4,000	16	80	200	2,000
Total V	**Total**	**ug/L**	5,000	20	100	250	2,500
ICP0437 Exp. Date 05/2024			5.0				
U	1,000	ug/L	5,000	20	100	250	2,500
ICP0448 Exp. Date 02/2019			5.00				
Ti	1,000	µg/L	5,000	20	100	250	2,500
Li	300	µg/L	1,500	6	30	75	750
Mo	300	µg/L	1,500	6	30	75	750
Sr	200	µg/L	1,000	4	20	50	500
P	1000	µg/L	5,000	20	100	250	2,500
ICP0469 Exp. Date 02/2024			5.0				
P	1,000	µg/L	5,000	20	100	250	2,500
Total P		µg/L	10,000	40	200	500	5,000
ICP0450 Exp. Date 09/2022			6.0				
B	1,000	ug/L	6,000	24	120	300	3,000
ICP0423 Exp. Date 03/2021			10.00				
Sn	1,000	ug/L	10,000	40	200	500	5,000
ICP0446 Exp. Date 01/2019			5.00				
Th	1,000	ug/L	5,000	20	100	250	2,500
ICP0458 Exp. Date 10/2023			2.50				
Zr	1,000	ug/L	2,500	10	50	125	1,250
ICP0436 Exp. Date 05/2021			12.50				
Si	1,000	ug/L	12,500	50	250	625	6,250
ICP0444 Exp. Date 01/2019			2.50				
Nb	1,000	ug/L	2,500	10	50	125	1,250
ICP0438 Exp. Date 6/2023			12.50				
Sb	1,000	ug/L	12,500	50	250	625	6,250

Room#		Balance/ Weight Set	Check Mass, g	Weight #1, g	Weight #2, g	Average Wt., g	Tolarance Acceptance
Humidity							± 2%
Temperature							± 2%

	Pipette s/n	Volumn, mL	Weight #1, g	Weight #2, g	Average Wt., g	Tolarance Acceptance
						± 2%
						±2%
						±2%
						±2%
						±2%
						±2%

ICP Metals

ICV/CCV - 2nd SOURCE STANDARDS

PREPARATION LOG

Prepared By: _____ Date Prepared: 7/18/2018 Exp. Date: 1/14/2019

Matrix: 5% HNO3 / 5% HCl

Stock Solution		Standard ID	071118-SS1						
Analyte	Conc. (ug/ml)	Final Vol (ml)	1000	Balance/ Weight Set	Check Mass, g	Weight #1, g	Weight #2, g	Average Wt., g	Tolarance Acceptance
ICP0472 Exp. Date 05/2020		Transfer vol.(ml)	1.00						± 2%
Pb	500	ug/L	500						± 2%
Se	200	ug/L	200						
Cd	150	ug/L	150	Pipette s/n	Volumn, mL	Weight #1, g	Weight #2, g	Average	Tolarance
Mn	100	ug/L	100						± 2%
Be	50	ug/L	50						±2%
Zn	150	ug/L	150						±2%
ICP0413 Exp. Date 07/2019		Transfer vol.(ml)	2.00						±2%
Fe	10000	ug/L	20,000						±2%
Ba	100	ug/L	200						±2%
Co	100	ug/L	200						
Cu	100	ug/L	200	Room#					
V	100	ug/L	200	Humidity					
ICP0451 Exp. Date 08/2020		Transfer vol.(ml)	1.00	Temperature					
As	500	ug/L	500						
Mo	100	ug/L	100						
ICP0473 Exp. Date 01/2022		Transfer vol.(ml)	4.00						
Ca	1000	ug/L	4,000						
K	400	ug/L	1,600						
Al	200	ug/L	800						
Na	200	ug/L	800						
Li	100	ug/L	400						
Cr	20	ug/L	80						
Ni	20	ug/L	80						
Sr	10	ug/L	40						
ICP0452 Exp. Date 08/2020		Transfer vol.(ml)	2.00						
Mg	1000	ug/L	2,000						
Sb	200	ug/L	400						
Tl	200	ug/L	400						
Ag	50	ug/L	100						
ICP0411 Exp. Date 01/2022		Transfer vol.(ml)	0.50						
U	1000	ug/L	500						
ICP0474 Exp. Date 7/2021		Transfer vol.(ml)	0.800						
B	100	ug/L	80						
Mo	1,000	ug/L	800						
Total Mo		ug/L	900						
Si	1,000	ug/L	800						
ICP0471 Exp. Date 09/2024		Transfer vol.(ml)	1.000						
Li	1,000	ug/L	1,000						
Total Li		ug/L	1400						
ICP0409 Exp. Date 03/2021		Transfer vol.(ml)	0.500						
Sn	1,000	ug/L	500						
ICP0390 Exp. Date 09/2020		Transfer vol.(ml)	0.500						
Th	1,000	ug/L	500						
ICP0445 Exp. Date 01/2019		Transfer vol.(ml)	0.500						
Zr	1,000	ug/L	500						
ICP0447 Exp. Date 01/2019		Transfer vol.(ml)	1.000						
P	1,000	ug/L	1000						
ICP0410 Exp. Date 09/2021		Transfer vol.(ml)	0.500						
Sr	1,000	ug/L	500						
Total Sr		ug/L	1440						
ICP0470 Exp. Date 06/2024		Transfer vol.(ml)	0.500						
Ti	1,000	ug/L	500						
ICP0355 Exp. Date 05/2020		Transfer vol.(ml)	0.800						
Nb	1,000	ug/L	800						

MATERIALS AND CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE		
Inductively Coupled Plasma – Mass Spectrometry Element/Metals *Including Tc^{99}* Sample Preparation and Analysis: Materials and Chemistry Laboratory Inc.	Approved: _____ MCLinc President _____ Quality Assurance Officer	 _____ Date _____ Date

1.0 PURPOSE

This document describes the procedures to determine elements/metals in properly prepared samples by inductively-coupled plasma – mass spectrometry (ICP-MS) based upon USEPA SW-846 Method 6020A-*C*. This document is also meant to determine elements/metals in properly prepared samples by ICP-MS based upon USEPA ORD Method 200.8. Any additional or slightly different requirements in Method 200.8 are given in Appendix 1.
The procedure for $Tc^{99}$is in Section 13.10 - 13.11.

2.0 SCOPE AND APPLICATION

2.1 Inductively coupled plasma – mass spectrometry (ICP-MS) determines trace elements/metals in solution. This method can be used for all elements/metals in Table 1. All matrices excluding filtered acidified groundwater samples and including other aqueous samples, industrial and organic wastes, soils, sludges, sediments and other solid wastes require digestion prior to analysis. Both non-digested and digested samples must be matrix-matched with the same type and concentrations of acids as found within the calibration standards.

Table 1 lists the elements that can be analyzed by this method. Elements other than those can be analyzed by this method if performance at the concentration levels of interest is demonstrated.

2.2 Users of this method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to the use of the method for analysis.

2.3 Use of this method is restricted to chemist/qualified operators who are knowledgeable in the correction of chemical and physical interferences described in this method. They must also have been appropriately trained on the instrumentation and its software.

2.4 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standard elements are ^{6}Li, ^{45}Sc, ^{74}Ge, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li so that interference from lithium native to the sample is minimized. The listed elements can be used as internal standards and other elements may need to be used as internal standards when samples contain significant native amounts of the recommended internal standard elements. MCL is routinely using ^{6}Li, ^{45}Sc, ^{74}Ge, ^{115}In, ^{159}Tb and ^{209}Bi.

3.0 RESPONSIBILITIES

The **MCLinc Project Manager** is responsible for assuring that project QA/QC is clearly defined to the ICP operator and sample preparation analyst and any health and safety issues are understood.

The **MCLinc Analyst** is responsible for routine operation, inventory of all required materials, upkeep of equipment, reviewing and reporting of results and the housekeeping of the work area associated with the equipment.

The **MCLinc Operations Manager** represents the first level of management, provides project oversight and is responsible for supplying the resources for proper upkeep of the required instrumentation.

4.0 SUMMARY OF METHOD

4.1 Prior to analysis, samples, except for filtered and acid preserved groundwater samples, must be digested using appropriate sample preparation methods. This includes all total and “acid-leachable” samples.

4.2 This method describes the multi-element determination of analytes by ICP-MS in environmental samples. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed, and valid corrections applied, or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents and constituents of the sample matrix.

5.0 DEFINITIONS

Applicable definitions are located throughout this SOP.

6.0 INTERFERENCES

6.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

6.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. The instrument software used corrects for isobaric and doubly-charged ion interferences. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. Examples include $^{75}ArCl^{+}$ ion on the ^{75}As signal and MoO^{+} ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature, the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics. Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^{+}$ at m/z 75 is a negligible 0.06% of the $^{40}Ar^{35}Cl^{+}$ signal):

Corrected arsenic signal (using natural isotopes abundances for coefficient approximations)

= (m/z 75 signal) – (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal)

where the final term adjusts for any selenium contribution at 77 m/z,

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^{+}$, (e.g., $^{81}BrH^{+}$ from bromine wastes).

Similarly,

Corrected cadmium signal (using natural isotopes abundances for coefficient approximations)

= (m/z 114 signal) – (0.027) (m/z 118 signal) – (1.63) (m/z 108 signal),

where last 2 terms adjust for any $^{114}Sn^{+}$ or $^{114}MoO^{+}$ contributions at m/z 114.

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^{+}$ ions contribute at m/z 108 but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^{+}$) and indirect ($^{90}ZrO^{+}$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients could be improved. The most appropriate coefficients for a particular instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 %) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. For example, this type of correction has been reported for oxide-ion corrections using ThO^{+}/Th^{+} for the determination of rare earth elements. The use of aerosol desolvation and/or mixed gas plasmas have been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met. Common isobaric, double charge and oxide formation corrections are included in the instrument software and are performed automatically.

6.3 Additionally, solid phase chelation may be used to eliminate isobaric interferences from both elemental and molecular sources. An on-line method has been demonstrated for environmental waters such as sea water, drinking water and acid-digested samples. Acid-digested samples refer to samples digested by methods similar to SW 846 methods 3052, 3051, 3050, or 3015. Samples with percent levels of iron and aluminum should be avoided. The method also provides a procedure for preconcentration to enhance detection limits simultaneously with elimination of isobaric interferences. The method relies on chelating resins such as imminodiacetate or other appropriate resins and selectively concentrates the elements of interest while eliminating interfering elements from the sample matrix. By eliminating the elements that are direct isobaric interferences or those that form isobaric interfering molecular masses, the mass region is simplified, and these interferences cannot occur. The method has been proven effective for the certification of standard reference materials and validated using SRMs. The method has the potential to be used on-line or off-line as an effective sample preparation method specifically designed to address interference problems.

6.4 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to

correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30% of the signals in the calibration standards) will be observed. Dilution of the sample fivefold (1+4) will usually eliminate the problem (see Section 13.7).

6.5 Memory interferences or carry-over can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler or skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

7.0 SAFETY

7.1 General laboratory protection (safety glasses, lab coat and disposable latex/nitrile gloves) should be worn at all times when handling standards or samples.

7.2 Acid solutions may pose potential health risks. Extreme care should be utilized when handling these solutions.

8.0 EQUIPMENT AND SUPPLIES

8.1 Inductively coupled plasma-mass spectrometer such as Perkin Elmer Elan 9000 with: (See Appendix 1 for Method 200.8 requirements)

8.1.1 Capability of providing resolution, better than or equal to 1.0 amu at 10% peak height.

8.1.2 Mass range from at least 6 to 240 amu.

8.1.3 Data system that has corrections for common isobaric, double charge and oxide interferences and the application of the internal standard technique.

8.2 Mass flow controller for argon nebulizer gas supply.

8.3 Peristaltic pump for delivery of sample to nebulizer.

8.4 Argon gas supply, high purity.

9.0 REAGENTS AND STANDARDS

9.1 Acids used in the preparation of standards and for sample processing must be of high purity. Nitric acid at less than 2% (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed when hydrochloric and sulfuric acids are used. Concentrations of antimony and silver between 50-500 µg/L require 1% (v/v) HCl for stability. For concentrations above 500 µg/L Ag, additional HCl will be needed. Consequently, accuracy of analytes requiring significant chloride molecular ion corrections (such as As and V) will degrade.

9.2 Reagent Water: All references to reagent water in the method refer to *ASTM Type II* (*>1.0* Mohms-cm) *water*.

9.3 Standard stock solutions are either purchased commercially as certified standards or prepared from ultra-high purity grade chemicals or metals (99.99% or greater purity).

9.4 Mixed calibration standard solutions are prepared by diluting the stock standard solutions to levels in the linear range for the instrument in a solvent consisting of 1% (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^{6}Li, ^{45}Sc, ^{74}Ge, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, ^{209}Bi. MCL is routinely using ^{6}Li, ^{45}Sc, ^{74}Ge, ^{115}In, ^{159}Tb and ^{209}Bi.

9.5 Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Fresh mixed standards should be prepared, as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard (see Section 9.7).

9.6 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The method blank is used to monitor for possible contamination resulting from the sample preparation procedure. The instrument blank is used to flush the system between all samples and standards.

9.6.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1% HNO_3 (v/v) in reagent water] along with the selected concentrations of internal

standards such that there is an appropriate internal standard element for each of the analytes.

9.6.2 The method (or preparation) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

9.6.3 The instrument blank consists of 1% to 3% HNO3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. If mercury is to be analyzed, the instrument blank should also contain 2 mg/L $AuCl_3$ solution.

9.7 The interference check solutions A and AB (ICS-A, ICS-AB) are prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

ICP-MS Interference Check Standards A (ICP0298) and AB (ICP0299) are to be analyzed with all runs that include any of the following metals: As, Cd, Cr, Co, Cu, Mn, Ni, Se, Ag, Ti, V, Zn. Dilute the purchased stock Interference Check Standards 10X each in separate vessels to yield concentrations in Table 2. Solution A contains the interference metals (Al, Ca, Fe, Mg, Na, P, K, S, C, Cl, Mo, Ti) and solution AB contains the interferent metals along with the analytes listed above that can experience isobaric interferences on the ICP-MS. After the closing CCV of analysis run, analyze the Interference Check Standards for all of the analytes listed above that are included for the samples, with the calibration curve used for the analysis run. End with another closing CCV. Percent recovery for each analyte is to be reported to the QAM.

9.8 The quality control standard is the second source standard used for initial calibration verification (ICV) which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration or from the same vendor but a different lot.

9.9 Continuing Calibration Verification (CCV) – The CCV is prepared from the same source and same acid matrix as calibration standards at mid-range concentration. The CCV is analyzed after every ten (10) samples including preparation QC samples such as LCS and MB, and at the end of analysis.

9.10 Mass spectrometer tuning solution is a solution containing elements representing all of the mass regions of interest to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 13.4). This solution is also used to verify that the

instrument has reached thermal stability. For the Elan 9000 ICP-MS, the tuning solution contains 10 µg/L Be, Mg, Co, Rh, In, Ba, Ce, Pb and can also contain Cu, Cd and U.

9.11 Dual detector cross-calibration solution is required for the Elan 9000 ICP-MS for the calibration of the detector in the crossover range between the pulse and analog ranges. This solution will contain 250 µg/L each of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Tl, Th, U, V, Zn, Na, Ca, Mg, K, Fe, Sc, Y, In, Rh, Tb, Ho, and Bi and 1250 µg/L Ge.

10.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

10.1 Sample collection procedures should address all considerations described in the Quality Assurance Project Plan, (MCL-7701).

10.2 Only polypropylene or fluorocarbon containers are suitable for collection of samples for Method 6020A.

10.3 Aqueous samples should be preserved with 1:1 HNO_3 to a pH <2.

11.0 QUALITY CONTROL

11.1 The type and frequency of the quality control program will be defined by the project. Depending upon the project defined program, the following quality control data, as defined in Table 3 may be included. The resulting data should be maintained and be available for easy reference or inspection.

11.2 Instrument detection limits (IDLs) are a useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. IDLs in µg/L can be estimated as the mean of the blank result plus three times the standard deviation of 10 replicate analyses of the reagent blank solution. (Use zero for the mean if the mean is negative). Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least once using new equipment, after major instrument maintenance such as changing the detector and/or as designated by a project.

11.3 The intensity of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below 30% of the intensity of that internal standard in the initial calibration standard, a significant matrix effect must be suspected. Under these conditions, the detection limit has degraded, and the correction ability of the internal standardization technique becomes questionable. The following procedure is used: First, make sure that the instrument has not just drifted by observing the internal standard intensities in the nearest clean matrix (calibration blank). If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration and reanalyze the affected samples. If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-

standard intensities rise above the 30% limit. Reported results must be corrected for all dilutions.

11.4 To obtain data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. For example, tungsten oxides can be very difficult to distinguish from mercury isotopes. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantitation and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferent itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections is required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element of molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Section 6.2) for each instrument system are acceptable corrections for use in this method.

11.5 Dilution test (DT) (serial dilution): This test may be applied for unusual matrices. If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the method blank, refer to Section 9.5.2), an analysis of fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected. One dilution test is be included for each 20 samples (or less) of each matrix in a batch.

11.6 Post-digestion spike addition (PDSA): An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125% of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect.

11.7 There will be two different laboratory control samples (LCS) analyzed with each batch of 20 or fewer samples using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples:

11.7.1 LCS shall be prepared and analyzed in duplicate and are solutions spiked to yield concentrations in the low to midrange of the calibration curve for each target analyte. The acceptance criterion is 100±30%.

11.7.2 LCSL (low) may be requested by the Quality Manager for special projects and are a solution spiked to yield concentrations 2-4x the concentration of the lowest calibration standard for each target analyte. The acceptance criterion will be determined based on historical results of ICP-MS.

11.8 Check the instrument calibration by analyzing appropriate quality control solutions as follows:

11.8.1 Check instrument calibration using a calibration blank and the ICV.

11.8.2 Verify calibration after every 10 analytical samples with the CCV and the calibration blank and after the last sample.

11.8.3 The results of the ICV and CCV must agree within ±10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-range calibration must be reanalyzed.

11.8.4 The results of the calibration blank must be less that 3 times the current IDL for each element. If this is not the case, the reason for the out-of-range condition must be found and corrected and affected samples reanalyzed.

11.9 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions. The analyst should be aware that precipitation from the ICS solutions may occur, particularly with silver.

11.10 The analysis of duplicate samples is project specific at the rate of one duplicate for every 20 or less samples. The acceptance criterion is ±20%.

11.10.1 The relative percent difference (RPD) between duplicate determinations is calculated as follows:

$$RPD = 100 \times \frac{| D_1 - D_2 |}{(D_1 + D_2)/2}$$

Where:
RPD = relative percent difference
D_1 = initial sample concentration
D_2 = duplicate sample concentration

A control limit of 35% RPD should not be exceeded for analyte values greater that 100 times the instrumental detection reporting limit. If this limit is exceeded, the reason for this situation

must be investigated and corrected if appropriate, and if any samples are affected, they should be reanalyzed.

11.11 Lower Reporting Limit Verification – After the ICV is analyzed and verified, the lower reporting limit (LRL) is verified by analyzing the lowest concentration calibration standard as a sample. The percent recovery should be ±30%.

11.12 A matrix spike (MS) and matrix spike duplicate (MSD) is project specific and is prepared at the frequency of one for every batch of 20 or fewer samples. Acceptance criterion is ±25%.

11.12.1 The % Recovery is calculated as follows:

$$\%R = 100 \times \frac{(MS - S)}{TV}$$

Where:
%R = % recovery
MS = concentration in matrix spike
S = concentration in sample
TV = theoretical concentration of the spike

12.0 CALIBRATION AND STANDARDIZATION

12.1 Conduct mass calibration and resolution checks in the mass regions of interest with the tuning solution. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less that 0.9 amu full width at 10% peak height.

12.2 Calibrate the instrument for the analytes of interest (recommended isotopes for analytes are given in Table 3), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Flush the system with the rinse blank between each standard solution. Use the average of at least 3 integrations for both calibration and sample analyses.
NOTE: Analysts have noted improved performance in calibration stability if the instrument is exposed to the interference check solution after cleaning sampler and skimmer cones. Improved performance is also realized if the instrument is allowed to rinse for 5 to 10 minutes before the calibration blank is run.

12.3 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are listed in Table 3.

12.4 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the ICV solution. When measurements exceed ±10% of the accepted value, the analyses must be terminated, the problem corrected, the instrument recalibrated, and the new calibration verified with ICV standard. Any samples

analyzed under an out-of-range calibration must be reanalyzed. During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift, but resloping must not be used as an alternative to reanalyzing samples following an unacceptable QC sample, such as a CCV. A recalibration must then be followed immediately by a new analysis of an ICV and a calibration blank before any further samples may be analyzed.

13.0 PROCEDURE

13.1 Sample Preparation

Samples should be prepared according to Acid Digestion for Metals (MCL-7746).

13.2 Initiate appropriate operating configuration of the instrument computer according to the instrument manufacturer's instructions.

13.3 Set up the instrument with the proper operation parameters according to the instrument method file defining reporting units (µg/L for liquid and mg/Kg for solids), calibration parameters, ICV and CCV frequency, acceptance criteria and corrective actions, ICS and LCS criteria. In the method file, also define by element the isotope(s) to be used and the specific plasma operational parameters.

13.4 Set up the Workspace file defining the analysis method, sample file, calibration file, data acquisition file, and the instrumental conditions file, which includes tuning, lens calibration and nebulizer calibration.

13.5 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 9.8) at least 4 times with relative standard deviations of ≤5% for the analytes contained in the tuning solution.

13.6 Calibrate the instrument following the procedure outlined in Section 12.0.

13.7 The sample run sequence will have an instrument blank immediately following each CCV as shown in this sequence example:

Calibration Blank (Section 9.5.1)
Calibration Standards, Lowest Concentration to Highest (Section 9.4)
ICV (Section 9.7)
LRL (Section 11.11)
Instrument Blank (Section 9.5.3)
ICS-A (Section 9.6)
ICS-AB (Section 9.6) LCSL (Section 11.7.2)
LCSN (Section 11.7.1)
Method Blank (Section 9.5.2)
Up to 10 Samples, including Duplicates and MS/MSD (MS/MSD only if required by project)

CCV (Section 9.7)
Instrument Blank
Up to 10 Samples, including Duplicates
PDSA (Section 11.6)
DT (Section 11.5)
CCV
Instrument Blank

The method preparation quality control samples: LCSL, LCSN, Method Blank, PDSA and DT are counted in the run sequence as samples, i.e., as one of the 10 samples between each ICV – CCV or CCV- CCV sequence.

13.8 Flush the system with the instrument blank solution (Section 9.5.3) until the signal levels return to the levels of quantitation defined in the method (usually about 30 seconds) before the analysis of each sample (see Section 12.3). Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the CCV solution (Section 9.7) and calibration blank (Section 9.5.1) at a frequency of at least once for every 10 analytical samples. Flow injection systems can be used as long as they meet the performance criteria of this method.

13.9 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate but less abundant isotope. The linearity of the alternate mass must be confirmed by appropriate calibration (see Section 12.2 and 12.4). Alternatively, apply solid phase chelation chromatography to eliminate the matrix interference as described in Section 6.3.

13.10 Final Prep and Analysis of Tc^{99} by ICP/MS. Prior to analysis, samples are prepared according to MCL-7754, Section 5.1 to 5.1.7. In addition to this, the following column separation procedure using Eichrom TEVA resin must be performed on the prepared sample.

13.11 Column Separation

13.11.1 For each sample aliquot analyzed, place a 2mL TEVA column in a column rack.
13.11.2 Place a beaker or tray below each column, remove the bottom plug from each column and allow each column to drain.
13.11.3 Pipet 5mL of 0.1m HNO3 into each column to condition the resin and allow to drain.
13.11.4 Transfer each sample aliquot into the appropriate column and allow to drain.
13.11.5 Rinse each sample container with 50mL 0.1M HNO3 and then transfer the rinse to the appropriate column. Allow the rinse solution to drain.
13.11.6 Discard all drain solutions collected to this point.
13.11.7 Place clean, labeled sample containers below each column.

13.11.8 Pipet 20mL of 11M HNO3 into each column to elute the Tc^{99}. Collect this solution for analysis.

13.11.9 The sample is now ready for analysis per Sections 13.3 – 13.9.

14.0 DATA ANALYSIS AND CALCULATIONS

14.1 The quantitative values shall be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/Kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values. All calculations must include appropriate interference corrections (see Section 6.2 for examples), internal-standard normalization, and the summation of signals at 206, 207 and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

14.2 For dissolved metals analyses:

$$\mu g/L = C \times DF$$

Where:
C = Sample concentration (µg/L)
DF = Dilution factor

14.3 For digested aqueous samples:

$$\mu g/L = \frac{C \times DF \times V}{W}$$

Where:
C = Digestate concentration (µg/L)
DF = Dilution factor
V = Final volume in L after sample preparation
W = Initial volume in L of sample used for sample preparation

14.4 Soil/Solid concentrations may be reported on the basis of the dry weight of the sample (a separate determination of % total solids must be performed):

$$\mu g/g \text{ (dry weight)} = \frac{C \times DF \times V \times S}{W}$$

Where:
C = Digest concentration (µg/L)
DF = Dilution factor
V = Final volume in L after sample preparation
W = Weight in g of wet sample
S = 100 / % solids

14.5 Air filter sample concentrations may be reported as total µg or total mg per filter or if the air volume sampled is given, as mg/cubic meter (mg/m^3):

Total µg = C x DF x V
Total mg = µg / 1000
$mg/m^3 = \frac{C \times DF \times V}{\text{Air volume in } m^3}$

Where:
C = Digest concentration (µg/L)
DF = Dilution factor
V = Final volume in L after sample preparation

15.0 METHOD PERFORMANCE

15.1 Refer to Table 1 for method detection limit information.

16.0 POLLUTION PREVENTION

16.1 To minimize hazardous materials generated with this method, minimal quantities of samples are digested (50-100 mL final digestate volume) and minimal quantities of standards are prepared.

17.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all applicable federal, state and local regulations governing waste management.

TABLE 1

ELEMENTS THAT CAN BE ANALYZED BY ICP-MS ACCORDING TO EPA METHOD 6020A AND DETECTION LIMITS

Element	Symbol	Lower Reporting Limit (µg/L)	Instrument Detection Limit (µg/L)	Method Detection Limit Soil (µg/g)	Method Detection Limit Water (µg/L)
Aluminum	Al	1.0	TBD*	TBD*	TBD*
Antimony	Sb	0.05	TBD	TBD	TBD
Arsenic	As	0.02	TBD	TBD	TBD
Barium	Ba	0.1	TBD	TBD	TBD
Beryllium	Be	0.02	TBD	TBD	TBD
Cadmium	Cd	0.02	TBD	TBD	TBD
Calcium	Ca	1.0	TBD	TBD	TBD
Chromium	Cr	0.05	TBD	TBD	TBD
Cobalt	Co	0.05	TBD	TBD	TBD
Copper	Cu	0.05	TBD	TBD	TBD
Iron	Fe	1.0	TBD	TBD	TBD
Lead	Pb	0.05	TBD	TBD	TBD
Magnesium	Mg	1.0	TBD	TBD	TBD
Manganese	Mn	0.1	TBD	TBD	TBD
Mercury	Hg	TBD	TBD	TBD	TBD
Nickel	Ni	0.05	TBD	TBD	TBD
Potassium	K	1.0	TBD	TBD	TBD
Selenium	Se	0.02	TBD	TBD	TBD
Silver	Ag	0.05	TBD	TBD	TBD
Sodium	Na	1.0	TBD	TBD	TBD
Thallium	Tl	0.02	TBD	TBD	TBD
Uranium	U	0.01	TBD	TBD	TBD
Vanadium	V	0.02	TBD	TBD	TBD
Zinc	Zn	0.1	TBD	TBD	TBD

* To be determined and placed in the instrument QA files

TABLE 2

RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	300.0	300.0
Fe	250.0	250.0
Mg	100.0	100.0
Na	250.0	250.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	2000.0	2000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.100
Cd	0.0	0.100
Cr	0.0	0.200
Co	0.0	0.200
Cu	0.0	0.200
Mn	0.0	0.200
Hg	0.0	0.020
Ni	0.0	0.200
Se	0.0	0.100
Ag	0.0	0.050
V	0.0	0.200
Zn	0.0	0.100

TABLE 3

RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Element of Interest	**Mass**
Aluminum	**27**
Antimony	121, **123**
Arsenic	**75**
Barium	138, 137, 136, **135**, 134
Beryllium	**9**
Bismuth (IS)	209
Cadmium	**114**, 112, **111**, 110, 113, 116, 106
Calcium (I)	42, 43, **44**, 46, 48
Chlorine (I)	35, 37, (77, 82)[a]
Chromium	**52**, **53**, **50**, 54
Cobalt	**59**
Copper	**63**, **65**
Holmium (IS)	165
Indium (IS)	**115**, 113
Iron (I)	**56**, **54**, **57**, 58
Lanthanum (I)	139
Lead	**208**, **207**, **206**, 204
Lithium (IS)	6[b], 7
Magnesium (I)	24, **25**, **26**
Manganese	**55**
Mercury	202, **200**, 199, 201
Molybdenum (I)	98, 96, 92, **97**, 94, (108)[a]
Nickel	58, **60**, 62, **61**, 64
Potassium (I)	**39**
Rhodium (IS)	103
Scandium (IS)	45
Selenium	80, **78**, **82**, **76**, **77**, 74
Silver	**107**, **109**
Sodium (I)	**23**
Terbium (IS)	159
Thallium	**205**, 203
Uranium	**238**
Vanadium	**51**, **50**
Tin (I)	120, **118**
Yttrium (IS)	89
Zinc	64, **66**, **68**, **67**, 70

NOTE: EPA Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes.

a These masses are also useful for interference correction (Section 6.2)

b Internal standard must be enriched in the 6Li isotope (Section 2.4)

TABLE 4

QUALITY ASSURANCE/QUALITY CONTROL

Description	**Frequency**	**Acceptance Criteria**	**Corrective Action**

Instrument Detection Limits (IDLs)	Per Section 11.2	See "Instrument Blank"	
Tuning Solution	Daily	RSD of ≤5%; Mass calibration <0.1 amu from true value; <0.9 amu full width at 10% peak height	Allow to warm up 30 minutes more
Calibration Blank	Before analysis of calibration curve standards	<3X current IDL	Allow instrument blank to flush system for 10-15 minutes and reanalyze
Calibration Curve Defining linear calibration range. 3 points minimum lower and upper defining reporting limits. 3rd point preferably near the lower	Before the analysis of the sample; after instrument repair or maintenance; when an ICV shows an existing calibration curve failed	Correlation Coefficient (R) > 0.998	Check standards, calibration range, operational parameters, Rerun calibration
Initial Calibration Verification Std (ICV) Standard containing all the target analytes prepared from a second source solution	After development of calibration curve	100%R ± 10%	Check both ICV and calibration standards preparation; recalibrate
Continuing Calibration Verification (CCV) Standard prepared from same source as calibration stds.	After every ten (10) samples including QC samples (LCS and MB) and at end of analysis	100%R±20%	Reanalyze CCV; check Preparation and re-prepare if Necessary; recalibrate
Instrument Blank	Immediately following every ICV/CCV	Less than *1/2* the current *LRL* for each element	Check tubing and calibration blank solution; remake solution
Internal Standards	Added to all blanks, calibration standards, samples, QC	In samples, the intensity of all internal standards should be 100±30% of that in the initial calibration solution	Check instrument drift, if drift present, recalibrate; If no drift, dilute sample 5X and reanalyze
Laboratory Control Sample (LCS) Spiked clean material containing all or defined elements processed through the entire preparation and analysis process	Two per batch of samples with a maximum of 20 samples per batch	100%R ± 20% or as defined by developing recovery studies	Re-prepare if fails review of all related QA/QC, and if necessary re-prepare and reanalyze all associated samples
Method Blank Sample composed of all reagents and processed through entire method	One per batch of samples with a maximum of 20 samples per batch	No analyte concentrations exceeding ½ the lower reporting limit	Qualify reported data
Lower Reporting Limit (LRL) Analysis of lowest concentration calibration standard as a sample	Once per day for each metal analyzed	100%R ± 30%	Internal MCL Inc requirement – Review with QA Manager
MS/MSD	*One set per batch*	*100%±25%*	*Evaluate for matrix effect – QA review*

APPENDIX 1
ADDITIONAL REQUIREMENTS OF EPA METHOD 200.8

TABLE 1-1
ELEMENTS THAT CAN BE ANALYZED BY ICP-MS ACCORDING TO EPA METHOD 200.8 AND DETECTION LIMITS

Element	Symbol	Lower Reporting Limit (µg/L)	Instrument Detection Limit (µg/L)	Method Detection Limit Soil (µg/g)	Method Detection Limit Water (µg/L)
Aluminum	Al	1.0	TBD*	TBD*	TBD*
Antimony	Sb	0.05	TBD	TBD	TBD
Arsenic	As	0.02	TBD	TBD	TBD
Barium	Ba	0.1	TBD	TBD	TBD
Beryllium	Be	0.02	TBD	TBD	TBD
Cadmium	Cd	0.02	TBD	TBD	TBD
Chromium	Cr	0.05	TBD	TBD	TBD
Cobalt	Co	0.05	TBD	TBD	TBD
Copper	Cu	0.05	TBD	TBD	TBD
Lead	Pb	0.05	TBD	TBD	TBD
Manganese	Mn	0.1	TBD	TBD	TBD
Mercury	Hg	TBD	TBD	TBD	TBD
Nickel	Ni	0.05	TBD	TBD	TBD
Selenium	Se	0.02	TBD	TBD	TBD
Silver	Ag	0.05	TBD	TBD	TBD
Thallium	Tl	0.02	TBD	TBD	TBD
Thorium	Th	TBD	TBD	TBD	TBD
Uranium	U	0.01	TBD	TBD	TBD
Vanadium	V	0.02	TBD	TBD	TBD
Zinc	Zn	0.1	TBD	TBD	TBD

18.0 EQUIPMENT AND SUPPLIES

18.1.1 Instrument resolution is 1 amu peak width at 5% peak height.

18.1.2 Mass range from 5-250 amu.

18.1.4 Radio-frequency generator compliant with FCC regulations.

18.1.5 If an electron multiplier detector is used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Changes in instrument response or damage to the multiplier may result with exposure to high ion flux. Samples having high concentrations of elements beyond the linear range of the instrument and with isotopes falling within scanning windows should be diluted prior to analysis.

NOTE: Equipment listed in Method 200.8 Sections 6.2 – 6.10 for the preparation of samples is listed in SOP# MCL-7746, MCL-7752 and MCL-7753.

19.0 QUALITY CONTROL

19.12 Initial Demonstration of Performance

19.12.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear calibration ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

19.12.2 Linear calibration ranges – Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limits must be diluted and reanalyzed. The LDRs should be verified whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

19.12.3 Quality control sample (QCS) – When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analysis of a QCS. To verify the calibration standards, the determined mean concentration from 3 analyses of the QCS must be within ±10% of the stated QCS value. If the QCS is used for determining acceptable on-going instrument performance, analysis of the QCS prepared to100 µg/L must be within ±10% of the stated value or within the acceptance limits listed in Table 5-1, whichever is greater.

19.13 Assessing Laboratory Performance (mandatory)

19.13.4 Instrument performance – For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration run the calibration blank and calibration standards as surrogate samples immediately following each calibration routine, after every ten analyses and at the end of the sample run. The results of the analyses of the standards will indicate whether the calibration remains valid. The analysis of all analytes within the standard solutions must be within ±10% of calibration. If the calibration cannot be verified within the specified limits, the instrument must be recalibrated. (The instrument responses from the calibration check may be used for recalibration purposes; however, it must be verified before continuing sample analysis.) If the continuing calibration check is not confirmed within ±15%, the previous 10 samples must be reanalyzed after recalibration. If the sample matrix is responsible for the calibration drift, it is recommended that the previous 10 samples are reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

19.14 Assessing Analyte Recovery and Data Quality

19.14.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix procedure is required.

19.14.2 The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples. In each case, the LFM aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the LFB. For solid samples, the concentration added should be 100 mg/Kg equivalent (200 µg/L in the analysis solution) except silver which should be limited to 50 mg/Kg. Over time, samples from all routine sample sources should be fortified.

19.14.3 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery of 70-130%. Recovery calculations are not required if the concentration of the analyte added is less than 30% of the sample background concentration.

19.14.4 If recovery of any analyte falls outside the designated range and laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the

unfortified sample is suspect due to either the heterogeneous nature of the sample or an uncorrected matrix effect.

20.0 PROCEDURE

20.1 Sample Preparation

NOTE: If mercury is to be analyzed, the digestion procedure must use mixed nitric and hydrochloric acids through all steps of the digestion. Mercury will be lost if the sample is digested when hydrochloric acid is not present. If it has not already been added to the sample as a preservative, Au should be added to give a final concentration of 2 mg/L to preserve the mercury and to prevent it from plating out in the sample introduction system.

20.1.1 Aqueous Sample Preparation – Dissolved Analytes (from EPA Method 200.8)

20.1.1.1 For the determination of dissolved analytes in ground and surface waters, pipet an aliquot (≥20mL) of the filtered, acid preserved sample into a 50 mL polypropylene (pp) centrifuge tube. Add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4mL (1+1) HNO_3 to a 20mL aliquot of sample). If direct addition is being used, add internal standards, cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

NOTE: If a precipitate is formed during acidification, transport or storage, the sample aliquot must be treated using the procedure in Section 13.1.2 prior to analysis.

20.1.2 Aqueous Sample Preparation – Total Recoverable Analytes (from EPA Method 200.8)

20.1.2.1 For the "direct analysis" of total recoverable analytes in drinking water samples containing turbidity <1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure described in Section 13.1.1.1 while making allowance for sample dilution in the data calculation. For the determination of total recoverable analytes in all other aqueous samples or for preconcentration drinking water samples prior to analysis follow the procedure given in Sections 13.1.2.2 through 13.1.2.8.

20.1.2.2 For the determination of total recoverable analytes in aqueous samples, transfer a 40mL aliquot from a well mixed, acid preserved sample to a 50mL pp digestion tube.

20.1.2.3 Add 2mL (1+1) HNO_3 and 1mL (1+1) HCL to the sample aliquot. Place the tube in a hot block at 95ºC and cover with a pp raised watch glass. Reflux

sample for 30-60 minutes. Do not boil. Some reduction in sample volume may occur.

20.1.2.4 Allow the sample in digestion tube to cool. Quantitatively transfer the sample solution to a labeled 50mL pp centrifuge tube. Dilute to 50mL with reagent water and mix.

20.1.2.5 Prior to analysis adjust the chloride concentration by pipetting 20mL of the prepared sample solution into a 50mL pp centrifuge tube. If the direct addition method is being used, add appropriate amounts of internal standards. Dilute to 50mL with reagent water and mix. The sample is now ready for analysis. All analyses should be performed as soon as possible after the completed preparation.

20.1.3 Solid Sample Preparation – Total Recoverable Analytes (from EPA Method 200.8)

20.1.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly to obtain a homogenous aliquot. Weigh 1.0 ± 0.10g of dry sample into a 50mL pp digestion tube.

20.1.3.2 Add 4mL (1+1) HNO_3 and 10mL (1+4) HCL carefully to avoid loss of sample. Place the digestion tube in the hot block (in an appropriate fume hood) at 95ºC. Cover with a raised pp watch glass.

20.1.3.3 Reflux the sample for 30 minutes at 95ºC. Slight boiling may occur, but vigorous boiling should be avoided to prevent loss of the HCl-H2O azeotrope. Some solution evaporation will occur.

20.1.3.4 Allow the sample to cool and quantitatively transfer the extract to a 100mL volumetric flask. Filter if necessary to remove undissolved solids. Take care to avoid potential contamination from filtration.

20.1.3.5 Prior to analysis, adjust the chloride concentration by pipetting 10mL of the prepared solution into a 50mL pp centrifuge tube. If the direct addition method is being used, add appropriate amounts of internal standards. Dilute to 50mL with reagent water and mix. The sample is now ready for analysis. All analyses should be performed as soon as possible after the completed preparation.

TABLE 5

ACCEPTANCE LIMITS FOR QC CHECK SAMPLE METHOD PERFORMANCE (µg/L)

Element	Symbol	QC Check Sample Concentration (µg/L)	Average Recovery %	Standard Deviation (S_r)	Acceptance Limits (µg/L)
Aluminum	Al	100	100.4	5.49	84-117
Antimony	Sb	100	99.9	2.40	93-107
Arsenic	As	100	101.6	3.66	91-113
Barium	Ba	100	99.7	2.64	92-108
Beryllium	Be	100	105.9	4.13	88-112
Cadmium	Cd	100	100.8	2.32	94-108
Chromium	Cr	100	102.3	3.91	91-114
Cobalt	Co	100	97.7	2.66	90-106
Copper	Cu	100	100.3	2.11	94-107
Lead	Pb	100	104.0	3.42	94-114
Manganese	Mn	100	98.3	2.71	90-106
Molybdenum	Mo	100	101.0	2.21	94-108
Nickel	Ni	100	100.1	2.10	94-106
Selenium	Se	100	103.5	5.67	86-121
Silver	Ag	100	101.1	3.29	91-111
Thallium	Tl	100	98.5	2.79	90-107
Thorium	Th	100	101.4	2.60	94-109
Uranium	U	100	102.6	2.82	94-111
Vanadium	V	100	100.3	3.26	90-110
Zinc	Zn	100	105.1	4.57	91-119

21.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Because all materials utilized in this procedure are potentially radioactive sources, all samples, waste, and standards will be appropriately labeled and handled according to MCL-7718 and MCL-7715.

The waste will be minimized by using small volumes and minimizing quantities utilized for sample preparation and standards preparation. Materials for disposal will be segregated and properly labeled. Where possible, the waste will be reduced by known treatment methodologies.

Rad waste will be measured and documented and where necessary turned over to an approved commercial handling and disposal service.

ICP-MS Metals

CALIBRATION SOLUTION STANDARD #1

PREPARATION LOG

****For BeO Filters Prep - Samples & LCS are NOT diluted ****

Make 250mL of Blank solution with 10mL conc H2SO4, 10mL conc HNO3 & 20mL conc HCl

Prepared By: _____ Expiration Date: 1/13/2019 Matrix: 16% Mixed Acid

Stock Solution		Standard ID	071618-Be-filters Stock Std	071618-01 ICPMS#1	071618-02 ICPMS#2	071618-03 ICPMS#3	071618-04 ICPMS#4	071618-05 ICPMS#5
Analyte	Conc. (ug/ml)	Final Vol (ml)	50	50	50	50	50	50
ICP0472 Exp. Date 05/2020		Transfer vol.(ml)	1.0	0.010	0.030	0.125	2.5	25
Be	50	ug/L	1.0	0.20	0.60	2.50	50	500

*50mL final vol - 2mL conc H2SO4, 2mL HNO3 and 4mL conc HCl
*100mL final vol - 4mL conc H2SO4, 4mL HNO3 and 8mL conc HCl
*250mL final vol - 10mL conc H2SO4, 10mL HNO3 and 20mL conc HCl

		Balance/ Weight Set	Check Mass, g	Weight #1, g	Weight #2, g	Average Wt., g	Tolarance Acceptance
Room#							
Humidity							± 2%
Temperature							± 2%

Pipette s/n	Volumn, mL	Weight #1, g	Weight #2, g	Average Wt., g	Tolarance Acceptance
					± 2%
					±2%
					±2%
					±2%
					±2%
					±2%

ICP-MS Metals

CALIBRATION SOLUTION #1; 2nd SOURCE STANDARDS PREPARATION LOG

Prepared By: _____ Date Prepared: 7/17/18 Exp. Date: 1/13/2019

Matrix:16% Mixed Acid

Stock Solution		Standard ID	Be-Filter-CCV-071618-SS				
Analyte	Conc. (ug/ml)	Final Vol (ml)	50				
ICP0443 Exp Date 8/2019		Transfer vol.(ml)	0.025				
Be	100	ug/L	50.0				

*50mL final vol - 2mL conc H2SO4, 2mL HNO3 and 4mL conc HCl
*100mL final vol - 4mL conc H2SO4, 4mL HNO3 and 8mL conc HCl
*250mL final vol - 10mL conc H2SO4, 10mL HNO3 and 20mL conc HCl

Room# _____
Humidity _____
Temperature _____

Balance/ Weight Set	Check Mass, g	Weight #1, g	Weight #2, g	Average Wt., g	Tolerance Acceptance
					± 2%
					± 2%

Pipette s/n	Volume, mL	Weight #1, g	Weight #2, g	Average Wt., g	Tolerance Acceptance
					± 2%
					±2%
					±2%
					±2%
					±2%
					±2%

MATERIALS AND CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE	
Determination of Uranium by a Modified Davies-Gray Titration: Materials and Chemistry Laboratory, Inc.	Approved: _____ _____ MCLinc President Date _____ _____ Quality Assurance Officer Date

1.0 PURPOSE

This procedure applies to samples of uranium compounds of the nature UxFz,, UxOyFz, UxOy and others relating to uranium contaminated scrap materials where interfering elements are kept to a minimum.

2.0 SCOPE

This procedure may also be applied to determine levels of uranium in aqueous and solid samples.

3.0 ROLES AND RESPONSIBILITIES

MCLinc analyst is responsible for performing the analysis on the samples per this procedure, reviewing the results, and reporting any problems.

The Operations Manager or Project Manager represents the first level of management and provides project oversight.

4.0 MATERIALS AND APPARATUS

- Platinum wire: 12"
- Orion Ag-AgCl Half-Cell Single Junction Reference Electrode
- *Thermo Scientific Orion Star pH/ISE Benchtop Meter* or equivalent
- Micro buret-2 ml, 0.002 ml graduations, Gilmont GS-1200A
- Magnetic stirrer
- Teflon coated stir bars
- Hot plate
- Fume hood
- Muffle or tube furnace

- Assorted laboratory glassware – cleaned in laboratory detergent solution and rinsed well in DI H_20
- Platinum or quartz boats
- Thermometer

5.0 REAGENTS

- Sulfuric acid (H_2SO_4): 96%, concentrated.
- Sulfamic acid (H_2NSO_3H): reagent grade.
- Phosphoric acid (H_3PO_4): 85%, concentrated.
- Ferrous sulfate ($FeSO_4.7H_2O$)), granular or crystal.
- Nitric acid (HNO_3): 70%, concentrated.
- Ammonium molybdate [$(NH_4)_6Mo_7O_{24}.4H_2O$], crystals.
- Vanadyl sulfate ($VOSO_4.nH_2O$), 99% pure.
- Potassium dichromate ($K_2Cr_2O_7$), Primary Standard Grade.
- Triuranium octaoxide, (U_3O_8), highly pure.
- Distilled or deionized water.
- Chromic acid for glassware cleaning.
- Sodium hydroxide, (NaOH), pellets or other caustic chemical for acid neutralization
- Laboratory detergent.

6.0 REAGENT PREPARATION

A. 1 M Sulfuric acid solution:

1. To a 2-liter volumetric flask, add ~ 1000 ml DI H_2O.
2. Carefully, while holding flask under the cold water faucet, add 110 ml of concentrated H_2SO_4 while swirling.
3. Allow to cool and then dilute to volume with DI H_2O.

Shelf life: ~ 6 months.

B. 1.5 M Sulfamic acid:

1. To a 1-liter volumetric flask, add 145.5 g of sulfamic acid and ~ 800 ml of DI H_2O.
2. Stir on a magnetic stirrer with gentle heat sufficient to dissolve the solids.
3. Cool and dilute to volume with DI H_2O.

Note: 100 ml of this solution is used in the preparation of the reagent in 6.0 D.

Shelf life: ~ 6 months.

C. 1 M Ferrous sulfate solution:

1. To a 100 ml volumetric flask, add ~65 ml DI H_2O.
2. Carefully add 10 ml of concentrated H_2SO_4.
3. Add 28 g of $FeSO_4.7H_2O$.
4. Carefully shake to dissolve, cool, and dilute to volume with DI H_2O

Shelf life: 2 days

D. Nitric-sulfamic acid solution with ammonium molybdate:

1. To a 1 liter storage bottle, add 400 ml of DI H_2O.
2. Add 4.0 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and dissolve.
3. Add 500 ml of concentrated HNO_3 and mix.
4. Add 100 ml of the sulfamic acid solution previously prepared in 6.0 B and mix well.

Shelf life: ~ 6 months

E. 0.027 N Potassium dichromate standard solution:

1. Dry *NIST* SRM 136*F* $K_2Cr_2O_7$ or equivalent primary standard grade for *2* hrs at 110 ^oC.
2. Cool in dessicator.
3. Weigh out about 1.325 g (accurately to 4 decimal places) of the dichromate for 1 liter of solution corrected for the assay.
4. Add the weighed dichromate to a 1-liter volumetric flask (calibrated), dissolve and dilute to volume with DI H_2O.
5. Transfer the solution to a 1 liter glass bottle.
6. Calculate the normality of the solution.

Normality ($K_2Cr_2O_7$) = mass(g) x assay x 1 mol/294.1844 g x 6 eq/mol x 1/vol. flask (L)

Shelf life: indefinite.

F. 0.008 N Potassium dichromate solution:

1. Dissolve 0.39 g $K_2Cr_2O_7$ in a 1-liter volumetric flask with DI H_20.
2. Bring to volume with DI H_2O.
3. This solution is used to oxidize impurities in the phosphoric acid, its normality does not have to be precise.

Shelf life: indefinite

G. Uranium standard solution, ~ 340 ppm U in 10% HNO_3.

1. Place a small quantity of NBS 950b U_3O_8 in a quartz or platinum boat.
2. Insert the boat into the tube furnace at 800 deg C for 1 h.
3. Cool in a dessicator to room temperature.
4. Weigh out ~0.4 g of U_3O_8 in a 200 ml tall form beaker.
5. Add 50 ml 10% HNO_3 and 50 ml conc. HNO_3.
6. Heat gently on a hot plate to dissolve.
7. Cool and transfer to a 1 liter calibrated volumetric flask using DI H_2O.
8. Add 45 ml of conc. HNO_3.
9. Dilute to volume with DI H_2O.
10. Transfer the solution to a 1 liter glass bottle.

Shelf life: indefinite

Calculation of uranium concentration in the standard solution.:

0.4000 g U_3O_8/1 L x 0.99968 g U_3O_8/1.00000 g U_3O_8 x 0.848001 g U/ 1.000000 g U_3O_8 x 1000 mg U/1 g U = 339.09 mg U/L

Standards are reanalyzed when the deviation from the accepted value exceeds 0.1 mg.

H. Uranium standard solution, ~ 42 ppm U in concentrated H_3PO_4.

1. Place a small quantity of NBS 950b U_3O_8 in a quartz or platinum boat.
2. Insert the boat into the tube furnace at 800 deg C for 1 h.
3. Cool in a dessicator to room temperature.
4. Weigh out ~0.05 g of U_3O_8 in a 200 ml tall form beaker.
5. Add ~25 ml concentrated H_3PO_4.
6. Heat gently on a hot plate to dissolve.
7. Cool and transfer to a 100 ml volumetric flask using concentrated H_3PO_4.
8. Dilute to volume with concentrated H_3PO_4.

Shelf life: U+4: Analyze within a week, total U indefinite

Calculation of uranium concentration in the standard solution.:

0.0500 g U_3O_8 x 0.99968 g U_3O_8/1.00000 g U_3O_8 x 0.848001 g U/ 1.000000 g U_3O_8 x 1000 mg U/1 g U = 42.386 mg U/L

Standards are reanalyzed when the deviation from the accepted value exceeds 0.1 mg.

7.0 PROCEDURE

A. Total U for samples dissolved in dilute HNO_3

1. To 300 ml tall form beaker add the following in order:
   a) Magnetic stir bar.
   b) 15 ml sample (pipetted).
   c) 3 ml conc. H_2SO_4 and swirl.
   d) 5 ml 1.5 M sulfamic acid and swirl.
   e) 40 ml conc. H_3PO_4 down the beaker walls and swirl.
   f) 3 ml DI H_2O and swirl.
   g) 1 ml 0.008 N $K_2Cr_2O_7$ and swirl.
   h) 5 ml 1 M $FeSO_4$ and swirl. (Allow 30-60s reaction time, adjust temperature to 40-43 deg C during this time period).
   i) 10 ml nitric-sulfamic acid solution and swirl. (Allow 3 min reaction time, weigh out vanadyl sulfate and prepare electrodes during this time period).
   j) 100 ml 1 M H_2SO_4 (wash down thermometer).
   k) 100 mg – 120 mg vanadyl sulfate.

2. Insert the electrodes and immediately titrate with 0.027 N $K_2Cr_2O_7$. (The endpoint is between 590-620 mv.) Rapidly add titrant until ~520 mv is reached. Then add titrant in 0.01 ml or 0.002 ml increments depending on uranium concentration, and record the potential at each addition of titrant. Use the second derivative method of calculating the endpoint.)

3. Place the remaining solution in the appropriate waste container.

B. Total U for samples dissolved in concentrated H_3PO_4.

1. To 300 ml tall form beaker add the following in order:
   a) Magnetic stir bar.
   b) 15 ml sample (pipetted).
   c) 3 ml conc. H_2SO_4 and swirl.
   d) 5 ml 1.5 M sulfamic acid and swirl.
   e) 28 ml conc. H_3PO_4 down the beaker walls and swirl.
   f) 11 ml DI H_2O and swirl.
   g) 1 ml 0.008 N $K_2Cr_2O_7$ and swirl.
   h) 5 ml 1 M $FeSO_4$ and swirl. (Allow 30-60s reaction time, adjust temperature to 40-43 deg C during this time period).
   i) 10 ml nitric-sulfamic acid solution and swirl. (Allow 3 min reaction time, weigh out vanadyl sulfate and prepare electrodes during this time period).
   j) 100 ml 1 M H_2SO_4 (wash down thermometer).
   k) 100 mg – 120 mg vanadyl sulfate.

2. Insert the electrodes and immediately titrate with 0.027 N $K_2Cr_2O_7$. (The endpoint is between 590-620 mv.) Rapidly add titrant until ~520 mv is reached. Then add titrant in 0.01 ml or 0.002 ml increments depending on uranium concentration, and record the potential at each addition of titrant. Use the second derivative method of calculating the endpoint.)

3. Place the remaining solution in the appropriate waste container.

C. Procedure for U^{+4} (sample must be dissolved in concentrated H_3PO_4)

1. To 300 ml tall form beaker add the following in order:
   a) Magnetic stir bar.
   b) 15 ml sample (pipetted).

Allow the beaker to stand while the rest of the reagents are added to a separate clean beaker.

2. To a separate clean 250 ml beaker, add:
   a) 15 ml conc. H_3PO_4 and swirl.
   b) 3 ml conc. H_2SO_4 and swirl.
   c) 5 ml 1.5 M sulfamic acid and swirl.
   d) 13 ml conc. H_3PO_4 down the beaker walls and swirl.
   e) 11 ml DI H_2O and swirl.
   f) 1 ml 0.008 N $K_2Cr_2O_7$ and swirl.
   g) 5 ml 1 M $FeSO_4$ and swirl. (Allow 30-60s reaction time, adjust temperature to 40-43 deg C during this time period).
   h) 10 ml nitric-sulfamic acid solution and swirl. (Allow 3 min reaction time, weigh out vanadyl sulfate and prepare electrodes during this time period).
   i) 100 ml 1 M H_2SO_4 (wash down thermometer)..
   j) Add this solution to the beaker containing the pipetted sample (steps 1a-1b).
   k) Add 100 mg – 120 mg vanadyl sulfate.

3. Insert the electrodes and immediately titrate with 0.027 N $K_2Cr_2O_7$. (The endpoint is between 590-620 mv.) Rapidly add titrant until ~520 mv is reached. Then add titrant in 0.01 ml or 0.002 ml increments depending on sample size, and record the potential at each addition of titrant. Use the second derivative method of calculating the endpoint.)

4. Place the remaining solution in the appropriate waste container.

8.0 CALCULATIONS

Sample Titration Data showing 2nd derivative method:

A Volume (ml)	B Potential (mV)	C d(B)/ d(A)	D d^2(B)/ d^2(A)
0.000	559		
0.008	576		
0.010	583		
		\	
		7,500	
		/ \	
0.012	598		+ 4,500
		\ /	
		12,000	
		/ \	
0.014	622		- 2,500
		\ /	
		9,500	
		/	
0.016	641		

Endpoint = 0.012 ml + 0.002 ml [4,500 / (4,500 + 2,500)] = 0.01329 ml

Sample Calculation for the Amount of Uranium:

[0.01329 ml - 0.0024 ml (blank)] x 0.027039 meq/ml x 1 mmol/ 2 meq x 238.03 mg U/ 1 mmol U = 0.035 mg U

Reporting limit – The reporting limit for this procedure is the amount of uranium corresponding to 0.005 ml of titrant after blank correction.

9.0 *POLLUTION PREVENTION AND WASTE MANAGEMENT*

Because all materials utilized in this procedure are potentially radioactive sources, all samples, waste, and standards will be appropriately labeled and handled according to MCL-7718 and MCL-7715.

The waste will be minimized by using small volumes and minimizing quantities utilized for sample preparation and standards preparation. Materials for disposal will be segregated and properly labeled. Where possible, the waste will be reduced by known treatment methodologies.

Rad waste will be measured and documented and where necessary turned over to an approved commercial handling and disposal service.

10.0 REFERENCES

1. W. Davies and W. Gray, "A Rapid and Specific Titrimetric Method for the Precise Determination of Uranium Using Iron (II) Sulfate as Reductant,"Talanta" 11, (1964), p. 1203.

2. Eberle et al., "Titrimetric Determination of Uranium in Product, Fuel, and Scrap Materials After Ferrous Ion Reduction in Phosphoric Acid," New Brunswick Laboratory Progress Report No. 252, July, 1970.

3. R.J. Jarabek, Transport Measurements of UF_5 Using a Precision Analysis for U^{+4}, K/PS-5017, Martin Marietta Energy Systems, Inc., Oak Ridge Gaseous Diffusion Plant, April 2, 1984.

4. D.A. Skoog and D.M. West, Fundamentals of Analytical Chemistry, Holt, Reinhart, and Winston, Inc., pp. 550-554, 2nd ed., 1969.

MATERIALS AND CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE		
Acid Digestion for Metals Based on EPA Method 3050B: **Materials and Chemistry Laboratory, Inc.**	Approved: MCLinc President	Date
	Quality Assurance Officer	Date

1.0. PURPOSE

This document provides the procedural steps and materials necessary to digest air filters, wipes, and other industrial hygiene samples, and solid samples including soils for total environmentally available metals for subsequent analysis by Flame atomic Absorption, GFAA, and Inductively Coupled Plasma

2.0. SCOPE

This procedure is based on the USEPA metals preparative Method 3050B as defined in SW-846 and NIOSH Method 7300 Elements by ICP.

3.0. ROLES AND RESPONSIBILITIES

MCLinc Analyst is responsible for following this procedure and reporting any anomalies that may occur and reviewing the results and properly documenting all elements as required in the procedure.

MCLinc Project Manager provides project oversight and is responsible to assure all users of this procedure on the project are trained and understand the procedure. The MCLinc Technical Director and QA Officer will provide support as needed.

4.0. REAGENTS/MATERIALS/EQUIPMENT

4.1. Reagents

Nitric Acid – concentrated, trace metals grade
Hydrogen peroxide – 30%
Nitric Acid Solution – 1:1 concentrated trace metals grade nitric/DI water.
Spiking Solutions
Hydrochloric Acid – concentrated, trace metals grade

4.2.Equipment

Glass beakers
Ribbed watch glasses capable of covering the beakers
Electronic Balance
Hot plate with temperature monitoring capabilities (i.e. thermometer in beaker of water)

Assorted laboratory glassware (volumetric flasks, graduated cylinders, pipets, etc.)
Funnels and Whatman # 41 filter paper or MCLinc approved equivalent.
Hot Block with temperature monitoring capability (i.e., thermometer in digestion tube of water *[For recording the Hot Block used and the location of the thermometer tube location, see Appendix A.*)
50mL digestion tubes to fit hot block
50mL centrifuge tubes

4.3. Miscellaneous

Latex/nitrile gloves
Tongue depressor or metal spatulas
DI water bottle
Paper towels
Sample Prep/lot Sheet
Polyethylene bottle

5.0. PROCEDURE

Note: Clean all glassware per MCL SOP for Glassware Cleaning, MCL-7753.

5.1. Sample Preparation

1. Identify beaker and tare on the balance.
2. Transfer 2g$\pm$0.1g using a clean unused tongue depressor to the tared beaker.
3. Record the MCL Sample No. and weight on the prep/lot sheet.
4. Add 10 ml of the 1:1 nitric acid solution to the beaker mix, cover with a watch glass and reflux at 95^{o}C$\pm$5^{o}C for a minimum of 10min without boiling.
5. Allow to cool, add 5 ml of concentrated nitric acid, replace the watch glass and reflux at 95^{o}C$\pm$5^{o}C for a minimum of 10 min without boiling.
6. If brown fumes appear repeat step 5 until there are no more brown fumes being generated.
7. Once the generation of brown fumes has stopped allow to heat until the volume has been reduce to approximately 15-20 ml. **Do not allow to go to dryness.**
8. Allow the sample to cool, add 2 ml of DI water and 3 ml of 30% peroxide. Add the peroxide slowly being careful not to allow the sample to effervesce out of the beaker. Continue to add peroxide in 1ml aliquots until all effervescing has stopped. Do not add more than 10ml total volume of peroxide.
9. Cover the sample and reflux at 95^{o}C$\pm$5^{o}C again reducing the volume to approximately 15-20 ml. **Do not allow to go to dryness.**
10. After cooling, filter using a funnel and Whatman #41 filter paper. Quantatively transfer the filtered sample to a 100 ml volumetric flask with DI water and bring up to volume.
11. Pour sample solution into properly labeled polyethylene sample bottle.

5.2. Sample Prep with Hot Block Digestion

1. Weigh Sample (2.0+/-0.1g in tared vials or carefully place air filters, wipes directly into the vials for hotblock digestion.)
2. Turn on hot block @ set point = 115 per manual *(95 ℃ ±5^{o}C)* temperature. *Check temperature for each set of samples.*

3. Weigh samples in tared vials for hot block digestion.
4. Add 10ml 8N HNO_3 and 3ml HNO_3 .
5. Digest for 1 hour.
6. Remove from hot block and cool.
7. Add 3-10ml H_2O_2.
8. Digest for 30 minutes.
9. Remove from hot block and allow to cool.
10. Filter into 50mL centrifuge tube containing 5mL conc HNO_3 <u>for ICP-OES analyses. For ICP/MS omit the 5mL conc. HNO_3</u>.
11. Bring to volume and run on ICP.

5.3. Special Instructions – Antimony

1. This procedure is for preparation for solid sample(s) requiring antimony analysis. If sample(s) require the analysis of other metals, use this digestion procedure for the preparation for all metals.
2. Add 2.5 mL conc. HNO_3 and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample in the hot block at *95°C ±5°C* and reflux for 15 minutes.
3. If the sample has not dissolved in the acid solution, proceed to Step 4. If the entire sample has dissolved in the digestate acid solution, filtration is not necessary. The final sample volume will be 50mL if 10 or fewer metals will be analyzed or 100mL if more than 10 metals are analyzed. Allow the digestate solution to cool. Quantitatively transfer the digestate solution to the proper size container and dilute to volume with reagent water.
4 Filter the sample/digestate solution through Whatman No. 41 filter paper or equivalent and collect filtrate in a clean 100mL volumetric flask. Wash the filter paper while still in the funnel with 5mL of hot (95±5°C) HCl, then with 5-10mL of hot reagent water. Collect the wash solutions in the same flask.
5. Remove the filter paper and residue from the funnel and place back in the digestion vessel. Add 5mL of hot HCl and place the digestion vessel back in the hot block. Heat at 95±5°C until the filter paper dissolves. Remove the tube from the hot block and rinse the watch glass and sides of tube with reagent water. Filter the residue and collect the filtrate in the same flask as in Step 4. Allow the filtrate to cool. If there is no precipitate present after cooling, dilute to volume with reagent water. If there is a precipitate present, see NOTE and proceed to Step 6. <u>NOTE</u>: High Concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates in these solutions upon cooling. If precipitation occurs, do not dilute to volume.
6. If a precipitate forms, add up to 10mL HCl. After precipitate has dissolved, dilute the sample to volume with reagent water.

5.4. *Special Instructions – Beryllium Oxide (BeO)*

For samples requiring the analysis of BeO, prepare samples per Operator Aid UU in MCLinc SOP MCL-7756.

5.5. Other Special Instructions

Radiological Screening Samples

1. Label the top of a 20 ml scintillation vial with the sample number.
2. Transfer 0.5- 2 ml of the final digestate solution from Step 10 above.
3. Proceed per MCL-7733 Section 6.6.1.11

Shipping metals digested sample

1. Label 250 ml plastic sample bottle with the MCL sample number, TM (for Total Metals) designator and Batch ID.
2. Fill bottle with final digestate solution; seal and stage for shipping

6.0. QUALITY CONTROL (QC)

Each batch of 20 or fewer samples will contain a minimum of *two* Laboratory Control Samples (LCS *and LCSD*) and a Method Blank (MB). Matrix Spike/Matrix Spike Duplicate (MS/MSD) will be added if required by project.

6.1. LCS

Since the metal requests vary by project, select appropriate standard spiking solutions for LCS*s* that match sample request. Spike levels should be within the calibration range of the metal. For the digestion of air filter samples or wipe samples, add a new filter or wipe to the LCS samples before digestion.

6.2. Method Blank

1. Run with each set of samples digested.
2. Using a clean beaker begin at Step 4 above in 5.1 and process with the rest of the samples.

6.3. MS/MSD

Matrix spike (MS) and matrix spike duplicate (MSD) are project specific and are used to determine accuracy. If required, one set of MS/MSD is included with each batch of 20 or fewer samples processed.

7.0. REPORTING

All recording of information shall be done on the Metals Sample Preparation Log Sheet. An example is presented in Appendix A.

8.0. POLLUTION PREVENTION AND WASTE MANAGEMENT

Because all materials utilized in this procedure are potentially radioactive sources, all samples, waste, and standards will be appropriately labeled and handled according to MCL-7718 and MCL-7715.

The waste will be minimized by using small volumes and minimizing quantities utilized for sample preparation and standards preparation. Materials for disposal will be segregated and properly labeled. Where possible, the waste will be reduced by known treatment methodologies.

Radioactive waste will be measured and documented and where necessary turned over to an approved commercial handling and disposal service.

9.0. REFERENCES

USEPA SW-846 Third Edition Revision 2, December 1996 Method 3050B Acid Digestion of Sediments, Sludges, and Soils.

NIOSH Method 7300 Elements by ICP, Fourth Edition, Issue 2, August 15, 1994.

Procedure: MCL-7746 or Be MCL-7756, App. UU Sample Type: Air Filters, Wipes, Solids, Soils, Oils

Date: _____ Prepared By: _____ Project ID: _____

Spike ID(s):A_____B_____C_____D_____

Used (check one): Class A Glass Pipets? ☐ Autopipet? ☐ Autopipet #: _____Verification Wt. _____ (DI H_2O) (g)

QA/QC Information	QC Sample ID	Matrix (soil, wipe, filter, DI H_2O)	Aliquot (g) or (mL)	Volume (mL) & Spike ID	Final Vol. (mL)	Comments

Sample Information	MCL Sample ID	Matrix (soil, filter, etc.)	Aliquot (g) or (mL)	Final Vol. (mL)	Digestion Temp (°C)	Comments	Chemicals/Reagents Used (include Prep Log Date)

Balance ID		Weight (g)				
Calibration ID		Actual (g)				
Weight Set ID		Actual (g)				
		Avg (g)				

Hot Block Used (circle one): **A** **B** **C** **D** Thermometer ID: _____

Temp. Blank Location:_____ Signature _____

APPENDIX A. HOT BLOCK LABELS

The hot blocks used for metals digestion are not moved from the laboratory or within the laboratory. The two large hot blocks are identified as A and B from left to right within the fume hood they are located within. The two small hot blocks are identified as C and D within the fume hood they are located within. Record on the prep sheet the Hot Block number and the well used for temperature determination. Move the thermometer to the next location with every set of samples digested.

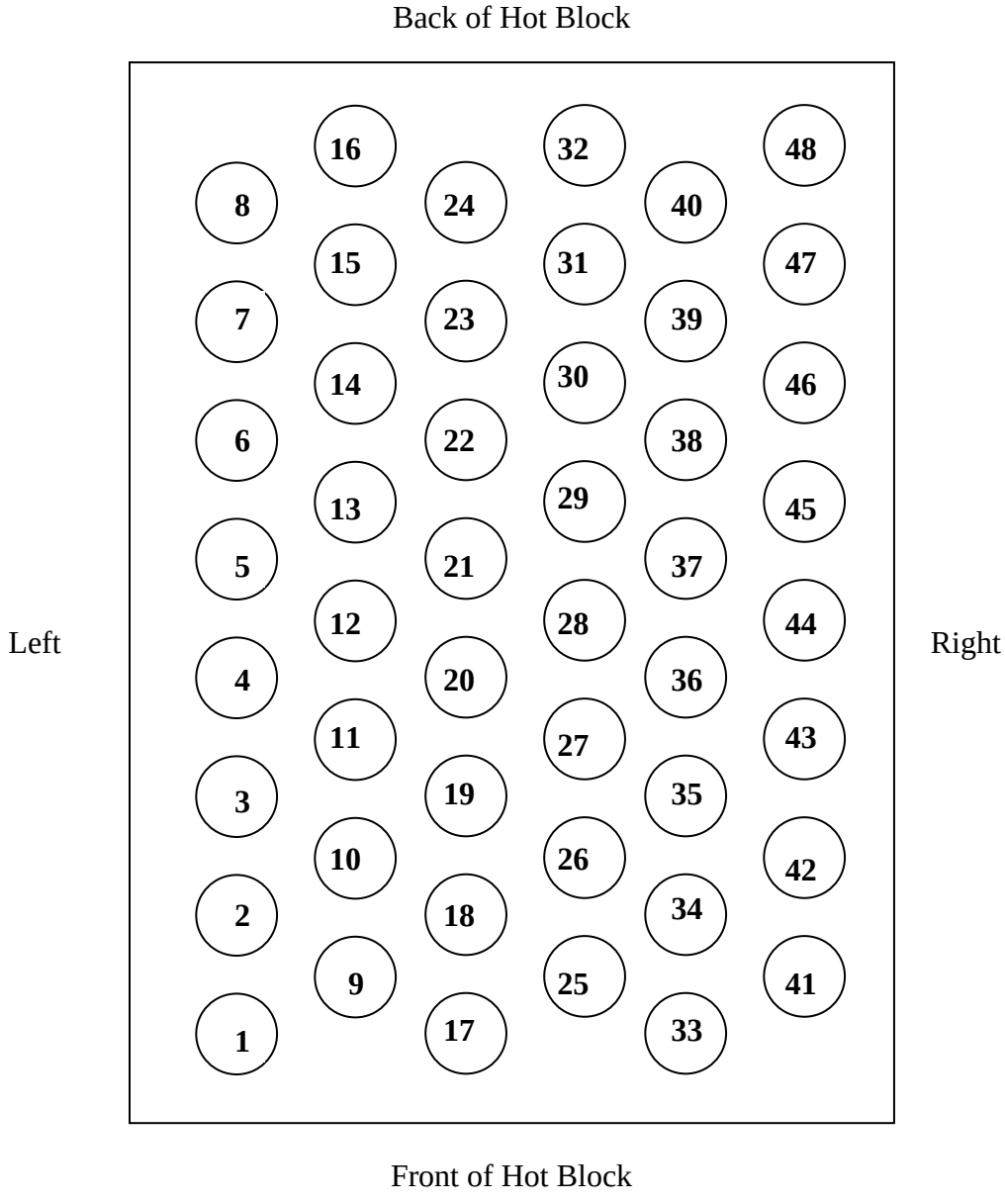


Figure 1. ***The wells within the Large Hot Blocks (A and B)are numbered from Left to Right, Front to Back in numerical order starting with 1.***

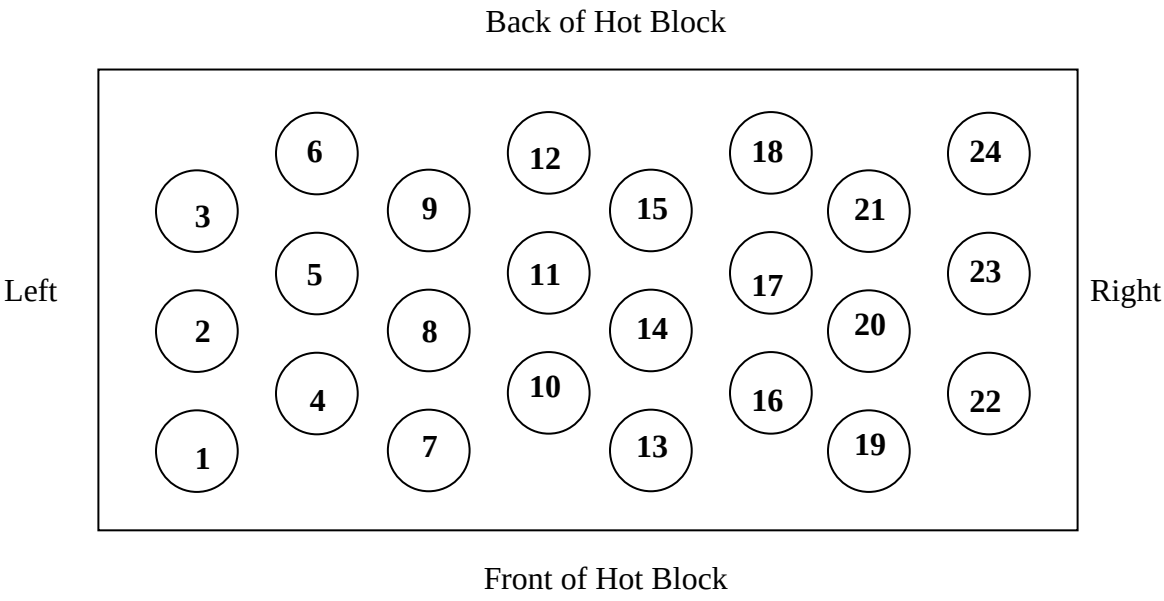


Figure 2. ***The wells within the Small Hot Blocks (C and D) are numbered from Left to Right, Front to Back in numerical order starting with 1***

MATERIALS & CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE		
Determination of pH Value: Materials & Chemistry Laboratory, Inc.	Approved: _____ MCLinc President _____ Quality Assurance Officer	 _____ Date _____ Date

1. Purpose

The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kPa. Because of difficulty in its use and the potential for poisoning the hydrogen electrode, the glass electrode commonly is used. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is determined by extrapolation.

Because single ion activities cannot be measured, pH is defined operationally on a potentiometric scale. The pH measuring instrument is calibrated potentiometrically with an indicating (glass) electrode and a reference electrode using National Institute of Standards and Technology (NIST) buffers.

a. In practice, samples will have varying ionic species and ionic strengths, both affecting H+ activity. This imposes an experimental limitation on pH measurement. Samples must be dilute aqueous solutions of simple solutes. (Choose buffers to bracket the sample.) Determination of pH cannot be made accurately in nonaqueous media, suspensions, colloids, or high-ionic strength solutions.

b. Interferences: The glass electrode is relatively free from interference from color, turbidity, colloidal matter, oxidants, reductants, or high salinity. pH measurements are affected by temperature in two ways: mechanical effects that are caused by changes in the properties of the electrodes and chemical effects caused by equilibrium changes. In the first instance, the Nernstian slope increases with increasing temperature and electrodes take time to achieve thermal equilibrium. This can cause long-term drift in pH. Because chemical equilibrium affects pH, standard pH buffers have a specified pH at indicated temperatures.

2. Apparatus

a. pH meter consisting of potentiometer, a glass electrode, a reference electrode, and a temperature-compensating device. A circuit is completed through the potentiometer when the electrodes are immersed in the test solution. Many pH meters are capable of reading pH or millivolts and some have scale expansion that permits reading to 0.001 pH unit, but most instruments are not that precise. For routine work, use a pH meter accurate and reproducible to 0.1 pH unit with a range of 0 to 14 and equipped with a temperature-compensation adjustment.

b. Upon immersion of a new electrode in a solution, the outer bulb surface becomes hydrated and exchanges sodium ions for hydrogen ions to build up a surface layer of hydrogen ions. This, together with the repulsion of anions by fixed, negatively charged silicate sites, produces at the glass–solution interface a potential that is a function of hydrogen ion activity in solution. Several types of glass electrodes are available. Combination electrodes incorporate the glass and reference electrodes into a single probe.

c. Beakers: Preferably use polyethylene or TFE* beakers; however, borosilicate glass beakers can be used.

d. Stirrer: Use either a magnetic, TFE-coated stirring bar or a mechanical stirrer with inert plastic-coated impeller.

3. Reagents

Calibrate the electrode system against standard buffer solutions of known pH. Because buffer solutions may deteriorate as a result of mold growth or contamination, use fresh buffers for accurate work.

4. Procedure

a. Instrument calibration: In each case, follow manufacturer’s instructions for pH meter and for storage and preparation of electrodes for use. Recommended solutions for short-term storage of electrodes vary with type of electrode and manufacturer, but generally have a conductivity greater than 4000 mhos/cm. A pH 4 buffer is best for the single glass electrode and saturated KCl is preferred for a calomel and Ag/AgCl reference electrode. Saturated KCl is the preferred solution for a combination electrode. Keep electrodes wet by returning them to storage solution whenever pH meter is not in use. Before use, remove electrodes from storage solution, rinse, blot dry with a soft tissue, and place in initial buffer solution. Select a second buffer within 2 pH units of sample pH and bring sample and buffer to same temperature, which may be the room temperature; a fixed temperature, such as 25°C; or the temperature of a fresh sample. Remove electrodes from first buffer, rinse thoroughly with distilled water, blot dry, and immerse in second buffer. Record temperature of measurement and adjust temperature dial on meter so meter indicates pH value of buffer at test temperature. Remove electrodes from second buffer, rinse thoroughly with distilled water and dry electrodes as indicated above. Immerse in a third buffer below pH 10, approximately 3 pH units different from the second; the reading should be within 0.1 unit for the pH of the third buffer. If the meter response shows a difference greater than 0.1 pH unit from expected value, look

for trouble with the electrodes or potentiometer. The purpose of standardization is to adjust the response of the glass electrode to the instrument. When only occasional pH measurements are made, standardize instrument before each measurement. When frequent measurements are made and the instrument is stable, standardize less frequently. If sample pH values vary widely, standardize for each sample with a buffer having a pH within 1 to 2 pH units of the sample.

b. Sample analysis: Establish equilibrium between electrodes and sample by stirring sample to ensure homogeneity; stir gently to minimize carbon dioxide entrainment. For buffered samples or those of high ionic strength, condition electrodes after cleaning by dipping them into sample for 1 min. Blot dry, immerse in a fresh portion of the same sample, and read pH. With dilute, poorly buffered solutions, equilibrate electrodes by immersing in three or four successive portions of sample. Take a fresh sample to measure pH.

5. Precision and Bias

By careful use of a laboratory pH meter with good electrodes, a precision of ± 0.02 pH unit and an accuracy of ± 0.05 pH unit can be achieved. However, ± 0.1 pH unit represents the limit of accuracy under normal conditions, especially for measurement of water and poorly buffered solutions. For this reason, report pH values to the nearest 0.1 pH unit. A buffer solution of pH 7.0 was analyzed electrometrically with a standard deviation of ± 0.11 pH.

MATERIALS & CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE	
Ferric Iron Analysis by Visible Light Spectroscopy (Colorimetric): Materials & Chemistry Laboratory, Inc.	Approved: MCLinc President — Date 11/11/2019 Quality Assurance Officer — Date 11/11/2019

1.0. PURPOSE

The purpose of this SOP is to establish guidelines for the preparation of soil samples for the spectroscopic analysis of Total and Ferrous (Fe^{2+}) Iron and subsequent calculation of Ferric (Fe^{3+}) Iron. Under acidic conditions, hydroxylamine hydrochloride reduces amorphous Fe^{3+} to Fe^{2+}, the latter of which is quantitatively measured by the phenanthroline colorimetric method. The reagent 1,10-phenathroline forms an orange-colored complex that is measured at 510 nm for the specific determination of ferrous iron. The concentration of ferric iron can then be calculated by the subtraction of the ferrous iron concentration from the total amorphous iron concentration.

2.0. PROCEDURE

2.1 Use **of the Spectrometer**:

- Turn on the spectrometer and allow to warm up for at least 30 minutes before use.
- Set wavelength to 510 nm.
- Zero the instrument while in %Transmittance mode.
- Insert a cuvette containing DI H_2O
- Set Transmittance to 100% (Absorbance 0)
- Measure the absorbance of calibration standards, creating a calibration curve
- Measure the absorbance of samples

3.0. EQUIPMENT

- Analytical Balance
- Volumetric Glassware
- Glass Cuvettes
- Spectrometer

4.0 REAGENT PREPARATION

4.1 Phenanthroline Solution: Dissolve 100 mg of 1,10-phenanthroline in 100 mL of DI H_2O and 2 drops of HCl, with stirring. Heat to 80°C if necessary, taking care not to bring to boiling. Discard the solution if it darkens.

4.2 Ammonium Acetate Buffer: Dissolve 250 g of Ammonium Acetate in 150 mL of DI H_2O. Add 700 mL of conc. Glacial Acetic Acid.

5.0 STANDARD PREPARATION

5.1 Ferrous Iron Calibration Standard:
Dilute purchased Ferrous Iron Standard Solution (50 mg/mL) with 0.25 M HCl. Add 5 mL of phenanthroline solution before measurement.

5.2 Ferrous Iron CCV Standard Solution:
Dissolve 1.404 g of ferrous ammonium sulfate hexahydrate in a mixture of 20 mL H_2SO_4 and 50 mL DI H_2O. Dilute to volume 1 L with DI H_2O. 1 mL of solution contains 200 µg Fe. Add 5 mL of phenanthroline solution before measurement.

Stock Standard Solution		Standard ID	Fe^{2+} CAL 1	Fe^{2+} CAL 2	Fe^{2+} CAL 3	CCV Standard Solution		CCV
Analyte	Conc. (µg/mL)	**Final Volume**	10	10	10	Analyte	Conc. (µg/mL)	10
Fe^{2+}	50	**Transfer vol.(mL)**	0.1	0.3	0.5	Fe^{2+}	200	0.1
		Conc. (µg/mL)	0.5	1.5	2.5			2.0
		Total µg	5	15	25			20

5.3 Total Iron Calibration Standard:
Dilute purchased Standard Solution (1000 µg/mL) with 0.25M Hydroxylamine Hydrochloride in 0.25M HCl. Add 5 mL of phenanthroline solution before measurement.

5.4 Total Iron CCV Standard Solution:
Dilute purchased Standard Solution (100 µg/mL) with 0.25M Hydroxylamine Hydrochloride in 0.25M HCl. Add 5 mL of phenanthroline solution before measurement.

Stock Standard Solution		Standard ID	Fe CAL 1	Fe CAL 2	Fe CAL 3	Fe CAL 4	Fe CAL 5	CCV Standard Solution		CCV
Analyte	Conc. (µg/mL)	**Final Volume**	10	10	10	10	10	Analyte	Conc. (µg/mL)	10
Fe	1000	**Transfer vol.(mL)**	0.1	0.2	0.3	0.5	0.8	Fe	100	0.3
Intermediate Standard Solution		**Conc. (µg/mL)**	0.5	1.0	1.5	2.5	4			3
Fe	50	**Total µg**	5	10	15	25	40			30

6.0 SAMPLE PREPARATION

6.1 Sample Preparation:

It is critical that the sample be well-homogenized before sampling and that extraneous material (wood chips, small pebbles, etc.) be excluded as much as possible from the sample aliquot. A portion of the moist soil or sediment will be used to determine the moisture content of the thawed, as-received sample. This data will be used to allow estimation of the dry-weight equivalent mass for soil aliquots.

6.2 Ferrous (Fe^{2+}) Iron Sample Preparation:

To 0.1 g of sample, add 5 mL of 0.5M HCl, gently swirl for 30 seconds, and allow to stand for 1 hour. To 0.1 mL of the sample extract*, add 1 mL of Ammonium Acetate Buffer and 5 mL of Phenanthroline Solution and mix for 15 seconds. Filter if necessary and dilute to 10 mL with DI H_2O. Measure the absorbance of the solution at 510 nm.

6.3 Total (Total Fe converted to Fe^{2+}) Iron Sample Preparation:

To 0.1 g of sample, add 5 mL of a 0.25M solution of Hydroxylamine Hydrochloride in 0.25M HCl, gently swirl for 30 seconds, and allow to stand for 1 hour. To 0.1 mL of the sample extract*, add 1 mL of Ammonium Acetate Buffer and 5 mL of Phenanthroline Solution and mix for 15 seconds. Add one mL of Ammonium Acetate Buffer. Filter if necessary and dilute to 10 mL with DI H_2O. Measure the absorbance of the solution at 510 nm.

*Note: The volume of sample extract used for analysis may be changed to remain within to the calibration range.

7.0 CALCULATIONS

7.1 Iron Concentration (µg/g):

$$= \frac{\text{Iron Measured (µg)}}{\text{sample weight (g)}} \times \frac{\text{Extraction Volume (mL)}}{\text{aliquot of sample extract (mL)}}$$

7.2 Ferric (Fe^{3+}) Iron (µg/g):

= Total Iron Concentration (µg/g) – Ferrous Iron Concentration (µg/g)

8.0 REFERENCES

Christensen, T.H.; P.L. Bjerg; S.A. Banwart; R. Jakobsen; G. Heron; H.J. Albrechtsen, (2000), *Characterization of redox conditions in groundwater contaminant plumes* [Review], Journal of Contaminant Hydrology, **45**, 165-241.

Lovely, D.R.; Phillips, E.J.P., 1987b. *Rapid assay for microbially reducible ferric iron in aquatic sediments.* Ppl. Environ. Microbiol. 53, 1536-1540.

Standard Methods for the Examination of Waste and Wastewater (SMEWW), 23rd Edition (2017), *Method 3500-Fe B: Phenanthroline Method.*

APPENDIX D-8

ALS ENVIRONNEMENTAL SIMI VALLEY SOPS

SAMPLE RECEIVING, ACCEPTANCE, AND LOGIN

DOCUMENT I.D. SMO-SMPL_REC

Approved By: Kate Kaneko Date: 5/29/18
Interim Laboratory Manager – Kate Kaneko

Approved By: Chaney Humphrey Date: 5/29/18
Quality Assurance Manager – Chaney Humphrey

Approved By: Date: 5-29-18
Sample Management Custodian – Al David

SOP CHANGE FORM

SOP Title: Sample Receiving, Acceptance, and Login
SOP Code: SMO-SMPL_REC
SOP Revision No.: 18
SOP Date: June 2, 2019
SOP Section(s) Affected by Change: 4.2, 10.3, 10.4

Description of Change:

Section 4.2: Update "*SOP for Waste Disposal*" to "*Simi Valley Lab Waste Management Plan*".

Section 10.3: Update reference to current DoD QSM version.

Section 10.4: Update reference ISO/IEC 17025:2005 to ISO/IEC 17025:2017.

Reason(s) for Change(s):

Section 4.2: The *SOP for Waste Disposal* has been replaced by the *Simi Valley Lab Waste Management Plan.*

Section 10.3: Update reference.

Section 10.4: Update reference.

Change(s) Submitted by: Chaney Arend	Date: 06/~~16~~19 CA 6/19/19

Approvals:

QA Manager Signature: Chaney Arend	Date: 6/19/19
Supervisor/Manager Signature:	Date: 6/19/19

Change(s) Effective Date: 06/19/19

Distribution: Original filed with original SOP
Copy attached to each controlled copy

Complete on hardcopy filed with original SOP
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1) Scope and Applicability

1.1 The purpose of this standard operating procedure (SOP) is to describe the requirements and guidelines necessary for effective sample receiving as well as the documentation associated with this process. Additionally, this document describes the procedures relating to the Sample Management Office for initiating any subcontract documentation.

1.2 This standard operating procedure (SOP) is applicable to all samples delivered to this laboratory and subcontracted out for analysis.

2) Summary of Procedure

2.1 For the purposes of this document sample receiving is considered to be an all-inclusive system, which comprises sample custody transfer, sample acceptance, and sample login.

2.2 This procedure is essential in identifying compromised samples and ensuring the validity of the laboratory's sample data. Improper sample handling affects the credibility and acceptability of analytical results, regardless of their accuracy and precision. Therefore, it is essential that all samples be properly received and handled and that the documentation maintained accurately reflects the integrity and processing of samples.

3) Definitions

3.1 Custody The guardianship or safe keeping of a sample. A sample is considered to be in a person's custody if it is physically in their possession, or it is in their view after being in their possession, or it was in their possession and then locked up or sealed to prevent tampering, or it is in a secure area.

3.2 Chain of Custody (COC) Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes the number and types of containers; the mode of collection; collector; time of collection; preservation; and requested analyses.

3.3 Internal Chain-of-Custody Procedures employed to record the possession of samples from the time of sample receipt until disposal/storage and are performed at the special request of the client. These protocols are handled electronically through LIMS.

3.4 Compromised Samples Those samples which are improperly sampled, insufficiently documented, improperly preserved, collected in improper containers, exceeding holding times and/or not received intact when delivered to a laboratory.

3.5 Holding Times (Maximum Allowable Holding Times) The maximum times that samples may be held prior to preparation and/or analysis and still be considered valid or not compromised. (40 CFR Part 136)

3.6 Preservation Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.

3.7 Service Request (SR) / Job File A unique, computer generated laboratory number which is assigned to a sample or group of samples submitted (at the same time) by the client representing one job or project. The job or project includes specific sample management information, analysis data, client correspondence, analysis report and other pertinent

information comprising a single sample submission containing one or more samples in a client's project.

3.8 COC Chain-of-Custody

3.9 SACF Sample Acceptance Check Form

3.10 LIMS Laboratory Information Management System

3.11 SMO Sample Management Office

3.12 PM Project Manager (may be referred to in other lab documents as PC/Project Chemist)

3.13 SMC Sample Management Custodian

3.14 SDG Sample Delivery Group

3.15 EDD Electronic Data Deliverable

4) Safety

4.1 Handle all samples as potentially hazardous. Gloves should be worn when handling all samples, safety glasses, and a lab coat shall be worn when handling liquid or soil (solid) samples. Always work under a hood when chemically preserving samples. Also place broken or leaking samples under the hood. Get assistance when confronted with any situation that appears to be dangerous.

4.2 In the event of broken liquid or soil samples, SMO needs to cleanup using one of the following procedures:

- Liquids: Broken glass is handled carefully using disposable gloves and disposed of in the Glass Disposal Box. Remaining sample and cleanup materials are disposed of in accordance with the *SOP for Waste Disposal*.
- Soils: Broken glass is disposed of in the Glass Disposal Box, and the soil is disposed of into the 55-gallon soil drum. This information is noted on the Service Request Form and the PM is notified. Soil that is still intact in a glass jar may be salvaged with client's approval.

5) Responsibilities

5.1 All employees involved with sample receiving, acceptance and login must ensure the procedures described in this document are followed. More specifically, SMO personnel, Project Managers and the Sample Management Custodian are responsible for complying with and implementing the procedures listed in this document.

6) Procedure

6.1 Upon sample receipt, the condition, including any abnormalities or departures from normal or specified conditions as described in the test method or method standard operating procedure must be recorded. All of the information including any other observances must be recorded on the Sample Acceptance Check Form (Attachment 2) and other associated documentation as detailed in the following procedures. Refer to Section 6.4 for the necessary procedures and documentation requirements dictated by abnormalities or departures.

6.2 Sample Custody

Upon delivery to the laboratory, the sample(s) must be transferred (as soon as possible) to a Sample Management Custodian (SMC) or a representative of the laboratory who accepts and assumes custody of the sample(s). Samples are transported to the laboratory by a number of means including courier, common carrier, sampler or client representative. The acceptance of a sample is achieved by presenting a signature, date and time of receipt in accordance with the requirements of the transmitter and client such as an electronic board (i.e. FedEx) and Chain of Custody Form. Sample shipping containers are examined for the presence and condition of custody seals, locks, shipping waybills, etc. After opening shipping containers, remove any other documents in order to evaluate login priority (see note below) and continue processing the samples.

Note: Rush requests and samples with short holding times are given top priority for processing. Sample Custodian alerts Project Manager and analysts by calling them and distributing copies of the COC and any other pertinent documentation. Refer to Appendix F in the Quality Assurance Manual for Sample Preservation and Holding Times which list maximum allowable hold times.

6.2.1 Shipping Receipts and Chain of Custody (COC) Forms

6.2.1.1 Packing Slips

A copy of the packing slip must be kept, whenever possible, as part of the permanent chain of custody process and placed in the job file.

6.2.1.2 Chain of Custody Forms

These forms may be identical to the one issued by the laboratory (see Figures 11-1 and 11-2 in the Quality Assurance Manual) or clients may submit samples using a similar form. The SMC or designee shall sign the COC and add the date and time of receipt. In addition, the service request number must be added to the COC form at the time of sample login.

6.2.2 Legal/Internal Chain of Custody (COC)

When samples are logged in using LIMS, the system automatically generates an internal chain of custody each time a sample is scanned into possession for use within the laboratory. This internal COC may be accessed anytime during the laboratory procedures and is provided to the client upon request.

6.3 Sample Receipt and Login

In order to evaluate the state of a sample upon receipt, the laboratory must evaluate certain parameters including container type, volume and preservation (thermal and chemical). Compare the findings against the specified criteria in Sample Preservation and Holding Times Tables in the most recent Quality Assurance Manual (Appendix F). Refer to Section 6.4 for the discrepancy/exception and the rejection of samples procedures.

Important: For odorous samples, refer to Section 6.9 for the handling procedure.

6.3.1 Service Request Form

A Service Request form (Attachment 3) shall be completed in LIMS for all samples received by the laboratory using the information provided on the sample receipt documentation (e.g., COC) and data collected by the SMC. A copy of this completed form shall accompany the sample(s). The following includes a description of the key components.

1. Service Request Number: Client's job file number (automatically assigned)
2. Report Name: Name of Client that shall be on report.
3. Reporting Address: Address of the Client that will be on the report.
4. Project Name: Client's referenced study or project name.
5. Project Number: Client's reference study or project number.
6. ISR Number (if applicable): Internal Service Request (between laboratories in the network using the same LIMS system)
7. Date Received: Date the laboratory actually received samples.
8. Purchase Order: Client's purchase order number or verbal notation (default).
9. Project Manager: The PM responsible for all client activity for job file.
10. TAT: Sample turnaround time (normal TAT, if not specified).
11. Initials: Initials of SMC or alternate logging in the sample(s).
12. Sample Type: Type/container of sample submitted by client.
13. Comments: Any comments concerning the sample or samples being submitted including short hold times.
14. Tier: QC level if one is given on the ISR or COC.
15. EDD: If EDD is required or not.
16. Method: Specified method for the samples to be analyzed.
17. Sample ID: Client's specified sample identification.
18. Test(s) Required: Number of methods for analysis on the samples.
19. Date Collected: Sampling date for each sample.
20. Time Collected: Sampling time for each sample.
21. Sample Type: Sample matrix for each sample.

Note: Some of the information (client's project name or number) may not be provided and will not be included on the form.

6.3.2 LIMS Login

Prior to sample arrival, the Project Manager may create a sample delivery group (SDG) in LIMS based on project information and in accordance with the *SOP for Project Management*. Analysis information associated with each sample is stored in this SDG. When samples arrive, the custodian uses this SDG as a template to create a job folder specific to the samples received. The custodian could either manually search SDG information from LIMS or find it by scanning the barcode of the bottle order form (also known as Bottle Order \ Sample Supplies Summary form).

Once the correct SDG has been selected, a sample template is chosen from the SDG template that best matches the analyses stated on the COC for each sample included on the COC. Once all the samples are chosen the custodian creates a unique job folder. Job folder is then edited as necessary (e.g., project name and number, date and time of sample collection, and client sample IDs).

Each sample container for a sample is given a unique lab code by the LIMS system. This lab code is express in the format of PYYJJJJJ-sss.ccc.

Where:

"P" is the current lab ID code for Simi Valley,
"YY" is the two-digit year code (e.g., 18 for Y2018),
"JJJJJ" is the five-digit job number (e.g., 00001 for the first project),
"sss" is a three-digit sample ID number;
"ccc" is the three-digit container ID number.

An example for the second container of the first sample for the first job of year for 2018 would be P1800001-001.002. The alphanumeric code before the dash is the job number, the number after the dash is sample ID and the number after the period is container ID.

6.3.3 Sample Acceptance Check Form The SMC shall complete and generate a Sample Acceptance Check form (Attachment 2) based on the information specified in this section. This form is given to the PM and electronically accessible so that Chemists may input additional preservation check information.

Once the samples have been checked and the SACF produced, the form is to be saved at G:\\STARLIMS\Sample Acceptance Check form (as SR#_Client_Project) so that additional information such as pH may be added.

6.3.3.1 Sample Acceptance Policy Sample containers are removed and organized according to the COC identification and analyses. The sample conditions are checked to ensure sample integrity has not been compromised. These steps are listed to complete the criteria for the acceptance or rejection of samples but they do not necessarily occur in this order. Each point is an evaluation requirement which must be used to complete the Sample Acceptance Check form.

- Sample submission documents are properly used, fully completed (in ink) and shall include the client, sample identification, project name or location, date and time of collection, collector's name, sample type, preservation type (if applicable) and any special remarks concerning the sample.
- Proper sample labeling is considered: unique sample identification (ID), durable labels (labels that are not easily removed) and the use of ink.
- Sample containers checked for integrity (broken, leaking, Tedlar® bags are received flat, under inflated or with the valve open, passivated stainless steel canisters are received under an unacceptable vacuum or with the valve open, etc.). Reject samples with broken or leaking containers.
- Sample container labels and/or tags agree with the sample documentation (ID, required analyses, etc.).
- Adherence to specified holding times (see Appendix F in the Quality Assurance Manual)
- Appropriate containers (size, type) are received for the requested analyses (see Appendix F in the Quality Assurance Manual).
- Proper temperatures of sample containers, if applicable (see Appendix F in the Quality Assurance Manual).

- Adequate sample volume (see Appendix F in the Quality Assurance Manual)
- Assessment of proper sample preservation, where applicable (see Appendix F in the Quality Assurance Manual). Reject samples preserved with the inappropriate preservatives for which the requested analysis has been compromised (e.g., cyanide samples preserved with acid).
- Any notation made by other persons accepting the sample and any evaluations made and noted on the associated documentation.

Once the samples have been checked against the Sample Acceptance Policy, the sample custodian must generate a Sample Acceptance Check form, sample identification labels, and Service Request form (optional). The Project Manager is responsible for generating and emailing the Sample Receipt Acknowledgment form (Section 6.5) if requested. The sample login forms and labels must be completed to properly track laboratory samples.

6.3.3.2 Measurement of Temperature The temperature of all coolers containing samples requiring thermal preservation shall be taken using a verified thermometer calibrated against NIST standards and the data recorded (with correction factor applied) on the Sample Acceptance Check form (Attachment 2).

An infrared thermometer shall be used to take the temperature reading of samples. Alternatively, a reading shall be taken by placing the thermometer in the cooler so as to give an accurate reflection of the cooler temperature (i.e. not directly on ice or blue ice and at approximate sample level or in the temperature blank, if supplied). The lid must be closed to allow enough time for the thermometer to reach equilibrium (i.e., a minimum of five minutes) before the temperature reading is taken and recorded. The arrival temperature check is considered acceptable if the following is adhered to:

- Samples have a temperature of +/-2˚C of the required temperature or the method specified range; or
- Samples with a required temperature of 4˚C have a temperature ranging from just above freezing of water to 6˚C; or
- IMPORTANT: The US EPA has published revisions to the Code of Federal Regulations at 40 CFR 136 and 40 CFR 141. These revisions, known as the Method Update Rule (MUR), became effective 4/11/07 and contains a revised approved methods tables and temperature requirements. A number of the methods have been updated and for those methods the temperature requirement has been updated to ≤6˚C. Refer to Appendix F in the most recent Quality Assurance Manual for the specific methods that are affected.

Note: Samples that are hand delivered to the laboratory immediately following collection may not meet these criteria. This is considered acceptable if there is evidence that the chilling process has begun such as arrival on ice. Include a notation on the Sample Acceptance Check Form.

6.3.3.3 Chemical Preservation A pH measurement may be required on certain tests, the pH value shall be documented on the Sample Acceptance Check

Form. Perform this check in accordance with the applicable method SOP and the *SOP for Laboratory Storage, Analysis, and Tracking.*

The pH of the sample shall be checked with a narrow ranged pH indicator strip (preferable). Take a small aliquot of the sample with a transfer pipette and place a few drops onto the pH indicator strip. Ensure that a new pipette is used for every sample container to prevent cross-contamination. Refer to Section 6.7 on specific information for subcontracted jobs.

6.3.3.4 Headspace Check for headspace in VOA vials. Pay close attention to samples that are opaque; bubbles may not be easily observed. Samples with heavy sediments may stick to the vial, making it appears to have no bubble when the vial is inverted. Any bubble in the sample should not exceed 5-6 mm.

6.3.3.5 Reusable media The pressure of each canister and glass bottle shall be checked and recorded to ensure the sample has the appropriate volume. Initial and final pressures are noted on the Service Request Form and on the back of the sample tag. Refer to the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters* for additional details.

At the time of sample submission, ambient air sampling canisters will likely have a vacuum (negative pressure). If the canister has a negative pressure, the gauge will read in inches of Mercury (inHg) or pounds per square inch (psig) depending on the gauge used. If the reading is inHg, the value must be converted to psig (A conversion chart may be used and is located in the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters* Attachment B). Vacuum readings entered in inHg to the system will be automatically converted to psig.

Returned canisters and glass bottles that are not samples are logged in and handled following the same procedures. Canisters received at an initial pressure *lower than* -9.8 psig (-20.0 inHg) are shelved on a canister rack outside SMO (P-102) for the canister department to clean. Canisters received that have an initial pressure *higher than* -9.8 psig (-20.0 inHg) are placed on a canister rack in SMO for screening before they are returned to the canister department for cleaning. This procedure must be performed in accordance with the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters.*

Thermal desorption tubes that are not samples are logged in according to their bar code ID and the analysis is marked cancelled.

6.3.3.6 Sample Login Contingency Plan This section is designed to detail the sample custody and receipt procedure for samples that are delivered to the laboratory late in the day or when the SMC or designee is not present. If sample(s) are delivered under thermal preservation, laboratory personnel shall evaluate the cooler temperature per Section 6.3.3.2. The temperature must be noted on the COC form along with the date and initial of the person making the notation. Refer to the Quality Assurance Manual for information on preservation requirements, which are listed by method and sample type. The person, following acceptance, evaluation and analysis (if performed), should place the samples in the appropriate storage location in accordance

with the *SOP for Laboratory Storage, Analysis, and Tracking* and submit the paper work to SMO in order for the login process to be completed.

6.3.3.7 Short Hold Times When samples are delivered to the laboratory with little remaining on the hold time it may be possible for the analysis to proceed prior to the login process. The following are circumstances where this is allowed.

- Tedlar bag samples only
- If there is no time for sample(s) evaluation and login prior to hold time expiration and an analyst is able to analyze the sample(s) immediately.

However, there are requirements that must be followed by the analyst(s) if the samples are to be analyzed prior to sample login.

- At a minimum, the analyst shall review/compare the chain of custody with the samples received to ensure that the sample identifications, etc. are correct.
- It is imperative that the client sample ID be referenced on all laboratory analytical documentation.
- Also, the analyst should check the integrity (i.e. leaking or flat Tedlar bag) of the samples and make any notations on the associated documentation.
- Additionally, once the samples have been analyzed they are to be immediately delivered back to SMO for the sample acceptance and login procedures detailed in this SOP.

6.3.3.8 Sample Identification Labels After samples have been logged into the computer and the lab ID assigned, the SMC shall print labels for each sample container received. Each computer-generated label is affixed to the appropriate sample container, where possible. Certain sample containers, such as solid adsorbent cartridges, are placed in a sealed bag identified with the job number and all the laboratory ID codes associated with each sample in the bag.

6.3.3.9 Sample Login/Labeling Verification After labels have been applied to the corresponding sample containers they should be verified by a second person to ensure proper labeling. Place all associated documentation into the job file and submit to the Project Manager.

- Once the documentation has been generated and the labeling verification has been performed, the custodian must complete the first section of the LIMS Sample Login Verification Form (Attachment 4).
- The Project Manager responsible for the project verifies login information. This process is documented on the LIMS Sample Login Verification form. It is only after this secondary review that the job folder is released out of the login console to the job in progress area, making the analysis information available to the analysts.

6.4 Discrepancy / Sample Rejection Procedures

Any discrepancies or concerns are noted on the Sample Acceptance Check Form (per Sample Acceptance Policy, see Section 6.3.3.1) and immediately communicated to the

appropriate Project Manager. If and when there is any doubt as to the suitability of a sample to be tested such as a leaking valve, broken container, etc. the SMC shall inform the PM. Regardless of the discrepancy, the PM shall be responsible for coordinating all correspondences and consulting with the client for further instructions before the laboratory may proceed. However, when there are short holding time constraints, the laboratory may complete the sample analysis, where possible for all samples in the client's job file including the sample in question.

6.4.1 Chemical Preservation for Water and Soil Samples Contact the PM and if the PM approves adding preservative to bring sample within the proper range, be sure to record the specific sample container identifications, preservative added, including type, lot number(s), and final pH on the Sample Acceptance Check form (Attachment 2) (even if subcontracting). Refer to Section 6.7 for information on sub-contracting and splitting samples, where appropriate. When chemical preservation is performed in the laboratory the Preservative Tracking Log (Attachment 2, *SOP for Media Request Fulfillment*) must be utilized for documentation purposes.

6.4.2 Login Revisions Changes to SR forms may be made by anyone authorized for sample login and Project Management capabilities; however, it is recommended that whenever possible documentation of the reasons for the changes and the person making those corrections is documented and any copies of the original must be retained and marked as obsolete.

6.5 Sample Receipt Acknowledgment

An acknowledgment form (Attachment 5) may be accessed and emailed to the client, along with a PDF of any other requested documentation.

6.6 Job File and LIMS Documentation

The sample documentation shall be maintained in each client's job file in accordance with current procedures and shall at a minimum include:

- Original chain of custody form (if utilized) with the laboratory job number
- Service Request Form
- Sample Acceptance Check Form
- Sample Login Verification Checklist
- Any documentation including memos or transmittal forms, which are transmitted to the laboratory by the common carrier, courier, sampler, or client.
- Any internal documentation which is pertinent to the handling and/or analysis of the samples.

Note: The original and all copies and revised versions of documentation must be kept in the associated job file.

Once the samples have been received, accepted (or rejected) and logged into the laboratory system, a job file (referencing the corresponding service request number) must be created and all receipt, acceptance and login documentation included. The COC is to be scanned into a PDF and attached to the LIMS job file. The job file must be submitted to the appropriate Project Manager for approval. The job file will be kept in a designated area for the inclusion of all the remaining documentation for the project including analytical data, invoices, etc.

6.7 Sample Transfer between Laboratories

The following must be adhered to for all samples, extracts, digestates and split samples

that are transferred, carried or shipped from one laboratory to another (between In-Network laboratories and to laboratories outside of the Network). Samples are generally prepared for shipping by packing bubble wrapped glass containers in a cooler filled with blue ice (or ice). Custody seals are signed and dated and placed on the front of the cooler. The cooler is then sealed with packaging tape.

Samples not analyzed at the laboratory are subcontracted to pre-approved laboratories (internal and or external). Samples are logged in for the required tests and assigned a subcontract lab (as assigned by the PM in the SDG, by flagging the team column of the folder with the appropriate sublab). A subcontract COC is printed from LIMS once the login has been completed. The subcontract COC is then placed in the job folder after a copy of document is made.

Note: If LIMS does not have the appropriate test or sub-contract laboratory code, a Request for Test Code or "Sublab" form is filled out and submitted to Kelso IT. In addition, if the sublab is not specified in the SDG, it will automatically be flagged and a subcontract lab must be selected. Contact the PM, if this occurs.

6.7.1 In-Network Sample Transfer This laboratory, when transferring samples to an In-Network laboratory, could either initiate a new chain of custody record or use a photocopy of the original chain of custody record. The SR number from the originating laboratory may remain the same when subcontracting to a laboratory within LIMS; and any documentation generated by the laboratory would be included in that job file.

6.7.1.1 A new chain of custody record may be initiated if the number of samples or analyses is small enough so that it is not too time consuming to write out the new chain of custody record. The sample custodian at this laboratory must accurately transfer the entire client and sample information to the new chain of custody record and sign and date relinquishing it and the samples.

6.7.1.2 A photocopy of the original chain of custody record may be used when the number of samples or analyses is large or the chain of custody record is complicated and it would take a lot of time to rewrite the client and sample information on a new chain of custody record. On the chain-of-custody-record-photocopy, the sample custodian preferably using blue ink must:

- Indicate which samples have been sent by crossing out the samples retained;
- Correct the number of sample containers actually being transferred by crossing out the number and writing the number of bottles sent;
- Indicate which analyses the subcontract network laboratory will be performing by highlighting the analyses to be performed and/or crossing out the analyses not subcontracted;
- Write the service request number of the originating laboratory on both the original chain of custody record and on the chain-of-custody-record-photocopy; and
- Sign the chain-of-custody-record-photocopy relinquishing it and the samples.

A photocopy of this completed document shall be placed in this laboratory's project file. The receiving network laboratory should treat this photocopied chain of custody record as its official chain of custody

record for their project file. This chain-of-custody-record-photocopy must be signed, preferably using blue ink, when the samples are received and logged in at the receiving network laboratory. It will be retained by the receiving network laboratory and a photocopy returned to the originating network laboratory with the final analytical report.

6.7.2 Sample Transfer to an Out of Network Laboratory (Interlaboratory Transfer)

The originating laboratory, when transferring samples to a laboratory outside the network, must initiate a new chain of custody record. This will help to protect the identity of our customer from the outside laboratory and maintain client confidentiality. The sample custodian will indicate that this laboratory is the client on this new chain of custody record and must accurately transfer all the sample and analysis information. Also, the purchase order number is to be included on the new chain of custody record. The new chain of custody record must be signed and dated relinquishing it and the samples.

6.7.3 pH Adjustment Certain methods require a pH check and adjustment to be recorded on the Sample Acceptance Check form. After performing pH adjustment place a yellow tape with the words "pH Check" and "date and time" of adjustment across the top of the bottle. Measure pH after 16 hours; adjust pH if necessary, and repeat the process until proper pH is obtained. The analyst will perform the pH check at the time of analysis.

If received within two weeks of collection, acid preserve upon receipt in the laboratory to lower pH to <2. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior to sending out to sub-contract network or out of network laboratory. If for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added, and the sample held for 16 hours until verified to be pH <2.

6.7.4 Splitting Samples Avoid splitting whole volume analysis samples; e.g., BNA, pesticides, PCBs. Make appropriate sample splits by pouring sample into containers with appropriate preservative already added.

6.8 Storage and Documentation Distribution

When all samples have been labeled and verified, they are to be placed in the designated storage areas per the *SOP for Laboratory Storage, Analysis, and Tracking*. Where necessary, there are refrigerators and freezers dedicated for specific storage requirements (e.g., Wet Chem, SVOA, etc.) and specific locations entered in the Sample Location module of LIMS.

All documentation (e.g. COCs, Sample Acceptance Check Form, Sample Login Verification, etc.) are to be placed inside the Job Folder and given to the PM. The PM will then distribute the folder to the appropriate department.

6.9 Odorous Sample Storage Odorous samples (ex., Tedlar bags or VOAs for sulfur) are to be placed in the SMO hood for login and labeled with a "HIGH SULFUR CONCENTRATION" caution sticker. The PM is to be contacted so that the best course of action may be taken to prevent any laboratory contamination. Following login, every possible precaution is to be taken when storing the samples; therefore, wherever they are stored must minimize any cross-contamination between stored samples and into the lab air for possible contamination into laboratory systems. Segregation of samples must be performed as necessary to ensure that no contamination occurs between samples,

extracts, and standards. After analysis, the odorous samples are returned to the SMO hood for disposal the next day upon PM approval.

7) Quality Assurance

7.1 Internal system audits shall be performed by the Quality Assurance Manager to assess adherence to the guidelines described in this SOP.

8) Documentation and Records

8.1 Forms, Checklists and other required documentation to be maintained are listed in Section 6.6.

9) Summary of Changes

Table 9.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
18.0	06/02/2018	C. Humphrey	Applied updated SOP formatting style to first two pages and header/footer. Sections reorganized and renamed as applicable to follow new SOP template format. Section references updated as needed.
			6.3.2 – updated year in example
			6.3.3.1 – changed "Summa" to "passivated stainless steel"
			6.3.3.2 – added infrared thermometer
			6.3.3.5 – removed "Summa" from first sentence; removed sentence regarding PUFs; updated rack number to 102
			6.6 – removed preservation tracking log from list – kept in logbook in SMO
			6.7 – removed last sentence of first paragraph regarding off-site extraction facility
			6.7.1.3 – removed section regarding off-site extraction facility
			10.2 – updated reference
			10.3 – updated reference
			Attachment 2 – updated
			Attachment 3 – updated
			Attachment 5 – updated

10) References and Related Documents

10.1 2009 TNI Standard and 2016 TNI Standard.

10.2 US EPA Methods Update Rule (MUR), effective 4/11/07.

10.3 DoD/DoE Quality Systems Manual, Version 5.1, 2017; and Version 5.1.1, 2018.

10.4 General Requirements for the Competence of Testing and Calibration Laboratories, ISO/IEC 17025, second edition, 2005-05-15.

10.5 Minnesota Administrative Rules, Department of Health, Chapter 4740, Laboratories; Accreditation Requirements.

11) Attachments

11.1 Attachments

Attachment 1	Training plan for Sample Receiving
Attachment 2	Sample Acceptance Check Form
Attachment 3	Service Request Form
Attachment 4	Sample Login Verification Form (also included in the *SOP for Project Management*)
Attachment 5	Sample Acknowledgement Form

Note: Forms are examples and may be modified as long as the minimum requirements of this document are met.

Attachment 1

Training Plan for Sample Receiving

Training Plan for Sample Receiving, Acceptance, and Login

Trainee _____ Trainer _____ Date _____

1. Read SOP — Trainer ____ Trainee ____ Date _____

2. Read Holding Time, Matrix Table (Appendix F of QA Manual) — Trainer ____ Trainee ____ Date _____

3. Demonstrated understanding of — Trainer ____ Trainee ____ Date _____

   Sample Acceptance Check Form & Chain of Custody Form

4. Demonstrated familiarity with related SOPs — Trainer ____ Trainee ____ Date _____

   SOP for Making Entries onto Analytical Records
   SOP for Laboratory Sample Storage, Analysis, and Tracking
   SOP for Nonconformance and Corrective Action
   SOP for Media Request Fulfillment

5. Sample Receipt — Trainer ____ Trainee ____ Date _____

   ☐Understands & knows Sample Hold Times for different methods, media and matrices (or where to find info.)
   ☐Understands Sample Receipt Procedures during business hours as well as after hours
   ☐Knows acceptable temperature for cooler/samples received and how to evaluate and document information
   ☐Knows how to check liquid samples for air bubbles and how to document information
   ☐Knows how to check samples for integrity & if they are compromised (& what this means), how to document
   ☐Knows appropriate containers for samples received according to requested analyses
   ☐Knows adequate sample volume for the analyses requested
   ☐Knows the proper preservation of samples received according to the requested analyses
   ☐Knows when & why the project manager needs to be notified
   ☐Knows how to check canister pressures

6. Sample Login — Trainer ____ Trainee ____ Date _____

   ☐Understands procedure of login and can successfully accomplish the task
   ☐Understands every field of the SR form
   ☐Able to generate a completed project/job – SR form
   ☐Understands the Sample Acceptance Check Form and how to utilize it for different media
   ☐Understands the Sample Receipt Acknowledgment Form and how to utilize it
   ☐Understands the SR form "Draft" copy and know when to utilize it
   ☐Understands the notes that are required at the top of the SR form (i.e., pressurize with helium) and why
   ☐Understands the documentation that must accompany canisters to pressurization
   ☐Understands when an NCAR must be generated in SMO
   ☐Able to submit hardcopy project requirements and how to document special requirements (& what is important to include) on SR form
   ☐Knows steps in documenting samples received outside of hold time
   ☐Know how to properly label samples during login

7. Freezer and Refrigerator Temperature Readings — Trainer ____ Trainee ____ Date _____

   ☐Read *SOP for Calibration and Use of Laboratory Support Equipment*
   ☐Logbooks (Calibration logbook & Freezer / Fridge Temperature logbook)
   ☐Knows required temperatures
   ☐Understands what to do if a temperature exceeds the required temperature (i.e., documentation, notification of QA)
   ☐Ability to calibrate thermometers using appropriate NIST traceable thermometer
   ☐Understands how to apply correction factors to applicable laboratory thermometers
   ☐Reset digital thermometers when appropriate

Attachment 2

Sample Acceptance Check Form

ALS Environmental
Sample Acceptance Check Form

Client: _____ Work order: _____
Project: _____
Sample(s) received on: _____ Date opened: _____ by: _____

Note: This form is used for all samples received by ALS. The use of this form for custody seals is strictly meant to indicate presence/absence and not as an indication of compliance or nonconformity. Thermal preservation and pH will only be evaluated either at the request of the client and/or as required by the method/SOP.

		Yes	No	N/A
1	Were **sample containers** properly marked with client sample ID?	☐	☐	☐
2	Did **sample containers** arrive in good condition?	☐	☐	☐
3	Were **chain-of-custody** papers used and filled out?	☐	☐	☐
4	Did **sample container labels** and/or tags agree with custody papers?	☐	☐	☐
5	Was **sample volume** received adequate for analysis?	☐	☐	☐
6	Are samples within specified holding times?	☐	☐	☐
7	Was proper **temperature** (thermal preservation) of cooler at receipt adhered to?	☐	☐	☐
8	Were **custody seals** on outside of cooler/Box/Container?	☐	☐	☐
	Location of seal(s)? _____ Sealing Lid?	☐	☐	☐
	Were signature and date included?	☐	☐	☐
	Were seals intact?	☐	☐	☐
9	Do containers have appropriate **preservation**, according to method/SOP or Client specified information?	☐	☐	☐
	Is there a client indication that the submitted samples are **pH** preserved?	☐	☐	☐
	Were **VOA vials** checked for presence/absence of air bubbles?	☐	☐	☐
	Does the client/method/SOP require that the analyst check the sample pH and if necessary alter it?	☐	☐	☐
10	**Tubes:** Are the tubes capped and intact?	☐	☐	☐
11	**Badges:** Are the badges properly capped and intact?	☐	☐	☐
	Are dual bed badges separated and individually capped and intact?	☐	☐	☐

Lab Sample ID	Container Description	Required pH *	Received pH	Adjusted pH	VOA Headspace (Presence/Absence)	Receipt / Preservation Comments

Explain any discrepancies: (include lab sample ID numbers): _____

RSK - MEEPP, HCL (pH<2); RSK - CO2, (pH 5-8); Sulfur (pH>4)

SACF.xls - Page 1 of 1 05/25/18 3:54 PM

Attachment 3

Service Request Form

Service Request Summary

Folder #: P1801631
Client Name: ALS Environmental - Simi Valley
Project Name: Phenova PT Study
Project Number: AE R21999
P.O. Number:

Report To: Chaney Humphrey
ALS Environmental - Simi Valley
2655 Park Center Drive, Suite A
Simi Valley, CA 93065
Phone Number: 805-526-7161
Cell Number:
Fax Number:
E-mail: chaney.humphrey@alsglobal.com

Project Chemist: Chaney Humphrey
Logged By: ADAVID
Date Received: 4/ 2/18
Time Received: 0900
Archive? N
Folder Due Date: 4/23/18
Internal Due Date: 4/19/18
QAP: LAB QAP
Qualifier Set: Lab Standard
Formset: Lab Standard
Report to MDL?: N
Merged?: Y Batch QC?: N
PC Approved?: Y
State of Sampling Location:
EDD: No EDD Specified

1 - 1 mL-Glass Vial Unpreserved

Location: P-04

Lab Samp No.	Client Samp No.	Matrix	Collected	TO-17/ VOC Sorbent	VOA GCMS AIR
P1801631-001	RR-VOATD-AIR	Air	3/29/18 0000	1	

Folder Comments:

See attached for analyte list. All QC Must Pass.

Test Comments:

Group	Test/Method	Samples	Comments
VOA GCMS AIR	VOC Sorbent/TO-17	1	Concentrations range from 5-100ng/tube.

Attachment 4

Sample Login Verification Form

Sample Login and Verification Checklist

Service Request Number, Client & Project Name	(place folder label here)	SDG Used	PM

Sample(s) delivered by: (circle) Client / ALS Emp. / DHL / GSO / FedEx / UPS / Other_____

Yes	No	N/A	SMO Verification	
			Project number has been correctly entered.	
			Sample IDs from the COC have been correctly entered.	
			Sample date and time collected for each sample has been entered correctly.	
			Date received is correct.	
			Container tags are reconciled and applied to correct containers.	By:
			Container tags have been verified by a second person.	By:
			The analyst and PM have been alerted of Short HT or Rush samples.	Notified:
			Sample receipt discrepancies have been noted on Sample Acc. Check Form.	
			Login Completed	By: Date:

Yes	No	N/A	Client Services Login Verification	
			Folder due date is correct.	
			Project Number, Dates, Times, and Sample IDs are correct.	
			Pricing and Rush charges are correct.	
			The subcontract containers have been tagged and sub COC has been generated.	Sub Lab:
			Samples requiring an MS/MSD are properly indicated in the folder.	
			All non-analytical tasks (encores, EDDs, etc.) are logged in and priced correctly.	
			Client has been notified regarding holding time exceedences and sample receipt discrepancies. Notified by email □ verbally □ voicemail □	By: Date:
			Login Approved (red button)	By: Date:

Yes	No	N/A	Client Services Folder Approval	
			Pricing is correct and approved. (Prepaid work is properly indicated with check or credit card.)	
			Hazardous waste designation has been set properly for each sample.	
			Report and/or EDD are complete.	
			Folder Release	By: Date:

Comments:

Attachment 5

Sample Acknowledgement Form

ACCREDITED IN ACCORDANCE WITH nelac

ALS Environmental
2655 Park Center Drive, Suite A
Simi Valley, CA 93065

Confirmation of Sample Receipt

To:	Chaney Humphrey	**From:**	Chaney Humphrey
Email:	chaney.humphrey@alsglobal.com	**Email:**	Chaney.Humphrey@alsglobal.com
Fax:		**Fax:**	805-526-7270
Phone:	805-526-7161	**Phone:**	805-526-7161 x2084

Samples for analysis have been received by ALS Environmental on 4/ 2/18 and assigned our Service Request number **P1801631**. **Please verify the following information and notify me of any corrections as soon as possible.**

The estimated completion date for this work is: **4/23/18**

Client: ALS Environmental - Simi Valley
Project: Phenova PT Study/AE R21999

EDD Required: No

Tier: I

Report To: Chaney Humphrey
ALS Environmental - Simi Valley
2655 Park Center Drive, Suite A
Simi Valley, CA 93065

Billing Address: Chaney Humphrey
ALS Environmental - Simi Valley
2655 Park Center Drive, Suite A
Simi Valley, CA 93065

Comments: See attached for analyte list. All QC Must Pass.

Thank you for your business!

A - Test is Authorized | H - Test is On Hold | HP - Test is On Hold Pending Inout | P - Test is Authorized for Prep Only | C - Test has been Cancelled | * - Test has assigned QC

				TO-17 VOC Sorbent
1801631-001	RR-VOATD-AIR	Air	[illegible]	A

Test Comments:

Group	Test/Method	Samples	Comments
VOA GCMS AIR	TO-17/VOC Sorbent	1	Concentrations range from 5-100ug/tube.

CLEANING AND CERTIFICATION OF SUMMA CANISTERS AND OTHER SPECIALLY PREPARED CONTAINERS

DOCUMENT I.D. SMO-CAN_CERT

Approved By: _____ Date: 11/6/18
Canister Conditioning and Shipping Team Leader – Sam Moh

Approved By: _____ Date: 11/7/18
Laboratory Supervisor – Wade Henton

Approved By: _____ Date: 11/6/18
Technical Services Manager – Chris Parnell

Approved By: _____ Date: 11/16/18
QA Manager – Chaney Arend

Approved By: _____ Date: 11/16/18
Laboratory Director – Kate Kaneko

TABLE OF CONTENTS

1) Scope and Applicability

1.1 This document describes the procedures required to prepare all passivated containers, including stainless steel canisters and glass bottles, for sample collection and use within the laboratory. It outlines the steps necessary to internally clean the containers (all volumes) and document their acceptability for re-use. Also included are procedures for leak checking, evaluation of the condition of canisters, canister repair, and maintenance of the cleaning apparatus. Canister cleaning and certification is needed to ensure that each sampling container is free of contaminants and leaks that could jeopardize the integrity of the analytical data. The process must uniformly and consistently render each canister clean enough to meet the criteria for all of the relevant test methods.

2) Summary of Procedure

2.1 After all analyses are complete on the canister sample in question, the analyst records the identification and concentration level of the most prominent compounds found in the sample on the sample identification tag. This includes not only target compounds from the analytical methods, but tentatively identified compounds and any anomalous observations. Only after the corresponding data is reviewed and approved including verification that all reporting and QA/QC requirements are met are the canisters released for cleaning and certification.

2.2 First, the canisters that contain elevated contaminant levels are pre-purged to remove the bulk of the sample from each canister. Then they are placed on a cleaning manifold inside an oven (ambient-level sample cans may be cleaned on manifolds without heating). The ovens are heated to 80 to 100C and the canisters are then serially filled and evacuated with humidified nitrogen. Following the cleaning process, a minimum of one canister per batch (10 to 16 canisters) is selected as the quality control (QC) canister. The canister(s) is analyzed by EPA Method TO-15 in accordance with the *SOP for Determination of Volatile Organic Compounds in Air Samples Collected in Specially Prepared Canisters and Gas Collection Bags by Gas Chromatography/Mass Spectrometry (GC/MS)*.

2.3 Following the cleaning procedure, the canisters are evacuated to approximately -14.3 psig (-29 "Hg) and held for a minimum of 24 hours to determine if any leaks exist. The pressure of each canister is evaluated using a calibrated pressure/vacuum gauge and the results recorded. All canisters that pass both the batch analyte concentration QC and individual leak check are certified and ready for use.

3) Definitions

3.1 Summa Canister A stainless steel air sampling canister whose inner surface has been electropolished by the proprietary "Summa" process to provide chemical inertness.

3.2 Silonite® Canister A stainless steel canister that has had the interior passivated with a fused-silica coating (Entech Instruments).

3.3 Bottle Vac A glass bottle (1000ml or 500ml) used for collecting whole air samples. The interior surface is chemically deactivated and the cap is fitted with a quick-connect style valve. Entech Instruments, Simi Valley, CA.

3.4 psig pounds per square inch gauge

3.5 GC/MS Gas Chromatography/Mass Spectrometry

3.6 ppbv parts per billion, volume

3.7 ppmv parts per million, volume

3.8 Pressurized Air Zero grade with <0.1ppmv of total hydrocarbons

3.9 QC Canister This is a quality control canister selected and analyzed in order for the cleaning batch to be certified as clean. There may be more than one canister selected within a cleaning batch to serve as a QC canister and this is dependent on a number of factors each of which are included in this standard operating procedure.

3.10 Standard Canister This is a canister labeled for containing standards; they are segregated from source and ambient canisters and are not to be sent to clients. Standard canisters may only be cleaned with other standard canisters on the manifolds. The most contaminated canister is analyzed in order to determine if the cleaning batch is to be certified as clean. There may be more than one canister selected within a cleaning batch to serve as a QC canister and this is dependent on a number of factors each of which are included in this standard operating procedure.

4) Responsibilities

4.1 It is the responsibility of all canister cleaning department technicians to accurately perform the procedures of this SOP and to complete applicable training documentation. Documented training plans must be completed by the trainee and trainer before submitting to the Quality Assurance department for final approval. This paperwork will be maintained by the QA department in an employee training file.

5) Interferences

5.1 Not applicable

6) Safety

6.1 Burns

Caution must be exercised when working with the canister cleaning system ovens because of the potential for burns from the hot canisters which are often heated to 100˚C. The oil from the rotary vane vacuum pumps is also hot enough to cause burns when operating at normal system temperatures. The operator should wait for the oil to cool prior to attempting to change the pump oil.

6.2 Contaminated Pump Oil

Besides the burn hazard, contact with used oil from the vacuum pumps should be avoided since it becomes contaminated during normal use with toxic organic residues from the canisters. Proper attire must be worn when working with used pump oil that must be disposed of as hazardous waste in accordance with the *Simi Valley Lab Waste Management Plan* and applicable regulations.

6.3 Electrical Shock

All electrical wiring should be periodically checked for insulation cuts and chafing as electrical shock can occur from exposed wires. If an exposed metal wire is discovered, it must be repaired immediately.

6.4 Fires

All flammable materials, especially solvents, shall be kept clear of the cleaning manifold and pumps since the canister heaters generate considerable heat. Also, all plugs must be securely seated in their receptacles.

6.5 Hydrochloric acid (HCl)

When Hydrochloric acid is used to prepare acidified water for manual cleaning, special care must be taken. Always wear protective eyewear and gloves when handling. Prepare mixture in a hood and keep tightly capped when transporting. Hydrochloric acid is a severe health and contact hazard.

7) Sample Collection, Containers, Preservation, and Storage

7.1 There are no requirements for sample collection in this document. The following are a list of canisters that may be cleaned, certified and maintained by this procedure. This list is not intended to be all-inclusive as it contains only the most requested and current canister types.

- Six-liter Summa passivated stainless steel canisters
- Six-liter Silonite® passivated stainless steel canisters
- Three-liter Silonite® passivated stainless steel canisters
- One-liter Summa passivated stainless steel canisters
- One-liter Bottle-Vacs

All canisters must be stored on the clearly designated shelves or rolling racks.

8) Apparatus and Equipment

8.1 The number and capacity of the pre-purge and cleaning manifolds may be increased or expanded depending on necessity as long as they are clearly identified. As long as the minimum requirements for identification, cleaning, certification and maintenance are met, additional manifolds may be added at any point during the effective dates of this document. Additionally, the equipment listed in this section may be modified as long as the performance of the equipment selected is at least equivalent and this may include the size of heating bands, pump horsepower, etc.

8.2 Pre-purge System

Each pre-purge manifold system consists of a vacuum pump and compressed nitrogen gas supply tube connected to a ten position manifold. The manifold is made of 1/4" 316 stainless steel and Teflon tubing with stainless steel or brass fittings. Pressure is read with an in-line pressure gauge. The canister valve fitting is attached to the manifold using a brass Swagelok nut and ceramic-filled Teflon ferrule.

The purge cycles are controlled manually or automatically with a three-way solenoid valve; one position connects to the nitrogen source, the second position connects to the pump, and the third position connects to the manifold. The canisters are pre-cleaned by serial evacuation and dilution with nitrogen. The solenoid valve is connected to a relay timer that can be programmed with the desired evacuation and fill time intervals and number of cycles. Programming is done using the keypad on the controller. The instruction for programming and starting the controller are found at the canister purge station.

8.3 Canister Cleaning System

The canister cleaning system is comprised of cleaning manifolds, nitrogen source with humidifiers, high vacuum pumps, digital vacuum/pressure gauges (in millitorr), electric ovens, and electronic control units each described below.

8.3.1 Canister Manifolds

Currently, there are six cleaning manifolds. The cleaning manifolds are split into three groupings with the sample type or size serving as the source of the manifold designation for cleaning.

Cleaning Manifolds #1 and 2 (Ovens)	(12) Source Canisters Each
Cleaning Manifold #3	(14) Ambient Canisters
Cleaning Manifold #5	(16) Ambient Canisters
Cleaning Manifold #6 (Oven)	(6) Ambient/Source Canisters
Cleaning Manifolds #7 and 8 (Ovens)	(12) Source Canisters Each
Cleaning Manifolds #9 and #10 (Ovens)	(24) 1-L Bottle Vacs each

The manifolds are constructed of 1/2" or 3/8" 316 stainless steel tubing and fittings. Canisters are attached to the manifold with a Swagelok brass nut and soft ferrule or canisters are attached to the oven manifold with a Swagelok brass nut or Swagelok stainless steel nut with aluminum finger-tight body and graphite/vespel ferrule. The proper fittings reduce the chance of damaging the stainless steel canister valve. Each manifold has its own pump and vacuum gauge, but may share a common gas source.

8.3.2 Gas Source with Hydrocarbon Trap and Humidifier

The manifolds use the gas from the auxiliary vapor outlet on the bulk liquid nitrogen tank. It is plumbed into the building with copper pipe, filtered through a hydrocarbon trap (if necessary), reduced in pressure, humidified, and connected to the gas inlet valves. Tubing is ¼" copper, stainless steel, or PFA Teflon. The fittings, humidifier, and single-stage regulator are 304 or 316 stainless steel. The vapor from the bulk tank ranges from 50 to 80psig, and is dropped to between 10 and 15psig before entering the humidifier via a regulator. The hydrocarbon trap may not be needed since this gas is typically ultra-clean.

8.3.3 Vacuum Pumps

For manifold 3 the vacuum pump is a dual-stage direct driven rotary-vane type, made by Alcatel Co. or Edwards Mfg. Co. Each is rated at 285 liters per minute and is capable of achieving a vacuum of <10mtorr. An activated alumina filled foretrap is used to protect vacuum pump oil from system impurities and to prevent oil vapors from backstreaming into the canisters. The exhaust port of each pump is vented to the hood with Tygon tubing.

Manifold #5 and the Entech 3100A systems for manifolds 1, 2, 6a and 6b, 7, 8, 9 and 10 use a two-stage oil-less pumping system comprised of a molecular drag pump backed by a diaphragm-type roughing pump. The rough pump evacuates the system to less than 2psig before activating the drag pump. The system on manifold #5 is a DriVac model BH200 (Vacuubrand MD4 roughing pump and Alcatel MDP 5011 drag pump combination) with integrated vacuum controller. The Entech systems use a Vacuubrand MZ2 or MZ2NT roughing pump and an Alcatel MDP 5011 drag pump combination.

8.3.4 Conditioner Vacuum Gauges

The gauges used to read the system pressure on each manifold are the Pirani digital type, capable of measuring between 0 and 2000 millitorr.

8.3.5 Electric Ovens and Heating Bands

During the cleaning process, each canister is heated to no more than 100˚C using an electric oven or heating band. The bands are made of fiberglass-reinforced silicone rubber, and range in size depending on the canisters to be cleaned. They are rated at 5 watts per square inch, and operate on 120 VAC.

8.3.6 Controller Unit

The canister cleaning manifolds are controlled through a remote I/O board and a custom designed PC-based software program. All electronic components of the system (except the power leads of the heating bands) are connected to an I/O board including solenoid valves, thermocouples, and vacuum gauges. The board is housed in a computer-style chassis with a 120 VAC, 60 Hz power supply. It is connected to the PC via a serial data port, and the interface software allows the operator to enter all the parameters necessary for automatic control of the cleaning process.

8.3.7 Laboratory Information Management System (LIMS)

The system (LIMS) has a number of essential functions including container history and maintenance, canister status (ready to be cleaned, etc.), cleaning set-up, post analysis information, and reports.

8.4 Pressure/Vacuum Gauge

A pressure/vacuum gauge that is calibrated and capable of measuring –14.7 psig (30 inHg) to 100psig is used to provide a more accurate reading of vacuum/pressure, so that the initial leak check reading can be monitored and recorded.

9) Standards, Reagents, and Consumable Materials

9.1 Edwards 450g Charge Activated Alumina
Purchased from Scientific Instrument Services

9.2 Vacuum Pump Oil #19
Purchased from VWR

9.3 Hydrochloric Acid

10) Preventive Maintenance

10.1 Preventive maintenance is one of the best ways to keep the conditioning systems running optimally. Maintenance log entries must be made each time work is performed on a system no matter the extent. Types of maintenance activities include: changing pump oil, changing in-line foretrap activated alumina media, and replacing worn ferrules.

A hardcopy maintenance logbook must be kept and remain current. An entry shall be made in the log every time maintenance is performed (no matter the extent). The log entry must include:

(a) The date of maintenance
(b) Who did the maintenance
(c) Description of the maintenance

(d) Proof that the maintenance activity was successful

A notation of a successful QC may serve as proof that the maintenance is complete and the system is in working order. The extent of the maintenance is not important, however, it is important that a notation be included for each maintenance activity.

10.2 Vacuum System

The mechanical vacuum pumps used in the canister cleaning system require periodic maintenance. The pump oil must be changed regularly, every *three months* or when the pump will no longer evacuate the system efficiently, whichever is more frequent. The pumps may also need to be returned to the manufacturer for rebuilding if they fail to perform to the necessary specifications.

Preventive Maintenance Schedules are as follows:

Rotary Vane Vacuum Pumps/Change Oil.....3 MONTHS
Foretraps/Change activated alumina media.....3 MONTHS

Diaphragm Dry Pumps/Replace diaphragms.....1 YEAR or as needed
Molecular Drag Pumps/Replace bearings.....As needed

10.2.1 Procedure for Changing Pump Oil

- Make sure there is a sufficient amount of fresh pump oil before the oil change begins.
- Wear safety glasses and gloves when changing oil.
- Set the control software to "EVAC ON"
- Open one position on the manifold so that air is pulled through the pump.
- Turn vacuum pump power switch to the off position and remove the power cord from the electrical outlet.
- Vent the pump from above the foreline trap.
- Detach the inlet and exhaust tubing from the pump.
- Place pump on a sturdy level surface and remove both fill and drain plugs.
- The pump oil is extremely hot and can cause severe burns. If possible, turn the pump off and let it sit for approximately 20 minutes to let the heat dissipate from the pump.
- Drain the oil into an appropriate hazardous waste container. Lift the motor end of the pump to get most of the used oil from the pump housing.
- Check for oil leaks at the pump seals and gaskets (*between the motor and the pump*), also at the drain and fill plugs.
- Install the drain plug and slowly refill with fresh vacuum pump oil.
- The vacuum pumps use a sight glass to measure the amount of oil in the pump. Fill to the designated mark on the sight glass and install the fill plug.
- Apply vacuum and exhaust tubing. Plug in the power cord into the electrical outlet and turn on power switch.
- The vacuum pump will take about an hour to prime to full vacuum.

10.2.2 Procedure for Changing Activated Alumina

- Make sure there is a sufficient amount of fresh activated alumina before the change begins.
- Wear gloves when handling the fore trap and the activated alumina.
- Set the control software to "EVAC ON"
- Open one position on the manifold so that air is pulled through the pump.

- Turn vacuum pump power-switch to the off position and remove the power cord from the electrical outlet.
- Vent the manifold from one of the canister positions with the evacuation valve open.
- Detach the inlet and exhaust tubing from the pump.
- Unscrew the cap from the fore trap and extract the activated alumina media holder. Unscrew the wing nut and remove the cover.
- Dispose of the used activated alumina as hazardous waste and refill the holder with fresh media.
- Install the cover and tighten the wing nut to the top of the holder. Place the media holder back inside of the fore trap and tighten the cap to the fore trap.
- Apply vacuum and exhaust tubing.
- Plug in the power cord into the electrical outlet and turn on power switch.
- The vacuum pump will take about an hour to prime to full vacuum.

10.3 Dry Pump Diaphragm Replacement

- Refer to the manufacturer's user's manual for detailed repair procedures. Replacement kits are available from VWR Inc.

  Models used: Vacuubrand MZ2, MZ2NT, and MD4

10.4 Oil Contamination

When canisters are cleaned on the conditioning manifolds, contaminates tend to remain in the pump oil and the activated alumina fore trap. This is normal and will not affect the normal workings of the pump and the conditioner. Occasionally, a canister will be conditioned that has high concentrations of a compound and will overwhelm the conditioning system. When this contamination occurs, the pump oil and the fore trap media must be changed. Additional conditioning cycles may be needed to purge the remaining contamination from the system. High contamination scenarios must be entered into the maintenance logbook.

10.5 Gas Source with Hydrocarbon Trap and Humidifier

- The step down pressure from the bulk nitrogen tank should be set to a minimum of 15psig.
- The water level in the humidifier should always be visible in the tubing and filled with ASTM Type II water of equivalent, such as boiled deionized water. When the water is low it shall be filled to the point where at least one inch of water is showing in the tubing.

11) Procedure

11.1 IMPORTANT:

1. Canister Conditioning Technicians Canister barcodes are *not* to be hand entered into LIMS unless the barcode cannot be scanned, in which case a new barcode label must be generated. If this procedure is unavoidable the hand entered canister barcode must be verified by a secondary reviewer. Additionally, complete comments must be entered for all changes and/or additions (after the fact) made in LIMS.
2. Analysts and Canister Conditioning Technicians If during analysis or attempted analysis, a canister is identified as leaking refer to Section 11.8.3 for the specific requirements.

11.2 Release of Canisters for Cleaning/Disposal

Canisters are grouped by job number and are shelved accordingly. Canisters ready for cleaning and disposal are released according to the *SOP for Laboratory Storage, Analysis, and Tracking*. Each canister in a group of canisters must include at least the concentrations of the primary or highest level compound(s) or a short description of the sample matrix if known. Samples which were not analyzed by a method that provides VOC matrix information and which are from suspected high-level sources should be segregated and processed separately. This may include individual QC for each canister.

11.3 Pre-Purging

All canisters containing samples with elevated contaminant levels, except canisters returned to the laboratory as unused, are evacuated and purged prior to cleaning. An exception may be made for canisters with very low analyte concentrations (<5000 ng/L). When pre-purging is performed, the operator selects a group of released canisters of similar analyte levels and places them on the pre-purge manifold. The pre-purge process may be performed manually or according to the following semi-automated procedure.

- Use a 9/16" wrench to attach the canisters to the manifold
- When the timer is off, the manifold is connected to the pump. Turn the manual three-way valve to the 'down' position to open the manifold to the solenoid valve.
- Turn on the pump and timer power strips.
- Open the canister valves, and the canisters will begin to evacuate.
- Set the current time on the timer to 1 AM (or whatever time has been programmed as the start time). Hold the CLOCK button down and use the HOUR and MIN buttons to set the time.
- Use the MANUAL button to select AUTO OFF. This activates the timer. The canisters will evacuate and fill according to the program entered into the timer.
- When the cycles have finished, close the canister valves.
- Turn the manual three-way valve to the 'closed' position.
- Turn off the pump and timer power strips.
- Remove the canisters from the purge manifold and place them onto the cleaning manifold and follow the procedure detailed in 11.4 below.

11.4 Bottle Vac Cleaning

New Bottle Vacs are typically cleaned for a minimum of five cycles at no more than 80C. A minimum of one bottle per oven must be QC checked.

11.4.1 The Micro-QT valves from Bottle Vac samples may be reused after special cleaning using the following procedure:

- Remove the valve from the sample bottle under an exhaust hood.
- Purge valve for several seconds by connecting to a clean gas source (air or nitrogen) at about 20psig using a female Micro-QT adapter.
- Place valves in a one-liter glass headspace vessel with Micro-QT valve cap with o-ring seal (available from Entech Instruments). Up to 120 valves will fit into a vessel.
- Connect vessel to an Entech 3100A canister cleaning oven by inverting and connecting to a port with a female Micro-QT adapter.
- Run cleaning cycles overnight (typically at least 40 cycles): evacuate to 100 mtorr/pressurize to 15 psia (0 psig), oven at 80C.

- Attach cleaned valves to a new passivated bottle (available from Entech Instruments) and then clean for a minimum of 5 cycles. A minimum of one bottle per oven must be QC checked.

11.5 Canister Cleaning

11.5.1 Cleaning Cycles

The oven temperature of the Entech 3100A systems should be set **no higher than 100C**. This is sufficient to remove contaminants from all but the highest-level samples and will prevent damage to the canister valves.

The number of cleaning cycles needed to sufficiently clean a canister is dependent on the concentration of the sample previously in the canister. The exact number of cleaning cycles is not significant as a canister is only accepted as clean upon passing the QC check criteria outlined in section 12.2.

Canisters are typically cleaned for twenty cycles as this is the number of cycles that can be performed during the overnight cleaning session. Shorter cleaning cycles are sufficient for low level canisters as these canisters do not require extensive cleaning in order to meet the QC check criteria. The following are examples of canisters where a minimum of five cleaning cycles may be sufficient:

- Canisters used for ambient air sampling
- Canisters that have been cleaned for sixteen cycles but still contain low levels of compounds
- Standard canisters
- Canisters returned by clients as unused

Cleaning cycles may also be cut short as long as the QC check criteria are met. Forty or more cycles are used for weekend canister conditioning to minimize the time canisters sit evacuated on the conditioner following the procedure.

If a QC canister fails to meet the QC requirements stated in Section 12.2 the operator and/or supervisor should determine if the problem is due to a high level canister in the set and decide whether to remove that canister (or canisters) before proceeding. If that canister is removed from the batch then the canister with the next highest levels must be analyzed as the batch QC. If the second can passes QC criteria the batch may be passed. Otherwise the entire batch must be cleaned again. Following the second reconditioning process, the canister that initially failed the QC must be analyzed unless that canister was removed from the set in which case the second highest canister must be analyzed. If the batch fails a second time, then either a third set of cleaning cycles may be performed or the entire batch taken off the conditioner and tagged for maintenance and manually cleaned. See Attachment 3 for a QC canister flow-chart and Section 12.2 for QC canister acceptance criteria and corrective action details.

11.5.2 Evacuation and Fill Setpoints

Typical cycle setpoints are 20 minutes for evacuation time and 10 minutes for fill time. The evacuation and fill times combined with the number of cycles necessary to sufficiently clean a canister are dependent on the sample previously in the canister. The evacuation and fill times may vary as long as the batch passes the QC check criteria in Section 12.2. The Entech 3100A systems use pressure setpoints as well as times. The canisters are filled to 10 to 15 psia (-5 to 0 psig) and typically evacuated to 1 psia using the rough pump and then below 500

mTorr with the molecular drag pump. Weekend setpoints will typically be longer as to minimize the time canisters sit evacuated on the conditioner following the procedure. Shorter setpoints may be used for the following:

- Canisters used for ambient air sampling
- Canisters that have been cleaned for sixteen cycles but still contain low levels of compounds
- Standard canisters
- Canisters returned by clients as unused
- Cleaning of new Bottle Vacs

11.5.3 Quality Control Canister Selection and Analyses

The following are strict guidelines that must be followed in order to ensure cleaning approval and that all documentation is complete and accurate.

- All canisters used for standards must be cleaned separately and the highest concentration standard selected as the QC canister.
- The canister or canisters, depending on the number of canisters within the batch (minimum of one per batch of 16 or fewer; two per batch of 20), selected for QC, must contain the highest level of contaminants as indicated on the back of the sample identification tag. When analyte concentrations in different canisters are within approximately 10%, the canister containing the analyte with the highest boiling point should be chosen as the QC canister. See Attachment 2 for TO-15 compounds listed in order by boiling point. If compound concentrations in different canisters are greater than approximately 10%, then the canister with the highest individual analyte concentration should be selected as the QC canister.
- Based on the analysis to be requested by the client, as may be indicated on the media request, the batch may be analyzed specifically for TO-15, sulfur compounds, methane (% level), or other analytes or methods not covered by TO-15. However, if the canisters are to be used for TO-15 analyses, they must be checked using this method and the acceptance criteria listed in Section 12.2 (as specified for the specific canister request, LIMS "Approved Container Orders").
- If the TO-15 analysis covers another method compound list, the QC canister may be analyzed by TO-15 for those compounds.
- A notation of the method and analytes or specific reference to the compound list that the batch is approved for must be noted in the log (*TO-15 is the default method; therefore, any method utilized other than TO-15 must be specified).*
- Make a notation in LIMS (Section 11.5.4) as to the canister or canisters selected as a QC canister.
- Make a notation on the sample identification tag that that canister was selected as the QC can, the manifold number and LIMS batch number.
- An electronic copy (pdf) of the quantitation report and chromatogram along with the acceptability of the batch (example, 75 + TICS states that the canister batch passed for the TO-15 75 compound list as well as tentatively identified compounds) must be kept by the laboratory and be available for review. IMPORTANT - A failing or passing result is to be entered into batch comments with the instrument ID, acquisition date and data file name as well.

Note: Refer to Section 12.2 for alternative uses for canisters that pass for specific compound lists.

11.5.4 LIMS

Once canisters are ready to be cleaned, they shall be placed on a conditioning manifold and the following steps taken to set-up and complete the cleaning procedure with respect to the Laboratory Information Management System (LIMS).

1) When LIMS is launched click the *Build/Update Batch* button.Click the *Create* button
2) Select the conditioning manifold
3) Type in the number of cycles
4) Scan in the canister barcodes
5) Click the *Save* button
6) Click the *Finish* button
7) When QC results are ready, click the *Open Existing* button
8) Enter QC instrument ID and filename in the comments field.
9) Select the pass or fail criteria
10) Click the *Save* button

11.5.5 Manifold Cleaning

Each canister batch must be entered into LIMS. This may be done upon completion of the cleaning cycles since the actual number of cycles may vary depending on when the system is stopped.

Perform the following procedure to clean canisters using manifolds 3 and 5:

- Remove canisters from the pre-purge manifold and secure on the cleaning manifold with a 9/16" wrench.
- Tighten the brass swagelok nuts ¼ turn past finger tight
- Cap any unused manifold positions.
- Perform a leak check prior to proceeding by:
  - Make sure the canister valves are closed; evacuate the manifold by using the manual control buttons on the main software window.
  - Activate the evacuation solenoid valve by clicking the "Evacuate" button, which will remain on until the "Evacuate Off" button is clicked.
  - With this valve on, the gauge reading should rapidly decrease to less than 100 millitorr within a few minutes. If the vacuum does not drop there is either a leak somewhere in the system, or there is a problem with the vacuum pump. As long as the vacuum gets below 400 millitor cleaning cycles may be initiated.
  - The problem must be isolated and fixed before proceeding. If there is a leak found refer to Section 11.8 for the appropriate maintenance activity.
  - If it is necessary to remove a canister (or cap) from the manifold, turn off the evacuation valve first.
  - If the leak check is successful, power on the canister heaters and open the canister valves.
  - Start the automated sequence at this point.
- Enter the parameters to be used for the automated sequence.
- Start the program by using the shortcut on the Windows 95 desktop or by locating and running the "clean.exe" file on the local hard drive. This should be located in the c:\vivid subdirectory. The setpoint window is accessed by

clicking the "Show Dialog Window" button in the lower left corner of the main window.

- Step 1 is the vacuum reading down to which the manifold pumps before going on to step 2. This should be set to less than 100 millitorr (as long as the requirements of this document are met the vacuum may be less).
- Step 2 is the time (using a 24 hour clock) that the program will wait before starting the cleaning cycles. This is used when a humidification step is necessary. Make sure the PC clock time is set accurately.
- Step 3 includes the number of fill/evacuate cycles to be performed. It also includes the times (in minutes) for each fill and evacuation period. Refer to Section 11.5.2 for this information.
- Step 4 is the final evacuation vacuum reading to be achieved, typically <100 millitorr. These setpoints are based on past experience, but other combinations may also be used if they can be demonstrated to achieve the QC criteria used to evaluate the canisters after cleaning.

- Start the sequence by clicking the "start/stop" button on the main window.
- After the cycles are completed and the canisters have been evacuated down to less than 100 millitorr, close the canister valves.
- Stop the sequence by clicking the "start/stop" button again.
- Follow the QC canister and leak check procedures detailed in Section 12.2 and 12.3 of this document.

Perform the following procedure to clean canisters using the Entech 3100A systems:

- Attach each canister using a brass nut with a graphite/vespel ferrule. Tighten no more than ¼ turn past finger tight. **Do Not Overtighten!** Make sure the canister valves are closed tightly.
- Using the software interface, evacuate the manifold manually by first clicking the **Rough Pump** button. If the pressure will not go below 1 psia check for leaks and then retry. If the pressure drops below 1 psia click the **H.V. Pump** button. The vacuum should drop below 2000 mtorr within about ten seconds and continue dropping to below 100 mtorr; if not, check for leaks and retry. As long as the vacuum gets below 400 millitor cleaning cycles may be initiated.
- Click the **All Off** button to isolate the manifold from the pumps.
- Load the desired cleaning method or edit the currently loaded method.
- Open the canister valves and turn on the oven.
- Click the **Go** button to start the cycles.
- When cycles are finished, turn the oven off and open the oven doors. Wait for the canisters to cool.
- Close the canister valves.
- Click the **Stop** button to terminate the method and isolate the manifold from the pumps.
- See section 11.6 for instructions to initiate the leak check procedure.

11.5.6 Manual Cleaning of Contaminated Canisters

If a canister is deemed too *highly contaminated* to be cleaned on a conditioner, or if it will not meet the QC cleaning criteria by the standard procedure, it may be necessary to manually rinse the can with acidified water. The analyst will make this determination from the analytical data obtained for a canister. The manual rinse is followed by a drying step, before once again placing it on the cleaning

manifold. This method will help remove semi-volatile compounds and particulates that may have entered the canister during sampling, as well as to dissolved salts which could have been deposited from condensed vapors. It may also help remove surface "lacquer" formed when the canisters are heated and contain condensed vapors.

1. Prepare a slightly acidic aqueous solution by diluting 3 or 4 drops of concentration hydrochloric acid (HCl) in a liter of distilled water. The pH will be approximately 3.
2. Using the appropriate pre-purge manifold, evacuate the canister to be cleaned (25"Hg is sufficient).
3. Attach a length of ¼" PFA Teflon tubing to the first canister using a brass nut and ferrule. It may be a removable type ferrule, such as Teflon or M-4.
4. The amount of acidified water used should be about 10% of the canister volume, i.e., 600mL for a 6L canister.
5. Place the free end of the tubing into the water, then open the can valve until the desired volume has be drawn into the can. Close the valve and leave under partial vacuum.
6. Remove the tubing and shake the can for at least one minute, making sure the entire inner surface come in contact with the liquid.
7. Place the canister in an oven set to approximately 80˚C overnight (or at least 12 hours).
8. Remove the can from the oven and pressurize to about 20psig with zero air, nitrogen or helium.
9. Hold the canister upside down over the sink and open the valve, allowing the pressure to blow out the liquid.
10. If liquid is discolored or there were a lot of particulates, repeat steps 4 through 6 using non-acidified distilled water.
11. Repeat step 8 and 9 until no more water comes out of the canister
12. Evacuate the can on the pre-purge manifold, leaving it under vacuum for at least 30 minutes.
13. Purge the canister two more times, which should remove enough residual liquid to allow the canister to be placed on the cleaning manifold.
14. Put the canister through the normal cleaning cycles. QC each canister that was manually cleaned.

11.6 Leak Check

The leak check is an individual canister certification. The two procedures listed in this section must be completed following the cleaning procedure detailed in Section 11.5.

- All canisters should be at full vacuum (less than 100 mtorr) before removing from the manifold except for laboratory standard canisters which should be left under positive pressure.
- A batch QC canister may be removed prior to evacuating the remaining canisters if it is in a position with its own isolation valve. Close all the other valves first and then evacuate the QC canister.
- Using LIMS, finish each respective cleaning batch by noting the date, time, and initial pressure of all canisters under the "Initial Vacuum" tab of "Build/Update Batch". Note: all non-QC canisters should have an initial pressure of -14.3 psig.
- Disconnect all of the canisters from manifold.
- Pressurize the QC canister(s) with humidified zero grade air (>20% RH) using the pressure/vacuum gauge to achieve the appropriate pressure (15psig).

- Alternatively, these canisters may be pressurized utilizing a canister zero grade air fill station with humidifier.
- Submit the QC canister(s) for analysis.

Note 1: If a stable reading is not achievable, then each canister pressure must be evaluated individually and the reading recorded accordingly.

- Allow each canister to sit for a minimum of 24 hours (Refer to Note 2 below).
- Measure the final pressure (using a calibrated digital pressure/vacuum gauge) and record the reading (under the "Final Vacuum" tab of "Build/Update Batch" in LIMS) as well as the time of the measurement.
- Acceptance criteria – a pressure change of <1.0psig (2 "Hg).
- If any canister is deemed to be leaking per this procedure then follow the steps in Section 12.3.

Note 2: All canisters including the QC canisters must be leak checked. If the leak check procedure is either not performed or cut short on any canister, it must done with the prior approval of the appropriate Project Manager. The person authorizing this departure from stated procedures as well as the specific reason for the departure must be noted in LIMS.

11.7 Batch Approval

Refer to Section 12.2 for information on batch approval requirements and approval with conditions.

Once the QC results have been submitted by the analyst, access the "QC Results" tab under "Build/Update Batch" in LIMS.

1) Select Batch
2) Select User
3) QC results button
   a) Select the appropriate passed for components
   b) Add any necessary comments
   c) Select the applicable update (batch or individual canisters)
   d) Select the canister IDs, where appropriate
   e) Select the analytes, where appropriate
   f) Next
4) Add QC results, where appropriate
5) Update QC results

11.8 Troubleshooting

11.8.1 Leaking Conditioning Manifold

- By far the most common cause for the manifold to fail to fully evacuate is a faulty canister valve. If a leak develops in the canister cleaning manifold, and it is not due to a leaking canister, then the manifold must be systematically checked until the leak is found. The most obvious symptom of leaking manifold is when the system will not pump down to its normal ultimate vacuum and the pirani gauge reading rises quickly after the pump isolation valve is closed.With a full set of canisters attached (or unused positions capped), close all the canister valves tightly. Open the pump isolation valve (Evac. on). The gauge should read <100mtorr. If it does not, close the manifold valves (or cap the 3100A positions) one at a time while watching

the gauge display. If the reading drops quickly after one valve is closed, the leak is at that position; proceed to the next step.

- Recheck the canister valve to be sure it is tightly closed. If the vacuum still does not go down to <100mtorr when that manifold valve is opened, the most common problem is a bad canister valve.
- Remove the canister from the leaking position and cap the end with a brass cap. Reopen the manifold valve and watch the gauge display. If it drops to <100mtorr, the problem was the canister valve. If it still does not drop, proceed to the next step.
- Close the manifold valve and replace the ferrule at the end of the flex hose. Recap the end and then open the valve. If this does not solve the problem, close the valve, remove the flex hose, and plug the valve fitting with a brass plug.
- Reopen the valve. If the vacuum still does not drop, replace the valve. Otherwise replace the flex hose and brass nut.
- For the Entech 3100A systems it is important to replace the graphite/vespel ferrules used to secure the cans to the manifold if they have been overtightened and become cracked. It may be necessary to replace the 3/8" graphite ferrules on the manifold pieces if a leak is isolated to the manifold itself.

If the system will not pump down even with all of the manifold valves closed, the leak must be in the manifold itself or the problem may be a faulty pressure isolation valve. This is an extremely rare situation. Diagnose the problem using the following steps:

- Disconnect the gas inlet tubing from the manifold. This will eliminate the solenoid valve from the system. Open the pump isolation valve and check the vacuum gauge. If it pumps down to <100mtorr, replace the pressure isolation valve.
- If the manifold still does not pump down, carefully tighten each fitting on the manifold using the appropriate wrenches. If this does not solve the leak, it may be necessary to reconnect the gas source and replace the nitrogen gas with helium. Pressurize the manifold with helium and use an electronic leak detector to check each fitting. Replace any leaking pieces with new tubing and ferrules.
- For the Entech 3100A systems it may be necessary to replace the 3/8" graphite ferrules on the manifold pieces if a leak is isolated to the manifold itself. Be very careful not to overtighten these fittings.

11.8.2 Contaminated Conditioning Manifold

- Clean the manifold by closing all of the manifold valves and clicking the "fill on" button on the screen. This will pressurize the system with UHP Nitrogen gas and can purge the stainless steel lines of the contaminant.
- Next use a heat source, i.e. heat gun, and start heating the fittings and the tubing at position one (1).
- Open the manifold valve at position one (1).
- Leave open for about one (1) minute and keep heating the tubing and the fittings surrounding the valve. This process will purge the contaminants from that valve's outlet and the heat will help volatilize the compounds from the inner surface of the stainless steel tubing.
- Close valve and move to the next valve.

- Continue this process for valves two (2) through remaining valves on the manifold in question.
- Refer to Section 11.3 for the pre-purging and canister cleaning procedure.

11.8.3 "Leaking" Canisters (Identified by Analysts or Other Such Sources)

This section is for those canisters that are suspected of leaking as identified by analysts using the AUTOCAN, during pressurization, or by other means and other individuals. This section is NOT for those canisters identified by the Canister Conditioning Department during the leak check or identified as leaking on the conditioner as those are required to go straight on Maintenance Hold.

Identified canisters are to be handled according to the following instructions and number 1 is to be completed first. This is regardless of the PM's or client's instructions to proceed.

1) Obtain a leaking canister or maintenance (yellow) tag, place it on the canister and label as leaking, add initials and date.
2) Also, make a note on the tag whether or not the analysis proceeded (e.g. "Analyzed" or "Canceled")
3) If canceled, then the Canister group can proceed and place the can on Maintenance Hold to perform a formal leak check or clean and perform the required 24hr leak check.
4) If analyzed, then the canister should be placed with the other canisters in the job and when cleaning is to take place then put the canister in question on Maintenance Hold.

IMPORTANT: All canisters that are suspected of leaking MUST have a yellow tag stating such and NO canister that is deemed to be leaking is to go without the *full* 24hr leak check.

12) Quality Control Requirements and Corrective Action

12.1 All corrective action plans must be developed in accordance with the *SOP for Nonconformance and Corrective Action*.

12.2 QC Canister Criteria

Once the cans have gone through the cleaning process, it is necessary to verify that all previous contaminants have been removed. This is accomplished by selecting a minimum of one canister per manifold/batch (10 or 16 or fewer) and two for a 20 canister batch (or fewer) to be analyzed for VOCs by GC/MS. However, all canisters that are to be analyzed for TO-15 (SIM mode) are individually analyzed/QC checked for the Client's specific compound list.

In order for a canister to be considered acceptable no analyte concentration may be at or exceed the canister cleaning requirement of 0.2ppbv. If the required reporting limit is lower than 0.2ppbV refer to the note below.

Analyte Exceptions	
Acetone	<1.26ppbv
Vinyl acetate	<0.85ppbv
Ethanol	<1.59ppbv
IPA	<0.31ppbv
1-Butanol	<0.30ppbv
2-Butanone	<1.0ppbv
Carbon Disulfide	<0.96ppbv
Acrolein	<0.65ppbv

- There must be no compound detected as a tentatively identified compound above the level specified in the associated TO-15 method SOP.
- If the canister has target contaminants above 0.2 ppbv or the MRL (if lower than the canister cleaning requirement), the entire batch is rejected and the cleaning process repeated.
- All canisters selected as QC canisters (all canisters for TO-15 SIM) for a cleaning batch must meet the requirements detailed above in order for the batch to be certified as "clean".

IMPORTANT NOTE: Method Reporting Limit – A client may request a certain method reporting limit for TO-15 that is lower than the 0.2ppbV canister cleaning requirement. In this case, it must be conveyed to the analyst. All TO-15 SIM reporting limits are lower than this canister cleaning requirement; therefore, they are all individually analyzed and approved.

DoD QSM Requirement Each canister must be individually certified. A canister is considered clean if no reported analytes are detected at >1/2 the LOQ.

Passed with Conditions

Depending on what the QC canister fails for, the laboratory may be able to use it or the batch for other media requests. For example, if the canister (SIM) or batch (SCAN) passes for BTEX only it may be entered into LIMS as "passed with conditions" and labeled accordingly. In this case, the canisters may be used to fulfill a media request for canisters for the BTEX compound target analyte list.

- A notation must always be made in LIMS if the QC canister(s) passed or failed.

12.2.1 Corrective Action for Failed QC Canister

If one QC canister has failed to meet the QC requirement stated above, or the batch may not be used for another analytical method, follow the procedure described in Section 11.5.1 and the corrective action guideline detailed in the flow chart in Attachment 3. The operator and/or supervisor should determine if the problem is due to a high level canister in the set and decide whether to remove that canister (or canisters) before proceeding. If the second QC can passes the batch may be passed otherwise a second cleaning run should be performed which will usually clean the batch sufficiently. However, following the reconditioning process the canister that initially failed the QC must be analyzed (if it has not been removed from the set, in which case the second highest must be evaluated). If the batch fails again, then either all of the canisters are taken off of the conditioner and put in a "Maintenance Hold" position, where they are

tagged as needing to be manually cleaned or a third set of cleaning cycles is performed. Otherwise, if the canisters pass the QC check, the batch is released for use.

If it is suspected or determined that the conditioning manifold is contaminated follow the cleaning procedure detailed in Section 11.8.2 and the corrective action in Section 12.4.

Note 1: The requirements listed above are the minimum actions that must be taken. There must be sufficient evidence (number of QC canisters analyzed within a single batch) to ensure that the entire batch of canisters meets the analyte concentration requirement of this document.

Note 2: No batch (SCAN) or canister (SIM) may be released unless all QC canisters have passed the analyte concentration requirements or it is safely selected for use for another method and analyte list.

12.3 Leak Check Criteria

There is no defined requirement for the initial reading; however, the initial reading for the vacuum should not be less than –28.0"Hg (i.e., 27.9, 27.8, etc.). The change in the initial and final readings must be <2.0"Hg.

12.3.1 Corrective Action for Failed Leak Check

Once a canister has failed the leak check, it must be placed on maintenance hold until repaired. All canister maintenance must follow the procedure detailed in Section 13.2.2.

The most common cause is a leaking valve seat, which may be caused by repeated over-tightening or debris falling into the valve and preventing it from closing. Another possibility is that the valve is not sufficiently tightened onto the canister. It may be necessary to find the exact position of the leak by utilizing one or more of the following procedures:

- It possible to find leaks by pressurizing the canister to 20 psig and submerging it in water and looking for a stream of air bubbles.
- A leaking canister may also be detected by pressurizing the canister to 20psig with UHP Helium gas and using a Helium gas leak detector to "sniff" out a leak. The operator will use the detector probe around the valve head, valve seat, valve body, valve stem and the fastener nut fitting of the canister to allow the detector to find the leak.

12.3.2 Corrective Action for Leaking Valve

If it is determined that a canister valve is leaking and needs to be replaced, a Entech TO-V or Nupro "H" Series stainless steel bellows seated valve should be used. The valve body has 1/4" male Swagelok end fittings and the only tools needed for changing a valve are a 13/16" and a 9/16" wrench.

12.3.3 Corrective Action for Leaking Valve Stem

If the leak is found at the valve stem, it may be replaced.

- Remove the valve body with a 9/16" wrench.
- Remove the valve stem with 11/16" wrench from the canister inlet nut.
- Use jewelers pick to remove any residual Teflon tape from the threads of the inlet nut.

- Wrap the new valve stem with Teflon tape, about 4 turns.
- Install the valve stem to the canister inlet nut and tighten with an 11/16" wrench.
- If the leak is from the center seam weld, the canister must be sent out for repair and the supervisor notified.

12.3.4 Corrective Action for Leaking Canister

If a leaking valve is identified, it should be replaced with an identical or equivalent valve. The canister is tagged as such with a yellow tag and repairs are specified on the tag. The laboratory supervisor should be contacted regarding this type of repair. After replacing the valve, the canister shall be put in "to be cleaned" mode in the tracking database. It must be part of a cleaning set and pass batch QC before being put back in service.

12.4 Corrective Action for Contaminated Manifold

If it is determined that a manifold is contaminated, changing the pump oil and foreline trap adsorbent will usually solve the problem. After maintenance is performed on the system (Section 11.8.2), the canister or set of canisters which caused the contamination should be removed and cleaned by the procedure described in Section 11.5.1. A minimum of two canisters shall be QC checked and meet the criteria in Section 12.2 before that set may be certified and further batches cleaned on that manifold.

12.5 Corrective Action for Leaking Manifold

If there is a leaking manifold, it must be repaired and any canister affected shall be reconditioned and a QC check performed. A leak check shall be performed (Section 11.8.1) following any maintenance to determine if the maintenance was successful.

Replacement fittings and tubing may be obtained in house. However, if parts must be ordered for the manifold, the unit will be in a "Lock Out" or unusable mode and a notation of the "Lock Out" status entered into the maintenance log.

13) Documentation and Records

13.1 Logbooks and Analytical Records All logbooks and records (electronic or hardcopy) must be completed in accordance with the requirements specified in this document and the *SOP for Making Entries onto Analytical Records*.

13.2 Documentation

13.2.1 Canister Conditioning

Information regarding each cleaning batch is maintained in LIMS. A notation is entered into LIMS for each cleaning batch regarding its QC status (Pass, Fail, etc.).

13.2.2 Canister Maintenance

Until the LIMS container tracking module has a functioning canister history component, colored tags must be utilized to track canister maintenance. A yellow tag must be used for canisters requiring any kind of repair, such as a leaking valve or fitting.The type of problem should be noted along with the date taken out of service. A red tag must be used for contaminated canisters that have failed batch or individual QC and need further cleaning and individual QC before they can be put back in service.

13.2.3 Manifold Maintenance

Manifold maintenance is documented in hardcopy logbooks. Information must be entered for scheduled and non-scheduled projects.

14) Method Performance

14.1 Not applicable

15) Pollution Prevention and Waste Management

15.1 Activated Alumina and pump oil is considered hazardous waste and must be disposed of in accordance with the *Simi Valley Lab Waste Management Plan.* Air purged from canisters via the vacuum pumps is discharged to an outside hood.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 In the case of unacceptable data being produced on a batch or specific canister, it shall be re-cleaned or put on maintenance hold for repair with the appropriate tag affixed. In certain cases a canister may become reclassified for use (ex. ambient to source).

16.2 Analysts must notify the canister cleaning department if canisters have concentrations in excess of 1 million ng/L. These canisters must be individually QC'd and assessed as to whether they can continue to be used for TO-15 Analysis. If not they will be relabeled for GC only use.

17) Training

17.1 Training shall be conducted in accordance with the *SOP for Training Policy*. The training plan, which includes all of the responsibilities and requirements included in this SOP, must be completed for each trainee. In addition, an initial demonstration of proficiency (IDP) shall be performed prior to independent performance of the procedures detailed in this document. The IDP must consist of two successful QC canisters, from two separate batches utilizing the acceptance criteria specified in this document.

18) Summary of Changes

Table 18.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
19.0	11/24/18	C. Arend	Approval page – updated
		C. Parnell	6.1 – revised
		C. Arend	6.2 – removed "Summa" from "Summa canisters"; replaced *SOP for Waste Disposal* with *Simi Valley Lab Waste Management Plan*
		C. Arend	7.1 – updated list
		C. Parnell	8.3 – removed heating bands
		C. Arend	12.3.4 – removed "Summa"
		C. Arend	12.2 – removed DoD QSM version number
		C. Arend	15.1 – updated *SOP for Waste Disposal* to *Simi Valley Lab Waste Management Plan*
		C. Arend	19 – updated reference section

19) References and Related Documents

19.2 *SOP for Determination of Volatile Organic Compounds in Air Samples Collected in Specially Prepared Canisters and Gas Collection Bags by Gas Chromatography/Mass Spectrometry (GC/MS)*, SOP ID: VOA-TO15

20) Attachments

20.1 Attachments

Attachment 1: Training Plan

Attachment 2: TO-15 Compounds Ordered by Boiling Point

Attachment 3: QC Canister Corrective Action Flow Chart

Attachment 1

Training Plan

Training Plan for Cleaning and Certification of Summa and Other Specially Prepared Canisters

Trainee _____ Trainer _____ Date _____

1. Read SOP — Trainer ____ Trainee ____ Date _____

2. Demonstrated understanding of the scientific basis of the Conditioning and Certification of Canisters — Trainer ____ Trainee ____ Date _____

3. Demonstrated familiarity with related SOPs — Trainer ____ Trainee ____ Date _____

   SOP for Making Entries onto Analytical Records
   SOP for Laboratory Storage, Analysis, and Tracking
   SOP for Nonconformance and Corrective Action

4. Observe performance of SOP — Trainer ____ Trainee ____ Date _____
   ___Canister selection
   ___Pre-purging of highly concentrated samples
   ___Conditioning batches and placement of canisters
   ___LIMS batch setup
   ___Using conditioning manifold and conditioning program
   ___QC canister selection and documentation
   ___Batch certification
   ___Leak check procedure and documentation
   ___LIMS approval and labeling
   ___Logbook documentation
   ___Racking canisters back into available inventory

5. Perform SOP with supervision — Trainer ____ Trainee ____ Date _____
   ___Canister selection
   ___Pre-purging of highly concentrated samples
   ___Conditioning batches and placement of canisters
   ___LIMS batch setup
   ___Using conditioning manifold and conditioning program
   ___QC canister selection and documentation
   ___Batch certification
   ___Leak check procedure and documentation
   ___LIMS approval and labeling
   ___Logbook documentation
   ___Racking canisters back into available inventory

6. Independent performance of the SOP — Trainer ____ Trainee ____ Date _____
   ___Canister selection
   ___Pre-purging of highly concentrated samples
   ___Conditioning batches and placement of canisters
   ___LIMS batch setup
   ___Using conditioning manifold and conditioning program
   ___QC canister selection and documentation
   ___Batch certification
   ___Leak check procedure and documentation
   ___LIMS approval and labeling
   ___Logbook documentation
   ___Racking canisters back into available inventory

7. Instrument operation and maintenance — Trainer ____ Trainee ____ Date _____
   ___Manual canister cleaning
   ___Canister maintenance and logbook entries
   ___Vacuum pump and manifold maintenance and logbook entries

8. Troubleshooting — Trainer ____ Trainee ____ Date _____
   ___Finding leaks in manifold system
   ___Detecting leaks in canisters

Attachment 2

TO-15 Compounds Ordered by Boiling Point

TO-15 Compounds Ordered by Boiling Point					
1	Propene	33	Ethyl tert-Butyl Ether	65	Styrene
2	Dichlorodifluoromethane (CFC 12)	34	1,2-Dichloroethane	66	o-Xylene
3	Chloromethane	35	1,1,1-Trichloroethane	67	n-Nonane
4	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	36	Isopropyl acetate	68	1,1,2,2-Tetrachloroethane
5	Vinyl Chloride	37	1-Butanol	69	Cumene
6	1,3-Butadiene	38	Benzene	70	alpha-Pinene
7	Bromomethane	39	Carbon Tetrachloride	71	n-Propylbenzene
8	Chloroethane	40	Cyclohexane	72	3-Ethyltoluene
9	Ethanol	41	tert-Amyl Methyl Ether	73	4-Ethyltoluene
10	Acetonitrile	42	1,2-Dichloropropane	74	1,3,5-Trimethylbenzene
11	Acrolein	43	Bromodichloromethane	75	alpha-Methylstyrene
12	Acetone	44	Trichloroethene	76	2-Ethyltoluene
13	Trichlorofluoromethane	45	1,4-Dioxane	77	1,2,4-Trimethylbenzene
14	Isopropyl Alcohol	46	Isooctane	78	tert-Butylbenzene
15	Acrylonitrile	47	Methyl Methacrylate	79	n-Decane
16	1,1-Dichloroethene	48	n-Heptane	80	Benzyl Chloride
17	tert-Butanol	49	cis-1,3-Dichloropropene	81	1,3-Dichlorobenzene
18	Methylene Chloride	50	4-Methyl-2-Pentanone	82	1,4-Dichlorobenzene
19	Allyl Chloride	51	trans-1,3-Dichloropropene	83	sec-Butylbenzene
20	Trichlorotrifluoroethane	52	1,1,2-Trichloroethane	84	p-Isopropyltoluene
21	Carbon Disulfide	53	Toluene	85	1,2,3-Trimethylbenzene
22	trans-1,2-Dichloroethene	54	2-Hexanone	86	1,2-Dichlorobenzene
23	1,1-Dichloroethane	55	Dibromochloromethane	87	d-Limonene
24	Methyl tert-Butyl Ether	56	1,2-Dibromoethane	88	n-Butylbenzene
25	Vinyl Acetate	57	Butyl Acetate	89	1,2-Dibromo-3-Chloropropane
26	2-Butanone (MEK)	58	n-Octane	90	n-Undecane
27	cis-1,2-Dichloroethene	59	Tetrachloroethene	91	1,2,4-Trichlorobenzene
28	Diisopropyl Ether	60	Chlorobenzene	92	Naphthalene
29	Ethyl Acetate	61	Ethylbenzene	93	n-Dodecane
30	n-Hexane	62	m- & p-Xylene	94	Hexachlorobutadiene
31	Chloroform	63	Bromoform		
32	Tetrahydrofuran	64	Cyclohexanone		

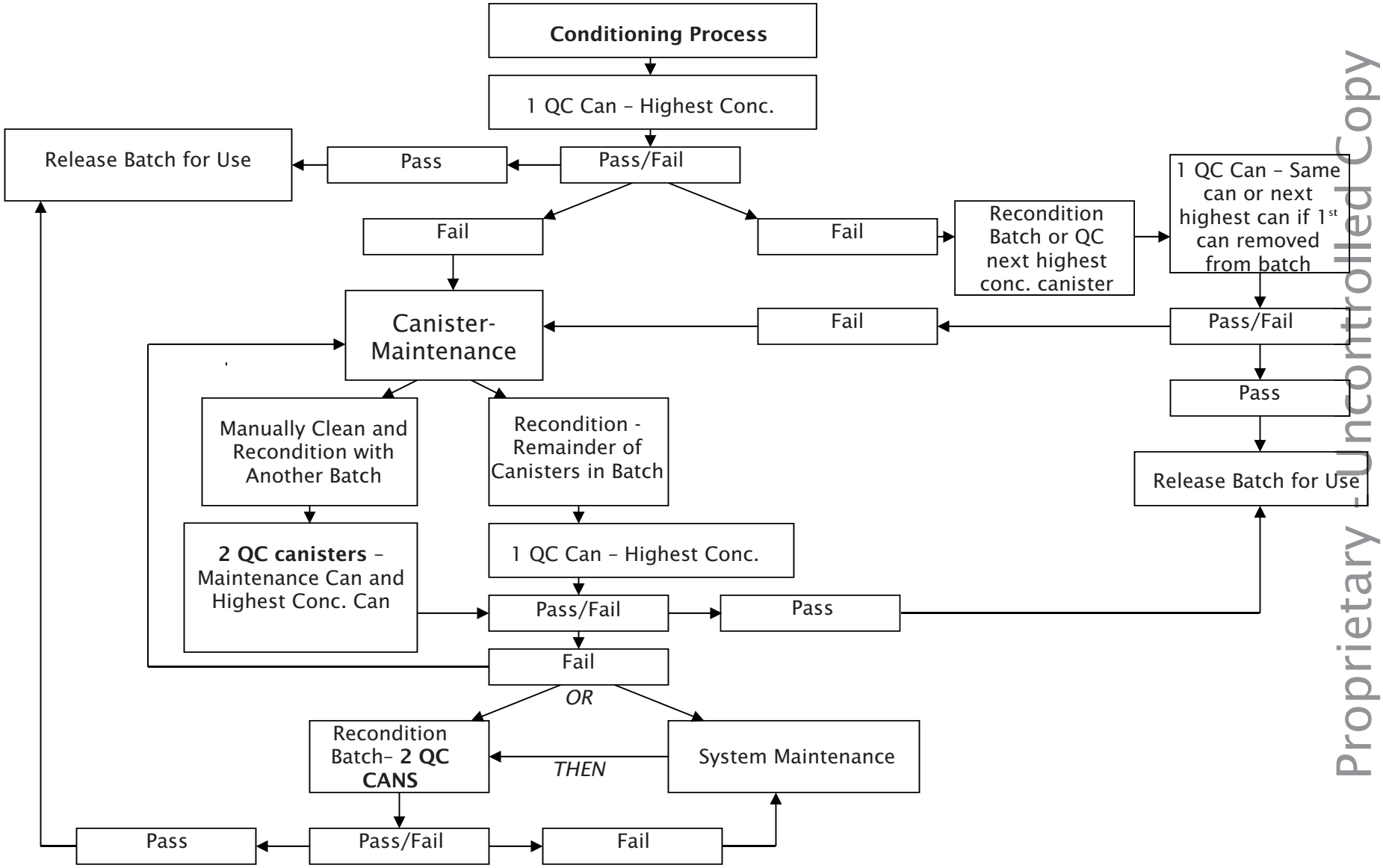
Selection of QC Canister

1. Analyte concentrations in different canisters within approximately 10%, select canister containing the analyte with the highest boiling point as the QC canister.
2. Analyte concentrations in different canisters greater than approximately 10%, select canister with the highest individual analyte concentrations as the QC canister.

Attachment 3

QC Canister Corrective Action Flow Chart

Note: This flow chart is designed for SCAN analyses, for SIM the number of QC canisters must include all of the canisters designated for SIM reporting. The 24 hour leak check is not included in this chart; however, the batch is to be released after all of the canisters have passed this check. Any canister failing the leak check is to be placed on maintenance hold.



Determination of Volatile Organic Compounds in Air Samples Collected in Specially Prepared Canisters and Gas Collection Bags by Gas Chromatography/Mass Spectrometry (GC/MS)

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1) Scope and Applicability

1.1 This procedure is based on and incorporates the requirements detailed in EPA Compendium Methods TO-15 and TO-14A and is used to quantify a wide range of volatile organic compounds (VOCs) in gaseous matrices collected in gas collection bags (method modification) and specially prepared stainless steel canisters or glass bottles. This method typically applies to ambient concentrations of VOCs 0.50ug/m3 (down to 0.10ug/m3 for low level ambient analyses) and above for the SCAN mode and 0.010ug/m3 and above for the SIM mode; however, refer to Tables 3 and 3A for the specific laboratory initial calibration ranges for each target compound. The method requires VOC enrichment by concentrating up to one liter of a sample volume, with a virtually unlimited upper concentration range using dilutions from source level samples.

In this document, Tables 2 and 2A (see Note 1 below) list compounds that can be determined by this procedure along with their corresponding laboratory method reporting limits (MRLs) and method detection limits (MDLs). The reported MRL may be adjusted higher; however, the capability of achieving lower MRLs for specific project requirements must be thoroughly demonstrated (by an acceptable initial calibration and method reporting limit check standard) and documented as long as the MRL is higher than the current method detection limit for each compound. Additional compounds may be analyzed according to this procedure as described in the referenced methods as long as the requirements of this document are adhered to. The number of samples that may be analyzed in a 24-hour period is about twenty. The number of sample results that may be reduced in an eight-hour day is approximately twenty.

2) Summary of Procedure

2.1 The analytical method involves using a high-resolution gas chromatograph (GC) coupled to a mass spectrometer (MS). The GC/MS utilizes a linear quadrupole system, which allows for it to be operated by either continuously scanning a wide range of mass to charge ratios (SCAN mode) or by Select Ion Monitoring mode (SIM), which consists of monitoring a small number of ions from a specified compound list.

An aliquot of an air sample is concentrated on a solid adsorbent trap (either cryogenically or fan cooled glass beads or stronger adsorbents at higher temperatures) to collect the analytes of interest. To remove co-collected water vapor, the concentrated sample then goes through a water removal (dry purge) step. After the sample is pre-concentrated on a trap, the trap is heated and the VOCs are thermally desorbed onto a refocusing cold trap. The VOCs are then thermally desorbed onto the head of a capillary column once the cold trap is heated. The oven temperature (programmed) increases and the VOCs elute and are detected by the mass spectrometer.

Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This method utilizes the internal standard calibration technique; refer to Section 3.16 for a complete definition.

3) Definitions

3.1 Cryogen A refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Liquid nitrogen (cryogen) is used for this purpose and it has a boiling point of -195.8°C.

3.2 Gauge Pressure Pressure measure with reference to the surrounding atmospheric (barometric) pressure, usually expressed in units of psig. Zero gauge pressure is equal to atmospheric pressure.

3.3 MS-SCAN Mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

3.4 MS-SIM Mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

3.5 Analytical Sequence The analytical sequence describes exactly how the field and QC samples in an analytical batch are to be analyzed.

3.6 Neat Stock Standard A purchased, single component assayed reference material having a stated purity used to prepare working calibration standards.

3.7 Stock Standards Solution A concentrated solution of one or more target analytes at a known concentration purchased from a reputable commercial vendor. Stock standard solutions are used to prepare working calibration standards.

3.8 Intermediate Calibration Standard A solution of one or more target analytes at a known concentration prepared either from one or more neat stock standards or from one or more stock standards solutions.

3.9 Working Calibration Standard A solution of all the target analytes at a known concentration prepared either from one or more intermediate calibration standards and/or from one or more stock standard solutions.

3.10 Calibration or Standard Curve A calibration or standard curve is a graph which plots the concentration of a compound (or an analyte) versus the instrument response to the compound.

3.11 Initial Calibration Verification (ICV) Standard A solution prepared in the laboratory containing known concentration(s) of analytes of interest. The solution is prepared from neat stock standards and/or stock standards solutions which are from a different source than the standards used to prepare the working calibration standards.

3.12 Continuing Calibration Verification (CCV) Standard A working calibration standard which is analyzed at specific intervals in order to verify that the instrument continues to meet the calibration criteria.

3.13 Field Sample A sample collected and delivered to the laboratory for analysis.

3.14 Manual Integration This term applies to a data file in which setpoints have been changed and reintegration has occurred under the changed setpoints; baselines have been adjusted; peak integration start and stop "ticks" have been changed; peak area, or peak height, are changed after the time of data collection and data file generation.

3.15 Batch Quality Control (QC) Batch QC refers to the QC samples that are analyzed in an analytical batch of field samples and includes the Method Blank (MB), Laboratory Control Sample (LCS) and Laboratory Duplicate (LD).

3.16 Internal Standard Calibration Compares the instrument responses from the target compound in the sample to the responses of specific standards (called internal standards), which are added to the sample or sample preparation prior to analysis. The ratio of the peak area (or height) of the target compound in the sample or sample preparation is compared to a similar ratio derived for each calibration standard.

3.17 May This action, activity, or procedural step is neither required nor prohibited.

3.18 Must This action, activity, or procedural step is required.

3.19 Shall This action, activity, or procedural step is required.

3.20 Should This action, activity, or procedural step is suggested, but not required.

3.21 SOP Standard Operating Procedure

3.22 Service Request A form generated, at the time of sample receipt, which details pertinent information such as client name, address, contact, client and laboratory sample identifications, sampling and receipt dates and times, requested analyses, sample type, canister pressures (initial and final), and the service request number (unique number for each submitted job) and serves as an inter-laboratory "custody" form which accompanies all samples throughout the laboratory.

3.23 Selectivity Selectivity of a method refers to the extent to which it can determine particular analyte(s) in a complex mixture without interference from other components in a mixture. Another definition is the extent to which a particular method can be used to determine analytes under given conditions in the presence of other components of similar behavior.

3.24 Limit of Detection (LOD) The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%. (DoD Clarification). For consistency purposes, the LOD may be referred to as the MDL once it is reported; however, full verification will be on file in the laboratory per the procedures detailed in this document.

3.25 Limit of Quantitation (LOQ) The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. (DoD Clarification). For consistency purposes and since the LOQ and MRL are equivalent with regards to laboratory procedure, the LOQ will be referred to as the MRL in this document and once it is reported. Full verification will be on file in the laboratory per the procedures detailed in the document.

3.26 Detection Limit (DL) / Method Detection Limit (MDL) The smallest analyte concentration that can be demonstrated to be different from zero or a blank concentration at the 99% level of confidence. At the DL, the false positive rate (Type 1 error) is 1%. (DoD Clarification). For consistency purposes, the DL may be referred to as MDL. Also, as far as reporting is concerned the MDL will be raised up (where necessary) to the verified LOD per the procedures defined in this document and reported accordingly.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP may perform analysis, interpretation and peer review of the results. Data reduction and/or peer review may be performed by another qualified employee. This employee must be

familiar with the analytical technique and have completed a data review training plan to ensure familiarity with specific analysis and requirements.

4.2 The supervisor/manager must ensure that method proficiency is documented initially and whenever significant changes in the instrument type, personnel, and matrix or test method are made.

4.3 The department supervisor/manager or designee shall perform final review and sign-off of the data.

5) Interferences

5.1 Canisters

Canisters shall be stored in a contaminant free location and shall be capped tightly during shipment to prevent leakage and minimize any compromise of the sample. The pressure/vacuum is checked prior to shipment and upon receipt from the field. Any problems with the sample from the field are noted and the Project Manager contacted.

Also, canisters must be cleaned and certified to be free from target analytes before being shipped to the field for sample collection. The procedure is described in detail in the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Containers* (refer to this procedure as well as Section 12.7 for the acceptance criteria).

Current laboratory practice entails the segregation of 6L canisters into ambient (low) level and source levels. All the ambient canisters are used for low level (indoor air, ambient air) projects and not intentionally for soil gas, SVE monitoring, or other higher level applications. It may be necessary to "retire" an ambient canister and re-assign for source level use if high concentrations are encountered. This decision will be made by management based on analytical concentrations and what compounds were encountered at these levels. If the level of any analyte is detected above 5,000ug/m*3* in the ambient can, then the supervisor/team leader must be contacted to determine if the canister(s) is to be retired. If retirement is decided upon, make a notation on the sample tag (or other color coded tag) of each canister in question. The notation must contain the analyte, threshold levels and retirement from ambient use (initial and date notation) so that the canister conditioning/management department may properly execute the retirement.

5.2 Analytical System

The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with buna-N rubber components must be avoided.

5.3 Carbon Dioxide

Excessive levels of carbon dioxide present in a sample may interfere with analysis by freezing up the cryogenic trap. A smaller aliquot must be analyzed to eliminate this problem, or the sample should be analyzed using the higher temperature multi-adsorbent trapping technique which allows carbon dioxide to pass.

5.4 Gas Collection Bags

This procedure covers the use of gas collection vessels such as Tedlar® or Mylar® bags. However, due to the nature of these types of bags it is not recommended that clients use this option for ambient air samples. Sample collection bags made out of Tedlar® have contaminants that are inherent to the manufacturing process. The two main

contaminants are phenol and N,N-Dimethylacetamide. However, this only becomes a problem when the concentration levels in the sample are low ppbv such as ambient air monitoring samples where more of the sample usually has to be concentrated and analyzed. To minimize the loss of sample integrity, a 72-hour hold time has been incorporated into the procedure.

5.5 Glassware

Interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware results in discrete artifacts and/or elevated baselines in the detector profiles should be minimized. All glassware associated with this method must be scrupulously cleaned to avoid possible contamination. The cleaning shall be performed in accordance with the procedure outlined in the *SOP for Glassware Cleaning*. The use of high purity water, reagents, and solvents helps to minimize these problems.

6) Safety

6.1 Each compound, mixture of compounds, standards, and surrogates, as well as samples, should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest level possible through the use of gloves (to minimize absorption through the skin) and hoods (to minimize inhalation). Refer to the laboratory's Safety Manual as it makes reference to the safe handling of chemicals and SDS location. Refer to the laboratory waste management plan for the safe disposal of chemicals and samples.

6.2 Safety Data Sheets (SDS)

The analyst should consult SDS for compounds being handled in the course of this procedure, and be familiar with proper safety precautions to be followed when handling hazardous chemicals. Care should be taken when handling standard material in a neat or highly concentrated form.

6.3 Liquid Nitrogen

Liquid nitrogen can cause serious tissue damage (frostbite) with only a few seconds of contact. The valves on the cryogen dewars should be opened slowly so leaky fittings can be identified. Neoprene or leather gloves should be worn when turning valves and handling tubing and fittings that have been in contact with the cryogen.

6.4 Protective Clothing

Personal protective clothing (safety glasses, gloves and lab coat) are required when preparing standards and handling standard material in neat form.

6.5 Pressurized Gases

The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp when not in use. The regulator should never remain on small "D" size cylinders following use. Sources of flammable gases (i.e. pressurized hydrogen) should be clearly labeled.

6.6 Syringes

The proper use of syringes should be part of employee training for this SOP. Care should be taken to avoid personal injury as a result or improper handling techniques.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Air samples are collected in the field and delivered to the laboratory and shall be collected in either a specially prepared, leak-free, passivated stainless steel canister (with valve) of desired volume (e.g., 6L), a glass sampling bottle (Bottle Vac, Entech Inntruments) or a sample collection bag (Tedlar). Canister samples may either be grab or time integrated (using a variable flow controller, refer to the *SOP for Flow Controllers and Critical Orifices*) utilizing the canister vacuum to draw the sample. Bags require the use of an upstream pump or a "lung machine."

7.2 There are no special preservation requirements for either canisters, Bottle Vacs or bags. However, bags should be stored in an environment free from puncture or deterioration sources (by hanging them from clips), labeled with the specific service request number, in accordance with the *SOP for Laboratory Storage, Analysis and Tracking*. Canisters and bottles should be stored on the appropriate shelves until they are to be analyzed.

7.3 Sample collection bags must be analyzed within 72 hours from the confirmed time of sampling. Samples received by the laboratory shall be analyzed within 30 days of sampling or sooner if project specific requirements dictate. Programs, which have shorter recommended or required hold times, include the Department of Toxic Substances Control (DTSC), which advises a 72 hour hold time. The Minnesota Pollutions Control Agency (MPCA) requires a 14 days hold time. Additionally, the MPCA does not allow the use of Tedlar bags for sampling or sample dilution. The DTSC requirement is an advisory notice, but the laboratory shall make every effort to comply. However, the following statement shall be added to each report where sample analyses do not meet the 72 hour hold time and the client project is intended to comply with DTSC requirements. "The recommended 72-hour hold time for the analysis of TO-15 was exceeded per the DTSC and LARWQCB Advisory – Active Soil Gas Investigations document dated January 28, 2003; however, this specific hold time statement is advisory and not considered as regulation. In addition, the samples were analyzed within the EPA Method TO-15 stated requirement of 30 days."

8) Apparatus and Equipment

8.1 Additional instruments and/or differing models may be utilized as long as they are equivalent and meet the minimum requirements of this document.

8.2 Gas Chromatograph (GC)

An instrument capable of temperature programming, with a column oven that may be cooled to sub-ambient temperature at the start of the gas chromatographic run to result in the resolution of the VOCs.

Hewlett Packard 5890 Series II Plus
Hewlett Packard 6890 Series
Hewlett Packard 6890A Series
Agilent 6890N Series
Agilent 7890A Series
Agilent 7890B Series

8.3 Autosampler

Tekmar-Dohrmann AUTOCan Autosampler: 14-ACAN-074

Markes Autosampler:	UNITY 2/CIA Advantage
Concentrating Trap (cryogenic trap, built-in):	14-6938-020
Cryofocusing Module w/split valve:	14-6520-A00
GAST Vacuum Pump:	DOA-P104-AA or equivalent

8.4 Mass Spectrometer (MS)

A MS capable of scanning from 34 to 350 amu every second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Bromofluorobenzene (BFB) which meets all of the criteria when 50ng or less of BFB is injected onto the GC/MS system.

Hewlett Packard 5972 Series
Hewlett Packard 5973 Series
Agilent 5973N
Agilent 5973 *inert*
Agilent 5975B *inert*
Agilent 5975C *inert*
Agilent 5977A

8.4.1 Ionization Gauge Controller

- Agilent: 59864B
- Granville-Phillips 330 Ionization Gauge Controller: 330001/2/3
- Hewlett Packard Ionization Gauge Controller: 59864B

8.5 Analytical Column

Any analytical column capable of separating the compounds of interest may be used. The capillary column should be directly coupled to the source of the mass spectrometer. The following are suggested columns; an alternative column may be used as long as sufficient peak resolution and separation is achieved.

- Restek Rxi-1ms Fused Silica Capillary Column; 30m x 0.25mm ID 1.0µm film thickness

  OR

- Restek Rxi-1ms Fused Silica Capillary Column; 60m x 0.25mm ID 1.0µm film thickness

8.6 Data Systems

IBM-compatible PC with Windows 95/98/NT/XP/7 (Microsoft Office EXCEL version 2003 or newer) and Hewlett Packard Chemstation software including EnviroQuant with Extracted Ion Current Profile (EICP), National Institute of Standards and Technology (NIST) library (2011 version or newer) or equivalent.

8.7 Canister Pressurization Station

Vacuum/Pressure Gauge [0 to –30 inHg; 0-90 or 100 psig]

8.8 Canister Sampling Devices

Refer to the *SOP for Flow Controllers and Critical Orifices* for specific calibration and other pertinent information.

- VICI Condyne Model 300 Flow Controller
- Critical Orifices (Laboratory manufactured)

8.9 Gas Collection Devices

- Lab Commerce, Aerosphere Model S6L, 6.0L Passivated Canisters or equivalent
- Lab Commerce, Stabilizer Model 22.4L, 2.4L Canisters or equivalent
- Restek Corporation, #24203, 3.0L Silco Canisters or equivalent
- Tedlar bags – 0.5L, 1L, 3L, 5L, 10L, 25L, and 40L (other sizes are available; however, the volumes that are listed encompass the majority of the bags supplied and the samples submitted to the laboratory).
- Entech Instrument, SiloniteTM Canisters or equivalent
- Entech Instruments, Bottle Vacs or equivalent

8.10 Dynamic Dilution System

- Entech Precision Diluter Model 4700
- Toshiba laptop computer Model 2210CDT/6.0 and Entech 4700 Version 2.1.2.9 Software

9) Standards, Reagents, and Consumable Materials

9.1 Reagents and Equipment

9.1.1 UHP Grade Helium (99.999%) (GC carrier gas, preconcentrator purge/sweep gas, pressurization gas)

9.1.2 Cryogen - Liquid nitrogen from bulk tank or 50 psig dewars (used to cool preconcentrator traps)

9.1.3 UHP/Zero Grade Air (canister pressurization)

9.1.4 ASTM Type II Water, DI water or equivalent

9.1.5 UHP Grade Nitrogen (99.999%) (additional pressurization gas, based on other methods requested – modification to method)

9.2 Standards

Standards are prepared for both SCAN and Selective Ion Monitoring (SIM) modes according to the procedures detailed in this section. The preparation of standards for the analysis of air samples is carried out by following the procedure, "Preparation of Gas Phase Standards for Ambient Air Analysis", Application Note, Spring 96, Vol. 6.5, *Tekmar*-DOHRMANN AutoCan User's Manual. Neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

9.2.1 Instrument Performance Check, Internal Standard and Surrogate Spiking Mixture
Prepare a standard solution of p-Bromofluorobenzene (BFB-used as both a tune check and surrogate compound), bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene, 1,2-dichloroethane-d4(surrogate), and toluene-d8(surrogate) at 500µg/m^3 each in humidified zero air (Section 9.2.1.2). Prepare this standard according to the procedure outlined in Volume 6.5 of the *Tekmar*-

DOHRMANN Application Note. This standard may also be prepared from a neat cocktail as in Section 9.2.2.2.1 or as stated in Section 9.2.1.3.

9.2.1.1 An intermediate standard is prepared from neat compounds in a glass static dilution bottle (SDB). After the volume of the SDB is determined, calculate the mass of each compound to be spiked to achieve a final concentration of 5.0µg/ml. Then use the density of each neat compound to calculate the microliter amount to be spiked into the SDB. The SDB is then heated for a minimum of one hour at ~60˚C to completely volatilize all components.

Concentration of the intermediate standard prepared in a SDB is 5.0µg/mL. The amount required to achieve this concentration is determined through the use of the following equation.

$$A = \frac{(C)(V)}{D} \qquad \text{(Equation 1)}$$

Where:

A Amount of each compound required to achieve the desired concentration of the standard in the SDB (µL)
C Desired concentration of SDB (µg/mL)
V Actual volume of the SDB (mL)
D Density of the compound in question (µg/µL)

Example:

Calculate the amount of neat bromochloromethane needed to achieve the final concentration of 5.0µg/mL of that compound in the SDB.

V = 2010mL
D = 1934.4µg/µL
C = 5.0µg/mL

$$A = \frac{\left(5.0\,\frac{\mu g}{mL}\right)2010\,mL}{1934.4\,\frac{\mu g}{\mu L}} = 5.2\mu L$$

Density (µg/µL)	Compound
1934.4	Bromochloromethane
1170.1	1,4-Difluorobenzene
1157	Chlorobenzene-d5
1307	1,2-Dichloroethane-d4
943	Toluene-d8
1593	BFB

9.2.1.2 The Working standard is prepared in a canister by spiking an aliquot of the stock SDB standard (Section 9.2.1.1) using a heated gastight syringe. Connect a cleaned, evacuated canister to a source of pure diluent gas (humidified zero air) using a Teflon line with a stainless steel tee directly above the canister valve. One port of the tee is fitted with a septum. Spike the SDB stock and following removal of syringe a small flow of diluent gas to flush the spike into the can. Pressurize the can to positive 83.3 psig with humid zero air, and allow the contents to equilibrate for approximately 24 hours before using.

Concentration of the working standard prepared in a canister is 500ng/L. The final pressure of the canister is 83.3psig; therefore, the pressurized volume is 40L, which is obtained through the use of the following equation.

PV = PDF(V) (Equation 2)

Where:

PV Pressurized canister volume (L)

PDF Pressure Dilution Factor, where PF = $\frac{P_{atm} + P_f}{P_{atm} + P_i}$

P_f Final Canister Pressure

P_i Initial Canister Pressure

V Volume of canister at 1atm

P_{atm} Atmospheric Pressure = 14.7psig

Example:

$\frac{14.7 + 83.3}{14.7 + 0}(6L)$ = 40L

In order to prepare the canister with a concentration of 500ng/L, it must be determined how much of the intermediate standard is required. This is achieved through the use of the following equation.

A= $\frac{(F)(V)}{(C)\left(1000\frac{ng}{\mu g}\right)}$ (Equation 3)

Where:

F Desired concentration of working standard (ng/L)

V Pressurized Volume of Canister (L)

C Concentration of prepared SDB (µg/mL)

A Amount of standard (mL) of the SDB required to obtain the desired working standard concentration

Example:

$$A = \frac{500\frac{ng}{L}(40L)}{\left(5.0\frac{\mu g}{mL}\right)\left(1000\frac{ng}{\mu g}\right)} = 4mL$$

9.2.1.3 Currently the working standard is purchased in a cylinder at a certified concentration of 500ng/L (prepared by Linde SPECTRA Environmental Gases, Alpha, NJ).

The internal standard (IS) cylinder comes from the vendor with a one year expiration date. These compounds should be stable in the high-pressure cylinder for five years or longer so the laboratory will extend the expiration date to two years from the date of preparation. The working standards are canisters filled directly from the main cylinder and are given a two month expiration when prepared in a 6L canister and a six month expiration when prepared in a 30L or greater canister. The method utilized relative response factors for target analyte quantitation so the IS concentrations are factored out since they appear in the numerator and denominator of the final calculation.

A quantitation report with chromatogram of a TO-15 blank run will be printed as soon as a new IS cylinder is put into use and again after one year. The latter will be checked for any unexpected peaks to look for possible degradation of the IS compounds in the cylinder. These shall be kept on file with the original certificate of analysis.

9.2.1.3.1 For SCAN analyses, the working standard is filled directly into a canister to a pressure of 70 to 80 psig.

9.2.1.3.2 For SIM analyses, the working standard is diluted and pressurized with humid zero air to the desired concentration using Equation 2 in Section 9.2.1.2. Typical concentrations will be 20ng/L, 40ng/L or 50ng/L.

9.2.2 Initial Calibration (ICAL) Standard Prepare the primary source calibration standards in canisters with nominal concentrations of 1ng/L (optional), 20ng/L and 200ng/L for analyses in SCAN mode and 0.1ng/L, 5.0ng/L, and 200ng/L for analyses in Selective Ion Monitoring (SIM) mode for each of the target analytes. Differing injection volumes will create the standard concentrations listed in Tables 3 (SCAN) and 3A (SIM) of this document. The full list of analytes which are analyzed according to this method can also be found in Tables 2 (SCAN) and 2A (SIM).

Standards are prepared by diluting the stock standard with humid zero air into a canister. The stock standard is a certified custom-blended cylinder (prepared by Linde SPECTRA Environmental Gases, Alpha, NJ). Refer to Tables 3 and 3A for the list of analytes and certified concentrations in the purchased cylinder.

9.2.2.1 Working standards are prepared into canisters using the Entech 4700 Precision Static Diluter. Turn on the power to the diluter ten minutes prior to using to allow for the components to come to thermal

equilibrium. Connect the computer and start the software. Connect a Zero Air source to the Diluent port on the back of the diluter and adjust the cylinder regulator to 50 psig. The ports for the stock standards are color-coded and use quick-connect fittings. Connect up to four stock standard cylinders to the inlet ports on the right side of the diluter using the Silonite-coated 1/8" stainless steel tubing and quick connects provided. Open the cylinder valve. Adjust the inlet pressures to 10psig.

Purge Diluter Lines: Click on Manual Control (left side of window), click Enable and choose channel for the desired standard. Move the slider bar to around 20% for a few seconds to purge the lines with the standard, then move back to 0%. Click Disable.

Set Configuration: Click the Settings button on top of window then click the Configuration tab. Enter the standard concentrations for each cylinder channel used. Save the file using the File tab. A previously saved configuration file can be loaded here also.

Dilution Settings: Click the Dilution button at top of window. Load a method or create a new method with the desired dilution parameters. Select the channel of the stock cylinder to be used for the dilution (check box in Use column). Multiple channels can be diluted into the same canister. Enter the target final concentration, final canister pressure (psia), canister volume and barcode ID, standards log ID, preparer's initials, and a brief description of the dilution. Save the file if desired.

Connect Canister: Spike 50µl clean DI water into the valve of a clean, evacuated canister and connect to the outlet port. Open the valve for a few seconds and then close it and watch the pressure reading in the software window. It should stabilize quickly and stop drifting. If there is a leak check the connection and the canister valve.

Start Dilution: Open the canister valve and start the dilution program. It will partially fill the canister with diluent air, then add the required amount of stock standard, and then fill to the final pressure. Remove the canister when finished.

Redilution: A serial dilution may be made from a standard canister. Create a configuration file as above with the first canister on channel 6 and then create a method using channel 6 as the stock. Connect the standard canister to position 6 Input (front of diluter) then continue as above with the evacuated canister.

9.2.2.2 When analysis of additional (extra) compounds are requested which are not in the purchased stock cylinders, the following preparation instructions should be used. In addition, the internal standard / surrogate standard may also be prepared in this manner (Sections 9.2.2.2.1 – 9.2.2.2.2) as mentioned in Section 9.2.1.

9.2.2.2.1 *Equi-mass "soup"* (contains compounds in equal mass amounts) or *cocktail* prepared from the neat compounds for a

large number of components. If additional SIM compounds are requested, the same cocktail may be used.

Cocktail Preparation:

Step 1: This cocktail is prepared by combining 25mg of each neat compound into a small glass vial. Use a microliter syringe to transfer each compound, cleaning with solvents in between. Put the vial in the freezer between aliquots to minimize volatilization. Take the density of each compound into account to determine the actual amount of each compound to spike into the cocktail by using the following equation.

$$S = \frac{A}{D} \qquad \text{(Equation 4)}$$

Where:

S Actual spike amount (µL)
A Desired amount for each compound (mg)
D Density (mg/µL); refer to Table 2 for the density

Example: The actual volume of acrolein to add to the cocktail is calculated by the following.

$$S(\text{Acrolein}) = \frac{25mg}{\left(0.840\,\frac{mg}{\mu l}\right)} = 29.8\mu L$$

Step 2: The concentration of each compound in the cocktail is determined by the following equation.

$$C = \frac{A}{V}\left(1000\,\frac{\mu g}{mg}\right) \qquad \text{(Equation 5)}$$

Where:

C Concentration of cocktail (µg/µL)
A Amount of each compound (mg)
V Final volume of cocktail (total spike volumes of each compound) (µL)

Example:

$$C = \frac{25mg}{631.8\mu L}\left(1000\,\frac{\mu g}{mg}\right) = 39.569\mu g/\mu L$$

9.2.2.2.2 *An intermediate standard* is prepared from neat compounds by spiking individual compounds into a glass static dilution

bottle (SDB) as described in Section 9.2.1.1 or spiking an aliquot of a cocktail into the SDB. The spike amount of a cocktail is determined by using the following equation.

$$S = \frac{C_1 V}{C_2} \qquad \text{(Equation 6)}$$

Where:

S Spike amount required in order to obtain the desired concentration (µL)
C_1 Desired concentration of SDB (µg/mL)
C_2 Concentration of cocktail (µg/µL)
V Volume of SDB (L)

Example: Determine the spike amount of the cocktail required to achieve the desired intermediate standard concentration.

$$S = \frac{\left(1\frac{\mu g}{ml}\right)(2010ml)}{27.81\frac{\mu g}{\mu L}} = 72.28\mu L$$

9.2.2.2.3 *Intermediate Standard Preparation (Gaseous Compounds*) As an alternative to the glass SDB method, if the extra compounds needed to be analyzed are gases at room temperature, use a gastight syringe to prepare an intermediate standard in a 1L Tedlar bag filled with humidified zero-grade air. Use the molecular weight of the compound to calculate the microliter amount to be spiked into the bag to achieve desired concentration. The spike amount is determined by using the following equation.

$$S = \frac{C * V * 24.46}{M * \left(1000\frac{ng}{\mu l}\right)}$$

S Spike amount required in order to obtain the desired concentration (µl)
C Desired concentration (ng/L)
V Volume of the Tedlar Bag (1L)
M Molecular Weight of the compound
24.46 Molar Volume of gas at 25°C, 1atm

Example:

Make a 100,000ng/L intermediate standard of Chloro-difluoromethane (Freon22) in a Tedlar Bag, where M=86

$$S = \frac{100{,}000\frac{ng}{L} * 1L * 24.46}{86 * \left(1000\frac{ng}{\mu l}\right)} = 28.44\mu l$$

9.2.2.2.4 *The Working standard* for extra compounds is prepared in a canister by spiking an aliquot of the intermediate standard (glass SDB or Tedlar bag) using a heated gastight syringe. The preparation of these standards shall follow the instructions detailed in Section 9.2.1.2. The concentrations for working standards are usually 20 and 200ng/L, however different concentrations can be chosen which work best for a particular project.

9.2.3 Initial Calibration Verification (ICV) - (Laboratory Control Sample - LCS) Prepare a secondary source standard (either a different manufacturer or different lot from the same manufacturer as the initial calibration standard) using the same procedures as the primary source. The ICV/LCS working standard should contain each target analyte present in the calibration working standard. Prepare the ICV/LCS working standard at a concentration of 200ng/L. Differing injection volumes account for the allowed concentrations listed in Table 4 for SCAN and 4A for SIM. The preparation of this standard shall follow the instructions detailed in Section 9.2.2, using the certified second-source standard cylinder.

9.2.4 Continuing Calibration Verification (CCV) Standard The CCV is the same as the initial calibration working standards detailed in Section 9.2.2.

9.2.5 Screening Standards Recommended procedure: Prepare a 0.5ug/mL and/or a 3.0ug/mL concentration standard so that the GC may be calibrated utilizing a few levels (may include approximately 0.5ng, 150ng and 600ng). However, other concentrations can be prepared depending on the desired range.

Any of the desired standard concentrations (primary and secondary) may change as long as the equations and the appropriate densities remain the same.

9.3 Storage and Expiration Dates

- All standards that are to be stored in a freezer shall be stored at ≤-10˚C for DoD projects.
- Neat Stock Liquids are stored at < -10˚C (-10˚C to -20˚C) as specified by the manufacturer or for a period of five years.
- Equi-Mass Primary Stock Standard is a cocktail or soup of neat compounds (containing compounds in equal mass amounts) used to in preparing intermediate gas phase standards and shall be stored in the freezer at < -10˚C (-10˚C to -20˚C) for up to six months. This is assuming that the soup is sealed with a septum-containing screw cap or Mininert™ valve. The selection of the compounds for the soup should be performed in accordance with the guidelines in Volume 6.5 of the *Tekmar*-DOHRMANN Application Note.

- Purchased Stock Standards Cylinders must be stored at laboratory temperature for a period of 2 years or as specified by the manufacturer before vendor re-certification or purchase of new standards. Expiration dates of the cylinders must be entered into the yearly wall calendar located next to the cylinders. Analysts must verify that the assigned expiration dates of prepared standard canisters do not exceed the parent standard expiration date.
- Intermediate Calibration Standards prepared by static dilution must be stored in an oven at a temperature of approximately 60°C to ensure analyte vaporization. Every time a standard is prepared from the static dilution bottle (SDB), the concentration changes. To increase the useful lifetime of an SDB standard, remove volumes of 25mL or less. The volume removed can be manipulated by increasing the SDB concentration or by adjusting the canister final volume/pressure. Depending upon the volume removed, an SDB intermediate standard is stable for approximately two months as long as new working standards made from this standard continue to meet acceptance criteria. These bottles must be in the oven for a minimum of one hour prior to use in preparing working standards. The guidelines for the storage and expiration date for the intermediate calibration standards are stated in Volume 6.5 of the *Tekmar*-DOHRMANN Application Note.
- Prepared Stock / Intermediate Calibration Standards prepared in canisters (1000ng/L) may be stored at laboratory conditions for up to three months in an atmosphere free of potential contaminants. Upon preparation, canister standards should be allowed to sit for approximately 24 hours prior to use in order for equilibration to take place. Shorter equilibration periods may be necessary and acceptable as long as performance criteria are met.
- Calibration or Working Calibration Standards prepared in canisters may be stored at laboratory conditions for one month in an atmosphere free of potential contaminants. Upon preparation, canister standards should be allowed to sit for approximately 24 hours prior to use in order for equilibration to take place. Shorter equilibration periods may be necessary and acceptable as long as performance criteria are met.

10) Preventive Maintenance

10.1 A maintenance log will be kept documenting maintenance performed on each analytical system. The serial numbers of each instrument shall be recorded, and each log entry must include a description of the maintenance performed and be initialed by the analyst performing or observing/authorizing maintenance by an outside contractor.

The instrument maintenance log must be kept current. An entry shall be made in the appropriate log every time maintenance is performed (no matter the extent). The entry in the log must include.

(a) The date of maintenance
(b) Who did the maintenance
(c) Description of the maintenance
(d) Proof that the maintenance activity was successful

A notation of a successful tune and continuing calibration or initial calibration and the file number that accompanies the data will serve as proof that the maintenance is complete and the instrument is in working order.

The extent of the maintenance is not important, however, it is important that a notation be included for each maintenance activity such as changing a column, tuning the instrument, changing the pump oil, cleaning the source, ordering a part. In addition, a

notation should be made in the logbook stating that no samples were analyzed during the days that the instrument was down and no active maintenance was being conducted (i.e., where no other notation was made in the logbook for those days).

10.2 Concentrating Trap

Routine maintenance includes periodic solvent cleaning of the Silco steel lines in the valve oven if contamination is suspected. Also, periodic replacement of the multi-sorbent or partial replacement of the trap if analyte specific deterioration is detected is required. See Attachment 5 for trap packing instructions. For specific trap information refer to the instrument maintenance logbook.

After repacking, the trap should be baked at 265°C for a minimum of three hours (or until a clean blank is generated) and a partial repacking requires baking (at 265°C) the trap for a minimum of 20 minutes (or until a clean blank is generated).

10.3 GC System

Column performance is monitored by observing both peak shapes and column bleed. Over time, the column will exhibit a poor overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced (see Section 8.5). Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column.

Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and "clean" (uniform, without fragmentation) by using the proper column-cutting tool. When removing any major portion of the column, which will affect the retention times and elution characteristics, a change in instrument conditions may be required to facilitate nominal analytical activity.

Declining performance can also be due to ineffective column ferrules, which should be replaced when a tight seal around the column is no longer possible. This can be detected with the use of a leak detector.

10.4 Mass Spectrometer

The Mass Selective Detector (MSD) ion source requires periodic cleaning to maintain proper performance. Symptoms of a dirty ion source include difficulty keeping the MSD in tune and fluctuating internal standard areas. The vacuum system should be serviced every six months, including changing the pump oil and checking the molecular sieve in the back-streaming trap.

10.5 Instrument Tuning

The instrument is tuned with guidance from the procedure described in the HP Operations Manual, when necessary.

10.6 Computer Troubleshooting

Computer care and troubleshooting is conducted by the IT department. Refer to Section 8.6 for the computer hardware and software requirements.

Computers are selected to meet or exceed operating system and or acquisition software requirements. Periodic upgrades of memory are performed to maintain or improve system performance and reliability. Upgrades may be performed on systems until instrument hardware configurations become the limiting factor.

Basic Troubleshooting Outline:

1) Document occurrence and severity in IT Log
2) Interview user(s)
3) Investigate any available logs (Event Logs, Acquisition Logs, etc.)
4) Determine if problem is isolated (single user or acquisition) or widespread (multi user or network).
5) If multiple possibilities exist for cause, then eliminate in systematic manner.
6) Hardware issues are addressed with component replacement (beginning with most suspect portion).
7) Software issues are addressed first with internet investigation (user blogs, software source updates/findings).
8) Network issues are investigated from the Server, to Switch, to Network Card; utilizing all available managed devices to help discover possible failure points.
9) In some cases, system corruption may require reload or complete system replacement.
10) Finalize documentation in IT Log with actions taken
11) Perform periodic follow-up with User and review any log found to have suspect events that suggested source of issue.

11) Procedure

11.1 Initial Calibration

The initial calibration is performed to determine instrument sensitivity and the linearity of the GC/MS response for the target compounds.

Initial calibration requirements are as follows:

1. A minimum of 5 concentrations must be used to calculate the calibration curve.
2. An initial calibration must be performed at a minimum initially per instrument, annually thereafter or whenever the continuing calibration verification standard does not meet the acceptance criteria.
3. Highest concentration, together with the lowest concentration, defines the calibration range.
4. The method reporting limit for any reported analyte must be at >/= the lowest calibration point.
5. The initial calibration event may not be interrupted by maintenance.
6. Only one value per concentration may be used.
7. Analyze calibration standards from lowest to highest concentration.
8. All ICAL analyses must be completed within the 24-hour tune window.
9. Only one calibration standard concentration may be replaced.
10. One of the calibration points from the initial calibration curve must be at the same concentration as the continuing calibration verification standard.
11. The upper end of the calibration range must not exhibit any peak saturation for any analyte or the range must be lowered accordingly.
12. The initial calibration model must be linear calibration using average of response factors and cannot be changed for any reason.
13. Point dropping policy
    - Minimum of 5 consecutive concentrations must be used to calculate the calibration curve.
    - Lowest concentration must be at or below the MRL (LOQ) and may not be dropped unless the MRL is changed to the concentration of the remaining lowest standard.

- Points at the high end may be dropped, but doing so lowers the calibration range.
- Points may not be dropped from the interior of the curve unless an assignable cause (i.e., gross dilution error, missing internal standards, purge malfunction, standard preparation error, or instrument malfunction) is accounted for and documented. In these instances, all the analytes in that calibration standard must be dropped from the calibration curve as the corrective action (the reason must be documented and the results maintained with the documentation for the final ICAL).
- Dropping individual compound points from the upper or lower end of the calibration range to improve linearity is not considered an error correction. The reason for dropping these points does not need to be documented but the ICAL documentation must state the revised calibration range if the MRL must be adjusted or the calibration range is lowered for a particular compound. This must be documented on the ICAL Review Checklist.

  When an individual compound point is dropped from an ICAL both the response and concentration fields in the compound database of the method must be cleared. This ensures the average ICAL RRF calculates correctly when executing the CCV check routine.

- One calibration standard may be re-analyzed if the first analysis of the standard has been dropped and other requirements in this policy are met (i.e., still within 24 hours).
- Once the ICAL has been used to calculate and report sample results it MUST not to be changed for any reason.
- It is recommended that if an analyte has a higher MRL than the lowest concentration analyzed that the low standard be automatically dropped from the curve (i.e., acetone MRL is 5, drop at least the 0.5ng point).

11.1.1 Calibration Points Analyze the calibration standards (analyze low to high) that span the monitoring range of interest of the samples. For SCAN, the range is typically 0.5ng-100ng on column; however, 0.1ng on column may be added if low level analyses are requested. For SIM, the range is 20pg on column to 50,000pg on column. The dynamic range is dependent on the sensitivity of a particular instrument as well as the required reporting limit for a given project and may be adjusted accordingly. Refer to Table 3 (SCAN) and Table 3A (SIM) for the concentrations of the compounds of interest in the initial calibration at each particular calibration concentration level.

Note: Refer to the EXCEL TO-15 Standard Concentration templates, located on the network at Q:\\TO15 Std. Concentrations\Std. Conc. Templates for both the SIM and SCAN templates. These templates must be utilized for the documentation of the standard canister concentration selection, final ICAL level concentrations and the determination of the correct injection volumes for the selected standard canister concentrations. If the primary or secondary stock standard cylinder concentrations are revised (upon re-certification or new purchases), the EXCEL spreadsheet templates, injection amounts and the ICAL concentrations in each instrument method must be adjusted accordingly. Other templates may be employed as long as they are validated and provide at least the same information.

SCAN

1. Determine if the lower end of the calibration range is to be 0.1ng or 0.5ng on column. If the low end is 0.1ng, then the 1ng/L standard must be utilized.
2. Determine if the 1ng/L or 20ng/L standard canister is to be used for the 0.5ng on column point.
3. Follow the instructions in the spreadsheet and save the file under the correct instrument folder and the initial calibration method identification.
4. Print the final ICAL concentration sheets and place into the corresponding ICAL folder

11.1.2 Recalibration Each GC/MS system must be recalibrated following any instrument maintenance which may change or effect the sensitivity or linearity of the instrument, if the continuing calibration verification acceptance criteria are not met and at least annually. The following procedure must be followed when updating an initial calibration method.

1. Open the most recent method.
2. Save the method with the new ICAL method ID using the "Save Method As" option. Date used in the method ID must be the date files were analyzed.
3. Quantitate midpoint standard and check retention times and integrations. Update retention times if necessary using QEdit or Easy ID (Tools → Easy ID). Requant if any changes are made and verify all peaks are identified correctly. Print.
   a. While midpoint standard is loaded update reference spectra (Continuing Calibration → Update Reference Spectra).
   b. With midpoint standard loaded update qualifier ion ratios and retention times (Initial Calibration → Update Levels → Select Update Level and then select Retention Times (Replace) and Replace Qualifier Ion Relative Responses).
   c. If necessary adjust integration parameters prior to processing remaining ICAL points.
4. Quantitate remaining ICAL standards. Review each peak for retention time, integration, and print. Review low level standards for acceptable signal to noise ratios and high level standards for saturation.
5. All responses must be cleared from ICAL before updating (Initial Calibration → Clear All Calibration Responses).
6. Update responses for each standard level (Initial Calibration → Update Levels) or (Initial Calibration → Quick Levels Update). If Quick Levels Update is used do not requant datafiles.
7. Save method.
8. Check Response Factor Report and evaluate whether any points should be dropped following the criteria outlined in this SOP.
9. Save method if any changes are made.
10. Verify calibration files listed on Response Factor Report are correct.
11. Verify file ID, acquisition time, quant time, update time, and last update information is correct on the Calibration Status Report.

11.1.3 Analytical Window If time remains in the tune window after meeting the acceptance criteria for the initial calibration, samples may be analyzed according to the procedure described in this document (see Section 11.5.2). If time does not remain in the analytical window, a new sequence shall commence with the analysis of the instrument performance check compound (BFB) and the continuing calibration verification standard.

11.1.4 Procedure The system should be operated using temperature and flow rate parameters equivalent to those in Section 11.6. Use the standard prepared in accordance with Section 9.2.2 of this SOP. Attach the calibration standard and internal standard/surrogate canisters to the designated inlets on the preconcentrator and open the canister valves. Analyzing different volume aliquots of the calibration standards produces differing concentrations.

Analyte responses (target ion areas) are tabulated and recorded using the Enviroquant program. Quantitation ions for the target compounds are shown in Table 2 and 2A and the primary ion should be used unless interferences are present, in which case the secondary ion may be used, but the reason documented in the initial calibration file and all subsequent quantitations utilizing that ICAL must be performed using the same ion selections. Refer to Section 13.2 for the required calculations and Section 12.4 for the acceptance criteria.

11.1.4.1 Additional Requirements The procedure for performing and generating a new initial calibration method must follow a few additional requirements.

1. If any analyte lacks the appropriate sensitivity (3 to 1 signal to noise ratio) at the low end of the calibration range, this point must be dropped from the curve and the MRL/LOQ raised accordingly.
2. No detector saturation may occur for any compound; the upper calibration level must produce no saturated peaks. Exhibited by:
   - The flattening of the response for the higher concentration standards as shown on the plot;
   - The presence of a reverse tail or rise on the front part of the peak;
   - The observed actual percent ratio of the secondary ion presence is lower than the expected percent ratio; or
   - The presence of a flat topped peak and again by the decline or saturation of the secondary ion compared with the expected % recovery.

11.1.4.2 LOQ Establishment, Verification and Acceptance Criteria

1. The LOQ must be set within the calibration range (≥ low std. of the current passing ICAL) prior to sample analysis.
2. The LOQ is verified by analyzing an LOQ verification QC sample containing the analyte at the claimed LOQ.
2. The LOQ for each analyte must be > the analyte's LOD.
3. The verification is acceptable if:
   a. The S/N ratio is at least 3:1 for each analyte.
   b. All ion abundances are acceptable per the requirements in this document.
   c. The % recovery for each analyte is within the laboratory generated control limits or 70-130% recovery for the annual Navy LOQ verification.
4. Using from 2 to 4 LOQ verification points, calculate the ongoing %RSD to demonstrate precision at the LOQ.
5. If the LOQ verification check fails, determine and document the cause. Additional LOQ verification checks must be performed at a higher level to set a higher LOQ.

6. Turn in all LOQ verification data (quantitation reports and software reports/checks) to QA regardless of pass or fail.
7. Verify the LOQ on each instrument quarterly. Navy accreditation requires an annual LOQ verification.
8. Annually, all results of the ongoing verification sample testing must be tabulated. All data representative of current operations must be used, if generated within the last two years. A minimum of seven points must be used. Refer to the *SOP for Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* for additional requirements.

11.1.5 Initial Calibration Review Analyst's calculation and assessment along with a peer review of all ICAL data and documentation as stated in Attachment 2 is required before the ICAL may be used to analyze samples. In the case where samples are placed on the autosampler and allowed to run overnight, the sample results may only be reported if the ICAL is reviewed and found to be acceptable. The ICAL checklist in Attachment 2 must be used to document the review and approval process.

Perform a review of specific aspects of the calibration which might compromise data quality such as inappropriate extension of the calibration range with detector saturation and/or a lack of sensitivity for any analyte. Analyte concentrations which do not meet the signal to noise ratio or exhibit saturation are not to be reported and must be eliminated from the initial calibration. These instances should be followed by a short explanation regarding the reason for the omission.

11.1.6 Initial Calibration File An ICAL file is to be created for each initial calibration performed per instrument into which is placed the following ICAL documents. The file shall remain in the laboratory and be filed by instrument and date.

- ICAL Checklist filled out, reviewed and approved
- BFB tune analysis report
- Calibration status report (aka Calibration History)
- Relative Response Factor Report / Percent Relative Standard Deviation
- Quantitation report for each calibration standard (including manual integration documentation – before and after manual integration)
- ICV quantitation report and % recovery report.
- TO-15 Standard Concentration Spreadsheet (exact ICAL level concentrations and ICV concentrations)
- Any manual integration documentation

11.2 Initial Calibration Verification Standard

Verify the initial calibration by analyzing an initial calibration verification standard (ICV). This standard shall be obtained or prepared from materials acquired from a different manufacturer or lot from that of the initial calibration and prepared according to Section 9.2.3.

Analyze 50ng or less (refer to Table 4 for the secondary source standard concentrations) of the ICV standard depending on the dynamic range of a given instrument and refer to Section 13.4 for the required calculations.

11.3 Sample Preparation

The pressure/vacuum is checked and the canister pressurized upon receipt by the laboratory, as needed. When necessary, canisters shall be pressurized with humidified zero grade air. However, if the samples are to be analyzed in accordance with EPA Method 3C then the samples must be pressurized with UHP Helium (refer to Section 11.11 for additional information). The client must be made aware of this in advance and given the option of either submitting two canisters for analysis or receiving a report with qualified results (TO-15 Modified).

Depending on the size of the canister and location of sampling and as specified in the SOP below, samples may be pressurized to approximately 1.0psig to 3.5psig. Additional information may be found in the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters*. Initial and final pressures are recorded in LIMS and should be repeated on the back of the sample tag. The dilution factor created by filling the sample canister is calculated using equation number 12 in Section 13.7.

11.4 Screening

The analyst must screen a sample or subset of samples if the source is of unknown origin. Typically, if the source is known to be indoor or ambient outdoor air, no screening is necessary. However, if screening is required make sure that the instrument is calibrated. A single point calibration is sufficient; however, the instrument may be calibrated utilizing a two point calibration. The ICAL points are recommended to be at approximately 0.5ng, 150ng and/or 600ng spanning the desired dynamic range. Refer to Section 9.2.5 for additional information.

Inject a 1mL or smaller aliquot of each sample into a GC/flame ionization detector (FID) system that has been calibrated with a standard containing a subset of the target analytes. This subset represents the most commonly found compounds in air samples, such as acetone, trichloroethylene, and toluene. Use the results to determine the maximum volume of sample to be analyzed by TO-15 by utilizing the following equation. Dilutions may be prepared as necessary according to Section 11.11.1.

$$I = \frac{C}{H}$$

Where:

I Injection volume (mL)
C Maximum calibration level (ng on column)
H Compound screening concentration (ng/mL)

Example: Select the compound with the highest concentration (toluene = 1.0ng/mL). If the upper calibration level is 100ng on column, then the following calculation determines the maximum injection volume to analyze.

$$\frac{100ng}{1.0ng/mL} = 100mL \text{ maximum injection volume}$$

11.5 Analytical Sequence and Data System Setup

11.5.1 Data System For the Tekmar AUTOCAN, fill in the sequence log of the Teklink program with the appropriate information. Refer to the Section 11.6.1 for the operating parameters.

For HP Chemstation, load the appropriate acquisition method for the GC/MS in the top window of the Chemstation program. Suggested GC/MS operating parameters are given in Section 11.6.2.

11.5.2 Analytical Sequence The analytical sequence must be completed for the analysis of ≤20 field samples. Re-runs, dilutions, and sample duplicates are not counted as separate samples. A method blank (MB) shall be run to monitor for laboratory introduced contamination. There must be at a minimum a laboratory duplicate (LD) analyzed in each batch to assess batch precision. The following generalized analytical sequence is to be followed:

Analytical Sequence Guideline

With Calibration	Tune Check[1] Calibration Standards (5 Standards Minimum) ICV Standard[2] (Acts as the ICV and LCS) QC Canister Checks[6] MB[7] Sample(s) – 1-20 Laboratory Duplicate[4]
With Continuing	Tune Check[1] CCV Standard[5] QC Canister Checks[6] MB[7] LCS[3] MRL Check Standard[8] Sample(s) – 1-20 Laboratory Duplicate[4]

[1] The instrument performance check solution must be analyzed initially and once per 24 hour (or as specified by the project) time period (sequence / tune window) of operation. All analyses for a sequence must be initiated (injected) prior to the expiration of the tune window.

[2] In this scenario, the ICV may also be evaluated as the LCS (differing acceptance criteria).

[3] An LCS shall be analyzed at a rate of 1 in 20 or fewer samples. The LCS is the second source calibration check standard analyzed at the lower end of the calibration curve (below the midpoint).

[4] A laboratory duplicate must be analyzed at a rate of 1 per 20 or fewer samples. The duplicate must be rotated among clients, whenever possible. Also, a duplicate laboratory control sample may be analyzed to assess precision to meet project requirements or due to sample matrix effects.

[5] A CCV must be analyzed at the beginning of every analytical sequence.

[6] Any number of QC check canisters may be analyzed in the sequence to determine a canister cleaning batch or batches acceptability.

[7] Any of the QC Check Canisters may serve as the method blank as long as the minimum requirements detailed in this document are met. A method blank shall be analyzed at a rate of 1 in 20 or fewer samples.

[8] A MRL check standard may be analyzed with each batch of 20 or fewer samples (when an initial calibration is not analyzed within the same batch). Additional information is included in Section 11.17.

Note: Client project batch specifications may require certain modifications to the analytical sequence; however, a batch may not be more lenient than that which is specified in this document.

11.6 Conditions

11.6.1 Sample Collection Conditions The suggested settings and system parameters are as follows:

Adsorbent Trap

Set Point:	35˚
Sample Volume:	up to 1L
Dry Purge:	300mL
Sampling Rate:	100mL/min (utilize for a sample injection volume of >100mL); 40mL/min (utilize for a sample injection volume of 25-100mL)
Desorb Temp.:	200˚C to 230˚C
Desorb Flow Rate:	8-10mL/min He, measured at refocuser split vent
Desorb Time:	3.0 minutes

Refocusing Trap

Temperature:	-180˚C
Injection Temp.:	160˚C
Injection Time:	1.0 min

Adsorbent Trap Reconditioning Conditions

Temperature:	265°C
Initial Bakeout:	3 hours or until clean blank is obtained
After each run:	5-8 minutes

Sample Run Time

Each analytical run is approximately 20 minutes long; the total cycle time is about 30 minutes between injections.

11.6.2 GC/MS System

Optimize GC conditions for compound separation and sensitivity.

Item	Condition
Carrier Gas	Helium

Flow Rate	1.0-1.6mL/minute
Temperature Program	Initial Temperature: ~20˚C Initial Hold Temperature: 3 minutes Ramp Rate: 5˚C/min to 80˚C 2nd Ramp: 10˚C/min to 160˚C 3rd Ramp: 20˚C/min to 240˚C for 5 min hold
Detector B (MSD *Interface)*	260˚C
Electron Energy	70 Volts (nominal)
Mass Range (Scan mode)	34 to 280 amu
Mass Range (SIM mode)	Scan masses corresponding to the target analytes
Scan Time	To give at least 10 scans per peak, not to exceed 1 second per scan.

Note: The instrument may be operated in Selective Ion Monitoring (SIM) mode if requested by the client.

11.7 Instrument Performance Check

Since the BFB tuning compound is included in the internal standard and surrogate standard canister and an autosampler is used, it is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to the reduction and approval of any data collection. The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or continuing calibration verification criteria) begins at the injection of the BFB, which shall be documented in laboratory records. Upon completion of the successful BFB tune, the tune report must be printed and retained on file for future reference.

The mass spectrum of BFB must be acquired in the following manner.

- Inject 50ng or less (on column)
- Three scans (peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.
- Background subtraction is conducted using a single scan prior to the elution of BFB.
- All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.
- The ion abundance criteria must not be changed from the requirement stated in this document (TO-15 or TO-14A, as requested).

All subsequent standards, samples and QC samples associated with a BFB analysis must use identical instrument conditions.

11.8 Continuing Calibration Verification Standard

Verify the calibration each working day, where necessary (e.g., an ICAL was not analyzed or the tune window has closed) by analyzing a continuing calibration verification (CCV) standard from the initial calibration standard canister. The concentration of the calibration verification may be varied between the low calibration standard and the midpoint of the calibration range; however, the concentration must be at one of the levels analyzed in the initial calibration. Refer to Table 3 for the standard concentrations. Refer to Section 13.3 for the required calculations.

DoD QSM Requirement: A CCV standard must be analyzed daily before sample analysis; after every 24 hours of analysis time; and at the end of the analytical batch run.

11.9 Canister Quality Control Check and Method Blank

The method blank must be a sample of a matrix similar to the batch of associated samples that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure, and in which no target or interferences are present at concentrations that impact the analytical results for sample analyses. Prepare a canister that has not left the building by pressuring with humidified zero air. Analyze an aliquot of one liter along with the same volume of internal standard and surrogate as standards and samples. Additionally, a blank must be analyzed whenever a high concentration sample is encountered and carryover is suspected. For all method blanks the unique laboratory barcode for the canister must be included in the sample analysis identification.

A Quality Control (QC) check canister pressurized with humidified zero air may serve as a method blank as long as the analyte concentration requirements stated in the canister quality control check section (Sections 12.7 and 12.8) and other requirements (refer to Section 12.12 for internal standard requirements) are met. Assuming continuing failure, another QC canister or a new canister must be prepared and analyzed in order to verify that no system contamination exists. For tracking purposes the unique laboratory barcode given to a canister shall be the information included in the sample analysis identification.

11.9.1 Sampling Systems Section 7.1 and 8.4 of Method TO-15 describe the setup and certification procedure for a specific sampling apparatus that has been used by the EPA for several of its large air monitoring programs. These systems are rarely used for the types of projects that make up the bulk of the laboratory's work. The vast majority of samples analyzed by the laboratory are taken into canisters either as grab samples or using a simple time integrated sampling device (flow controller), as in Section 8.2.1 of the method, so these procedures are not part of the typical protocol for providing sampling materials to clients. The laboratory has developed an SOP for the cleaning and certification of the materials it provides its clients for obtaining air samples to be analyzed by method TO-15. Refer to the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Containers* for additional information.

It is this laboratory's interpretation that the sampler system certification procedure described in Section 8.4.4 of the TO-15 method applies to the specific sampling apparatus described in the method and not to the sampling procedures used by our clients. The laboratory does not maintain a dynamic calibration manifold or canister sampler apparatus as described in the method and thus performance of the relative accuracy certification procedure described in section 8.4.4 is not possible.

11.10 Laboratory Control Sample

The laboratory control sample is a sample matrix, which is free from the analytes of interest and spiked with a standard containing known amounts of analytes. The laboratory control sample is an injection of the initial calibration verification standard. Inject the LCS (ICV) at concentrations below the midpoint of the calibration curve. Make sure that all of the pertinent information is included on the quantitation report including the sample identification (LCS), concentration, standard used, and analyst.

11.11 Sample Analysis

Prior to analysis, all sample containers (canisters and bags) should be at temperature equilibrium with the laboratory.

- Attach sample canisters to Tekmar AUTOCan using a 9/16" wrench. Bottle Vacs use a proprietary quick connect fitting (Micro-QT, Entech Instruments). Tedlar bags can be connected using soft silicone tubing or a 3/16" fitting with a reusable ferrule.
- Before opening the valve, check for leaking fittings by running the leak check program in the Teklink software. Quick connect fittings must be leak checked before connecting the sample container.
- If system is leak tight, open the canister valves and start the automated preconcentration procedure. Make sure the Chemstation data acquisition software has been readied.
- Maintain the trap at an elevated temperature until the beginning of the next analysis.

Check all target compounds using the QEdit routine in Enviroquant, making sure all extracted ion chromatogram peaks are integrated properly (see Section 11.15).

Note 1: The secondary ion quantitation is only allowed if there is sample matrix interference with the primary ion. If the secondary ion quantitation is performed, document the reasons in the instrument run logbook and/or on the quantitation report (initial and date any notation).

Note 2: Each female Micro-QT fitting must be purged after use to remove any remaining sample residue and prevent contamination from subsequent usage. Connect a male Micro-QT fitting to a source of ultrapure or carbon-filtered gas. Adjust the pressure to about 10 psig using an inline regulator. Connect the female fitting for several seconds, then remove and place in an oven kept at 60ºC until the next use. Do not heat the fitting higher than 80ºC.

SCAN Mode - The instrument is normally operated in the SCAN mode, where the following procedure may be followed.

- Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic range from 34 to 270 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning allows identification of unknown compounds in the sample through searching of library spectra. See operating conditions in Section 11.6.
- Generate a quantitation report for each run.
- If reporting Tentatively Identified Compounds (TICs), refer to Section 11.11.2 for identification criteria.

SIM Mode - When the client requests SIM mode, select SIM instead of SCAN mode and identify a minimum of two ions per analyte of interest. Also, a minimum of two ions for each internal standard and surrogate compound should be selected.

Helium Pressurization – If a canister is pressurized with helium, a correction factor is applied to sample volumes extracted from the canister via auto sampler. This is due to the difference in thermal properties between helium and air. A correction factor worksheet has been generated to determine the exact volume taken from a canister and may be found at J:\\A-GCMS\Helium Pressurization. Save file, print the sheet and include with the data. Refer to the instruction page in the template for all of the instructions and calculations including backfilled canisters.

AutoCAN Leak Checks – Canisters should be put on at least two different AutoCAN positions to confirm a "leak". In addition, the valve threads should be inspected for defects which may prevent a good seal with the AutoCAN. Once a canister has "failed" the leak check it must be tagged, an NCAR initiated, and the PM notified. Regardless of what the client or PM specifies as the fate of the sample, the canister must be put on maintenance hold to complete a full 24-hour leak check. The leaking canister must be documented on the Sample Review Checklist (or yellow sheet). This is a fixed QA procedure with no allowance for deviation.

11.11.1 Sample Dilution If any target analyte results are above the highest level of the initial calibration, a smaller sample aliquot should be analyzed. The dynamic range of volume aliquots for the automatic cryogenic concentrator is 15ml to 1L. If a volume smaller than 15ml is to be analyzed, a dilution should be made in a Tedlar bag, or the sample directly injected using a gastight syringe. Guidance in performing dilutions and exceptions to this requirement are given below.

- Refer to Section 11.6.1 (Adsorbent Trap Sampling Rate) for the required sampling rate if less than 100mL is to be analyzed.
- Use results of the original analysis to determine the approximate dilution factor required and get the largest analyte peak within the initial calibration range.
- The dilution factor must be documented (and included in the final report) and chosen in such a way as to keep the response of the analyte peak for a reported target compound in the upper half of the initial calibration range of the instrument.

Tedlar bag dilution:

- Make a dilution by filling a Tedlar bag with 1.0 liter of humidified zero air using a one-liter gas syringe.
- Calculate the volume of balance gas needed to obtain the required dilution.
- Remove the difference in the balance gas using a syringe.
- Add the calculated sample amount using a gastight syringe.

Direct injection:

- Make a direct injection by attaching a clean, humidified zero air filled canister to the preconcentrator autosampler using 1/4" stainless steel or teflon tubing with a "tee" septum port. This canister should be the same canister that may be used as the method blank.
- Inject the sample through the septum while the preconcentrator withdraws a 200cc aliquot from the canister.

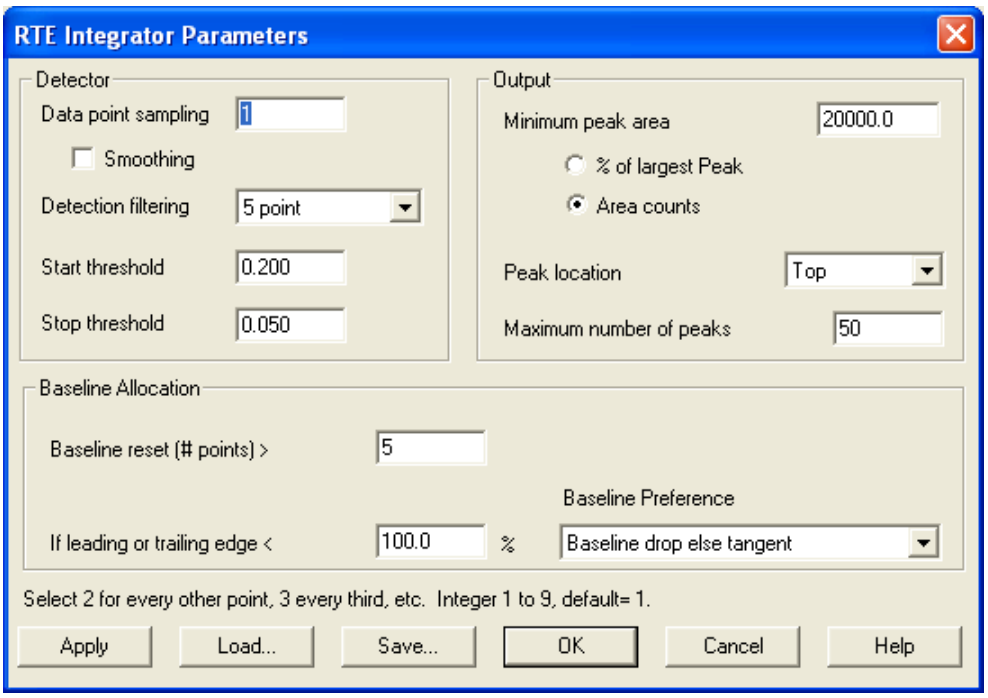
11.11.2 Tentatively Identified Compounds When requested, a mass spectral library search may be made for the purpose of tentatively identifying sample components not associated with the calibration standards. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system mass spectral library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

Certain programs may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. The following guidelines are used for making tentative identifications.

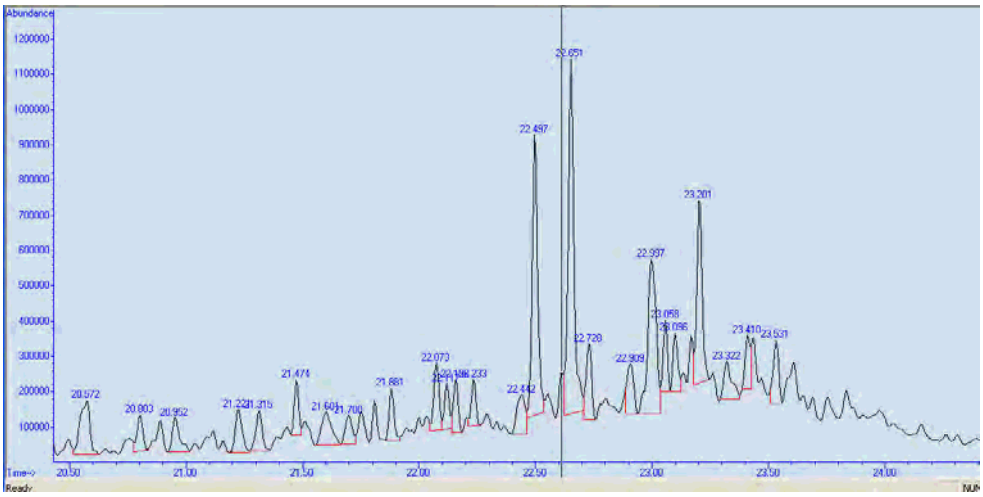
- Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. For example, for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30 and 70%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.
- The concentration of the tentatively identified compound is estimated by assuming a response factor of 1.0 and comparing the response of the tentatively identified compound to the response of the nearest internal standard.
- If non-target analytes are not Q-deleted from the quant report, the analyst must evaluate whether these compounds should be reported as TICS.

Procedure for Reporting Tentatively Identified Compounds (TICs) for samples and associated Method Blanks

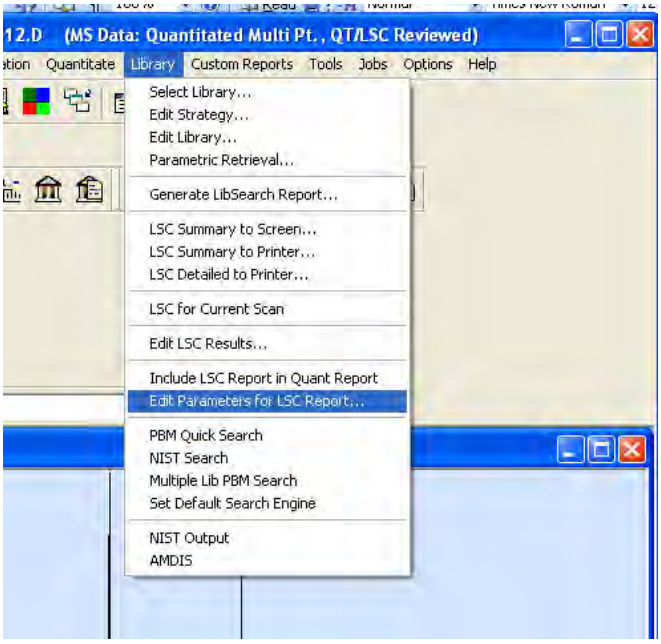
1. Load the datafile in the main Enviroquant window.
2. Load the TIC integration parameters (LSCINT.p). Typical setpoints are as shown below.



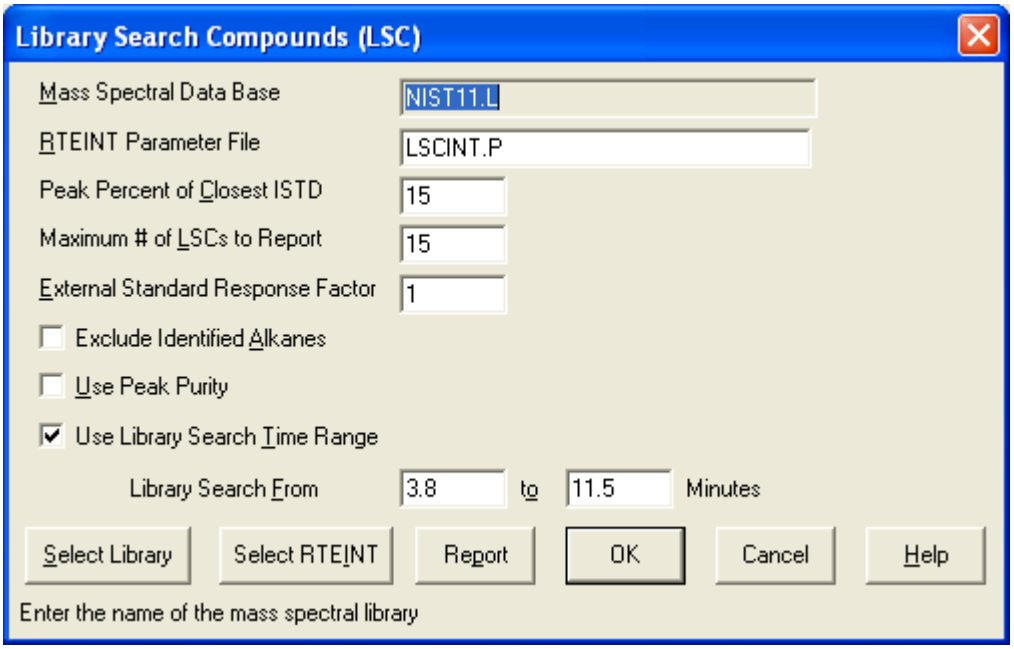
3. Integrate the chromatogram and inspect the peak integrations. Adjust the parameters as needed to achieve integration that will:
   - Resolve closely-eluting peaks that only have a small valley separating them.
   - Not include excess area below the peak in a complex matrix with an elevated baseline.
   - Include peak tailing when necessary.
   - Yield a sufficient number of peaks that will ensure that the internal standards are included.



4. Edit the parameters to be used in generation the library search report:



Select the most current mass spectral library database available, the correct integration parameters file, the area threshold (as a percent of IS area), number of peaks to report, and a time range of the chromatogram to search (set to start after the CO2 peak).



5. Run the LSC routine from the Library menu. You may choose 'LSC Summary to Screen' (Calculate/Generate Report) to get a quick view of the results and then proceed if they seem acceptable. Set the default printer to 'Adobe PDF' and then choose 'LSC Detailed to Printer'.
6. Open the pdf file and inspect the LSC summary (last page). Check the internal standard areas and confirm that they are correct. If any IS area is biased high due to a coeluting peak use the 'Edit LSC Results' routine to switch all associated TICs to use a different IS. If all three IS peaks have coelutions substitute the areas from the daily method blank in the calculations.
7. Use the LSC Summary as a guide and inspect the chromatogram in the data analysis window. Integrate the chromatogram from the Integrate menu and look for peaks that may have been missed by the LSC routine. Possible reasons for missed peaks are excessive tailing (organic acids), RT close to a target compound, coeluting peaks with no valley between them. These will need to be added manually.
8. Use the DOSCAN routine from the Tools menu to search individual missed peaks one by one. This will add them to the LSC list.
9. Go back into the Edit LSC Results routine and make any necessary changes to compound names and/or the internal standard used for quantitation.
10. Run the macro "QT '0,0,C' by clicking the Custom Tool 1 button. This will update the LSC list to the quant.csv file.
11. Run the LSC Detailed to Printer routine from the Library menu (Generate Report *only*). This will print the file to pdf.

12. Excel Reporting
    1. In Excel, open the TIC reporting template (I:\A-GCMS\TICS\System\StarLIMS_TICQ).
    2. Enter the service request number and click ok.
    3. Click the Get Samples button. Select the samples to be reported. Delete any samples that are not to be reported (right click/delete row).
    4. Click the Update PEF button.
    5. Click the Get TICs from CSV button. Enter the date analyzed and select the instrument ID.
    6. Click the Apply to all Samples button. Change the date for any sample that was analyzed on a different date.
    7. Click the Apply Instrument to all Samples button.
    8. Enter file number in column E (i.e. enter 07 for file 12301507.d).
    9. Click the Copy Data button. This copies the TIC info to the report sheets.

11.12 Duplicate

A duplicate must be analyzed to assess laboratory precision and samples selected for duplicate analysis shall be rotated among client samples, where applicable. Some projects or sample matrix issues may require the analysis of a duplicate laboratory control sample (DLCS).

11.13 Internal Standard (IS)

The concentration of internal standard added to each standard, field sample and QC sample must be consistent from that of each current ICAL standard.

11.14 Surrogates

Internal standards/surrogates must be added at the same volume for every standard, sample and QC sample. Surrogate compound recoveries are requested by a number of clients, but are more appropriately used as system monitoring compounds. This is due to the fact that the compounds are introduced directly into the analytical system and not into the canisters or bags. It is for this reason that they are not considered to be true surrogates and a fixed window is applied. Additionally, surrogates are not included in the ICAL because they are not required by the method and are only system monitoring compounds.

11.15 Manual Integration and Q Deletion

A list of abbreviations (codes) that may be used to give a reason for performing either of these procedures are listed in the *SOP for Data Review and Reporting*.

11.15.1 Manual Integration The integration for each peak must be legally defensible and shall be checked to ensure that it has been integrated properly and consistently between samples, standards and QC samples. All peak reviews and manual integrations must follow the requirements specified in the *SOP for Manual Integration* and the *SOP for Laboratory Ethics and Data Integrity.* The requirements in the above stated procedure include when manual integrations are performed, raw data records shall include a complete audit trail for those manipulations (i.e., chromatograms showing both the integration prior to any manual integrations and those depicting the corresponding manually integrated peaks), and notation of rationale, date, and initials of person performing the manual integration operation. In addition, manual integrations must be reviewed and approved by a second reviewer and the manual integrations maintained in the appropriate job file.

Reporting Requirements Certain project requirements including samples which are submitted under the Department of Defense (DoD) QSM require that the case narrative include an identification of samples and analytes for which manual integration is required. Refer to project requirements to determine if this is necessary.

11.15.2 Q Deletion Q deleting may be performed to either delete a false positive or delete non-target compounds.

11.16 Detection Limits and Limits of Detection

The MDL shall be performed in accordance with the procedure outlined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.* The detection limit shall be used to determine the LOD for each analyte.

11.16.1 Performance and Acceptance Criteria

1. The MDL must be <0.5ppbV for each analyte (Method 11.11.1).
2. Following the MDL study perform a Limit of Detection (LOD) verification on all instruments (performing this method). Spike the LOD at 2-4x the MDL; the spike level establishes the LOD.
3. LOD Acceptance
   - Analyte must be detected reliably and identified by the method-specific criteria (i.e, ion confirmation) and produce a signal that is at least 3 times the instrument's noise level (3:1 signal to noise ratio).
   - It is specific to each combination of analyte, matrix, method and instrument configuration.
   - The LOD must be verified quarterly on each instrument (spiked at LOD) using the criteria listed above.
4. If the LOD verification fails (per #3), repeat the detection limit determination and LOD verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.
5. The laboratory shall maintain documentation for all detection limit determinations and LOD verifications (regardless of pass or fail).

11.17 Method Reporting Limit Check Standard

It is recommended to analyze a MRL check standard at the current MRL or required MRL for the batch (per client requirements) of twenty or fewer samples if the CCV fails low for any target compound. A MRL check standard may also be required per client specifications.

This check standard can also serve as the LOQ verification if it meets the specific requirements listed in Section 11.1.4.2. Apply the requirements and retain all documentation accordingly. Refer to Attachment 4 for Minnesota specified MRL check standard criteria.

11.18 Method Modifications

Method modifications are not allowed under TNI standards; therefore, a statement, however worded, must be included in the final report indicating that data reported does not fall under the laboratory's NELAP certificate of approval. In addition, the following items are considered to be method modifications and must be reported accordingly.

- Sample collection in gas collection bags

- The pressurization of canisters with nitrogen or helium (if EPA Method 3C is requested) refer to Section 11.11.

12) Quality Control Requirements and Corrective Action

12.1 To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.2 Corrective actions shall follow the procedures outlined in the *SOP for Nonconformance and Corrective Action*, where appropriate. Any maintenance which may alter instrument sensitivity or linearity must result in the re-analysis of the entire sequence including the tune compound, ICAL or CCV or any batch QC.

12.3 Instrument Performance Check

12.3.1 Acceptance Criteria

Refer to Tables 1 and 1A for the required ion abundance criteria.

12.3.2 Corrective Action Perform auto tune or manual tune and then re-analyze BFB. If the BFB acceptance criteria are still not met, the MS must be retuned according to the procedure outlined in the instrument user's manual. Perform necessary maintenance and make notations in the instrument maintenance logbook. It may be necessary to clean the ion source, or quadrupole, or take other necessary actions to achieve the acceptance criteria. An acceptable tune is required for sample results to be calculated and reported.

12.4 Initial Calibration

12.4.1 Acceptance Criteria Refer to the following acceptance criteria for the initial calibration.

- The RRT for each target compound at each calibration level must be within 0.06RRT units of the mean RRT for the compound.
- The calculated %RSD for the RRF for each compound in the calibration standard must be less than 30% with at most two exceptions up to a limit of 40% (this may not be true for all projects).

  DoD QSM/Navy Requirement: The two exceptions of %RSD up to 40%, allowed by the method, are not allowed.

- For each Internal Standard the area response (Y) at each calibration level must be within 40% of the mean area response $\overline{Y}$ over the initial calibration range.
- The retention time shift for each of the internal standards at each calibration level must be within 20s of the mean retention time over the initial calibration range for each internal standard.

  Navy Requirement: The absolute retention time for each of the internal standard and calibrated analytes must be within ±0.20 minutes (12 seconds) of the mean retention time for the corresponding internal standard or analyte over the initial calibration range.

- All of the following information must be retained to permit reconstruction of the initial instrument calibration: calibration date, test method, instrument, analysis date, analyte identification, analyst's initials, concentration and responses, and response factors.

- All initial instrument calibrations must be verified with an acceptable ICV.

12.4.2 Corrective Action Follow the initial calibration requirements detailed in Section 11.1 for information on re-analyzing or dropping points and the restriction of maintenance performed during the analysis of the initial calibration standards.

If the initial calibration results are outside the established acceptance criteria, corrective actions must be performed and all associated samples reanalyzed, if reanalysis of the samples is not possible, data associated with an unacceptable initial calibration shall be reported as estimated with the appropriate data qualifiers.

12.5 Initial Calibration Verification Standard (ICV)

12.5.1 Acceptance Criteria The percent recovery for each compound in the ICV must be between 70%-130% for all analytes except vinyl acetate, which must be within 50-150%. Exceptions to this allowance for the vinyl acetate recovery are project specific requirements and any DoD type project, which shall adhere to the 70-130% requirement for all target compounds.

12.5.2 Corrective Action If the initial calibration verification technical acceptance criteria are not met, reanalyze and if it fails again, prepare a new canister and analyze. If the criteria are still not met inspect the system for possible sources and perform any necessary maintenance and make a notation in the maintenance logbook of any steps taken. It may be necessary to clean the ion source or change the column. Perform a new initial calibration if any performed maintenance has altered instrument linearity and/or sensitivity. Perform another initial calibration or if reanalysis is not possible, data associated with an unacceptable ICAL/ICV shall be reported as estimated with the appropriate data qualifiers.

12.6 Continuing Calibration Verification (CCV)

12.6.1 Acceptance Criteria All compounds must be evaluated prior to rounding. The percent difference for each target analyte must be within plus or minus 30% of the initial calibration average RRFs.

12.6.2 Corrective Action If the continuing calibration verification technical acceptance criteria are not met, reanalyze and if it fails again, prepare a new canister and analyze. If the criteria are still not met inspect the system for possible sources of the problem and perform any necessary maintenance and make a notation in the maintenance logbook of any steps taken. It may be necessary to clean the ion source or change the column.

If any corrective action and/or reanalysis fails to produce continuing calibration verification within acceptance criteria (analyzed immediately following the initial failure), then either two consecutive successful verifications must be performed following corrective action or a new initial calibration must be performed; however, refer to 16.6.2.1 below.

DOD Requirement: If a CCV fails, the laboratory must immediately analyze two additional consecutive CCVs (The two consecutive CCVs must be analyzed within one hour).

- Both of these CCVs must meet acceptance criteria in order for samples to be reported without reanalysis.

- If either of these two CCVs fail or if the laboratory cannot immediately analyze two CCVs, the associated samples cannot be reported and must be reanalyzed.
- Corrective action(s) and recalibration must occur if the above scenario fails.
- Flagging data for a failed CCV is only appropriate when the affected samples cannot be reanalyzed. The laboratory must notify the client prior to reporting data associated with a failed CCV.

12.6.2.1 Method Reporting Limit Check Standard

If a per batch MRL check standard is analyzed due to a failing CCV or client requirement and is unacceptable for any compound (sensitivity; ratio or %D), reanalyze at the same or higher level within the same batch and report data with the CCV flag and case narrative notes accordingly. Reporting data with these conditions must be acceptable per project and client requirements otherwise corrective action must be initiated and samples reanalyzed.

Refer to Section 11.1.4.2 for annual (NELAP and Navy) and quarterly (DoD) LOQ verification requirements.

12.7 Canister Quality Control Check

The actual cleaning procedure, number of cans to select for analysis (to release a cleaning batch) and corrective actions are covered in the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters* and are not covered in this section. However, the procedure for analyzing and certifying a cleaning batch is included. If a canister passes as a QC canister it meets all of the requirements for a method blank (Method, TNI Standards, and Department of Defense Quality Systems Manual – DoD QSM, etc.).

12.7.1 Scan Analyses A canister is considered "clean" for normal SCAN analyses if the analysis shows <0.2ppbv of any target analyte (analyte exceptions listed in table below). If a canister passes as a QC canister it meets all of the requirements for a method blank (Method, TNI Standards, and Department of Defense Quality Systems Manual - DoD QSM, etc.).

Low Level SCAN Analyses For those analytes with a MRL of 0.1ug/m3, the QC criteria of <MRL is acceptable; otherwise, <0.2ppbV is required (analyte exceptions listed in table below).

SIM Analyses Results <MRL will be acceptable as this complies with the <0.2ppbV method requirement.

DoD QSM Requirement Each canister must be individually certified. A canister is considered clean if no reported analytes are detected at >1/2 the LOQ.

ANALYTE EXCEPTION LIST					
Compounds	ppbV	On Column (ng)	Compounds	ppbV	On Column (ng)
Target Analytes	0.2	0.50	Acrylonitrile	0.2	0.43
Chloromethane	0.2	0.41	Acetone	1.5	3.5
1,3-Butadiene	0.2	0.44	Ethanol	1.9	3.5
Acetonitrile	0.2	0.33	Vinyl acetate	0.99	3.5
Acrolein	0.31	0.70	1-Butanol	0.23	0.70
Isopropanol	0.57	1.4	Carbon Disulfide	0.22	0.70
2-Butanone	0.24	0.70			

Document the status of the check in LIMS and return the canister to the canister conditioning room. Additionally, if the check was found to be acceptable, the quantitation report must be kept on file for future reference

12.7.2 Tentatively Identified Compounds (TIC) If the batch of canisters are to be used for tentatively identified compounds (TIC) analysis, any non-target peaks present in the QC check canister analysis must be evaluated and determined to be less than the TIC reporting limit (10% of the internal standard). The concentration is estimated by assuming a RRF of 1.0 and comparing the response of the TIC to the response of the nearest internal standard.

12.8 Method Blank

12.8.1 Acceptance Criteria

- The concentration of a targeted analyte in the blank cannot be at or above the MRL, AND be greater than 1/10 of the amount measured in any associated sample. For any project that requires reported results less than the MRL, all associated measurements found in the MB should result in a qualifier; however, project requirements may differ and must be followed. Refer to DoD requirements listed below.
- The method blank should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.
- For DoD samples, the method blank will be considered to be contaminated if:

  1. The concentration of any target analyte in the blank exceeds 1/2 the reporting limit or is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);
  2. The concentration of any common laboratory contaminant (acetone, ethanol, carbon disulfide, and methylene chloride) in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
  3. The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

The laboratory shall evaluate whether reprocessing of the samples is necessary based on the above criteria.

12.8.2 Corrective Action If the analyte concentration results in the blank do not meet the acceptance criteria repeat analysis with remaining QC canisters until results are acceptable or prepare a canister per Section 11.9. If the analyte results in the

blank still do not meet the acceptance criteria the source of the problem must be investigated and measures taken to eliminate the source. Each method blank must be critically evaluated as to the nature of the interference and the effect on the analysis of each sample within the batch. Determine whether the contamination is from the instrument or due to contamination in the blank container (if results from the new can are not acceptable then the system is probably contaminated). In all cases, the corrective action (reprocessing or data qualifying codes) must be documented. However, the specific corrective action depends on the type of project the blank is utilized for; therefore, refer (below) to the reporting/reprocessing requirements.

DEPARTMENT OF DEFENSE (DoD) QSM PROJECT: Any sample associated with a blank that fails the criteria shall be reprocessed in the same or subsequent analytical batch, except when the sample analysis resulted in a non-detect. If reanalysis is not performed, the results shall be reported with appropriate data qualifier.

OTHER PROJECT TYPE: Appropriate corrective measures must be taken and documented before sample analysis proceeds. However, if this is not a possibility and the results must be reported follow the reporting requirements stated in Section 16.4.

12.9 Laboratory Control Sample (LCS)

12.9.1 Acceptance Criteria Round all results to the nearest whole number prior to determining if the acceptance criteria have been met. The percent recoveries must be within the laboratory-generated limits and are referenced in the electronic TO-15 Method Manual. However, Arizona requires the percent recovery for each compound in the LCS to be 70%-130% (to match the ICV requirement). Therefore, the ICV exception for vinyl acetate stated in Section 12.5 requires the percent recovery for AZ samples to be 50-150%.

Note: Client project requirements and DoD requirements shall take precedence over the AZ requirement for AZ samples. Meaning if a sample is collected for a DoD project in AZ, DoD requirements specified in this document and the project specific QAPP (if supplied) are to be followed.

DoD Requirement: In the absence of client specified LCS reporting criteria, the LCS control limits outlined in the DoD QSM Appendix C tables shall be used when reporting data for DoD projects.

12.9.2 Corrective Action If the LCS criteria are not met, determine whether the cause is instrumentation or the result of a poor injection. If the problem is instrumentation, perform maintenance and if the problem is with the injection re-analyze the LCS. DoD considers the same analyte exceeding the LCS control limits two out of three consecutive LCS to be indicative of non-random behavior; therefore, this trend should be monitored and the appropriate corrective action taken when it occurs.

12.10 Sample Results

12.10.1 Acceptance Criteria

- Sample results must be quantitated from the initial instrument calibration and may not be quantitated from any continuing instrument calibration verification.

- The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, initial calibration verification technical acceptance criteria described in this document.
- All target analyte peaks must be within the initial calibration range, diluted or reported with the appropriate data qualifier.

12.10.2 Corrective Action

- If the retention time for any internal standard within the sample changes by more than 20 sec from the latest daily calibration or initial calibration mid-point standard, the GC/MS system must be inspected for malfunctions, and maintenance performed as required. Repeat sample analysis as needed.

  Navy Requirement: The absolute retention time for each of the internal standard and calibration analytes must be within ±0.20 minutes (12 seconds) of the mean retention time for the corresponding internal standard or analyte over the initial calibration range.

- If the area for any internal standard changes by more than ±40 percent between the sample and the most recent calibration, check for possible matrix interferences and re-analyze at a greater dilution. If the requirement is still not met and matrix interference is not detected the GC/MS system must be inspected for malfunction and maintenance made where necessary.
- When corrective actions are made, samples analyzed while the instrument was not functioning properly must be re-analyzed or the appropriate data qualifiers must be attached to the results.

  To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.11 Laboratory Duplicate

12.11.1 Acceptance Criteria The relative percent difference must fall within ±25%. This RPD criterion also applies to duplicate laboratory control samples (DLCS).

12.11.2 Corrective Action If the duplicate results do not meet the technical acceptance criteria, perform another duplicate analysis. If the results are still unacceptable and the associated samples are not reanalyzed then all of the sample results in the associated batch must be flagged accordingly.

12.12 Internal Standards

12.12.1 Acceptance Criteria The following acceptance criteria must be applied to each run (except the ICAL – see Section 12.4).

- The area response for each internal standard in the blank must be within ±40 percent of the area response for each internal standard in the most recent valid calibration. (CCV or mid-point from the initial calibration, whichever is most current).
- The retention time for each internal standard must be within ±0.33 minutes of the retention time for each internal standard in the most recent valid calibration. (CCV or mid-point from the initial calibration, whichever is most current).

Navy Requirement: The absolute retention time for each of the internal standard and calibration analytes must be within ±0.20 minutes (12 seconds) of the mean retention time for the corresponding internal standard or analyte over the initial calibration range.

12.12.2 Corrective Action

- Internal Standard Responses If the problem is with the instrument, perform maintenance. If the problem is with a sample, check for interferences. If the response is high, it is likely that interference is present. In this case, lower the volume or aliquot of the sample and re-analyze. If the problem persists, report the results with the best quality and qualify the results. If the problem is corrected with the lower volume analysis, report those results.
- Internal Standard Retention Times If the retention time for any internal standard within the sample changes by more than 20 sec from the latest daily calibration or initial calibration mid-point standard, the GC/MS system must be inspected for malfunctions, and maintenance performed as required. Repeat sample analysis where required.

12.13 Surrogates

12.13.1 Acceptance Criteria Since the matrix precludes the use of true surrogates and there is no established method criterion, acceptable surrogate recoveries are based on a fixed window of 70 - 130%. This is the typical requirement from clients. Additionally, these limits are referenced in SW-846 for use as guidance in evaluating recoveries. These limits are sufficient for evaluating the effect indicated for the individual sample results.

12.13.2 Corrective Action Poor surrogate recovery should be followed by re-analyzing a smaller aliquot to mitigate any matrix interferences. Evaluate the out of control surrogate for the effect on individual sample results.

12.14 Method Reporting Limit Check Standard

12.14.1 Acceptance Criteria Per client requirements or if the CCV is biased low for any compound, then evaluate the MRL check standard. Analyte must be detected reliably and identified by the method-specific criteria (i.e, ion confirmation) and produce a signal that is at least 3 times the instrument's noise level (3:1 signal to noise ratio). A percent difference +/-50% is recommended but program and client specific requirements must be followed if applicable.

12.15 Sample Holding Time Expired

The customer is to be notified that the sample's holding time was missed and the customer is to decide if the sample analysis is to continue. The documentation of missed holding time and the client's decision to proceed must be included in the corresponding job file. A statement dictating all holding time occurrences must accompany the sample results in the final report.

13) Data Reduction and Reporting

13.1 This method has specific requirements including the use of canisters; any modification must be reported accordingly. All reports that fall under the laboratory's certificate of approval (in accordance with TNI standards) must include a statement(s) clarifying any

deviations from the scope of this certification. Refer to Section 13.10 for additional information and specific items, which require this clarification.

13.2 Initial Calibration

Tabulate each of the following:

13.2.1 Equation Number 1 - **Relative Response Factor (RRF):**

$$RRF = \frac{A_x C_{is}}{A_{is} C_x}$$ where:

A_x is the area response of the analyte quantitation ion.
A_{is} is the area response of the corresponding internal standard quantitation ion.
C_{is} Internal standard concentration, ng.
C_x Analyte concentration, ng.

Note: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC samples is the same from run to run.

13.2.2 Equation Number 2 - **Average (or Mean) RRF:**

$$\overline{RRF} = \frac{\sum_{i=1}^{N} RRF_i}{N}$$ where:

RRF_i are the individual RRFs from each concentration level in the initial calibration curve.

N is the number of calibration concentration levels.

13.2.3 Equation Number 3 - **Standard Deviation, SD:**

$$SD = \sqrt{\sum_{i=1}^{N} \frac{\left(RRF_i - \overline{RRF}\right)^2}{N-1}}$$ where:

RRF_i are the individual RRFs from each concentration level in the initial calibration curve.
$\overline{RRF}$ Average (or Mean) RRF of all concentration levels in the initial calibration curve.
N total number of calibration concentration levels

13.2.4 Equation Number 4 - **Percent Relative Standard Deviation, %RSD:**

$$\%RSD = \frac{SD}{\overline{RRF}}(100)$$ where:

SD Standard Deviation calculated in equation number 3
$\overline{RRF}$ Average or Mean RRF

13.2.5 Equation Number 5 - **Relative Retention Time (RRT):**

$$RRT = \frac{RT_C}{RT_{is}}$$ where:

RT_C Retention time of the target compound, seconds.
RT_{is} Retention time of the internal standard, seconds.

13.2.6 Equation Number 6 - **Mean Relative Retention Time ($\overline{RRT}$):**

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT_i}{n}$$ where:

$\overline{RRT}$ Mean relative retention time (seconds) for the target compound for all initial calibration levels.
RRT_i Relative retention time for the target compound in level i.
n Number of calibration levels

13.2.7 Equation Number 7 - **Mean Area Response ($\overline{Y}$):**

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$ where:

Y_i Area response for the primary quantitation ion for the internal standard for each initial calibration standard.
n number of calibration concentration levels

13.2.8 Equation Number 8 - **Mean Retention Times ($\overline{RT}$):**

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$ where:

$\overline{RT}$ Mean retention time, seconds
RT_i Retention time for the internal standard for each initial calibration standard, seconds.
n number of initial calibration levels

13.3 Continuing Calibration Verification

- Calculate the (RRF) of each target compound using equation number 1.

13.3.1 Equation Number 9 - **Percent Difference, %D:**

$$\%D = \frac{RRFx - \overline{RRF}}{\overline{RRF}}(100)$$ where, for any given analyte:

RRF_x is the RRF from the CCV being evaluated.
$\overline{RRF}$ is the mean RRF from the current calibration curve.

13.4 Percent Recovery – ICV, LCS, Surrogates, MRL Check Standard

13.4.1 Equation Number 10 - **Percent Recovery (%R):**

%R = X/TV x 100

where
X = Concentration of the analyte recovered
TV = True value of amount spiked

13.5 Duplicate Analysis

13.5.1 Equation Number 11 - **Relative Percent Difference (RPD):**

$$\frac{x_1 - x_2}{\bar{x}}(100)$$ where:

x_1 First measurement value
x_2 Second measurement value
$\bar{x}$ Average of the two values

13.6 Internal Standards (IS)

- Calculate the mean area response $\overline{Y}$ for each internal standard using equation number 7.
- Calculate the mean of the retention times for each internal standard using equation number 8.

13.7 Pressure Dilution Factor (PDF)

13.7.1 Equation Number 12 - **PDF**, for samples collected in canisters:

$$PDF = \frac{P_{atm} + P_f}{P_{atm} + P_i}$$ where:

P_{atm} is the ambient atmospheric pressure, 14.7 psi at sea level.
P_f is the final sample canister pressure, in psig.
P_i is the initial sample canister pressure, in psig. This will most often be a negative value (sub-ambient initial pressure).

13.8 Results

If a canister has been pressurized with Helium and the Tekmar AutoCan was utilized, refer to Section 11.11.

13.8.1 Equation Number 13 - For calculating analyte concentrations in a sample, the starting point is the nanogram amount generated by the HP Enviroquant software, which appears on the quantitation report.

$$ng_x = \frac{A_x ng_{is}}{A_{is}\,\overline{RRF}}$$ where:

ng_x is the nanogram amount of analyte *x*.
A_x is the area response of the analyte's quantitation ion.
A_{is} is the area response of the corresponding internal standard's quantitation ion.
ng_{is} is the internal standard amount, in nanograms.
$\overline{RRF}$ is the average or mean RRFs

13.8.2 Equation Number 14 - The final analyte concentration, C_x, in units of micrograms per cubic meter (µg/m³), is then calculated from the following:

$$C_x = \left(\frac{ng_x PDF}{V}\right)\left(\frac{1\mu g}{1000 ng}\right)\left(\frac{1000 l}{1 m^3}\right)$$ where:

V is the sample volume analyzed, in liters.
PDF is the sample canister pressure dilution factor.

13.8.3 Equation Number 15 - To convert to units of parts per billion volume (ppbv):

$$ppbv = \frac{\mu g / m^3}{MW} x 24.46 \qquad \mu g / m^3 = \frac{ppbv}{24.46} x MW$$ where:

MW is the molecular weight (Table 2) of the analyte, in g/mole.
24.46 is the molar volume of an ideal gas at 298 K (25 °C) and 760 mmHg (1 atm), in liters per mole (l/mol).
C_x the final analyte concentration in micrograms per cubic meter.

13.8.4 Equation Number 16 – Helium Pressurization (Injection Amount)

Applicable to canisters pressurized with helium and injected utilizing the mass flow controller of the AutoCAN. For full instructions and calculations, refer to the 1st tab of the template located at: J:\A-GCMS\Helium Pressurization\System\HE Pressurization Template.

13.9 Data Review

The analyst must review data on a real time basis for all calibration and QC data. The QC data must be evaluated by analytical sequence following the Daily QC review checklist (Attachment 3). The data shall be reviewed and the sample results calculated and assessed by one analyst and reviewed by a second qualified analyst. The Sample Review checklist (Attachment 3) is used to document sample review per service request and once completed, initialed and dated must be filed with each job file.

Initial calibrations must be reviewed in the same manner as QC data with all ICAL documentation retained in a separate file organized by instrument and date. Refer to the initial calibration checklist in Attachment 2 for the review guideline. The ICAL file must contain all the pertinent information stated in Section 11.1.6.

13.10 Reporting

The results of each test shall be reported clearly, unambiguously and objectively, and shall include all the information necessary for the interpretation of the test results and information required by this laboratory's policy, TNI standards, DoD Manual (applicable version, see reference section), client projects, and the TO-15 method including modifications, observances, data qualifiers, and certification information.

If the project requires that results be reported below the MRL (LOQ), but above the LOD all of the requirements specified for normal reporting apply (3:1 S/N ratio and ion abundance). This is regardless of the fact that the results will be qualified as estimated.

13.10.1 Analysis Observations / Case Narrative Summary Form

This form, which is included in the *SOP for Laboratory Storage, Analysis and Tracking*, may be generated when there are specific sample composition information or analysis issues and/or observations. In addition, during the analysis, specific identification information or problems, interferences, calibration issues, flags, and additional/expanded explanation of flags should be added to the form. This form may be modified as long as the sections and basic concepts are reserved. All data qualifiers and flags should follow those listed in the most recent Quality Assurance Manual or as defined in any client requirements.

This form may be used as a means for documentation. This form, among other information, will be reviewed when compiling the final report and case narrative. Alternatively, information may be included on the Daily QC and Sample Review Checklists (Attachment 3). All information regarding the job shall remain in the file, in order that sufficient documentation is available to recreate the job from sample receipt through analysis, data reduction, and reporting.

13.10.2 NELAP\TNI Requirements

The following items do not comply with TNI standard requirements and must be reported accordingly. A statement, however worded, must be included in the final report indicating that data reported does not fall under the laboratory's NELAP certificate of approval.

- Reporting any compound which is not included in the second source standard (ICV or LCS) does not meet NELAP requirements.
- In addition, a report that contains a compound not included on the NELAP certificate of approval must also include the statement listed above.

13.10.2.1 Modifications

Method modifications are also not allowed under TNI standards; therefore, a statement, however worded, must be included in the final report indicating that data reported does not fall under the laboratory's NELAP certificate of approval. In addition, the following items are considered to be method modifications and must be reported accordingly.

- Sample collection in gas collection bags
- The pressurization of canisters with nitrogen or helium (if EPA Method 3C is requested) refer to Section 11.11.

13.10.3 Surrogates

Only report surrogates at the request of the client. If any surrogate is out of control, all samples results (with surrogates requested) associated with the surrogate must be reported with the appropriate data qualifier.

13.10.4 DoD Requirements

Report results with the appropriate data qualifiers, if samples cannot be reanalyzed for any reason. In addition and at a minimum, the following situations are to be noted in the case narrative: manual integrations, CCV out of control, and results exceeding the calibration range.

13.11 Storing Electronic Data

The initial calibration data must be stored in a quantitation method (on the server) using a unique filename and may not be overwritten at any time in order to maintain an accurate audit trail. There are multiple quantitation methods, which are subsets of the compound list in Table 2. Therefore, files will be named with a notation indicating the compound list and the date of the corresponding initial calibration. In addition, all data files including method blanks, continuing calibration verification, laboratory control samples and client submitted samples files are saved in a unique sub-directory on the server.

13.12 Sufficient raw data records must be retained on file of all laboratory analyses described in this document including passing QC canister checks, tune checks, instrument calibrations, verifications, sample analyses and dilutions, QC checks, and method detection limit studies. The information that is required includes: analysis/calibration date and time, test method, instrument, sample identification, analyte identification, analyst's initials, concentrations and responses, as well as standards used for the analysis and calibrations, all manual calculations including sample dilutions and manual integrations to permit reconstruction of analyses. Information entered and reported on the quantitation report and instrument run log must be complete and accurate. All data shall be obtained following defensible and ethical practices in accordance with the most recent Quality Assurance Manual and the *SOP for Laboratory Ethics and Data Integrity*.

Note: All data records must explicitly connect data to the initial instrument calibration. This includes all samples, continuing calibrations and QC samples.

13.13 The essential information to be associated with analysis, such as computer data files, run logs, etc. shall include: Sample ID code, date and time (if the holding time is 72 hours) of analysis, instrument operating conditions/parameters (or reference to such data), analysis type, all manual calculations including dilutions and manual integrations, analyst's initials, sample preparation (pressure readings and balance gas if pressurized with helium), standard and reagent origin, receipt, preparation, and use, as well as

calibration criteria, frequency and acceptance criteria, data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions.

14) Method Performance

14.1 An on-going assessment of method performance is conducted in order to ensure that the laboratory is capable of reporting results which are acceptable for its intended use. Validation of the method is confirmed by the examination and provision of objective evidence that these requirements are met.

14.2 Method Detection Limit (MDL)

The procedure used to determine the method detection limits are as stated in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as defined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation*. The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is distinguishable from method blank results. The MDL concentrations are listed in Tables 2 and 2A for both SCAN and SIM modes and were obtained using spiked canisters prepared with humidified zero air, making at least seven replicate measurements of the compounds of interest, computing the standard deviation, and multiplying this value by the appropriate Student's t value for 99 percent confidence. Additionally, at least seven method blank results were processed according to the procedure described in this document. Refer to the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* for the method blank MDL calculation and additional requirements for establishing the MDL. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. All MDLs, regardless of the mode of operation, meet the method performance criteria of <0.5ppbV.

14.3 Accuracy and Precision

Refer to Section 11.4 in the referenced method for information on replicate precision criteria for method performance. Single laboratory accuracy is presented as the second source initial calibration verification standard, which meets the method performance criteria of 30%. Additionally, laboratory generated control limit data for LCSs are presented for the analytes of interest and may be referenced in the electronic TO-15 Method Manual. Refer to Section 11.1.4.2 for the accuracy and precision requirements for concentrations at the LOQ/MRL.

14.4 Selectivity

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification.

It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak must be acquired. Scanning also allows identification of unknown compounds in the sample by searching through library spectra.

The sample analysis using the GC/MS is based in part on a combination of retention times and relative abundances of selected ions. The retention time of each chromatographic peak should be ±0.10 minutes of the library/reference retention time of the compound. The acceptance level for relative abundance should be set at ±20% of the expected abundance. The data should be manually examined by the analyst to determine the reason for the # flag [(#) = qualifier out of range], if present and whether the compound should be reported as found or if there is matrix interference. A background subtraction may aid in this determination. Manual inspection of the qualitative results should also be performed to verify concentrations outside the expected range.

Specific selectivity information is provided in this section and document (such as relative retention time) as well as in the referenced method. Refer to the method for additional information on selectivity.

- Use NIST Library 2011 or newer version
- The *reference spectra updates* must be performed with every new ICAL utilizing the mid-level standard (minimum). If needed, the reference spectra may be updated sooner with the continuing calibration standard.
- *Retention time updates* must be performed using EasyID and not by updating to the method (InitCal \ Update Calibration). Refer to the Help selection of the software.

14.5 Demonstration of Capability

This laboratory has continuously performed this method since before July 1999. Therefore, ongoing demonstration of capable shall be performed and documented; however, the initial demonstration of method capability is not required.

14.6 Proficiency Testing (PT) Program

The laboratory shall participate in an air and emissions PT study for TO-15. The testing shall be performed in accordance with this document and meet the frequency and proficiency requirements detailed in the DoD QSM.

Proficiency testing samples including all accredited compounds are not available. Therefore, in addition to third party PT samples, intra laboratory comparisons must be performed biannually to meet the DoD QSM proficiency testing requirements. Eight QC analyses from various analysts and instruments shall be compiled and statistical validity evaluated using a Z-score.

15) Pollution Prevention and Waste Management

15.1 All waste disposals shall be carried out in accordance with the requirements detailed in the *Simi Valley Lab Waste Management Plan.* In addition, canisters must be cleaned in accordance with the requirements detailed in the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Containers.*

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 The following is specific information on how to report unacceptable data. If the data requires a data qualifier flag, as specified in this SOP, refer to Appendix D of the most recent version of the Quality Assurance Manual for the appropriate data qualifier.

16.2 Initial Calibration and/or Initial Calibration Verification

All results reported with an unacceptable ICAL must be reported as estimated and all data shall be reported using defined qualifiers or flags or explained in the case narrative

accordingly.

16.3 Continuing Calibration Verification

All results associated with an unacceptable CCV must be reported with the appropriate data qualifier or flag and explained in the case narrative.

1. When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported with a qualifier or flag and explained in the case narrative. The case narrative may include information stating the data quality is not affected.
2. When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples with detects, then those detects must be reported with a qualifier or flag and explained in the case narrative.
3. If however, the acceptance criteria for the continuing calibration verification are exceeded low, i.e., low bias, and there are associated samples that are non-detects, then those non-detects must be reported with qualifiers or flags and explained in the case narrative as having less certainty. However, along with the data qualifiers, the case narrative may include information stating the fact that the results were not significantly affected if:
   a. *An MRL check standard was analyzed and found to be acceptable. The MRL must be the same as that analyzed in the MRL check standard for those analytes that were biased low in the CCV. Adjust MRLs (if required), flag data and state the certainty in the case narrative where the sensitivity of the instrument was demonstrated at the MRL; therefore, results were not significantly affected.*
   b. *With the reporting limit adjusted to the next level in the calibration curve (typically 5 times higher) to prove the nonexistence of a false negative and note procedure in case narrative.*
4. If the acceptance criteria was exceeded (biased high) for the CCV and there were detectable results in a sample, the results may be "qualified" if the results exceeded the regulatory/decision limit (this is to be stated in the case narrative along with the data qualifiers or flags).
5. Data associated with a biased low CCV may be fully useable if the results reported exceed a maximum regulatory limit/decision level.

16.4 Method Blank

- If an analyte in the blank is found to be out of control and the analyte is also found in associated samples, those sample results shall be "flagged" in the report and the method blank results reported.
- If the analyte is found in the blank but not in the sample then the results for the sample may be reported without a qualifier.

16.5 Laboratory Control Sample

All results associated with an out of control laboratory control sample must be reported with the appropriate data qualifier. An indication of whether the LCS was out high or low should also be included.

16.6 Surrogate

Report sample results with the appropriate data qualifier.

16.7 Laboratory Duplicate

All batch sample results associated with an out of control laboratory duplicate must be flagged with the appropriate data qualifier.

16.8 Internal Standard

All target analytes associated with an out of control internal standard must be flagged with the appropriate data qualifier.

16.9 Estimated Sample Results

16.9.1 Sample Hold Time All occurrences of missed holding times must be included on the final report including those samples received and/or analyzed outside of the specified hold times detailed in this SOP.

16.9.2 Matrix Interference Sample data associated with matrix interference must be flagged with the appropriate data qualifier.

16.9.3 Results Outside Initial Calibration Range All sample results not bracketed by initial calibration standards (within calibration range) must be reported as having less certainty by reporting with the appropriate data qualifier.

17) Training

17.1 Demonstration of Capability

All analysts must be trained in accordance with the guidelines detailed in the *SOP for Training Policy*. Demonstrations shall also be performed in accordance with the TNI Standards and DoD Quality Systems Manual. Attachment 1 shall be used to document the training plan for new analysts' initial demonstration. Additionally, these demonstrations are performed anytime there is a change in instrument type, personnel or method.

Once performance is found to be acceptable, a required certification statement must be completed by the QA Manager and either the immediate supervisor or Laboratory Manager and retained on file as a demonstration of compliance.

17.1.1 Quarterly Demonstration A demonstration of method sensitivity must be performed *quarterly on each instrument* performing this method.

1) A spike at the current LOD must be analyzed.

2) Verification of precision and bias at the LOQ must be performed.

Refer to Section 11.1.4.2 (LOQ) and 11.16.1 (LOD) for additional information on how these demonstrations are to be performed as well as the acceptance criteria.

17.1.2 Annual Demonstration Each analyst must perform a demonstration of capability initially and annually. For the initial demonstration analyze four LCS standards at 1-4x the MRL (LOQ) either concurrently or over a period of days as a verification of precision and bias of the quantitation range. The standard deviation (n-1) and average percent recovery of the four replicates are compared against the method requirement for precision (±25%) and current laboratory control limits for bias/LCS.

17.1.3 Change in Personnel, Instruments, Method and/or Matrix The requirements in Sections 17.1.1 and 17.1.2 must be performed per the schedule noted and when there is a change in personnel, instruments, method or matrix. "Change" refers to any change in personnel, instrument, test method, or sample matrix that

potentially affects the precision and bias, sensitivity, or selectivity of the output (e.g., a change in the detector, column type, matrix, or other components of the sample analytical system, or a method revision).

All completed attempts at this demonstration must be turned into the QA department for retention.

18) Summary of Changes

Table 18.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
26.0	10/26/2019	C. Arend	Applied updated SOP formatting style to first page
			5.1 – 2nd paragraph – updated SOP title
			6.1 – added 3rd sentence
			7.3 – removed 14 day hold time for Region 9 samples collected in canisters
			8.10 – updated first and second bullet
			9.2.2.1 – updated section to reflect new Entech Precision Diluter
			11.1 - #9 updated to align with 2016 TNI Standard; #13 6th bullet revised to align with 2016 TNI Standard, 8th bullet revised "0.4ng point" to "0.5ng point"
			11.1.4.2 - #2 changed "at 1-2X the claimed LOQ" to "at the claimed LOQ" to align with 2016 TNI Standard; #8 – new
			11.9.1 – 1st paragraph – updated SOP title
			11.15.1 – updated 1st SOP title
			12.7.1 – updated table based on current MRLs
			15.1 – updated reference to first document. Updated SOP title.
			16.3 – updated first paragraph and #1 to align with 2016 TNI Standard; #2 and #3 – minor wording revision to better align with current procedure
			19.3 - updated
			19.7 - updated
			Tables 2, 3, 3A, 4, 4A – updated values
			Attachment 1 - #4 3rd SOP title updated
			Attachment 4 – removed EPA Region 9 hold time requirement

19) References and Related Documents

19.1 EPA Method TO-14A, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA/625/R-96/010b, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1997.

19.2 EPA Method TO-15, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA/625/R-96/010b, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1997.

19.3 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, January 1999.

19.4 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Addendum, January 17, 2002.

19.5 TNI Standard 2009 and 2016, Volume 1, *Management and Technical Requirements for Laboratories Performing Environmental Analysis.*

19.6 *Preparation of Gas Phase Standards for Ambient Air Analysis,* Tekmar-DOHRMANN Application Note, Spring 96, Vol. 6.5.

19.7 DoD/DoE QSM, *Department of Defense (DoD), Department of Energy (DoE) Quality Systems Manual (QSM) for Environmental Laboratories*, Current Version.

19.8 Arizona Administrative Code, Title 9. Health Services, Chapter 14. Department of Health Services Laboratories, October 1, 2016.

19.9 Florida Department of Environmental Protection, Chapter 62-160.

19.10 Minnesota Department of Health, 4740.2065, *Standard Operating Procedures*, Statutory Authority: MS s 144.97; 144.98; History: 31 SR 446, Posted: October 09, 2006, Revised April 16, 2010.

20) Attachments

20.1 Tables

Table 1: Instrument Tune Check Ion Abundance Criteria (TO-15)

Table 1A: Instrument Tune Check Ion Abundance Criteria (TO-14A)

Table 2: Volatile Organic Compounds, EPA Compendium Method TO-15 (SCAN)

Table 2A: Volatile Organic Compounds, EPA Compendium Method TO-15 (SIM)

Table 3: Standard Concentrations (SCAN) (Primary Sources)

Table 3A: Standard Concentrations (SIM) (Primary Sources)

Table 4: Standard Concentrations (SCAN) (Secondary Sources)

Table 4A: Standard Concentrations (SIM) (Secondary Sources)

20.2 Attachments

Attachment 1 – Training Plan

Attachment 2 – Initial Calibration Checklist

Attachment 3 – Daily QC and Sample Review Checklists

Attachment 4 – State and Project Specific Requirements

Attachment 5 – Tekmar AutoCan Trap Packing Instructions

TABLE 1

Required BFB Key Ions and
Ion Abundance Criteria for Method TO-15

Mass	Ion Abundance Criteria[1]
50	8.0 to 40.0 percent of m/e 95
75	30.0 to 66.0 percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/e 95
173	Less than 2.0 Percent of m/e 174
174	50.0 to 120.0 Percent of m/e 95
175	4.0 to 9.0 Percent of m/e 174
176	93.0 to 101.0 Percent of m/e 174
177	5.0 to 9.0 Percent of m/e 176

[1] All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 1A

Required BFB Key Ions and
Ion Abundance Criteria for Method TO-14A

Mass	Ion Abundance Criteria
50	15 to 40 percent of m/e 95
75	30 to 60 percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5 to 9 Percent of m/e 95
173	Less than 2 Percent of m/e 174
174	>50 Percent of m/e 95
175	5 to 9 Percent of m/e 174
176	>95 and <101 Percent of m/e 174
177	5 to 9 Percent of m/e 176

Note: The criteria listed in Tables 1 and 1A shall be met or exceeded in order for EPA Compendium Methods TO-15 or TO-14A to be referenced.

TABLE 2 - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	**CAS Number**	**Molecular Weight**	**Density**	**Primary Ion[2]**	**Secondary Ion(s)[2]**	**MRL[3] (µg/m³)**	**MDL[3] (µg/m³)**	**IS[4]**
Bromochloromethane (IS1)	74-97-5	-	-	130	128, 132	-	-	-
Propene	115-07-1	42.08	NA	42	39,41	0.53	0.13	IS1
Dichlorodifluoromethane (CFC 12)	75-71-8	120.9	1.329	85	87, 101, 103	0.53	0.087	IS1
Chloromethane	74-87-3	50.49	0.911	50	52	0.53	0.086	IS1
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	76-14-2	170.9	1.455	135	137	0.53	0.084	IS1
Vinyl Chloride	75-01-4	62.50	0.9106	62	64	0.54	0.057	IS1
1,3-Butadiene	106-99-0	54.09	0.6149	54	39, 53	0.53	0.088	IS1
Bromomethane	74-83-9	94.94	1.6755	94	96	0.54	0.074	IS1
Chloroethane	75-00-3	64.52	0.8902	64	66	0.54	0.066	IS1
Ethanol	64-17-5	46.07	0.7893	45	46	5.2	0.37	IS1
Acetonitrile	75-05-8	41.05	0.7857	41	40	0.53	0.13	IS1
Acrolein	107-02-8	56.06	0.840	56	55	1.0	0.15	IS1
Acetone	67-64-1	58.08	0.7845	58	43	5.3	1.2	IS1
Trichlorofluoromethane	75-69-4	137.4	NA	101	103	0.53	0.081	IS1
Isopropyl Alcohol	67-63-0	60.10	0.7809	45	43	2.1	0.22	IS1
Acrylonitrile	107-13-1	53.06	0.8060	53	52	0.53	0.11	IS1
1,1-Dichloroethene	75-35-4	96.94	1.213	96	61	0.54	0.074	IS1
tert-Butanol	75-65-0	74.12	0.7887	59	57,41,43	1.1	0.16	IS1
Methylene Chloride	75-09-2	84.94	1.3266	84	49	0.53	0.15	IS1
Allyl Chloride	107-05-1	76.53	0.9376	41	76	0.54	0.072	IS1
Trichlorotrifluoroethane	76-13-1	187.38	1.5635	151	101	0.54	0.076	IS1

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	**CAS Number**	**Molecular Weight**	**Density**	**Primary Ion[2]**	**Secondary Ion(s)[2]**	**MRL[3] (µg/m³)**	**MDL[3] (µg/m³)**	**IS[4]**
Carbon Disulfide	75-15-0	76.14	1.2632	76	78	1.1	0.16	IS1
trans-1,2-Dichloroethene	156-60-5	96.94	1.2565	61	96	0.54	0.074	IS1
1,1-Dichloroethane	75-34-3	98.96	1.1757	63	65	0.55	0.078	IS1
Methyl tert-Butyl Ether	1634-04-4	88.15	0.7402	73	57	0.54	0.063	IS1
Vinyl Acetate	108-05-4	86.09	0.9317	86	43	5.4	1.2	IS1
2-Butanone (MEK)	78-93-3	72.11	0.7999	72	43	1.1	0.11	IS1
cis-1,2-Dichloroethene	156-59-2	96.94	1.2837	61	96	0.53	0.075	IS1
Diisopropyl Ether	108-20-3	102.18	0.7241	87	45,59,43	0.54	0.070	IS1
Ethyl Acetate	141-78-6	88.106	0.9003	61	70	1.1	0.28	IS1
n-Hexane	110-54-3	86.18	0.6548	57	86	0.54	0.11	IS1
Chloroform	67-66-3	119.4	1.4832	83	85	0.54	0.071	IS1
1,2-Dichloroethane-d4(S)	17060-07-0	-	-	65	67	-	-	IS1
Tetrahydrofuran	109-99-9	72.11	0.8892	72	71,42	0.55	0.067	IS1
Ethyl tert-Butyl Ether	637-92-3	102.176	0.7519	87	59,57	0.54	0.064	IS1
1,2-Dichloroethane	107-06-2	98.96	1.2351	62	64	0.54	0.059	IS1
1,4-Difluorobenzene(IS2)	540-36-3	-	-	114	88	-	-	-
1,1,1-Trichloroethane	71-55-6	133.4	1.3390	97	99, 61	0.54	0.066	IS2
Isopropyl acetate	108-21-4	102.13	0.8718	61	87,43	1.1	0.17	IS2
1-Butanol	71-36-3	74.1224	0.8098	56	41	1.0	0.14	IS2
Benzene	71-43-2	78.11	0.8765	78	77	0.53	0.077	IS2
Carbon Tetrachloride	56-23-5	153.8	1.5940	117	119	0.53	0.074	IS2

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	**CAS Number**	**Molecular Weight**	**Density**	**Primary Ion[2]**	**Secondary Ion(s)[2]**	**MRL[3] (µg/m³)**	**MDL[3] (µg/m³)**	**IS[4]**
Cyclohexane	110-82-7	84.16	0.7739	84	69,56	1.1	0.15	IS2
tert-Amyl Methyl Ether	994-05-8	102.176	0.7703	73	87,55,43	0.54	0.065	IS2
1,2-Dichloropropane	78-87-5	113	1.1560	63	62	0.54	0.066	IS2
Bromodichloromethane	75-27-4	163.8	1.980	83	85	0.54	0.077	IS2
Trichloroethene	79-01-6	131.4	1.4642	130	132	0.54	0.072	IS2
1,4-Dioxane	123-91-1	88.11	1.0337	88	58	0.54	0.063	IS2
Isooctane	540-84-1	114.23	0.6877	57	41	0.54	0.080	IS2
Methyl Methacrylate	80-62-6	100.12	0.944	100	69	1.1	0.19	IS2
n-Heptane	142-82-5	100.2	0.6837	71	57,100	0.54	0.085	IS2
cis-1,3-Dichloropropene	10061-01-5	111	1.224	75	77	0.52	0.083	IS2
4-Methyl-2-Pentanone	108-10-1	100.2	0.7965	58	85	0.53	0.073	IS2
trans-1,3-Dichloropropene	10061-02-6	111	1.217	75	77	0.53	0.11	IS2
1,1,2-Trichloroethane	79-00-5	133.4	1.4397	97	83	0.54	0.054	IS2
Chlorobenzene-d5(IS3)	3114-55-4	-	-	82	117	-	-	-
Toluene-d8(S)	2037-26-5	-	-	98	100	-	-	IS3
Toluene	108-88-3	92.14	0.8669	91	92	0.54	0.065	IS3
2-Hexanone	591-78-6	100.16	0.8113	43	58	0.54	0.066	IS3
Dibromochloromethane	124-48-1	208.3	2.451	129	127	0.54	0.070	IS3
1,2-Dibromoethane	106-93-4	187.9	2.1791	107	109	0.54	0.062	IS3
n-Butyl Acetate	123-86-4	116.16	0.8825	43	56, 73	0.55	0.073	IS3
n-Octane	111-65-9	114.23	0.6986	57	114	0.54	0.12	IS3

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	**CAS Number**	**Molecular Weight**	**Density**	**Primary Ion[2]**	**Secondary Ion(s)[2]**	**MRL[3] (µg/m³)**	**MDL[3] (µg/m³)**	**IS[4]**
Tetrachloroethene	127-18-4	165.8	1.6227	166	164	0.52	0.069	IS3
Chlorobenzene	108-90-7	112.6	1.1058	112	114	0.54	0.071	IS3
Ethylbenzene	100-41-4	106.2	0.8670	91	106	0.54	0.075	IS3
m-, p-Xylenes	179601-23-1	106.2	0.8642, 0.8611	91	106	1.1	0.14	IS3
Bromoform	75-25-2	252.8	2.899	173	175	0.54	0.11	IS3
Styrene	100-42-5	104.1	0.9060	104	78, 103	0.53	0.086	IS3
o-Xylene	95-47-6	106.2	0.8802	91	106	0.54	0.077	IS3
n-Nonane	111-84-2	128.26	0.7176	43	57, 85	0.54	0.089	IS3
1,1,2,2-Tetrachloroethane	79-34-5	167.9	1.5953	83	85	0.54	0.074	IS3
4-Bromofluorobenzene(S)	460-00-4	-	-	174	176	-	-	IS3
Cumene	98-82-8	120.2	0.8618	105	120	0.54	0.077	IS3
alpha-Pinene	80-56-8	136.24	0.8582	93	77	0.54	0.082	IS3
n-Propylbenzene	103-65-1	120.1938	0.8670	91	120,65	0.54	0.077	IS3
3-Ethyltoluene	620-14-4	120.2	0.8645	105	120	0.53	0.072	IS3
4-Ethyltoluene	622-96-8	120.2	0.8614	105	120	0.54	0.085	IS3
1,3,5-Trimethylbenzene	108-67-8	120.2	0.8652	105	120	0.53	0.077	IS3
alpha-Methylstyrene	98-83-9	118.19	0.9106	118	103,117	0.54	0.085	IS3
2-Ethyltoluene	611-14-3	120.2	0.8807	105	120	0.54	0.068	IS3
1,2,4-Trimethylbenzene	95-63-6	120.2	0.8758	105	120	0.54	0.074	IS3
n-Decane	124-18-5	142.28	0.7300	57	71,85	0.54	0.072	IS3
Benzyl Chloride	100-44-7	126.59	1.1004	91	126	1.1	0.12	IS3

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	CAS Number	Molecular Weight	Density	Primary Ion[2]	Secondary Ion(s)[2]	MRL[3] (µg/m³)	MDL[3] (µg/m³)	IS[4]
1,3-Dichlorobenzene	541-73-1	147	1.2884	146	148	0.54	0.080	IS3
1,4-Dichlorobenzene	106-46-7	147	1.2475	146	148	0.54	0.082	IS3
sec-Butylbenzene	135-98-8	134.2206	0.8601	105	134,91	0.54	0.073	IS3
p-Isopropyltoluene	99-87-6	134.2206	0.8573	119	134,91	0.55	0.081	IS3
1,2,3-Trimethylbenzene	526-73-8	120.1938	0.8944	105	120	0.55	0.073	IS3
1,2-Dichlorobenzene	95-50-1	147	1.3059	146	148	0.54	0.079	IS3
d-Limonene	5989-27-5	136.24	0.8402	68	93	0.54	0.11	IS3
1,2,Dibromo-3-Chloropropane	96-12-8	236.33	2.093	157	75, 39	0.53	0.10	IS3
n-Undecane	1120-21-4	156.31	0.7402	57	71, 85	0.54	0.14	IS3
1,2,4-Trichlorobenzene	120-82-1	181.5	1.459	180	182, 184	0.54	0.13	IS3
Naphthalene	91-20-3	128.17	1.0253	128	129	0.52	0.13	IS3
n-Dodecane	112-40-3	170.34	0.7487	57	71,85	0.52	0.15	IS3
Hexachlorobutadiene	87-68-3	260.8	1.556	225	227	0.53	0.11	IS3
Cyclohexanone	108-94-1	98.14	0.9478	55	42, 98	0.50	0.083	IS3
tert-Butylbenzene	98-06-6	134.22	0.867	119	134	0.54	0.080	IS3
n-Butylbenzene	104-51-8	134.22	0.867	91	134	0.54	0.077	IS3

(S) = Surrogate (IS1) = Internal Standard 1 (IS2) = Internal Standard 2 (IS3) = Internal Standard 3
NA = Not Available

Note 1: Additional compounds may be reported as long as the minimum requirements of this document are met. The compounds listed in this table are reported using TO-15 SCAN. The Selected Ion Monitoring (SIM) compounds are a subset of this list and are included in Table 2A.

Note 2: These are suggested primary and secondary ions. However, any ions in the analyte spectra that are sufficient enough in response to reach the desired reporting limit and having a limited amount of interference, is acceptable for both the primary and secondary ion selection. Analyst experience should be utilized in determining appropriate ions.

Note 3: The laboratory performs three concentration level analyses (SIM, SCAN and Low Level SCAN). The method reporting limit listed is the standard SCAN limit (at or above lowest concentration in the initial calibration curve), but may change with each new initial calibration performed. Therefore, current reporting limits for the three analysis levels, MRLs in ppbv, and those from the Low Level SCAN should be reviewed in the electronic TO-15 Method Manual.

Note 4: The listing of the internal standard by which the compounds are quantitated is for TO-15 SCAN only. SIM compounds (SCAN subset) and their corresponding ions and internal standards are listed in Table 2A.

Note 5: m/e 101 is ~10% or less of m/e 85 (the base peak) and may not be present for low level results. Retention times must be carefully verified.

Table 2A – Volatile Organic Compounds, EPA Compendium Method TO-15 (SIM)					
Compound	**Primary Ion[1]**	**Secondary Ion[1]**	**MRL[2] (ug/m3)**	**MDL[2] (ug/m3)**	**IS**
Dichlorodifluoromethane	85	87	0.050	0.017	IS1
Chloromethane	52	50	0.050	0.019	IS1
Vinyl Chloride	62	64	0.025	0.0076	IS1
1,3-Butadiene	54	39	0.050	0.014	IS1
Bromomethane	94	96	0.025	0.0093	IS1
Chloroethane	64	66	0.025	0.0085	IS1
Acrolein	56	55	0.20	0.039	IS1
Acetone	58	43	2.5	0.056	IS1
Freon 11	101	103	0.050	0.015	IS1
1,1-Dichloroethene	96	98,61	0.025	0.0086	IS1
Methylene Chloride	84	49	0.10	0.013	IS1
Trichlorotrifluoroethane	151	153	0.025	0.0089	IS1
trans-1,2-Dichloroethene	96	98,61	0.025	0.0073	IS1
1,1-Dichloroethane	63	65	0.025	0.0061	IS1
Methyl tert-Butyl Ether	73	57	0.025	0.0093	IS1
cis-1,2-Dichloroethene	96	98,61	0.025	0.0092	IS1
Chloroform	83	85	0.10	0.018	IS1
1,2-Dichloroethane	62	64	0.025	0.0084	IS1
1,1,1-Trichloroethane	97	99	0.025	0.0059	IS1
Benzene	78	77	0.075	0.020	IS1
Carbon Tetrachloride	117	119	0.025	0.012	IS1
1,2-Dichloropropane	63	62,76	0.025	0.0073	IS2
Bromodichloromethane	83	85	0.025	0.0069	IS2
Trichloroethene	130	132	0.025	0.0085	IS2
1,4-Dioxane	88	58	0.10	0.0085	IS2
cis-1,3-Dichloropropene	75	77,39	0.025	0.0062	IS2
trans-1,3-Dichloropropene	75	77,39	0.025	0.0055	IS2
1,1,2-Trichloroethane	83	97,61	0.10	0.0079	IS2
Toluene	91	92	0.10	0.011	IS2
Dibromochloromethane	129	127	0.025	0.0088	IS3
1,2-Dibromoethane	107	109	0.025	0.0079	IS2
Tetrachloroethene	166	164	0.025	0.0082	IS2
Chlorobenzene	112	114	0.10	0.0092	IS3
Ethylbenzene	91	106	0.10	0.0097	IS3
m-&-p-Xylene	91	106	0.10	0.019	IS3
Styrene	104	103	0.10	0.0074	IS3
o-Xylene	91	106	0.10	0.0089	IS3
1,1,2,2-Tetrachloroethane	83	85	0.025	0.0072	IS3
1,3,5-Trimethylbenzene	105	120	0.10	0.0073	IS3
1,2,4-Trimethylbenzene	105	120	0.10	0.0083	IS3
1,3-Dichlorobenzene	146	148	0.025	0.0085	IS3
1,4-Dichlorobenzene	146	148	0.025	0.0081	IS3
1,2-Dichlorobenzene	146	148	0.025	0.0083	IS3
1,2-Dibromo-3-chloropropane	157	75	0.10	0.0095	IS3
1,2,4-Trichlorobenzene	182	184	0.050	0.013	IS3
Naphthalene	128	129	0.10	0.016	IS3
Hexachlorobutadiene	225	227	0.10	0.0092	IS3
Bromobenzene	77	156, 158	0.10	0.0042	IS3

NA = Not Available (IS1) = Internal Standard 1 (IS2) = Internal Standard 2 (IS3) = Internal Standard 3

Note 1: These are suggested primary and secondary ions. However, any ions in the analyte spectra that is sufficient enough in response to reach the desired reporting limit and having a limited amount of interference, is acceptable for both the primary and secondary ion selection. Analyst experience should be utilized in determining appropriate ions.

Note 2: The method reporting limit listed is the standard SIM limit (lowest concentration in the initial calibration curve; must be higher than MDL), but may change with each new initial calibration performed. Therefore, current reporting limits should be reviewed. MDLs in ppbV may be reviewed in the electronic TO-15 Method Manual.

Table 3
Standard Concentrations (SCAN) (Primary Sources)[1]

Compound Name	0.1ng	0.2ng	0.5ng	1.0ng	5.0ng	25ng	50ng	100ng
Bromochloromethane (IS1)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Propene	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
Dichlorodifluoromethane (CFC 12)	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
Chloromethane	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	0.105	0.210	0.525	1.05	5.25	26.25	52.5	105
Vinyl Chloride	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
1,3-Butadiene	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
Bromomethane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Chloroethane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Ethanol	0.521	1.042	2.605	5.21	26.05	130.25	260.5	521
Acetonitrile	0.105	0.210	0.525	1.05	5.25	26.25	52.5	105
Acrolein	0.103	0.206	0.515	1.03	5.15	25.75	51.5	103
Acetone	0.533	1.066	2.665	5.33	26.65	133.25	266.5	533
Trichlorofluoromethane	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
Isopropyl Alcohol	0.210	0.420	1.050	2.10	10.50	52.50	105.0	210
Acrylonitrile	0.105	0.210	0.525	1.05	5.25	26.25	52.5	105
1,1-Dichloroethene	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
tert-Butanol	0.216	0.432	1.080	2.16	10.80	54.00	108.0	216
Methylene Chloride	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
Allyl Chloride	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Trichlorotrifluoroethane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Carbon Disulfide	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
trans-1,2-Dichloroethene	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
1,1-Dichloroethane	0.109	0.218	0.545	1.09	5.45	27.25	54.5	109
Methyl tert-Butyl Ether	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Vinyl Acetate	0.535	1.070	2.675	5.35	26.75	133.75	267.5	535
2-Butanone (MEK)	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
cis-1,2-Dichloroethene	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
Diispropyl Ether	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Ethyl Acetate	0.217	0.434	1.085	2.17	10.85	54.25	108.5	217
n-Hexane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Chloroform	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
1,2-Dichloroethane-d4 (S)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Tetrahydrofuran	0.109	0.218	0.545	1.09	5.45	27.25	54.5	109
Ethyl tert-Butyl Ether	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
1,2-Dichloroethane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
1,4-Difluorobenzene(IS2)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
1,1,1-Trichloroethane	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
Isopropyl acetate	0.211	0.422	1.055	2.11	10.55	52.75	105.5	211
1-Butanol	0.208	0.416	1.040	2.08	10.40	52.00	104.0	208

Table 3 - Continued
Standard Concentrations (SCAN) (Primary Sources)[1]

Compound Name	0.1ng	0.2ng	0.5ng	1.0ng	5.0ng	25ng	50ng	100ng
Benzene	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
Carbon Tetrachloride	0.105	0.210	0.525	1.05	5.25	26.25	52.5	105
Cyclohexane	0.212	0.424	1.060	2.12	10.60	53.00	106.0	212
tert-Amyl Methyl Ether	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
1,2-Dichloropropane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Bromodichloromethane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Trichloroethene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
1,4-Dioxane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Isooctane	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
Methyl Methacrylate	0.215	0.430	1.075	2.15	10.75	53.75	107.5	215
n-Heptane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
cis-1,3-Dichloropropene	0.104	0.208	0.520	1.04	5.20	26.00	52.0	104
4-Methyl-2-Pentanone	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
trans-1,3-Dichloropropene	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
1,1,2-Trichloroethane	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
Chlorobenzene-d5 (IS3)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Toluene-d8 (S)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Toluene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
2-Hexanone	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
Dibromochloromethane	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
1,2-Dibromoethane	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
n-Butyl Acetate	0.109	0.218	0.545	1.09	5.45	27.25	54.5	109
n-Octane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
Tetrachloroethene	0.104	0.208	0.520	1.04	5.20	26.00	52.0	104
Chlorobenzene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
Ethylbenzene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
m- & p-Xylene	0.214	0.428	1.070	2.14	10.70	53.50	107.0	214
Bromoform	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
Styrene	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
o-Xylene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
n-Nonane	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
1,1,2,2-Tetrachloroethane	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
4-Bromofluorobenzene (S)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Cumene	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
alpha-Pinene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
n-Propylbenzene	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
3-Ethyltoluene	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
4-Ethyltoluene	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
1,3,5-Trimethylbenzene	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
alpha-Methylstyrene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
2-Ethyltoluene	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
1,2,4-Trimethylbenzene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107

Table 3 - Continued
Standard Concentrations (SCAN) (Primary Sources)[1]

Compound Name	0.1ng	0.2ng	0.5ng	1.0ng	5.0ng	25ng	50ng	100ng
n-Decane	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
Benzyl Chloride	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
1,3-Dichlorobenzene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
1,4-Dichlorobenzene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
sec-Butylbenzene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
p-Isopropyltoluene	0.109	0.218	0.545	1.09	5.45	27.25	54.5	109
1,2,3-Trimethylbenzene	0.109	0.218	0.545	1.09	5.45	27.25	54.5	109
1,2-Dichlorobenzene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
d-Limonene	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
1,2-Dibromo-3-Chloropropane	0.105	0.210	0.525	1.05	5.25	26.25	52.5	105
n-Undecane	0.108	0.216	0.540	1.08	5.40	27.00	54.0	108
1,2,4-Trichlorobenzene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
Naphthalene	0.103	0.206	0.515	1.03	5.15	25.75	51.5	103
n-Dodecane	0.104	0.208	0.520	1.04	5.20	26.00	52.0	104
Hexachlorobutadiene	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
Methacrylonitrile	0.106	0.212	0.530	1.06	5.30	26.50	53.0	106
Cyclohexanone	0.100	0.200	0.500	1.00	5.00	25.00	50.0	100
tert-Butylbenzene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107
n-Butylbenzene	0.107	0.214	0.535	1.07	5.35	26.75	53.5	107

Note 1: The concentrations detailed in this table may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Table 3A - Standard Concentrations (SIM) (Primary Sources)[1]

Compound Name	20pg	50pg	100pg	500pg	1000pg	2000pg	5000pg	10,000pg	25,000pg	50,000pg
Freon-12	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000
Chloromethane	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000
Vinyl Chloride	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
1,3-Butadiene	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000
Bromomethane	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
Chloroethane	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
Acrolein	20.6	51.5	103	515	1030	2060	5150	10300	25750	51500
Acetone	106.6	266.5	533	2665	5330	10660	26650	53300	133250	266500
Freon-11	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000
1,1-Dichloroethene	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
Methylene Chloride	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000
Freon-113	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
trans-1,2-Dichloroethene	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
1,1-Dichloroethane	21.8	54.5	109	545	1090	2180	5450	10900	27250	54500
Methyl tert-Butyl Ether	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
cis-1,2-Dichloroethene	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000
Chloroform	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
1,2-Dichloroethane	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
1,1,1-Trichloroethane	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
Benzene	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000
Carbon Tetrachloride	21.0	52.5	105	525	1050	2100	5250	10500	26250	52500
1,2-Dichloropropane	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
Bromodichloromethane	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
Trichloroethene	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
1,4-Dioxane	21.6	54.0	108	540	1080	2160	5400	10800	27000	54000
cis-1,3-Dichloropropene	20.8	52.0	104	520	1040	2080	5200	10400	26000	52000
trans-1,3-Dichloropropene	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000
1,1,2-Trichloroethane	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
Toluene	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
Dibromochloromethane	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
1,2-Dibromoethane	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
Tetrachloroethene	20.8	52.0	104	520	1040	2080	5200	10400	26000	52000
Chlorobenzene	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
Ethylbenzene	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
m,p-Xylenes	42.8	107.0	214	1070	2140	4280	10700	21400	53500	107000
Styrene	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000
o-Xylene	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
1,1,2,2-Tetrachloroethane	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
1,3,5-Trimethylbenzene	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000
1,2,4-Trimethylbenzene	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
1,3-Dichlorobenzene	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
1,4-Dichlorobenzene	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
1,2-Dichlorobenzene	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
1,2-Dibromo-3-chloropropane	21.0	52.5	105	525	1050	2100	5250	10500	26250	52500
1,2,4-Trichlorobenzene	21.4	53.5	107	535	1070	2140	5350	10700	26750	53500
Naphthalene	20.6	51.5	103	515	1030	2060	5150	10300	25750	51500
Hexachloro-1,3-butadiene	21.2	53.0	106	530	1060	2120	5300	10600	26500	53000

Table 3A - Standard Concentrations (SIM) (Primary Sources)[1] – Continued

Compound Name	20pg	50pg	100pg	500pg	1000pg	2000pg	5000pg	10,000pg
Bromobenzene	21.2	53.0	106	530	1060	2120	5300	10600

Note 1: The concentrations detailed in Table 3A may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Table 4 - Standard Concentrations (SCAN) (Secondary Sources)[1]

Compound Name	25ng	Compound Name	25ng	Compound Name	25ng
Bromochloromethane (IS1)	**12.5**	1,1,1-Trichloroethane	26.75	alpha-Pinene	26.50
Propene	26.25	Isopropyl acetate	52.50	n-Propylbenzene	26.75
Dichlorodifluoromethane (CFC 12)	26.25	1-Butanol	53.25	3-Ethyltoluene	26.75
Chloromethane	26.50	Benzene	26.25	4-Ethyltoluene	26.25
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	25.75	Carbon Tetrachloride	26.00	1,3,5-Trimethylbenzene	26.50
Vinyl Chloride	26.50	Cyclohexane	52.75	alpha-Methylstyrene	26.50
1,3-Butadiene	26.50	tert-Amyl Methyl Ether	26.75	2-Ethyltoluene	26.75
Bromomethane	26.50	1,2-Dichloropropane	26.75	1,2,4-Trimethylbenzene	26.50
Chloroethane	26.75	Bromodichloromethane	27.25	n-Decane	26.75
Ethanol	132.50	Trichloroethene	27.00	Benzyl Chloride	26.75
Acetonitrile	26.75	1,4-Dioxane	27.00	1,3-Dichlorobenzene	26.75
Acrolein	25.75	Isooctane	26.75	1,4-Dichlorobenzene	26.75
Acetone	133.50	Methyl Methacrylate	53.75	sec-Butylbenzene	26.50
Trichlorofluoromethane	26.50	n-Heptane	26.75	p-Isopropyltoluene	27.25
Isopropyl Alcohol	52.75	cis-1,3-Dichloropropene	26.75	1,2,3-Trimethylbenzene	27.00
Acrylonitrile	26.50	4-Methyl-2-Pentanone	26.50	1,2-Dichlorobenzene	26.75
1,1-Dichloroethene	26.75	trans-1,3-Dichloropropene	26.50	d-Limonene	26.50
tert-Butanol	53.75	1,1,2-Trichloroethane	26.75	1,2-Dibromo-3-Chloropropane	26.75
Methylene Chloride	26.25	**Chlorobenzene-d5 (IS3)**	**12.5**	n-Undecane	27.00
Allyl Chloride	26.75	**Toluene-d8 (S)**	**12.5**	1,2,4-Trichlorobenzene	27.00
Trichlorotrifluoroethane	27.00	Toluene	26.50	Naphthalene	26.50
Carbon Disulfide	26.50	2-Hexanone	27.00	n-Dodecane	26.50
trans-1,2-Dichloroethene	26.75	Dibromochloromethane	26.75	Hexachlorobutadiene	26.75
1,1-Dichloroethane	26.50	1,2-Dibromoethane	26.75	Methacrylonitrile	26.50
Methyl tert-Butyl Ether	26.75	Butyl Acetate	27.25	Cyclohexanone	25.25
Vinyl Acetate	133.25	n-Octane	27.00	tert-Butylbenzene	26.50
2-Butanone (MEK)	26.50	Tetrachloroethene	26.00	n-Butylbenzene	26.75
cis-1,2-Dichloroethene	26.50	Chlorobenzene	26.75		
Diisopropyl Ether	27.00	Ethylbenzene	26.50		
Ethyl Acetate	54.00	m- & p-Xylene	53.25		
n-Hexane	27.00	Bromoform	26.75		
Chloroform	26.75	Styrene	26.50		
1,2-Dichloroethane-d4 (S)	**12.5**	o-Xylene	26.75		
Tetrahydrofuran	27.50	n-Nonane	26.75		
Ethyl tert-Butyl Ether	26.75	1,1,2,2-Tetrachloroethane	26.75		
1,2-Dichloroethane	26.75	**4-Bromofluorobenzene (S)**	**12.5**		
1,4-Difluorobenzene(IS2)	**12.5**	Cumene	26.75		

Note 1: The concentrations detailed in this table may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Table 4A – ICV/LCS Standard Concentrations (SIM) (Secondary Sources)[1]

Compound Name	1000pg
Freon-12	1050
Chloromethane	1060
Vinyl Chloride	1060
1,3-Butadiene	1060
Bromomethane	1060
Chloroethane	1070
Acrolein	1030
Acetone	5340
Freon-11	1060
1,1-Dichloroethene	1070
Methylene Chloride	1050
Freon-113	1080
trans-1,2-Dichloroethene	1070
1,1-Dichloroethane	1060
Methyl tert-Butyl Ether	1070
cis-1,2-Dichloroethene	1060
Chloroform	1070
1,2-Dichloroethane	1070
1,1,1-Trichloroethane	1070
Benzene	1050
Carbon Tetrachloride	1040
1,2-Dichloropropane	1070
Bromodichloromethane	1090
Trichloroethene	1080
1,4-Dioxane	1080
cis-1,3-Dichloropropene	1070
trans-1,3-Dichloropropene	1060
1,1,2-Trichloroethane	1070
Toluene	1060
Dibromochloromethane	1070
1,2-Dibromoethane	1070
Tetrachloroethene	1040
Chlorobenzene	1070
Ethylbenzene	1060
m,p-Xylenes	2130
Styrene	1060
o-Xylene	1070
1,1,2,2-Tetrachloroethane	1070
1,3,5-Trimethylbenzene	1060
1,2,4-Trimethylbenzene	1060
1,3-Dichlorobenzene	1070
1,4-Dichlorobenzene	1070
1,2-Dichlorobenzene	1070
1,2-Dibromo-3-chloropropane	1070
1,2,4-Trichlorobenzene	1080
Naphthalene	1060
Hexachloro-1,3-butadiene	1070
Bromobenzene	1080

Note 1: The concentrations detailed in this table may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Attachment 1

Training Plan

Training Plan for Analysis of VOCs by GC/MS

Trainee _____ Trainer _____ Instrument _____ Training Completion Date _____

1. Read SOP *Training Duration* _____ Trainer ____ Trainee ____ Date _____

2. Read Methods TO-14A & TO-15A *Training Duration* _____ Trainer ____ Trainee ____ Date _____

3. Demonstrated understanding of the scientific basis of the analysis Trainer ____ Trainee ____ Date _____
   Whole air sample preconcentration techniques
   Gas chromatography *Training Duration* _____
   Mass spectrometry

4. Demonstrated familiarity with related SOPs Trainer ____ Trainee ____ Date _____
   SOP for Batches and Sequences; Rev. ___
   SOP for Making Entries onto Analytical Records; Rev. ___ *Training Duration* _____
   SOP for Manual Integration; Rev. _____
   SOP for Significant Figures; Rev. ____
   SOP for Nonconformance and Corrective Action; Rev. ____
   SOP for Performing MDL Studies and Establishing Limits of Detection and Quantitation; Rev. _____
   SOP for Cleaning and Certification of Summa Canisters; Rev. ____

5. Observe performance of SOP *Training Duration* _____ Trainer ____ Trainee ____ Date _____
   ___sample preparation/dilution and sample loading and analysis
   ___analytical sequence setup
   ___standard preparation
   ___BFB tuning evaluation
   ___initial calibration (model, calculations, manual integrations)/initial calibration verification
   ___manual integrations
   ___continuing calibration verification
   ___EnviroQuant introduction (recognizing saturation and sensitivity issues)
   ___data reduction and reporting including reporting req. for various agencies, autotexts, documentation
   ___canister and bag handling (including leakers)

6. Perform SOP with supervision *Training Duration* _____ Trainer ____ Trainee ____ Date _____
   ___sample preparation/dilution and sample loading and analysis
   ___analytical sequence setup
   ___standard preparation
   ___BFB tuning evaluation
   ___initial calibration (model, calculations, manual integrations)/initial calibration verification
   ___manual integrations
   ___continuing calibration verification
   ___EnviroQuant use (recognizing saturation and sensitivity issues)
   ___data reduction and reporting including reporting req. for various agencies, autotexts, documentation
   ___canister and bag handling (including leakers)

7. Independent performance of the SOP *Training Duration* _____ Trainer ____ Trainee ____ Date _____
   ___sample preparation/dilution and sample loading and analysis
   ___analytical sequence setup
   ___standard preparation
   ___BFB tuning evaluation
   ___initial calibration (model, calculations, manual integrations)/initial calibration verification
   ___manual integrations
   ___continuing calibration verification
   ___EnviroQuant proficiency (recognizing saturation and sensitivity issues)
   ___data reduction and reporting including reporting req. for various agencies, autotexts, documentation
   ___canister and bag handling (including leakers)
   ___initial demonstration of competency (4 Laboratory Control Samples)

8. Instrument operation and maintenance Trainer ____ Trainee ____ Date _____
   ___autosampler *Training Duration* _____
   ___GC and capillary column installation *Training Duration* _____
   ___mass spectrometer *Training Duration* _____
   ___data system *Training Duration* _____

Attachment 2

Initial Calibration Checklist

Initial Calibration Review Checklist - EPA Compendium Method TO-15

ICAL Date:_____ ICAL ID:_____ LIMS ICAL ID:_____

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan Scan Low Level (0.1ng): ☐ Yes ☐ No

Analyst		Reviewer
☐	1. Is the required documentation in the ICAL file?	☐
	☐ BFB Tune analysis Report	☐
	☐ Calibration Status Report (aka Calibration History)	☐
	☐ Response Factor Report/Percent RSD	☐
	☐ Quant Report for each calibration std (including manual integration documentation)	☐
	☐ ICV Quantitation Report	☐
	☐ TO-15 Standard Calculation Spreadsheet	☐
☐	2. Was the ICAL performed continuously (not interrupted for maintenance or sample analysis)?	☐
☐	3. Have all the calibration standards been analyzed within 24 hours of each other?	☐
☐	4. Does the BFB tune check standard analysis at the start meet the tune criteria?	☐
☐	5. Are all the analytes in the blank analysis <MRL?	☐
☐	6. Does each analyte's ICAL include a minimum of 5 concentrations at 5 consecutive levels?	☐
☐	7. Were the standards analyzed from low concentration to high concentration?	☐
☐	8. For each analyte, are there no levels skipped?	☐
☐	9. For each analyte, is there only one value used for each calibration level?	☐
☐	10. For each analyte, is the lowest standard's concentration at or below the analyte's MRL?	☐
☐	11. For each analyte, is the corresponding signal to noise ratio at least 3:1 at the lowest point on the curve?	☐
☐	12. For each analyte, are the corresponding upper levels free from saturation?	☐
☐	13. If a calibration level is dropped, are all the responses for each target analyte dropped and is the information noted in the ICAL explaining the reason?	☐
☐	14. Is the average RSD ≤30% for all analytes, with no more than two exceptions ≤40%?	☐
☐	15. DoD/Navy: Is the average RSD ≤30% for all analytes?	☐
☐	16. Is the response Y at each calibration level within 40% of the mean area response over the initial calibration range for each internal standard?	☐
☐	17. Percent recovery for each analyte in the ICV 70%-130% (AZ: 50-150% for VA)?	☐
☐	18. Was the RRT for each target compound at each calibration level within 0.06RRT units of the mean RRT for the compound?	☐
☐	19. Is the retention time shift for each of the internal standards at each calibration level within 20s of the mean retention time over the initial calibration range for each standard?	☐
☐	20. If there are any manual integrations, are they performed correctly according to the corresponding SOP? If so, initial and date the appropriate pages.	☐
☐	21. Is the ICAL good at 0.5ng (or 0.1ng)–100ng (Scan) or 10-20000pg (SIM) for all compounds? ☐ Yes ☐ No Note exceptions and corresponding MRLs below – *Specify applicable range...*	☐
☐	22. Are ALL of the peak selections for each analyte correct according to retention time (all RTs must be checked by both the initial and peer reviewer)?	☐

COMMENTS:

Analyst: _____ Secondary Reviewer: _____

Attachment 3

Daily QC and Sample Review Checklists

EPA Compendium Method TO-15 - Daily QC Review Checklist

(Note exceptions in Comments and include Analysis Observations/Case Narrative Summary Form as appropriate)

Method: ☐ EPA TO-15 ☐ EPA TO-14A **Analysis Date:** _____

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan **Scan Low Level (0.1ng):** ☐ Yes ☐ No **DOD:** ☐ Yes ☐ No

Analyst **Reviewer**

☐ 1. Is the required documentation present? ☐
- ☐ CORRECT BFB Tune analysis Report
- ☐ CCV analysis Quantitation Report & %D Report
- ☐ LCS analysis Quantitation Report
- ☐ MB analysis Quantitation Report

☐ 2. BFB **tune** check standard analysis meet the tune criteria for the method indicated above? ☐

☐ 3. Analyses within the tune's **24-hr window or** ☐ **Client's 12hr window requirement**? ☐

☐ 4. Does the **CCV** have a difference ≤30% for all analytes? ☐
[Note <u>all</u> outliers biased high and/or low]

☐ 5. **DoD**: Does the **Closing CCV** have a difference ≤30% for all analytes? ☐
[Note <u>all</u> outliers biased high and/or low]

☐ 6. All **IS** retention times within 20 seconds of the CCV RT or the RT from the midpoint (ICAL)? ☐

☐ 7. All **IS** responses within ±40% of CCV or the midpoint in the ICAL? ☐

☐ 8. All **surrogate** recoveries (in CCVs, MB, LCSs, etc.) within acceptance limits (70%-130%) ☐

☐ 9. All analytes in the **MB** <MRL? (DoD <1/2MRL, except Acetone, MeCl2, EtOH, Carbon Disulfide)? ☐

☐ 10. **LCS** %R within lab control limits for all analytes except AZ samples (70%-130%, VA 50%-150%)? ☐

☐ 11. All analytes in the **Lab Duplicate / DLCS** within ±25% or the client specified limits? ☐

☐ 12. **DoD/Navy**: **DLCS** analyzed? ☐

<u>Air-Phase Petroleum Hydrocarbons</u>

☐ 1. Does the **CCV** meet the following criteria? ☐
- Percent difference ≤30%.
- One compound or range can be >30%, but less than 50%.
- No single analyte or range may be >50%.

[Note outliers biased high and/or low in comments below]

☐ 2. Does lab **duplicate** meet an RPD of ≤30% for results >5x MRL? Repeat analysis if: ☐

RPD >30 (where both analyses are >5x RL	1st analysis detect @ >5x MRL, Dup=ND
1st analysis ≤5x RL; Dup=ND (RPD not calculable)	

☐ 3. Are the analytes in the **LCS** within 70%-130% recovery? ☐

COMMENTS:

Analyst/LIMS Run Approval: _____ Secondary/LIMS Supervisor Approval: _____

EPA Compendium Method TO-15 - Sample Review Checklist
(Note exceptions in Comments and include Analysis Observations/Case Narrative Summary Form as appropriate)

Method: ☐ EPA TO-15 ☐ EPA TO-14A **Analysis Date:** _____ **Project #:** _____

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan **Scan Low Level (0.1ng):** ☐ Yes ☐ No **DOD:** ☐ Yes ☐ No

Analyst		**Reviewer**
☐	1. All analyte hits in the samples within the **calibration range** and/or noted?	☐
☐	2. All **peak integrations** acceptable?	☐
☐	3. All **manual integrations** flagged and documented?	☐
☐	4. Have **Q values** been verified for each peak?	☐
☐	5. All **calculations** correct?	☐
☐	6. Has the analyst initialed and dated each **quantitation report**?	☐
☐	7. For **TICs** are the relative intensity and other requirements met (associated MB reported)?	☐
☐	8. **Auto report** correct?	☐
☐	9. **MRL** = _____ ☐ ng ☐ pg (ethanol, acetone, vinyl acetate = 5.0ng)	☐
☐	10. Pressurized with **Helium**? Is the worksheet completed for all samples?	☐
☐	11. Report to **MDL**? ☐ Yes ☐ No	☐
☐	12. **Global Minimum Detection Limit** = _____ ☐ ng ☐ pg	☐
☐	13. **DOD:** Are **manual integrations** notated in the **case narrative?**	☐

Air-Phase Petroleum Hydrocarbons

☐	1. Are all manual **integrations** flagged and documented (except for HC ranges)?	☐
☐	2. Are the associated ICAL responses correct?	☐
☐	3. Does the lab **duplicate** meet RPD ≤30% for results >5x the MRL? Otherwise, repeat analyses if:	☐

RPD >30 (where both analyses are >5x RL	1st analysis detect @ >5x MRL, Dup=ND
1st analysis ≤5x RL; Dup=ND (RPD not calculable)	

COMMENTS:

☐	1. **CASE NARRATIVE COMPLETED?**	☐

Analyst/LIMS Run Approval: _____ Secondary/LIMS Supervisor Approval: _____

Attachment 4

State and Project Specific Requirements

Minnesota Requirements	
Item	**Criteria**
Holding Time (HT)	14 days
Tedlar bags	Not allowed for sampling or sample dilution
Canisters and flow controllers	Individually certified Individually leak checked before shipment
	Samples with concentrations outside of the calibration curve will have a zero canister analysis performed to check for carryover. If carryover is detected, system bake out shall be performed and documented. Additionally, in instances where the laboratory has evidence on file that a particular compound when present at a high concentration does not exhibit carry-over, the samples will not be reanalyzed. When samples are analyzed that have a higher concentration than the evidence on file, the above requirements must be followed. Also, samples that have hits below the MRL will not be reanalyzed when analyzed after a sample with concentrations over the calibration range.
Method Reporting Verification Check	Analyze a Method Reporting Verification at the beginning of the sequence prior to analyzing samples. Acceptance criteria ±40%.
Duplicates	10 percent laboratory duplicates
Record retention	MN/NELAP 5 years MPCA (Minnesota Pollution Control Agency) compliant samples 10 years
Tier level	TIII

Arizona Requirements	
Item	**Criteria**
LCS	70-130% (vinyl acetate 50-150%)

Department of Toxic Substances Control (DTSC) Requirements	
Item	**Criteria**
Holding Time (HT)	72 hour hold time for canisters

Attachment 5

Tekmar AutoCan Trap Packing Instructions

Tekmar AutoCan Trap Packing Instructions

The internal sample trap on the AutoCan is a 1/8" x 12" thin-walled stainless steel tube, usually coated with fused silica (Silcosteel). It is packed with a combination of graphitized carbon black and carbon molecular sieve adsorbents, with the weakest adsorbent at the top (inlet) and the strongest at the bottom (outlet). Each bed is separated by a small plug of untreated glass wool. Untreated is used because DCMS-treated wool will release siloxanes when heated to the temperatures used for TO-15 analysis.

The adsorbents listed below are further refined at the lab by sifting in an 80-mesh sieve. This removes the smaller particles and leaves a very uniform product of about 60-mesh size. Getting rid of the "fines" helps ensure good flow through the trap during sampling and reduces the pressure drop across the trap. A tightly-packed trap can lead to problems such as poor reproducibility, slowed flow rates, and channeling (small spaces in the beds that let analytes pass through).

Adsorbent	Mesh	Supplier	Catalog #	Packing Amount (mg)
Carbosieve SIII	60/80	Supelco	10184	40
Carbosieve G	60/80	Supelco	10198	30
Carbopack Z	60/80	Supelco	20273	30
Tenax TA	20/30 or 45/60	Supelco	10257	rest of trap

Old traps can be reused if unpacked carefully and cleaned and baked out properly. Use a glass wool puller to remove the wool plugs, and gently tap the sorbent out onto a piece of paper. If necessary, use the other end of the puller to loosen the sorbent bed, being careful not to scratch the inside of the trap. Discard the old sorbent. Rinse the empty trap with methanol, then bake in a GC oven for 30 minutes at 150°C.

The total length of the adsorbent bed is 12 to 13cm. You want to leave 2 to 3cm of space above the top of the last glass wool layer to ensure that all of the material is within the heated zone of the AutoCan trap heater.

With clean hands (no lotion!) place a small amount of glass wool, about 10-15mg, into the top of the trap and work it in with a piece of wire or tubing. Then use the trap packing tool (the larger steel rod that just barely fits inside the trap) to hold the plug in the trap while you pull away any loose strands of wool. Then use the long steel tube to push the plug down about 15cm. The idea is to keep the plug very compact, so it is a good idea to use the trap packing tool to push up from the bottom while pushing the wool in from the top, meeting 15cm down. The plug should not move too easily when pushed.

Weigh out the first sorbent (Carbosieve SIII) on weighing paper using the analytical balance. Using the glass funnel and a short piece of silicone tubing, pour the sorbent into the top of the trap. Tap on counter to get it all out of the funnel, then remove the funnel and tap some more to settle the sorbent into a compact bed. It is very important that there are no air spaces in the bed. However, it is also very important not to compress the sorbents too much, so be very careful when placing the glass wool plugs.

Place a glass wool plug on top of the first bed, starting as described above for the first plug. Push it gently onto the top of the sorbent with very little pressure.

Proceed with the other three packings in the table above (Carbosieve G, Carbopack Z, and Tenax TA).

After placing the last glass wool plug on top, turn the trap over and gently tap it on a piece of white paper to see if any sorbent comes out. If it does, you need to add more glass wool.

Now the trap needs to be conditioned in the trap heater. The sorbent manufacturers recommend that they be conditioned at succeedingly higher temperatures, with the final temperature being about 20-30˚C higher than the desorb temperature. The reason is that the sieves hold a lot of air and moisture and it is better to drive these off at lower temperatures to avoid damage to the material, such as cracking and oxidation which creates active sites. The temperatures and times are:

80˚C for 30 minutes, 50 to 100ml/min nitrogen or helium flow
200˚C for 30 minutes
265˚C for at least 3 hours

These temperatures are set using the variable power controller and thermocouple meter. Repeat for the other temperatures (low to high). Make sure the gas toggle valve in back is open, and measure flow at the top of the trap.

Analysis of C1-C6+ using Gas Chromatography with Flame Ionization Detection (FID) in Accordance with a Modification of EPA Compendium Method TO-3

DOCUMENT ID: VOA-TO3C1C6, REV 14

Approved By: Kate Kaneko Date: 6/10/19
Laboratory Director – Kate Kaneko

Approved By: Chaney Arend Date: 5/24/19
Quality Assurance Manager – Chaney Arend

Approved By: Date: 5/24/19
Technical Manager (Volatiles GC) – Wade Henton

Doc Control ID:	UNCONTROLLED	Archived Date:	

TABLE OF CONTENTS

1) Scope and Applicability

1.1 This gas chromatographic method is used in the analysis of methane, ethane, ethene, acetylene, propane, propene, n-butane, n-pentane, n-hexane and hydrocarbon ranges from C2 to greater than C6 by a modification of EPA Compendium Method TO-3 and modified ASTM D1945-03. In addition a value for Total Volatile Petroleum Hydrocarbons (TVPH), Non-methane Organic Hydrocarbons (NMOHC), or Total Gaseous Non-methane Organics (TGNMO) can be reported. These terms are interchangeable and can be reported as methane or as hexane as requested by the client.

1.2 This method applies to but is not limited to the following sample matrices: ambient air, source emissions, landfill gases, digester gases, and vehicular exhaust.

1.3 The range of this method for quantifying target analyte gases, depending on the concentration of the samples, is approximately 0.5ppm to percent values. The upper limit may be extended by diluting the sample with an inert gas or by using a smaller injection volume.

1.4 The number of samples, which may be analyzed in one eight hour day, is approximately twenty. The reporting limits for these analytes are listed in Attachment D of this standard operating procedure. The method reporting limit for a compound is defined as the minimum reliably quantifiable concentration of that compound.

2) Summary of Procedure

2.1 Samples are collected as vapor in Tedlar bags, glass bottles, or specially prepared canisters and delivered to the laboratory for analysis. An aliquot is drawn from the sampling container using a gas tight syringe and injected onto a packed chromatographic column where the analytes are separated and measured using a flame ionization detector (FID). Analytes and hydrocarbon ranges are identified and quantified based on their retention time, which is compared with that of a known standard under identical conditions.

3) Definitions

3.1 Relative Standard Deviation (RSD) The RSD is the coefficient of variation (CV; ratio of the standard deviation to the mean) multiplied by 100 to convert the CV to a percentage of the mean.

3.2 Analytical Sequence The analytical sequence describes exactly how the field and QC samples in an analytical batch are to be analyzed.

3.3 Field Sample A sample collected and delivered to the laboratory for analysis.

3.4 Batch QC Batch QC refers to the QC samples that are analyzed in an analytical batch of field samples and includes the Method Blank (MB), Laboratory Control Sample (LCS) and Laboratory Duplicate (LD), etc.

3.5 Calibration Standard (Initial Calibration – ICAL) A certified calibration standard is a purchased from an outside vendor. A calibration standard is analyzed at varying concentrations and used to calibrate the response of the measurement system with respect to analyte concentration.

3.6 Initial Calibration Verification (ICV) Standard An initial calibration verification standard (ICV) is a second source certified standard that is purchased from an outside vendor and

is analyzed after the measurement system is calibrated, but prior to sample analysis in order to verify the calibration of the measurement system.

3.7 Continuing Calibration Verification (CCV) Standard A continuing calibration verification standard (CCV) is a midrange calibration standard that is analyzed periodically to verify the continuing calibration of the measurement system.

3.8 Method Blank (MB) The method blank (MB) for this method is ultra-pure nitrogen that is analyzed to verify the zero point of the analytical system and to verify freedom from carryover. Refer to Section 11.7 and Attachment 7 for NAVSEA specific requirements.

3.9 Laboratory Control Sample (LCS) For the purposes of this document, a laboratory control sample (LCS) shall be a calibration standard of known concentration. The percent recovery of the analyte(s) in the LCS is used to assess method performance.

3.10 Laboratory Duplicate Aliquots of a sample taken from the same container under laboratory conditions which are processed and analyzed independently. A duplicate client sample or duplicate laboratory control sample may be analyzed.

3.11 Precision Precision of a method is how close results are to one another, and is usually expressed by measures such as standard deviation, which describe the spread of results.

3.12 Bias The bias of a method is an expression of how close the mean of a set of results (produced by the method) is to the true value.

3.13 Manual Integration This term applies to a data file in which setpoints have been changed and reintegration has occurred under the changed setpoints; baselines have been adjusted; peak integration start and stop "ticks" have been changed; peak area, or peak height, are changed after the time of data collection and data file generation.

3.14 Limit of Detection (LOD) The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%. (DoD Clarification). For consistency purposes, the LOD may be referred to as the MDL once it is reported; however, full verification will be on file in the laboratory per the procedures detailed in this document.

3.15 Limit of Quantitation (LOQ) The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. (DoD Clarification). For consistency purposes and since the LOQ and MRL are equivalent with regards to laboratory procedure, the LOQ will be referred to as the MRL in this document and once it is reported. Full verification will be on file in the laboratory per the procedures detailed in the document.

3.16 Detection Limit (DL) / Method Detection Limit (MDL) The smallest analyte concentration that can be demonstrated to be different from zero or a blank concentration at the 99% level of confidence. At the DL, the false positive rate (Type 1 error) is 1%. (DoD Clarification). For consistency purposes, the DL may be referred to as MDL. Also, as far as reporting is concerned the MDL will be raised up (where necessary) to the verified LOD per the procedures defined in this document and reported accordingly.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review and reporting per the corresponding standard operating procedures. Analysis and interpretation of results must be performed by personnel in the laboratory who have demonstrated the ability to

generate acceptable results utilizing this SOP.

4.2 The department supervisor/manager or designee shall perform final review and sign-off of the data.

5) Interferences

5.1 Contamination

5.1.1 Column Conditioning Conditioning of the chromatographic column is required prior to use of the system. The column should be conditioned with a continuous flow of chromatographic grade helium and temperature programmed from 35˚C to 200˚C at a rate of five degrees per minute. The column should be held at 200˚C for at least four hours.

5.1.2 Contamination in the Sample Care must be taken to prevent ambient air intrusion into the sample container during canister pressurization and laboratory analysis. When using adapters and fittings the dead volume must be evacuated and replaced with the sample gas prior to sampling from the container. The sampling syringe shall then be flushed with the sample gas to remove residual ambient air. An aliquot greater than is needed is drawn, and the syringe plunger is adjusted to the appropriate volume *immediately* before injecting.

5.1.3 Carrier Gas Contamination To prevent system contamination, UHP/ZERO grade helium (99.999% purity) is used as the carrier gas. Also, a purifier and an oxygen trap are incorporated into the analytical system as additional insurance against possible contamination.

5.1.4 Injection Port Maintenance When performing injection port maintenance and when the injection port septa is replaced a back end chromatographic bleed can be observed. When this occurs, sample analysis for the heavier hydrocarbons (C5-C6) cannot be performed. To "clean" the system, raise the injection port temperature to 180˚C and the oven temperature to 270˚C, let bake overnight for 1 to 3 days. During the day instrument blanks should be analyzed.

6) Safety

6.1 Each compound, mixture of compounds and standards, as well as samples, should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest level possible through the use of gloves (to minimize absorption through the skin) and hoods (to minimize inhalation). Refer to the laboratory's Environmental Health and Safety Manual as it makes reference to the safe handling of chemicals, SDS location, as well as the *Simi Valley Lab Waste Management Plan* for the proper disposal of chemicals and samples.

6.2 Safety Data Sheets (SDS) Safety data sheets (SDS) are available and should be reviewed as part of employee training.

6.3 Protective Clothing Personal protective clothing (safety glasses and gloves) should be used when preparing standards, handling standards in neat form or performing maintenance on pressurized systems.

6.4 Pressurized Gases The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. The regulator should not remain on size "D" cylinders when not in use. Sources of flammable gases (i.e. pressurized hydrogen) should be clearly labeled.

6.5 Syringes Care should be taken to avoid personal injury as a result of improper handling techniques.

7) Sample Collection, Containers, Preservation, and Storage

7.1 The samples are collected and delivered to the laboratory for analysis in either Tedlar bags, specially prepared canisters, or glass sampling bottles (Bottle Vac. Entech instruments).

7.2 Samples collected in bags must be analyzed within 72 hours after sample collection unless otherwise specified by the client.

7.3 Samples delivered in cleaned, evacuated specially prepared canisters and glass bottles do not have specified holding times for atmospheric gases but should be analyzed within 30 days from the date of collection.

8) Apparatus and Equipment

8.1 Gas Chromatograph

8.1.1 GC7 and GC8 HP 5890A, Series II or equivalent (i.e., HP 6890) equipped with a flame ionization detector, and having a temperature programmable oven with sub-ambient cooling capability. The column shall be 60m, 0.53mm ID RT_x-1 or equivalent with a 5µm film thickness.

8.1.2 GC10 Hewlett-Packard Model 5890 Series II Gas Chromatograph or equivalent equipped with a flame ionization detector (FID). The column shall be J&W MXT-QPlot, 053mm x 30m or equivalent.

8.2 Regulators Regulators are used on the gas cylinders supplying the GC and for preparing cylinder standards.

8.3 Data System A data system with the ability to collect data from the GC detector, integrate the peaks and perform the appropriate quantification calculations shall be used. This laboratory currently uses HP Chemstation/Enviroquant GC software.

8.4 Syringes Gas tight syringes of the following volumes: 10mL, 2.5mL, 1.0mL, 0.5mL and 0.25mL.

8.5 Tedlar Bags/Glass Bombs Glass "bombs" of volumes 125 or 250mL and new Tedlar bags are used for diluting very concentrated samples, which fall outside of the initial calibration range.

9) Standards, Reagents, and Consumable Materials

9.1 All samples and standards must be stored separately. The concentration, preparation and expiration date as well as analyst's initials must be identified on the standard label. Each standard must also be uniquely identified with a laboratory ID number.

9.2 All certificates shall be maintained (turned in to the quality assurance department) and noted with the standard identification number, date received and initials of the receiving analyst. For additional information on these and other requirements, refer to the *SOP for Handling Consumable Materials.*

9.3 Carrier and Calibration Standard Balance Gas

9.3.1 Helium UHP/ZERO (99.999%) or higher in purity

9.3.2 Nitrogen UHP/ZERO (99.999%) or higher in purity

9.3.3 Hydrogen 99.999%, fuel source for FID

9.3.4 Zero Air Ultra

9.4 Standards

9.4.1 Purchased Standards

These standards must be stored in accordance with the requirements described in the *SOP for Handling Consumable Materials*. These standards may be stored for a period of 2 years or as recommended by the manufacturer.

9.4.1.1 Scott Specialty Gas cylinders (or similar)

Compound	Concentration			
Methane	1%	1000ppm	100ppm	15ppm
Ethane	1%	1000ppm	100ppm	15ppm
Propane	1%	1000ppm	100ppm	15ppm
n-Butane	1%	1000ppm	100ppm	15ppm
n-Pentane	1%	1000ppm	100ppm	15ppm
n-Hexane	NA	1000ppm	100ppm	15ppm
Balance Gas: Nitrogen				

Note: Specific concentrations of these standards may change with each purchase.

9.4.1.2 Scotty Mix 48 or Equivalent

Compound	Approximate Concentration (ppm by volume)
Methane	15
Ethylene	15
Ethane	15
Propane	15
Acetylene	15
Propylene	15
Propyne	15
n-Butane	15
Balance Gas	Nitrogen

Note: These stock standards contain compounds that are not reported. The actual concentrations of these standards may change with each purchase.

9.4.1.3 Neat Standards

Compound	Approximate Concentration (ppm)
Carbon dioxide	990,000
Ethylene (Ethene)	990,000
Methane	990,000
Propylene	990,000

Propane	990,000
Ethane	990,000

Note: The specific concentrations of these standards may change with each purchase. If utilizing an ultra-high purity (UHP) gas cylinder, the certificate must be on file and it shall meet all of the minimum UHP requirements with respect to impurity content.

9.4.1.4 Matheson Specialty Gas (or similar)

Compound	Concentration
Methane	1000ppm
Ethane	1000ppm
Propane	1000ppm
n-Butane	1000ppm
n-Pentane	1000ppm
n-Hexane	1000ppm
Balance Gas: Nitrogen	

Note: Two different lots or manufacturers of this type of standard are purchased for use as the primary and the secondary source standards. The specific concentrations of these standards may change with each purchase.

9.4.1.5 Scott Specialty Gas (or similar)

Compound	Concentration
Methane	40000ppm

9.4.1.6 Scott Specialty Gas (or similar)

Compound	Concentration
Methane	99.0+%

9.4.1.7 Aldrich Chemical Company (or similar)

Compound	Concentration
n-Hexane	99.0+%

9.5 Calibration Standards

9.5.1 Initial Calibration (ICAL) and Continuing Calibration Verification (CCV) Standards
Working standards shall be prepared from higher concentration stock standards purchased from commercial vendors (see Section 9.4).

9.5.1.1 Procedure Aliquots of the stock standards are spiked into a cleaned and evacuated 6.0 liter canister (*SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Containers)* by using gastight syringes. The canister is then balanced with helium or nitrogen

per the *SOP for Evaluation and Pressurization of Specially Prepared Canisters*.

Step 1: Determine the actual pressurized volume of the 6L canister by the use of the following equation.

PV = PDF(V) (Equation 1)

Where:

PV = Pressurized canister volume (L)

PDF = Pressure Dilution Factor, where PDF = $\frac{p_{atm} + p_f}{p_{atm} - p_i}$

P_f = Final Canister Pressure

P_i = Initial Canister Pressure

V = Volume of canister at 1atm

p_{atm} = Pressure at 1atm = 14.7

Example:

$\frac{14.7 + 65}{14.7 - 0}(6L)$ = 32.53L

Step 2: Determine the amount required to achieve the desired concentration(s) by utilizing the following equation.

$S = \frac{(C_1)(PV)}{(C_2)} x \frac{1000mL}{1L}$ (Equation 2)

Where:

S = Spike amount required in order to obtain the desired concentration (mL)

C_1 = Desired concentration (ppm)

C_2 = Concentration of source (ppm)

PV = Pressurized volume of canister determined in Step 1 (L)

The concentrations listed in this table are based on the purchased neat standards listed in Section 9.4.1.3 and may change with each purchased standard. However, the nominal concentrations should remain close to that listed below.

Compound	Source Conc. (ppm)	Introduce (mL)	Nominal Conc. (ppm)
Carbon dioxide	998,000	326	10,000
Methane	990,000	82.15	2,500
Ethene	10,000	1626.5	500
Ethane	990,000	16.43	500
Propane	990,000	16.43	500
Propene	10,000	1626.5	500

Note: The exact volumes injected, to make a working standard, must be used to determine the final concentration of the standard.

In order to achieve all of the desired concentrations for each analyte in the ICAL or CCV, additional standard dilutions may be required. These dilutions may be prepared in glass dilution bombs (i.e., 125mL) or Tedlar bags and are achieved by following step 3 below.

Step 3: Determine the correct injection amount based on the desired final concentration for a target analyte by utilizing the following equation.

Using $C_1V_1 = C_2V_2$

Where:

C_1 = Initial concentration (i.e., 2500ppm methane stock solution)
C_2 = Final desired concentration (i.e., 2.5ppm)
V_2 = Final volume (125mL or 125000uL – glass dilution bomb)
V_1 = Solve for V_1 (uL)

Step 4: To perform the ICAL or to analyze a CCV, determine the correct instrument injection volume for an analyte by utilizing the following equation.

$$I = \frac{C_2}{C_1}$$

where:

I = required injection (mL)
C_1 = Source (initial) concentration (ppm)
C_2 = Desired concentration (ppm)

9.5.2 Initial Calibration Verification (ICV) Standard This standard must be from a second source (manufacturer or lot) and used as a verification of the initial calibration. Prepare the ICV as specified in Section 9.5.1.

9.5.3 Laboratory Control Sample Spike The same standard as detailed in Section 9.5.2 may be used to spike the LCS and LCSD.

9.6 Storage and Expiration Dates

9.6.1 Stock Standards

The stock standards are purchased in gas cylinders and are stored at ambient temperature. Expiration dates are either assigned by the manufacturer or by an analyst for two years from receipt.

9.6.2 Calibration Standards (ICAL, ICV and CCV)

Store each standard at an ambient temperature for a period detailed below, depending on the container.

Specially Prepared Canister - Two years

Tedlar Bags and Glass dilution bombs - Three days

10) Preventive Maintenance

10.1 A maintenance log shall be kept documenting maintenance performed on each analytical system and the instrument maintenance log must be kept current. The serial numbers of each instrument shall be recorded in the front of the logbook. An entry shall be made in the appropriate log every time maintenance is performed (no matter the extent). The extent of the maintenance is not important, however, it is important that a notation be included for each maintenance activity such as changing a column, tuning the instrument, or cleaning the source. The entry in the log must include:

(a) The date of maintenance
(b) Who did the maintenance
(c) Description of the maintenance
(d) Proof that the maintenance activity was successful

A notation of a successful continuing calibration or initial calibration shall serve as proof that the maintenance is complete and the instrument is in working order.

10.2 Carrier Gas Purifier If in-line purifiers or scrubbers are in place, these purifiers must be changed as recommended by the supplier.

10.3 GC System

10.3.1 Column Performance should be monitored by observing peak shapes and column bleed. Over time, the column may exhibit a poor overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur depends on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced. Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column.

Clipping off a small portion of the head of the column often enhances chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column-cutting tool. When removing any major portion of the column, which will affect the retention times and elution characteristics, a change in instrument conditions may be required to facilitate nominal analytical activity.

Decreasing performance can also be due to ineffective column ferrules, which should be replaced when a tight seal around the column is no longer possible. This can be detected with the use of a leak detector.

10.3.2 Injection Port Injection port maintenance includes changing the injection port liner and column ferrule as needed. Liners should be changed when recent sample analyses predict a problem in chromatographic performance.

10.3.3 Injector Septa Septa should be changed monthly or whenever there is a noticeable change in peak definition. For best results with air analyses, two septa are placed into the injector in order to eliminate loss during manual injections.

10.3.4 Detector Clean FID jet as needed.

11) Procedure

11.1 GC Configuration

11.1.1 Temperature Program The carrier gas flow rate and sub-ambient GC oven temperature programming must be set to completely elute all of the target analytes. The temperature program ramps up to a high temperature, not exceeding the maximum temperature rating of the column in use, and holds there to allow all heavier hydrocarbons to elute, in order to prevent carryover to the next injection.

The settings and system parameters are as follows:

PARAMETERS	HP 6890 (GC7)	HP 5890 (GC8)	HP 5890 (GC10)
Sample Inlet	GC	GC	GC
Injection Source	Manual	Manual	Manual
Injection Location	Back	Front	Front
Run Time	14.27	16.00	~10.0min
OVEN			
Initial Temp.	-20˚C	-30˚C	55˚C
Max. Temp.	325˚C	325˚C	250˚C
Initial Time	1.0min	1.0min	2.0min
Equilibration Time	0.0min	0.0min	0.0min
RAMP			
Rate	22˚C /min	20˚C /min	20˚C /min
Final Temp.	250˚C	250˚C	250˚C
Final Time	3.0min	1.0min	0.5min
INJECTOR			
Mode	Packed Column	Packed Column	Packed Column
Temp.	150˚C	150˚C	100˚C
Pressure	11psi at -20˚C oven temp	24psi at -30˚C oven temp	20psi at 55˚C oven temp
COLUMN			
Model No.	RTx-1	RTx-1	J&W MXT-QPlot
Max. Temp.	325˚C	325˚C	250˚C
Nominal Length	60m	60m	30m
Nominal Diameter	0.53mm ID	0.53mm ID	0.53mm ID
Film Thickness	5um	5um	NA
DETECTOR			

Make-up Gas	35mL/min	40mL/min	30mL/min (N2)
Hydrogen Flow	35mL/min	36mL/min	30mL/min
Air Flow	400mL/min	375mL/min	350mL/min

11.2 Analytical Sequence and Data System Setup

11.2.1 Data System Load the appropriate acquisition method file for the correct GC temperature program (ex. J:\GC7\Method\TO3.m). Load the appropriate analytical sequence (ex. J:\GC7\Sequence\TO3.s). Enter the analytical sequence information in the table window, including standard name, sample name and injection volume. Load the appropriate quantitation method file (ex. J:\GC7\Method\current ICAL method). Run the sequence and inject the standards and samples per the guidelines in Section 11.2.2.

11.2.2 Analytical Sequence The analytical batch must be completed for the analysis of ≤ 20 field samples. Re-runs, laboratory duplicates (LD), and sample dilutions are not considered separate samples. Batch QC samples may be analyzed anywhere in the analytical sequence, with the exception of the method blank which must be analyzed prior to sample analysis in order to demonstrate a contamination free system.

Analytical Sequence Guideline[1]

Sample Description(w/ICAL)	*Sample Description*
Calibration Stds.[2]	CCV[3]
ICV[4]	MB[5]
MB[5]	LCS[6]
LCS[6]	Samples 1-10
Samples 1-10	CCV[3]
CCV[3]	Samples 11-19
Samples 11-19	LD[7]
LD[7]	CCV[3]
CCV[3]	

[1]The batch QC may be analyzed in an order other than the one listed in this document; the analytical sequence specified below is a guideline.
[2]The initial calibration must be generated in accordance with the guidelines detailed in Section 11.3 of this document.
[3]In cases, where the ICAL is not performed the analytical sequence must begin with the analysis of a CCV standard. In addition, a CCV must be analyzed every ten sample injections and the analytical sequence shall end with an acceptable CCV.
[4]Every ICAL must be followed by a second source standard (ICV) which contains all of the target analytes.
[5]The method blank must be analyzed prior to any samples within the sequence.
[6]Every analytical sequence must include a laboratory control sample. A LCS shall be analyzed at a rate of one per twenty samples or fewer for each analyte.
[7]A laboratory duplicate must be analyzed at a frequency of 1 in 20 or fewer samples. A duplicate client sample or duplicate laboratory control sample may be analyzed to assess precision.

11.3 Initial Calibration

The instrument must be calibrated initially and whenever the laboratory takes corrective action (maintenance), which may change or affect the initial calibration criteria, or if the

continuing calibration acceptance criteria have not been met. Introduce each initial calibration concentration standard (at least five levels, analyzed from low concentration to high concentration) by direct injection using a gas tight syringe. Perform all calibration runs according to the analytical portion of the sample analysis described in Section 11.9.

Note: The concentrations of the initial calibration may change as long as the low standard analyzed is the same as the reporting limit for each analyte or lower.

Refer to Section 13.1 for the required calculations and Section 12.4 for the acceptance criteria and corrective action.

11.3.1 Initial Calibration Requirements

Once a set of ICAL standards is analyzed and used to report samples, the previous ICAL may no longer be used to analyze new samples and it must be archived. The only time an archived ICAL can be used thereafter is to review or re-evaluate samples(s) previously processed using that ICAL.

1. A minimum of 5 concentrations must be used to calculate the calibration curve.
2. Highest concentration, together with the lowest concentration, defines the calibration curve.
3. Lowest concentration must be at or below the method reporting limit.
4. A blank should be analyzed prior to beginning the analysis of the calibration standards.
5. The initial calibration event may not be interrupted by maintenance.
6. Only one value per concentration may be used.
7. Analyze calibration standards from low to high concentration.
8. All ICAL analyses must be completed within 48 hours.
9. If 5 calibration standards are in the ICAL, one standard may be re-analyzed. If 6 to 10 calibration standards are in the ICAL, two calibration standards may be re-analyzed.
10. Point dropping policy
    - Minimum of 5 consecutive concentrations must be used to calculate the calibration curve.
    - Lowest concentration must be at the MRL and may not be dropped unless the MRL is changed to the concentration of the remaining lowest standard.
    - Points at high end may be dropped, but doing so lowers the calibration curve.
    - Points may not be dropped from the interior of the curve unless an assignable cause (i.e., gross dilution or standard preparation error, or instrument malfunction) is accounted for and documented in a nonconformity and corrective action report (NCAR). In these instances, all the analytes in that calibration standard must be dropped from the calibration curve as the corrective action.
    - If a point or a calibration standard is dropped, the reason must be documented (and the results maintained with the documentation for the final ICAL).
    - A calibration standard may be re-analyzed if the first analysis of the standard has been dropped and other requirements in this policy are met (i.e., still within 48 hours).

- Once the ICAL has been used to calculate and report sample results, it is not to be changed.

11. Concentrations for calibration curves can been found in Attachment E and Attachment F. However these concentrations might change due to the availability of the standards. Other concentrations can be used as long as all other guidelines for the analysis of initial calibration are followed.

11.3.2 ICAL Update Procedure

1. Open most recent method.
2. Save to new ICAL method ID. The date used in method ID is the date files were analyzed.
3. Clear all responses prior to update initiation and/or clear levels if different concentrations are to be used (Initial Calibration → Clear All Calibration Responses; Initial Calibration → Clear All Calibration Levels).
4. Quantitate standard
5. Review all peaks for retention time, integration, etc.
6. Update responses for standard
7. Repeat for all standards
8. If necessary load midpoint standard and update retention times.
9. Save method.
10. Verify Calibration Files listed on Response Factor Report are correct (Both Primary and Secondary Reviewer).
11. Verify responses of Page 3 of Edit Compounds are correct (Both Primary and Secondary Reviewer).
12. Verify file ID, acquisition time, quant time, update time, and last update information is correct on the Calibration Status Report (Both Primary and Secondary Reviewer).
13. Save Method. Confirm that no other copies of the method are open on other computer workstations.

Note: It is also acceptable to quantitate all standards and review all peaks before updating responses but steps 1-2 still must be completed initially. Step 3 also must be done prior to beginning ICAL update.

11.3.3 Initial Calibration Review

Analyst's calculations and assessment along with a peer review of all ICAL data and documentation as stated in Attachment B is required before the ICAL may be used to analyze samples. Sample results may only be reported if the ICAL is reviewed and found to be acceptable.

11.3.4 Initial Calibration File

An ICAL file is to be created for each initial calibration performed per instrument into which is placed the following ICAL documents. The file shall remain in the laboratory and be filed by instrument and date.

- ICAL Checklist filled out, reviewed and approved
- Blank analysis quantitation report
- Calibration status report (a.k.a. Calibration History)
- Relative Response Factor Report / Percent Relative Standard Deviation
- Quantitation report for each calibration standard (including manual integration documentation – before and after manual integration)

- ICV quantitation report and evaluate continuing calibration report (a.k.a. Percent Difference Report)

11.3.5 Initial Calibration Verification Verify the initial calibration by analyzing an independent calibration verification standard (ICV). Refer to Section 13.2 for the required calculations and Section 12.5 for the acceptance criteria and corrective action.

11.4 LOQ Establishment, Verification and Acceptance Criteria

A) The LOQ must be set within the calibration range (≥ low std. of the current passing ICAL) prior to sample analysis.
B) The LOQ for each analyte must be > the analyte's LOD.
C) Initially a passing demonstration of precision and bias must be performed at the LOQ
D) Run CCV 2 times at the LOQ and:
   1) Evaluate the LOQ for precision and bias using current control chart limits.
   2) Check the signal to noise ratio (S/N) using the software. The S/N ratio must be at least 3:1 for each analyte.
E) If anything fails, verify at higher level and notify reporting. Also, make a note in the ICAL documentation.
F) Turn in all LOQ verification data (quant reports and software reports/checks) to QA (regardless of pass/fail).
G) Verify the LOQ on each instrument quarterly by running the CCV at the LOQ and verifying that ongoing precision and bias requirements are met.

NAVSEA Requirement (Annual): Project analytes must be spiked at concentrations up to two times the Laboratory Reporting Limit. Recoveries must be within ±30% of their true concentration.

11.5 Retention Time (RT) Windows

Retention time windows for each target analyte must be generated initially and whenever there is a major change in instrument conditions including flow rates. In addition, retention time windows must be generated when standard analyses result in analyte retention times outside the established windows. The procedure for determining the retention time windows for this method is as follows. For range analysis, retention times from the most recent CCV shall be used to establish the range.

1. The system must be operating reliably and be optimized for the target analytes in the sample matrix to be analyzed.
2. The retention times from a minimum of four initial calibration points spanning the calibration range shall be used as they will show shifts in RTs due to analyte concentrations (higher concentrations lead to wider peaks).
3. Record the retention time for each single component analyte to three decimal places. Calculate the mean and standard deviation of the four absolute retention times for each single component analyte and surrogate
4. If the standard deviation of the retention times for the target compound is 0.000, then additional ICAL points may be included or the use of a default standard deviation of 0.01 minutes.
5. The width of the retention time window for each analyte is defined as ±3 times the standard deviation of the mean absolute retention time established using the ICAL points. If the default standard deviation of 0.01 is used, the width of the window will be 0.03 minutes.

6. Establish the center of the retention time window for each analyte by using the absolute retention time for each analyte from the continuing calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

Retention time windows must be calculated for each analyte on each instrument. New retention time windows must be established when a new column is installed.

11.6 Continuing Calibration Verification

A continuing calibration standard must be analyzed every ten field sample injections or every 12 hours, whichever is more frequent. The analytical batch must also begin and end with the analysis of a CCV standard and shall not exceed a 24 hour period. The concentration of the calibration verification may be varied within the established calibration range. Refer to Section 13.3 for the required calculations and Section 12.6 for the acceptance criteria and corrective action.

11.7 Method Blank

The method blank shall be obtained using ultra high purity nitrogen directly injected in the same manner as the standards and samples. A method blank must be analyzed prior to analysis of samples. A method blank must also be analyzed if carryover contamination is suspected. Refer to Section 12.7 for the acceptance criteria and corrective action.

NAVSEA Requirement: The method blank shall be Zero air contained in a glass bottle (Bottle-Vac™).

11.8 Laboratory Control Sample

The laboratory control sample shall be an injection of the continuing calibration or initial calibration verification standard. Make sure that all of the pertinent information is included on the quantitation report including the sample identification (LCS), concentration, standard used, and analyst. Refer to Section 13.4 for the required calculations and Section 12.8 for the acceptance criteria and corrective action.

11.9 Analysis

11.9.1 Container Pressurization Sample analysis must be made using the same instrument parameters as that of the calibration standards. Refer to the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters* for the procedure of how canisters and glass bottles are to be pressurized prior to analysis. The analyst shall record the appropriate pressures on the Service Request form. This includes noting the difference between the initial (as received pressure) and the pressure prior to pressurization for which the appropriate corrective actions have been detailed and must be followed accordingly.

11.9.2 Sample Analysis Sample analysis shall be performed by a direct injection technique using gas tight syringes. Insert the syringe through the Tedlar bag septum or canister or glass bottle fitted with an adapter. When using adapters and fittings the dead volume must be evacuated and replaced with the sample gas prior to sampling from the container. The sampling syringe shall then be flushed with the sample gas to remove residual ambient air and vented into a waste bag. This procedure entails drawing an aliquot greater than is needed, and adjusting the syringe plunger to the appropriate volume *immediately* before injecting. Refer to Section 13.5 for the required calculations and Section 12.9 for the acceptance criteria and corrective action.

Bottle Vacs use a proprietary quick connect fitting (Micro-QT, Entech Instruments). Each female Mirco-QT fitting must be purged after use to remove any remaining sample residue and prevent contamination from subsequent usage. Connect a male Mirco-QT fitting to a source of ultrapure or carbon-filtered gas. Adjust the pressure to about 10 psig using an inline regulator. Connect the female fitting for several seconds, then remove and place in an oven kept at 60ºC until the next use. Do not heat the fitting higher than 80ºC.

11.9.3 Sample Dilution If any target analyte results are above the highest level of the initial calibration, a smaller sample aliquot or a dilution in a Tedlar bag or glass dilution bomb must be analyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

- Use results of the original analysis to determine the approximate dilution factor required getting the largest analyte peak within the initial calibration range.
- The dilution factor chosen should keep the response of the analyte peak for a reported target compound in the upper half of the initial calibration range of the instrument. Additional compounds may be reported as long as they are within the calibration range.
- Analysis involving dilution should be made with high purity nitrogen and must be reported with a dilution factor.

Tedlar bag dilution:

- Calculate the sample amount and volume of balance gas needed to obtain the required dilution.
- Fill a new 1.0L tedlar bag with nitrogen using the appropriate gas tight syringe.
- Remove the difference in the balance gas using the appropriate gas tight syringe.
- Add the calculated sample amount using a gas tight syringe.

11.9.4 Quantitative Analysis Prior to integration, verify that each peak is within calibration range. A smaller injection volume or dilution may be required. Integrate the entire range of hydrocarbons that elute prior to and include the n-alkane peak (Branched alkanes of the same molecular weight will elute prior to the n-alkane.). For example, C3 as propane, integrate the range of peaks that elute after the ethane peak to the end of the propane peak.

The >C6 as hexane may be integrated as one group or separated into >C6_1 as hexane, >C6_2 as hexane, and >C6_3 as hexane. If the analysis is for the n-chain alkanes and alkenes only, manual integration is generally unnecessary unless the peaks are misidentified, not integrated or the baseline needs to be adjusted. Refer to Section 11.11 for manual integration guidelines.

11.10 Laboratory Duplicate

Analyze two separate aliquots from the same sample container. A laboratory duplicate must be analyzed a frequency of 1 in 20 field samples. The laboratory duplicate should be rotated among clients, whenever possible. Alternatively, a duplicate laboratory control sample may be analyzed to assess precision. Refer to Section 13.6 for the required calculations and Section 12.10 for the acceptance criteria and corrective action.

NAVSEA Requirement: A duplicate client sample and a duplicate laboratory control sample must be analyzed per batch of 20 samples.

11.11 Manual Integration

For single component analysis, the integration(s) for each sample is checked to ensure that it has been integrated properly. For the hydrocarbon range analysis the computer software is not programmed to perform the integration; therefore, manual integration must be performed. In this instance, the software integrations of a before chromatograph printout is not necessary. Assuming an incorrect automatic integration the analyst shall conduct the manual integration in accordance with the *SOP for Manual Integration* including all documentation and reviews associated with the process. The review should include the analyst and peer reviewer initialing and dating the manual integration as an indication of acceptability and approval.

Client samples that are received in Tedlar bags may have the noticeable artifacts of N,N-dimethylacetamide and Phenol from the Tedlar manufacturing that is above the reporting limit for the greater than C6 portion of the chromatogram. These peaks may have to be excluded from the manual integration process if they add an amount of area that will lead to a false positive result. The retention time of these peaks have been identified and are maintained on file.

11.12 Detection Limits and Limits of Detection

If results are to be reported below the MRL, an MDL study must be performed in accordance with the procedure outlined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.* Method detection limits must be determined initially and each time there is a change in the test method that affects how the test is performed, or when a change in instrumentation is such that it affects the sensitivity of the analysis. The MDL study shall be performed on each instrument. All supporting data must be approved and retained.

The detection limit shall be used to determine the LOD for each analyte. Once determined on each instrument, the highest LOD (for each analyte from all instrument determinations) shall be used as the uniform LOD.

11.12.1 Performance and Acceptance Criteria

1. Perform Limit of Detection (LOD) verification on all instruments (performing this method) immediately following the MDL study. Spike the LOD at 2-4x the MDL; the spike level establishes the LOD.
2. LOD Acceptance
   - Analyte must be detected reliably and identified by the method-specific criteria and produce a signal that is at least 3 times the instrument's noise level (3:1 signal to noise ratio).
   - It is specific to each combination of analyte, matrix, method and instrument configuration.
   - The LOD must be verified quarterly on each instrument (spiked at LOD) using the criteria listed above.
3. If the LOD verification fails (per #2), repeat the detection limit determination and LOD verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.
4. The laboratory shall maintain documentation for all detection limit determinations and LOD verifications (regardless of pass or fail).

Note: Per DoD QSM and TNI Standard, it is not necessary to perform a MDL study when results are not to be reported below the LOQ/MRL.

11.13 Cleaning Tedlar Bags and Static Dilution Bombs

Tedlar Bags Fill with nitrogen and evacuate several times. In the final cleaning step partially fill the bags with nitrogen, heat at 60°C for 20 minutes, and evacuate using a pump.

Static Dilution Bombs Heat to 60°C for 30 minutes and purge for approximately 30 seconds from the liquid nitrogen dewer.

11.14 Method Modifications The modification for EPA Compendium Method TO-3 includes the fact that the analysis is conducted without cryogenic preconcentration. In addition, the sample is introduced onto the system using a manual injection technique with a gas-tight syringe.

Method ASTM D1945-03 references the use of a TCD or equivalent. An FID is used for this analysis. Additionally, the backflush procedure described in the ASTM D1945-03 method is not performed.

12) Quality Control Requirements and Corrective Action

12.1 This section of the standard operating procedure contains technical acceptance criteria and preferred corrective actions to data nonconformities. Corrective actions shall follow the procedures outlined in the *SOP for Nonconformance and Corrective Action*, where appropriate.

12.2 To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.3 It must be determined if there are any instrumentation problems contributing to the occurrence of any out of control data. If it is decided that problems do exist then the analyst must determine if the effects have caused any modification in the data from client submitted samples. This being the case, all samples (including QC) that are affected by instrumentation problems must be re-analyzed following any necessary maintenance activity.

12.4 Initial Calibration

12.4.1 Acceptance Criteria The percent relative standard deviation (%RSD) of the analytes of each of the levels must be less than 20% for the calibration to be considered acceptable.

12.4.2 Corrective Action If the initial calibration technical acceptance criteria are not met, inspect the system for possible sources. It may be necessary to change the column or take other corrective actions to meet the initial calibration technical acceptance criteria. Also, check standards for a bad injection and re-analyze standard. If a bad injection is not evident, perform maintenance and attempt another initial calibration (make notation in maintenance logbook regarding any steps taken). A demonstration of an in-control system is required before proceeding with the analysis.

Note: No ICAL may be interrupted by any maintenance procedure; therefore, all the ICAL standards must be reanalyzed.

12.5 Initial Calibration Verification Standard (ICV)

12.5.1 Acceptance Criteria The percent difference (%D) for each calculated target analyte must be within ±15% of the actual concentration of the standard.

12.5.2 Corrective Action If the initial calibration verification fails to meet the acceptance criteria, it should be re-analyzed. A second failed ICV must initiate corrective action and two consecutive standards must pass in order for the ICAL to be deemed acceptable. It may be necessary to prepare either new ICAL or ICV standards or both, perform maintenance and reanalyze the initial calibration.

12.6 Continuing Calibration Verification (CCV)

12.6.1 Acceptance Criteria The percent difference (%D) for each calculated target analyte must be within ±15% of the actual concentration.

12.6.2 Corrective Action If the criteria are not met, reanalyze (no more than two injections may be made before corrective action is initiated) or prepare a fresh CCV standard and reanalyze. If routine corrective action procedures fail to produce an acceptable calibration verification, a new initial calibration must be performed. However, sample data associated with unacceptable calibration verification may be reported as qualified data only under the following special condition:

> *When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the sample affected by the unacceptable CCV shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.*

DoD QSM REQUIREMENT: If a CCV fails, the laboratory must immediately analyze two additional consecutive CCVs (immediately is defined as within one hour).

- Both of these CCVs must meet acceptance criteria in order for samples to be reported without reanalysis.
- If either of these two CCVs fail or if the laboratory cannot immediately analyze two CCVs, the associated samples cannot be reported and must be reanalyzed.
- Corrective action(s) and recalibration must occur if the above scenario fails. All affected samples since the last acceptable CCV must be reanalyzed.
- Flagging data for a failed CCV is only appropriate when the affected samples cannot be reanalyzed. The laboratory must notify the client prior to reporting data associated with a failed CCV.

12.7 Method Blank

12.7.1 Acceptance Criteria The method blank result for any target analyte must not be greater than the method reporting limit or contribute more than 10% of the sample concentration.

For DoD and NAVSEA samples, the method blank will be considered to be contaminated if:

1. The concentration of any target analyte in the blank exceeds 1/2 the reporting limit and is greater than 1/10 the amount measured in any

sample or 1/10 the regulatory limit (whichever is greater);
2. The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
3. The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

The laboratory shall evaluate whether reprocessing of the samples is necessary based on the above criteria.

12.7.2 Corrective Action If the analyte results in the blank do not meet the acceptance criteria the source of the problem must be investigated and measures taken to eliminate the source. Determine whether the contamination is from the instrument or due to contamination in the nitrogen, syringe or other source. Regardless, appropriate corrective measures must be taken and documented before further sample analysis proceeds. *If the results are the same, the blank along with all associated samples must be reported to the client with the appropriate qualifier as specified in Section 16.*

12.8 Laboratory Control Sample (LCS)

12.8.1 Acceptance Criteria The percent recovery must be within the control limits designated in Attachment D (unless updated after the revision of this document, refer to the most current control limits). Fixed limits of 70-130 will be used if insufficient points are available to generate control charts.

NAVSEA Requirement: An LCS and LCS Duplicate must be analyzed per batch of 20 samples. All project analytes must recover within ±30% or within in-house limits (whichever is more stringent). The RPD between the LCS and LCS Duplicate must be ±15% or within in-house limits (whichever is more stringent).

12.8.2 Corrective Action If the LCS criteria are not met, determine whether the cause is instrumentation or the result of a poor injection. If the problem is instrumentation, perform maintenance and reanalyze the associated sample(s). If the problem is with the injection, reanalyze the LCS. If the results are still unacceptable and there does not appear to be any instrumentation problems refer to Section 16 for the appropriate reporting information.

12.9 Sample Analysis

Sample results must be quantitated from the current instrument initial calibration and may not be quantitated from any continuing calibration verification standard.

12.9.1 Acceptance Criteria The field samples must be analyzed along with a laboratory method blank that has met the blank criteria in Section 12.7. All target analyte peaks must be within the initial calibration range. The retention time of each target analyte must fall within the retention time window using the CCV as the absolute retention time. For range analysis, retention times from the most recent CCV shall be used to establish the range.

12.9.2 Corrective Action To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measures shall be reported with the appropriate data qualifier(s) as detailed in this document and the most current Quality Assurance Manual.

- When corrective actions are made, samples analyzed while the system was not functioning properly must be reanalyzed.
- Results not bracketed by initial instrument calibration standards (within calibration range) must be reported as having less certainty, e.g., defined qualifiers or flags.

12.10 Laboratory Duplicate

12.10.1 Acceptance Criteria The selected samples should be rotated among client samples whenever possible so that various matrix problems may be noted and/or addressed. Alternatively, a duplicate laboratory control sample may be analyzed to assess precision. The results must meet the relative percent difference criteria stated in Attachment D. A fixed RPD of 25 will be used if insufficient data points are available for control charts.

NAVSEA Requirement: A replicate injection of a field sample must be analyzed in addition to a duplicate laboratory control sample per batch of 20 samples. For field sample duplicates, when one or both results is >RL for a project analyte, the RPD must be ≤25%.

12.10.2 Corrective Action If the replicate results do not fall within the technical acceptance window, the sample should be re-analyzed. If the results are still unacceptable and there does not appear to be any matrix effects, interfering peaks, or instrument problems, the results for both injections shall be reported to the client with the appropriate qualifier as specified in Section 16.

12.11 Sample's Holding Time Expired

The client is to be notified (best attempt) that the sample's holding time was missed and the client is to decide if the sample analysis shall continue. The documentation of missed holding time and the client's decision to proceed must be included in the corresponding job file. A statement dictating all holding time occurrences must accompany the sample results in the final report.

13) Data Reduction and Reporting

13.1 Initial Calibration

The initial calibration curve must be saved with a two-character identification (C1) followed by the date of the analysis (mmddyy). This file shall be saved in an appropriate directory (J:\GC#\Method\). No curve may be overwritten at any time to ensure a complete audit trail.

- Tabulate the peak area along with standard concentration injected to determine the response factor (RF) for each analyte at each concentration using equation number 1.
- Calculate the percent relative standard deviation (%RSD) of the mean RF (equation number 2) for each analyte over the range of each concentration of the calibration standards using equation numbers 4 and 5.

13.2 Initial Calibration Verification

- Calculate the concentration for each analyte using equation number 3.
- Calculate the percent difference (%D) between the calculated concentration (equation number 3) and the actual concentration using equation number 6.

13.3 Continuing Calibration Verification

- Calculate the concentration of each analyte using equation number 3.
- Calculate the percent difference (%D) between the calculated concentration (equation number 3) and the actual concentration using equation number 6.

13.4 Laboratory Control Sample

- Calculate the concentration of each analyte using equation number 3.
- Calculate the percent recovery (%R) for each analyte using equation number 8.

13.5 Sample Analysis

- Calculate the concentration of each range using equation number 3.
- Calculate the dilution factor if necessary using equation number 9.

13.6 Laboratory Duplicate

- Calculate the concentration of each range using equation number 3.
- Calculate the relative percent difference (RPD) using equation number 7.

13.7 Calculations

13.7.1 Equation Number 1

Response Factor (RF)

The response factor, for analyte *x* is given by:

$$RF = \frac{A_x}{C_x}$$

where:

A_x = Area of the analyte in the standard

C_x = Concentration of the analyte in the standard

13.7.2 Equation Number 2

Average (or Mean) RF

$$\overline{RF} = \frac{\sum_{i=1}^{N} RF_i}{N}$$

where:

RF_i are the individual RFs from each concentration level in the initial calibration curve.

N is the number of calibration concentration levels.

13.7.3 Equation Number 3

Concentration (C):

$$C = \frac{Area}{\overline{RF}} \times \frac{D_{inj}}{A_{inj}}$$

where:

Area	is the area obtained from the chromatogram
$\overline{RF}$	Average (or Mean) RF of all concentration levels in the initial calibration curve
D_{inj}	default injection volume (mL)
A_{inj}	actual injection volume (mL)

13.7.4 Equation Number 4

Standard Deviation, SD:

$$SD = \sqrt{\sum_{i=1}^{N} \frac{\left(RF_i - \overline{RF}\right)^2}{N-1}}$$

where:

RF_i	are the individual RFs from each concentration level in the initial calibration curve.
$\overline{RF}$	Average (or Mean) RF of all concentration levels in the initial calibration curve.
N	total number of calibration concentration levels

13.7.5 Equation Number 5

Percent Relative Standard Deviation, %RSD:

$$\%RSD = \frac{SD}{\overline{RF}}(100)$$

where:

SD	Standard Deviation calculated in equation number 3
$\overline{RF}$	Average or Mean RF

13.7.6 Equation Number 6

Percent Difference, %D,

The %D is used for evaluating ICV and CCV vs. the initial calibration

$$\%D = \frac{C_{CCVorICV} - C_{std}}{C_{std}}(100)$$

where, for any given analyte:

$C_{CCVorICV}$ is the concentration being evaluated
C_{std} is the concentration from the current calibration curve

13.7.7 Equation Number 7

Relative Percent Difference (RPD)

$$\frac{|R_1 - R_2|}{\left(\frac{R_1 + R_2}{2}\right)} x100$$

where:

R_1 First measurement value
R_2 Second measurement value

13.7.8 Equation Number 8

Percent Recovery (%R):

$$\%R = \frac{C}{S} x100$$

where

C = Concentration of the analyte recovered
S = Spiked amount

13.7.9 Equation Number 9

Dilution Factor

$$DF = \frac{V_T}{V_S}$$

Where:

DF = dilution factor
V_S = volume of sample (mL) used
V_T = total volume of dilution (mL)

13.8 Data Review

The analyst must review data on a real time basis for all calibration and QC data. The QC data must be evaluated following the data review checklist in Attachment C. The data shall be reviewed and the sample results calculated and assessed by one analyst and reviewed by a second qualified analyst. The data review checklist shall be used to document the review process. Once it has been completed, the checklist must be initialed, dated and filed with each job file.

Initial calibrations must be reviewed in the same manner as QC data with all ICAL documentation retained in a separate file. Refer to the initial calibration checklist in Attachment B for the review guideline. The ICAL file must contain all the pertinent information stated in Section 11.3.4.

13.9 Reporting

The results of each test shall be reported clearly, unambiguously and objectively, and shall include all the information necessary for the interpretation of the test results. The analyst shall ensure that all of the requirements specified in this document and the *SOP for Data Review and Reporting*.

13.10 Sample Preparation and Analysis Observations / Case Narrative Summary Form

This form, which is included in the *SOP for Laboratory Storage, Analysis, and Tracking*, must be generated when there are any specific sample composition information, sample preparation, analysis issues and/or observations. In addition, during the analysis, specific identification information or problems, interferences, calibration issues, flags, and additional/expanded explanation of flags should be added to the form. This form may be modified as long as the sections and basic concepts are reserved.

This form is necessary as a means for documentation. This form, among other information, will be reviewed when compiling the final report and case narrative. All information regarding the job shall remain in the file, in order that sufficient documentation is available to recreate the job from sample receipt through preparation, analysis, data reduction, and reporting.

13.11 The initial calibration data must be stored in a quantitation method (on the server) using a unique filename and may not be overwritten at any time in order to maintain an accurate audit trail. There are multiple quantitation methods, which are subsets of the compound list in Attachment D. Therefore, files should be named with a two-character notation indicating the compound list and the date of the corresponding initial calibration. In addition, all data files including method blanks, continuing calibration verification, laboratory control samples and client submitted samples files shall be saved in a unique sub-directory on the server. An example of how the analyst should store analytical data is as follows:

Instrument Number/Data/Method ID/yr_month/.d*

* Injection (automatically assigned based on order of injection)

13.12 The essential information to be associated with analysis, such as computer data files, run logs, etc. shall include: Sample ID code, date of analysis, time of analysis, instrument

operating conditions/parameters (or reference to such data), analysis type, any manual calculations including dilutions and manual integrations, analyst's initials, sample preparation (pressure readings), standard and reagent origin, sample receipt, calibration criteria, frequency and acceptance criteria, data and statistical calculations, review, confirmation, interpretation, and assessment and reporting conventions.

13.13 Sufficient raw data records must be retained of the analysis, instrument calibrations and method detection limit studies including: analysis/calibration date and time, test method, instrument, sample identification, each analyte name, analyst's initials, concentration and response, and standards used for the analysis and calibrations, any manual calculations including sample dilutions and manual integrations. All information entered and reported on the quantitation report must be complete and accurate.

14) Method Performance

14.1 An on-going assessment of method performance is conducted in order to ensure that the laboratory is capable of reporting results which are acceptable for its intended use. Validation of the method is confirmed by the examination and provision of objective evidence that these requirements are met.

14.2 Method Detection Limit (MDL)

The procedure used to determine the method detection limits are as stated in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as defined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation*. The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. MDLs can be obtained using standards at a concentration of about 0.1ppm and making at least seven replicate measurements of the compounds of interest, computing the standard deviation, and multiplying this value by the appropriate Student's t value for 99 percent confidence.

The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. Refer to Section 11.12.1 for the LOD verification criteria.

Note: Per DoD QSM and TNI Standard, it is not necessary to perform a MDL study when results are not to be reported below the LOQ/MRL.

14.3 Accuracy and Precision

Refer to Section 12.10 for information on replicate precision criteria for method performance. Single laboratory accuracy is presented as the second source initial calibration verification standard, which meets the method performance criteria of 15%. Additionally, laboratory generated control limit data for LCSs are presented for the analytes of interest and may be referenced in attachment D. Refer to Section 11.4 for the accuracy and precision LOQ requirements.

14.4 Demonstration of Capability

This laboratory has continuously performed this method since before July 1999. Ongoing demonstration of capable shall be performed and documented; however, the initial demonstration of method capability is not required.

14.5 Proficiency Testing (PT) Program

Proficiency testing samples are not available from a third party for this method. Repeatability studies will be performed biannually to meet the DoD QSM proficiency testing requirements. A minimum of eight QC analyses performed over multiple days or

on the same day will be compiled. Statistical validity will be assessed by evaluating results against LCS control limits and an RSD of 15%.

15) Pollution Prevention and Waste Management

15.1 All waste management must be carried out in accordance with the requirements detailed in the *Simi Valley Lab Waste Management Plan*.

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 Analysis quality control results (CCV, MB, LD, and LCS recoveries) are out-of-control

If the associated samples are within holding time, re-analyze the sample. Alternatively, evaluate the effect on the sample results and report the results with qualifiers and/or discuss in the case narrative as detailed below.

16.1.1 CCV Refer to Section 12.6.2 for specific information on reporting data with an unacceptable continuing calibration verification standard (biased high).

16.1.2 Method Blank If an analyte in the blank is found to be out of control and the analyte is also found in associated samples, those sample results shall be "flagged" in the report. If the analyte is found in the blank but not in the sample and all other quality control meets acceptance criteria then the results for the sample may be reported without a qualifier. However, if other QC is out of control then an evaluation must be made and the results reported accordingly.

16.1.3 Laboratory Control Sample All samples processed with an out of control LCS will require re-analysis or data qualifiers to be attached to the analytical results.

16.1.4 Laboratory Duplicate The appropriate data qualifier must be included for results associated with an out-of-control laboratory duplicate and/or discussed in the case narrative.

16.2 Sample quality control results are out-of-control

Examine the sample results for matrix interference and for carryover. Reanalyze the sample(s) and/or reanalyze the sample(s) at a lower aliquot. If the out-of-control results are due to matrix interference, report the results with a matrix interference qualifier.

Holding time qualifiers must be included for those samples not analyzed within holding time.

17) Training

17.1 Training shall be conducted in accordance with the *SOP for Training Policy*. An initial demonstration of proficiency shall be performed prior to independent analyses of samples. In addition, a continuing demonstration must be performed annually. See Attachment A for the training plan.

17.2 Demonstration of Capability

Demonstrations are to be performed in accordance with the SOP stated above, TNI standard, and DoD QSM. Additionally, these demonstrations are performed anytime there is a change in instrument type, personnel, or method.

Once performance is found to be acceptable, a required certification statement must be completed by the QA Manager and either the immediate supervisor or Laboratory Manager and retained on file as a demonstration of compliance.

17.2.1 Quarterly Demonstration A demonstration of method sensitivity must be performed *quarterly on each instrument* performing this method.

1) A spike at the current LOD must be analyzed.

2) Verification of precision and bias at the LOQ must be performed.

Refer to Section 11.4 (LOQ) and 11.12.1 (LOD) for additional information on how these demonstrations are to be performed as well as the acceptance criteria.

17.2.2 Annual Demonstration Each analyst must perform this demonstration both initially and annually. Analyze four LCS standards (at 1-4x the MRL (LOQ) for initial) either concurrently or over a period of days as a verification of precision and bias of the quantitation range. The standard deviation (n-1) and average percent recovery of the four replicates are compared against current laboratory control limits for precision and bias. See attachment D.

17.2.3 Change in Personnel, Instruments, Method and/or Matrix The requirements in Sections 17.2.1 and 17.2.2 must be performed per the schedule noted and when there is a change in personnel, instruments, method or matrix. "Change" refers to any change in personnel, instrument, test method, or sample matrix that potentially affects the precision and bias, sensitivity, or selectivity of the output (e.g., a change in the detector, column type, matrix, or other components of the sample analytical system, or a method revision).

All attempts at this demonstration must be completed and turned into the QA department for retention.

18) Summary of Changes

Table 18.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
14.0	06/22/2019	C. Arend	Applied updated SOP formatting style to first two pages and header/footer. Sections renamed and reorganized to align with *SOP for Preparing Standard Operating Procedures*. Section references updated throughout.
			2.1 – removed "Summa"
			3.8 – added last sentence
			3.10 – added last sentence
			6.1 – updated reference
			7.3 – removed "Summa"
			9.5.1.1 – removed "Summa" and updated title of first SOP
			9.6.2 – removed "Summa"
			11.2.2 – revised second sentence; revised footnote 3 to clarify 10 field sample injections; added second sentence to footnote 7
			11.4 – added NAVSEA requirement
			11.5 – new section
			11.6 – clarified 10 field sample injections
			11.7 – added NAVSEA requirement
			11.9.2 – removed "Summa"

			11.9.4 – 2nd paragraph, 1st sentence – added >C6_3 as hexane
			11.10 – revised to clarify requirement and add NAVSEA requirement
			11.11 – Updated title of SOP
			12.7.1 – added "NAVSEA" to section
			12.8.1 – added NAVSEA requirement
			12.9.1 – added last two sentences
			12.10.1 – revised to clarify and added NAVSEA requirement
			Information previously in section 13 removed – redundant to information covered in section 12.
			15.1 – updated reference
			Information previously in section 17 removed – redundant to information covered in administrative SOPs.
			17.2.2 – revised 2nd sentence to add clarification
			19.2 – updated reference
			19.3 – updated reference
			19.4 – new reference
			20.1 – added Attachment 7
			Attachment 1 - #4 updated 3rd SOP title
			Attachment 2 – revised #5; #15 – updated SOP title
			Attachment 3 - #6 updated to clarify requirement; #7 added RT window requirement for target analytes; #8 revised to clarify and add requirement; #9 and #10 revised to include NAVSEA requirements; #11 revised to include NAVSEA/DoD requirement
			Attachment 4 – updated GC10 MDLs/MRLs and GC08 Control Limits
			Attachment 7 - new

19) References and Related Documents

19.1 EPA Compendium Method TO-3, "Method for the Determination of Volatile Organic Compounds in Ambient Air using Cryogenic Preconcentration Techniques and Gas Chromatography with Flame Ionization and Electron Capture Detection", Revision 1, April 1984.

19.2 DoD/DoE QSM, *Department of Defense (DoD), Department of Energy (DoE) Quality Systems Manual (QSM) for Environmental Laboratories*, Current Version.

19.3 TNI 2009 and 2016, Volume 1, *Management and Technical Requirements for Laboratories Performing Environmental Analysis*.

19.4 *Naval Sea Systems Command Laboratory Accreditation Program (LAP),* S0005-AC-TED-010, Revision 3, July 31, 2013.

20) Attachments

20.1 Attachments

Attachment 1 – Training Plan

Attachment 2 – Initial Calibration Checklist

Attachment 3 – Data Review Checklist

Attachment 4 – Target Analytes with Corresponding Method Reporting and Control Limits

Attachment 5 – Calibration Curve Concentrations (GC07 and GC08)

Attachment 6 – Calibration Curve Concentrations (GC10)

Attachment 7 – NAVSEA Method Specific Criteria

Attachment 1

Training Plan

Proprietary - Uncontrolled Copy

Training Plan for Analysis of C1 to C6 Hydrocarbons by GC/FID

Trainee _____ Trainer _____ Instrument _____

1. Read SOP (VOA-TO3C1C6) Trainer ____ Trainee ____ Date _____
2. Read Method: EPA Compendium Method TO-3 Trainer ____ Trainee ____ Date _____
3. Demonstrated understanding of the scientific basis of the analysis

   Gas chromatography Flame Ionization Detector Trainer ____ Trainee ____ Date _____
4. Demonstrated familiarity with related SOPs Trainer ____ Trainee ____ Date _____
   SOP for Batches and Sequences
   SOP for Making Entries onto Analytical Records
   SOP for Manual Integration
   SOP for Significant Figures
   SOP for Nonconformance and Corrective Action
   SOP for Performing MDL Studies and Establishing Limits of Detection and Quantitation
5. Observe performance of SOP Trainer ____ Trainee ____ Date _____
   ___sample preparation (gas-phase dilutions)
   ___standard preparation
   ___analytical sequence setup
   ___initial calibration and initial calibration verification
   ___continuing calibration verification
   ___sample analysis
   ___EnviroQuant introduction
   ___data reduction and reporting

6. Perform SOP with supervision Trainer ____ Trainee ____ Date _____
   ___sample preparation (gas-phase dilutions)
   ___standard preparation
   ___analytical sequence setup
   ___initial calibration and initial calibration verification
   ___continuing calibration verification
   ___sample analysis
   ___EnviroQuant use
   ___data reduction and reporting
7. Independent performance of the SOP Trainer ____ Trainee ____ Date _____
   ___sample preparation (gas-phase dilutions)
   ___standard preparation
   ___analytical sequence setup
   ___initial calibration and continuing calibration verification
   ___sample analysis
   ___EnviroQuant proficiency
   ___data reduction and reporting
   ___initial demonstration of competency
      ___ Four consecutive laboratory control samples
8. Instrument operation and maintenance Trainer ____ Trainee ____ Date _____
   ___gas chromatograph and capillary column installation
   ___detector (FID) setup and maintenance
   ___data system

Attachment 2

Initial Calibration Checklist

Analysis: C1-C6+ per TO-3 Mod

ICAL Date: _____

Instrument: ☐GC7 ☐GC8 ☐GC10 ☐GC___

Initial Calibration Checklist

Analyst **Reviewer**

☐ 1. Is the required documentation in the ICAL file? ☐
- ☐ Sequence report ☐
- ☐ Blank analysis Quantitation Report ☐
- ☐ Calibration Status Report (aka Calibration History) – Initial ☐
- ☐ Response Factor Report ☐
- ☐ Quantitation Report for each calibration standard (including manual integration documentation – before and after printouts) ☐
- ☐ ICV Quantitation Report and Evaluate Continuing Calibration Report (aka Percent Diff. report) ☐

☐ 2. Was the ICAL performed continuously (i.e., not interrupted for maintenance or sample analysis)? ☐

☐ 3. Was the ICAL performed within 24 hours? ☐

☐ 4. Were the standards analyzed from low concentration to high concentration? ☐

☐ 5. Are all the analytes in the blank analysis ≤1/2 MRL? ☐

☐ 6. Does each analyte's ICAL include a minimum of 5 consecutive concentrations? ☐

☐ 7. For each analyte, is there only one value used for each calibration level? ☐

☐ 8. If a point is dropped, is information noted in the ICAL explaining the reason? ☐

☐ 9. Does this follow the laboratory's point dropping policy (including re-analysis within 24 hrs)? ☐

☐ 10. For each analyte, is the lowest standard's concentration at or below the MRL? ☐

☐ 11. For each analyte, does the ICAL include 5 consecutive levels? ☐

☐ 12. For each analyte, are there no levels skipped? ☐

☐ 13. Does the calibration curve give a %RSD of <20%? ☐

☐ 14. For the ICV analysis, is the percent recovery for each analyte 85-115%? ☐

☐ 15. Are all peak integrations including manual integrations (per *SOP for Manual Integration*) acceptable? *If so, initial and date the appropriate pages.* ☐

COMMENTS:

_____

_____

_____

Analyst _____ Secondary Reviewer _____

Date _____ Date _____

Attachment 3

Data Review Checklist

C1-C6 per Modified EPA Method TO-3
Data Review Checklist

Analysis Date _____ Instrument ☐GC7 ☐GC8 ☐GC10 ☐GC___

Client _____ QC level _____

Project # _____ Due Date _____

Analyst **Reviewer**

Initial Calibration

☐ 1. Referenced ICAL the most recent ICAL performed? ☐
2. Referenced ICAL peer reviewed and all associated documentation including the ICAL review checklist available for review? ☐
3. All associated requirements within the specified limits? ☐

Continuing Calibration

☐ 4. CCV raw data submitted? ☐
☐ 5. Was the %D for the CCV ±15% between the calculated and actual concentration? ☐
☐ 6. Was a CCV analyzed at the beginning of the sequence, every 10 sample injections and the end of the sequence? ☐

Sample Data

☐ 7. Is all sample data present and correct? ☐
___Sample raw data?
___All target analyte responses within calibration range?
___All peak integrations acceptable?
___All manual integrations flagged and properly documented?
If so, initial and date.
___All target analyte retention times within generated RT window?
___All calculations correct?
___First quantitation report initialed and dated by analyst?

QC Data

☐ 8. Duplicate sample / DLCS analyzed 1 per 20 or fewer samples? (NAVSEA – client sample duplicate required in addition to DLCS) ☐
☐ 9. Lab Dup - For analyte concentrations >10x the MRL, is the RPD acceptable? (NAVSEA >MRL) ☐ (within the lab generated limits or 25% if lab generated limits not available)
☐ 10. LCS % recoveries within lab generated limits? (70-130% if lab generated limits not available) ☐
NAVSEA: LCS/LCSD ±30% or within in-house limits (whichever is more stringent).
RPD between LCS/LCSD must be ±15% or within in-house limits (whichever is more stringent).
☐ 11. All the analytes in the MB <MRL? (NAVSEA & DoD: ≤1/2 MRL) ☐

Reporting Information

☐ 12. Sample Prep and Analysis Observations/Case Narrative Summary completed if applicable? ☐
☐ 13. Appropriate flags indicated on a Sample Prep and Analysis Observations/Case Narrative Summary form if applicable? ☐
☐ 14. **DOD:** Are manual integrations notated in the case narrative? ☐

COMMENTS:

_____

☐ LIMS Run Approval ☐ LIMS Supervisor Approval

Analyst _____ Reviewer _____

Date _____ Date _____

Attachment 4

Target Analytes with Method Reporting and Control Limits

Target Analytes with Method Detection Limits, Method Reporting Limits and Control Limits
EPA Compendium Method TO-3 (Modified) for the Analysis of C_1-C_6+

ANALYTE	GC8 MDL ppm (mg/m3)	GC8 MRL ppm (mg/m3)	GC10 MDL ppm	GC10 MRL ppm
Methane	0.11 (0.072)	0.50 (0.33)	0.28	1.0
Ethene	N/A	N/A	0.074	0.30
Ethane	0.057 (0.070)	0.50 (0.61)	0.042	0.30
Propene (Propylene)	N/A	N/A	0.052	0.30
Propane	0.055 (0.099)	0.50 (0.90)	0.046	0.30
Acetylene	N/A	N/A	0.034	0.25
Butane	0.044 (0.10)	0.50 (1.2)		
Pentane	0.049 (0.14)	0.50 (1.5)		
Hexane	0.064 (0.23)	0.50 (1.8)		
C6+	N/A	1.0 (3.5)		
TGNMO as Hexane	N/A	0.17 (0.60)[1]		
TGNMO as Methane	N/A	1.0		
TVPH as Hexane	N/A	0.17 (0.60)[1]		
TVPH as Methane	N/A	1.0		
NMOHC as Hexane	N/A	0.17 (0.60)[1]		
NMOHC as Methane	N/A	1.0		

[1] The MRL is based on the MRL for C6+/6 and converted to mg/m3.

Note 1: The method detection and reporting limits may change with each new MDL study and ICAL performed, check the current documentation for verification.

Note 2: The terms TGNMO, TVPH, and NMOHC are interchangeable.

CONTROL LIMITS (GC8)

Analyte	LCS - LCL (%R)	LCS -UCL (%R)	LD (RPD)
Methane	94	110	6
Ethane	91	113	11
Propane	94	120	14
Butane	91	121	17
Pentane	86	118	19
Hexane	87	126	21
>C_6	N/A	N/A	30*

* = Fixed Limit

Note: New limits may be established prior to the revision of this document, refer to the most recent control limits.

Attachment 5

Calibration Curve Concentrations

GC07 and GC08

Calibration Curve Concentrations (ppm unless noted as %)						
ICAL	Methane	Ethane	Propane	n-Butane	n-Pentane	n-Hexane
1	0.5	0.5	0.5	0.5	0.5	0.5
2	2	2	2	2	2	2
3	50	50	50	50	50	50
4	500	500	500	500	500	500
5	1000	1000	1000	1000	1000	1000
6	2000	2000	2000	2000	2000	
7	3%					
8						5000

ICAL	Amount of standard spiked onto instrument
1	0.05 ml of a 10ppm C1 to C6 standard[1]
2	0.2 ml of a 10ppm C1 to C6 standard[1]
3	0.05 ml of a purchased 1000ppm C1 to C6 standard (see section 9.4.1.1)
4	0.5 ml of a purchased 1000ppm C1 to C6 standard (see section 9.4.1.1)
5	1.0 ml of a purchased 1000ppm C1 to C6 standard (see section 9.4.1.1)
6	2.0 ml of a purchased 1000ppm C1 to C6 standard (see section 9.4.1.1)
7	0.75 ml of a purchased 4% methane standard

[1]10ppm standard is made by introducing 10 ml of a purchased 1000ppm standard into 990 ml of nitrogen in a Tedlar bag.

Note: An approximate 5000ppm n-hexane standard can made by introducing 30ul of 99%+ n-Hexane into 1 liter of nitrogen in a Tedlar bag. The calculation is as follows with the following constants. The density of n-hexane is 0.6548mg/ul. The gas constant is 24.46L/mole at 25degrees C and 1 atm. The molecular weight of n-hexane is 86.18g/mole.

30ul * 0.6548mg/ul = 19.644mg (spike into 1 liter) = 19.644mg/L
19.644mg/L * 1000L/m3 = 19644mg/m3
19644mg/m3 * 24.46 / 86.18 = 5575ppm

The Calibration Curve Concentrations Define the Calibration Range	
Methane	0.5ppm – 30000ppm
Ethane	0.5ppm – 2000ppm
Propane	0.5ppm – 2000ppm
n-Butane	0.5ppm – 2000ppm
n-Pentane	0.5ppm – 2000ppm
n-Hexane	0.5ppm – 2000ppm

Attachment 6

Calibration Curve Concentrations

GC10

Calibration Curve Concentrations (ppm unless noted as %)					
ICAL	Methane	Ethene	Ethane	Propene	Propane
1	0.2	0.1	0.1	0.1	0.1
2	0.4	0.2	0.2	0.2	0.2
3	0.8	0.4	0.4	0.4	0.4
4	1.5	1.5	1.5	1.5	1.5
5	7.5	7.5	7.5	7.5	7.5
6	50	25	25	25	25
7	125	125	125	125	125
8	625	625	625	625	625
9	4%				
10	5%				
11		5%			
12			5%		
13				5%	
14					5%

ICAL	Amount of standard spiked onto instrument
1	100ul of a 2ppm/1ppm MEEPP standard[1]
2	200ul of a 2ppm/1ppm MEEPP standard[1]
3	400ul of a 2ppm/1ppm MEEPP standard[1]
4	100ul of a 15ppm MEEPP standard
5	500ul of a 15ppm MEEPP standard
6	1ml of a 50ppm/25ppm MEEPP standard
7	100ul of a 1250ppm ME standard
8	500ul of a 1250ppm MEEPP standard
9	500ul of a purchased 4% Methane standard
10	50ul of a purchased 100% Methane standard
11	50ul of a purchased 100% Ethene standard
12	50ul of a purchased 100% Ethane standard
13	50ul of a purchased 100% Propene standard
14	50ul of a purchased 100% Propane standard

[1]2ppm/1ppm standard is made by introducing 1.25 ml of a standard that is 200ppm methane and 100ppm all other analytes into a 125ml glass dilution bottle with UHP Helium.

The Calibration Curve Concentrations Define the Calibration Range	
Methane	0.2ppm – 50000ppm
Ethene	0.1ppm – 50000ppm
Ethane	0.1ppm – 50000ppm
Propene	0.1ppm – 50000ppm
Propane	0.1ppm – 50000ppm

ICAL	Acetylene	Amount of Standard Spiked onto Instrument
1	0.075ppm	250ul of a 0.3ppm standard
2	0.15ppm	500ul of a 0.3ppm standard
3	1.5ppm	100ul of a 15ppm standard
4	7.5ppm	500ul of a 15ppm standard
5	15ppm	1ml of a 15ppm standard

Attachment 7

NAVSEA Method Specific Criteria

NAVSEA Method Specific Criteria		
Quality Control Element	**Minimum Frequency**	**Acceptance Criteria**
Sample Batch	Every sample and QC sample	Samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents/gas standards. An analytical batch is composed of prepared samples which are analyzed together as a group with a single analytical sequence. The number of field samples in an analytical sequence must not exceed 20. Note: In addition to field samples, each batch must contain batch QC samples (Method Blank, LCS, and LCS Duplicate) that are prepared using the glass bottles and treated in exactly the same manner as field samples).
Sample Container	Every sample and field QC sample	Bottle-Vac™ Sampler
Laboratory Reporting Limit Verification	Annual and when significant changes that may affect quality have been made to the SOP or instrument.	A glass bottle that is spiked with all project analytes at concentrations up to two times the laboratory reporting limit (RL). Recoveries must be within ± 30% of their true concentration.
Initial Calibration Curve	At initial set-up of the method and as needed by the failure of a calibration standard (second source calibration verification or CCV), major changes in instrumentation, or instrument run parameters (e.g., ramp rates, injection volume)	At a minimum 5 standards must be used. If a quadratic fit is used, a minimum of 6 standards must be used. Omission of a calibration point within the calibration range is not allowed without technical justification. The lowest calibration standard must be ≤ the RL. The laboratory's RL must be ≤ the project's RL. The RSD of the calibration curve for each target analyte must be < 20%. If not, the correlation coefficient of the calibration curve must be ≥ 0.990.
Second Source Calibration Verification	After each initial calibration, before any samples or QC samples are analyzed	Must include all analytes found in the initial calibration. All analytes must recover within ± 15% of their true concentration
Retention Time (RT)	Evaluated in all standards, blanks, batch QC samples, and field samples. Established at method set-up and whenever there are changes to GC	RT window widths must be set as ±3 times standard deviation for each target analyte using corresponding retention times from the ICAL as various standard concentrations, or 0.03 minutes, whichever is greater. For range analysis, RTs from the most recent CCV shall be used to establish the range.

NAVSEA Method Specific Criteria		
Quality Control Element	**Minimum Frequency**	**Acceptance Criteria**
	conditions, a new column is installed, or when a standard falls outside the previously generated windows.	
Continuing Calibration Verification (CCV)	On days when an initial calibration is not analyzed, before samples and batch QC samples are analyzed and after every ten (10) field samples. All samples and QC samples must be bracketed by a passing second source calibration verification standard and passing CCV for the first samples following a calibration curve, and bracketed by two passing CCVs for all brackets thereafter.	Each project analyte must recover within ±15% of its true concentration.
Instrument Blank (IB)	Prior to initial calibration and daily, when in use, prior to sample analysis	The concentration of each project analyte must be ≤ ½ the laboratory RL.
Method Blank (MB)	One per batch of 20 or fewer samples	Zero air contained in a Bottle-Vac™ Sampler. The concentration of each project analyte must be ≤ ½ the RL and no greater than 1/10 the amount measured in any sample, or 1/10 the regulatory limit, whichever is greater. Results must be reported with field sample results.
Laboratory Control Sample (LCS)	One per batch of 20 or fewer samples	All project analytes must recover within ±30% or within in-house limits (whichever is more stringent). Results must be reported with field sample results.
LCS Duplicate	One per batch of 20 or fewer samples	All project analytes must recover within ±30% or within in-house limits (whichever is more stringent). The RPD between the LCS and LCS Duplicate must be ±15% or within in-house limits (whichever is more stringent).

NAVSEA Method Specific Criteria		
Quality Control Element	**Minimum Frequency**	**Acceptance Criteria**
		Results must be reported with field sample results.
Laboratory Replicate (LR)	One per batch of 20 or fewer samples	Replicate injection of one field sample. When one or both results is > RL for a project analyte, the RPD must be ≤ 25%. Results must be reported with field sample results.

Analyte	Program Limit (ppm)	CAS #
Methane	25	74-82-8
Ethane	50	74-84-0
Ethene	20	74-85-1
Propane	10	74-98-6

APPENDIX D-9

ALS ENVIRONMENTAL WINNIPEG, SOPS

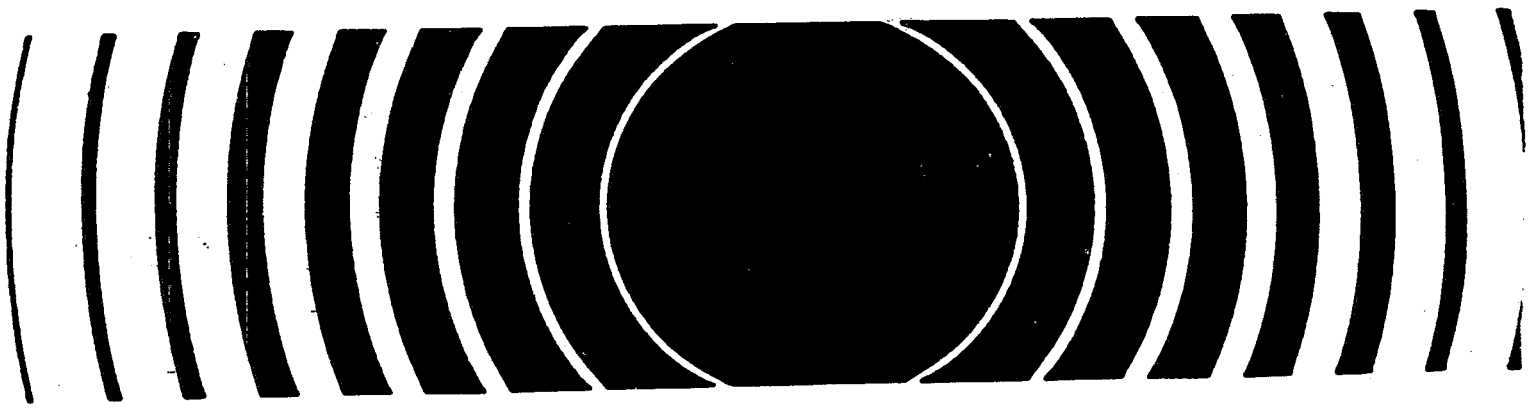
United States
Environmental Protection
Agency

Air and
Radiation
(6604J)

EPA 402-R-92-004
July 1992

EPA

Indoor Radon And Radon Decay Product Measurement Device Protocols



EPA-402-R-92-004

INDOOR RADON AND RADON DECAY PRODUCT MEASUREMENT DEVICE PROTOCOLS

July 1992

Prepared for:

U.S. Environmental Protection Agency
Office of Radiation Programs (6604-J)
401 M Street, S.W.
Washington, D.C. 20460

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
AIR AND RADIATION

12/1/92

MEMORANDUM

Subject: Corrections to the Document "Indoor Radon and Radon Decay Product Measurement Device Protocols" (EPA 402-R-92-004).

From: Tom Peake Tom Peake
EPA Radon Division (6604J)

To: Users of the "Indoor Radon and Radon Decay Product Measurement Device Protocols"

The 1992 document, "Indoor Radon and Radon Decay Product Measurement Device Protocols" (EPA 402-R-92-004; National Technical Information Service PB-92-206-176), updates and replaces the 1989 document, "Indoor Radon and Radon Decay Product Measurement Protocols" (EPA 520/1-89-009). Please note that there are two corrections, and they are discussed below. In addition, the corrected pages are attached.

Correction 1.

On page 2-3, continuous radon monitor section 2.1.7.2, the sentence, "The CR monitor should be programmed to run continuously, recording periodically (hourly or more frequently) the radon concentration for at least 48 hours" should be changed to "The CR monitor should be programmed to run continuously, recording periodically the radon concentration for at least 48 hours."

Correction 2.

The EPA document listed in the reference section, page R-4, as "Protocols for Radon and Radon Decay Product Measurements in Homes" is not a final document as of October 28, 1992. It should be listed as (Summer Draft) "Protocols for Radon and Radon Decay Product Measurements in Homes."

Attachment

CONTENTS

Section 3: INDOOR RADON DECAY PRODUCT MEASUREMENT DEVICE PROTOCOLS

LIST OF EXHIBITS

DISCLAIMER

Mention of trade names or commercial products in this document does not constitute EPA endorsement or recommendation for their use.

ACKNOWLEDGEMENTS

This document represents the cumulative efforts of many dedicated individuals within the radon measurement community and the U.S. Environmental Protection Agency. Several key components of this document were prepared by the authors acting as interpreters of the substantial field experience and technical knowledge provided by these individuals, and their assistance is gratefully acknowledged.

SIGNIFICANT CHANGES IN THIS REVISION

This protocol document updates and supersedes the U.S. Environmental Protection Agency (EPA) document entitled, "Indoor Radon and Radon Decay Product Measurement Protocols," and issued in March, 1989 (U.S. EPA 1989a). The updating reflects new information, new procedures, and new measurement devices, including a new interim protocol for unfiltered track detectors. The EPA's testing recommendations are summarized in Section 1.2. This measurement strategy reflects the changes made in the most recent edition of "A Citizen's Guide to Radon" (U.S. EPA 1992a). More information is also provided in the EPA measurement guidance document, "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c). Guidance on radon measurements in schools and for real estate transactions is also available (U.S. EPA 1989b, 1992b).

This edition contains some clarifications and new information on quality assurance. The addition of a Glossary provides definitions and formulas for several of the technical terms used in the document, including accuracy, precision, and the values used to quantify these parameters.

The two previous editions of these protocols (U.S. EPA 1986, 1989a) used the value coefficient of variation (COV), defined as the standard deviation divided by the mean, as the expression used for the goal (at 4 pCi/L or 0.02 WL) of 10 percent for precision. The COV should decrease with increasing concentration. This edition explains that there is a variety of ways to calculate and express precision, including the COV and the relative percent difference, defined as the difference between two duplicates divided by their mean. It is important to monitor precision over the entire range of radon levels that are encountered routinely in the measurement program, and that a systematic and documented method for evaluating changes in precision be part of the standard operating procedures. While a limited precision error is desirable (e.g., COV of $\leq$ 10% at 4 pCi/L), it is most important to maintain the total error of any individual device (including both errors in precision and accuracy) to within $\pm$ 25 percent of the "true" radon or decay product concentration for concentrations at or above 4 pCi/L (0.02 Working Levels when the equilibrium ratio is 0.5).

To limit errors in accuracy, this edition recommends that users calibrate their measurement systems at least once every 12 months. Participation in the National Radon Measurement Proficiency (RMP) Program will not satisfy the need for annual calibration, as this Program is a performance test, not a calibration procedure.

The 1986 and 1989 versions of the measurement protocols recommended that known exposure measurements, or spikes, be conducted at a rate of a few percent of the total number of measurements. These measurements are those for which the detectors are exposed to a known radon concentration in a calibration chamber and analyzed routinely. The results are used to monitor the accuracy of the entire system. This edition clarifies

this recommendation, specifying that spikes be conducted at a rate of three per 100 measurements, with a minimum of three per year and a maximum required of six per month. This reduces the number of spikes necessary for large users and clarifies the need for spikes by all users.

A significant change in this version of the Measurement Protocols is the requirement that all devices used for measurements in homes, schools, or workplaces be deployed for a minimum of 48 contiguous hours. It is important to understand that this minimum measurement period applies to all cases when the result of the measurement is given to a homeowner or building official to determine the need for further measurements or remedial action. The exceptions to the 48-hour measurement period are for those cases when the results will not be reported to a homeowner or building official, but will be used by a mitigator or researcher within the context of their project or research. For example, in-progress diagnostic measurements made in the process of performing mitigation can help to determine points of radon influx. Results of these measurements will be used to assist the contractor to better understand the dynamics of radon within that building, and will be part of a series of measurements, including pre- and post-mitigation 48-hour measurements. Radon researchers testing the effects of mitigation techniques, measurements methods, or strategies may also need to perform measurements of flexible durations.

The Agency has implemented a requirement for a minimum measurement period for several reasons. First, it will help ensure consistency among measurement programs, thereby ensuring that measurement results of at least a minimum quality become the basis for decisions by homeowners, school officials, and others responsible for authorizing further measurements or mitigation. This will become increasingly important as radon is measured in more and different types of buildings, and as a more diverse group of people, many without technical backgrounds, find the need to compare and understand these results. Second, a minimum measurement period will guarantee that a certain number of hours, including daily radon cycles, will be incorporated into the result reported to the persons responsible for making a decision about that building.

A period of 48 hours for the minimum measurement period is a policy decision that was arrived at after careful scrutiny of the possible options. It is important that the complete measurement result includes the effects of daily fluctuations in radon levels, so the minimum period needed to be a multiple of a 24-hour day. The Agency deems a single 24-hour period as too short because of the possibility of unforeseen circumstances occurring during the 24 hours; this possibility is diminished if two 24-hour periods form the duration of the measurement. One possible unforeseen circumstance is the improper implementation of closed-building conditions. A longer measurement period increases the chance of identifying such occurrences and helps minimize their impact. Finally, it was deemed important to include two daily cycles so that periods of low and high radon concentrations are well represented in the overall result.

There may be some situations when it is impossible to terminate the measurement at exactly 48 hours; therefore, a grace period of two hours will be allowed. A measurement made over a period of at least 46 hours is sufficient and is considered a two-day measurement. This grace period applies to all measurement methods.

Concerns have been raised regarding the requirement of a minimum distance of 30 inches from the floor for placement of detectors. The change from 20 inches to 30 inches was made in the March 1989 Protocols (U.S. EPA 1989a). This distance is not thought to be critical, so this version again recommends a minimum distance of at least 20 inches. In addition, the 1989 edition was not specific regarding the minimum distance between the measurement location and an exterior wall; this revision clarifies that distance to be about one meter, or three feet. Suspended detectors should also be about six to eight feet above the floor (i.e., within the general breathing zone).

Sections 2.6 (Evacuated Scintillation Cells), 2.7 (Pump/Collapsible Bags), and 2.8 (Radon Grab Sampling) of the previous protocol document (U.S. EPA 1989a) describe methods that share common features. For this reason, the three measurement methods are combined into one section in this revision. In addition, the Appendices A and B of the previous document are now part of their corresponding protocols. The radon grab sampling and pump/collapsible bags methods are not appropriate for purposes of determining the need for further measurements or for mitigation because they do not comply with the 48-hour minimum measurement period.

This revision also reflects the method designations used in the National RMP Program. A two letter code for each method has been adopted, although ATDs (AT), RPISUs (RP), and EICs/ECs (ES or EL) may still be referred to by their traditional acronyms. The new designations are as follows:

RADON AND RADON DECAY PRODUCT MEASUREMENT METHODS

METHOD CATEGORY	Abbreviations	
	Common	RMP Method
Continuous Radon Monitors	CRM	CR
Alpha Track Detectors	ATD	AT
Electret Ion Chambers Short Term Long Term	EIC/EC	 ES EL
Activated Charcoal Adsorption Devices (formerly called charcoal canisters)	CC	AC
Charcoal Liquid Scintillation	CLS	LS
Three-day Integrating Evacuated Scintillation Cells		SC
Pump/Collapsible Bag Devices (24 hour sample)		PB
Grab Radon Sampling Scintillation Cells Activated Charcoal Pump-Collapsible Bag		 GS GC GB
Unfiltered Track Detectors	UTD	UT
Continuous Working Level Monitors	CWLM	CW
Radon Progeny Integrating Sampling Units	RPISU	RP
Grab Sampling - Working Level		GW

Section 1: GENERAL CONSIDERATIONS

1.1 INTRODUCTION AND BACKGROUND

The risk of lung cancer due to exposure to radon and its decay products is of concern to State and Federal health officials. There is increased awareness that indoor radon concentrations may pose a significant health threat, and that there are areas in the country where some indoor levels are such that even short-term exposures can cause a significant increase in risk. It is extremely important that homes and other buildings be tested to determine if elevated radon levels are present indoors. However, in the process, the collection of unreliable or misleading data must be avoided.

There are many Federal, State, university, and private organizations now performing measurements or planning measurement programs. It is important for these different groups to follow consistent procedures to assure accurate and reproducible measurements, and to enable valid intercomparison of measurement results from different studies.

The objective of this document is to provide information, recommendations, and technological guidance for anyone providing measurement services using 15 radon and radon decay product measurement methods. The EPA has evaluated these techniques and found them to be satisfactory. However, the Agency has not conducted large-scale field tests using the unfiltered track detection technique, and an interim protocol has been prepared with the assistance of researchers who have field experience with this method. As the EPA and others acquire more experience with this interim technique, the guidelines may be revised.

These Protocols provide method-specific technological guidance that can be used as the basis for standard operating procedures. In keeping with good laboratory practices, each radon measurement company should develop its own detailed instrument-specific procedures that incorporate recommendations found in this and other radon-related EPA protocol and guidance documents. Mere duplication of sections of this report will not constitute an adequate standard operating procedure.

The recommendations contained in this report are similar to those being developed by industry and other groups (e.g., the American Society of Testing and Materials [ASTM 1991] and the American Association of Radon Scientists and Technologists [AARST 1991a]). This report is a guidance document; however, one condition of participation in the EPA National Radon Measurement Proficiency (RMP) Program is conformance with these protocols.

1.2 GENERAL GUIDANCE ON MEASUREMENT STRATEGY, MEASUREMENT CONDITIONS, DEVICE LOCATION SELECTION, AND DOCUMENTATION

1.2.1 Measurement Strategy

The choice of measurement strategy depends upon the purpose of the radon measurement and the type of building where the measurement is made, such as a home, school or workplace. EPA's recommendations for measuring radon in various situations are outlined in documents such as the second edition of "A Citizen's Guide to Radon" (U.S. EPA 1992a), the EPA "Home Buyer's and Seller's Guide to Radon" (U.S. EPA 1992b), the "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c), and in "Radon Measurements in Schools: An Interim Report" (U.S. EPA 1989b). The following discussion on measurement conditions, device location selection, and documentation apply to measurements made in all types of buildings.

1.2.2 Measurement Conditions

The following conditions should exist prior to and during a measurement period to standardize the measurement conditions as much as possible. This list may be applied to each of the measurement methods discussed in Sections 2 and 3. However, there may also be method-specific conditions that are mentioned in the applicable protocol.

- Short-term measurements lasting 90 days or less should be made under closed-building conditions. To the extent reasonable, all windows, outside vents, and external doors should be closed (except for normal entrance and exit) for 12 hours prior to and during the measurement period. Normal entrance and exit includes opening and closing a door, but an external door should not be left open for more than a few minutes. These conditions are expected to exist as normal living conditions during the winter in northern climates. For this reason, short-term measurements should be made during winter periods whenever possible.

- In addition to maintaining closed-building conditions during the measurement, closed-building conditions for 12 hours prior to the initiation of the measurement are a required condition for measurements lasting less than four days, and are recommended prior to measurements of up to a week in duration.

- Internal-external air exchange systems (other than a furnace) such as high-volume attic and window fans should not be operating during measurements and for at least 12 hours before measurements are initiated. Air conditioning systems that recycle interior air may be operating. Normal

operation of permanently installed air-to-air heat exchangers may also continue during closed-building conditions.

- In buildings where permanent radon mitigation systems have been installed, these systems should be functioning during the measurement period.

- Short-term tests lasting just two or three days should not be conducted if severe storms with high winds (e.g., > 30 mph) or rapidly changing barometric pressure are predicted during the measurement period. Weather predictions available on local news stations can provide sufficient information to determine if these conditions are likely.

- In southern climates, or when measurements must be made during a warm season, the closed-building conditions are satisfied by meeting the criteria listed above. The closed-building conditions must be verified and maintained more rigorously, however, when they are not the normal living conditions.

1.2.3 Measurement Device Location Selection

The following criteria should be applied to select the location of the detector within a room. For further guidance on selecting an appropriate area in a building in which to place the measurement device, the reader should refer to the relevant documents mentioned in section 1.2.1. The following list may be applied to each of the measurement methods discussed in Sections 2 and 3. However, there may be method-specific location criteria that will be mentioned in the applicable protocol.

- A position should be selected where the detector will not be disturbed during the measurement period and where there is adequate room for the device.

- The measurement should not be made near drafts caused by heating, ventilating and air conditioning vents, doors, fans, and windows. Locations near excessive heat, such as fireplaces or in direct sunlight, and areas of high humidity should be avoided.

- The measurement location should not be within 90 centimeters (3 feet) of windows or other potential openings in the exterior wall. If there are no potential openings (e.g., windows) in the exterior wall, then the measurement location should not be within 30 centimeters (1 foot) of the exterior walls of the building.

- The detector should be at least 50 centimeters (20 inches) from the floor, and at least 10 centimeters (4 inches) from other objects. For those detectors that may be suspended, an optimal height for placement is in the general breathing zone, such as 2 to 2.5 meters (about 6 to 8 feet) from the floor.

- In general, measurements should not be made in kitchens, laundry rooms, closets, or bathrooms.

1.2.4 Documentation

The operator of the measurement device must record enough information about the measurement in a permanent log so that data interpretation and comparison can be made.

The results of radon decay product measurements should be reported in Working Levels (WL). If the WL value is converted to a radon concentration which is also reported to a homeowner, it should be stated that this approximate conversion is based on a 50 percent equilibrium ratio. In addition, the report should indicate that this ratio is typical of the home environment, but any indoor environment (especially in schools and workplaces) may have a different and varying relationship between radon and decay products.

The following list may be applied to each of the measurement methods discussed in Sections 2 and 3. However, there may be method-specific documentation requirements that will be mentioned in the applicable protocol.

- The start and stop times and dates of the measurement;
- Whether the standardized measurement conditions, as discussed in Section 1.2.2, are satisfied;
- The exact location of the device, on a diagram of the room and building if possible;
- Other easily obtained information that may be useful, such as the type of building and heating system, the existence of a crawl space or basement, the occupants' smoking habits, and the operation of humidifiers, air filters, electrostatic precipitators, and clothes dryers;
- The serial number and manufacturer of the detector, along with the code number or description which uniquely identifies customer, building, room, and sampling position; and
- The condition (open or closed) of any crawl space vents.

1.3 QUALITY ASSURANCE

The objective of quality assurance is to ensure that data are scientifically sound and of known precision and accuracy. This section discusses the four general categories of quality control measurements; specific guidance is provided for each method in the relevant section.

Anyone providing measurement services using radon and radon decay product measurement devices should establish and maintain quality assurance programs. These programs should include written procedures for attaining quality assurance objectives and a system for recording and monitoring the results of the quality assurance measurements described below. The EPA offers general guidance on preparing quality assurance plans (U.S. EPA 1980); a draft standard prepared by a radon industry group is also available (AARST 1991b). The quality assurance program should include the maintenance of control charts and related statistical data, as described by Goldin (Goldin 1984) and by the EPA (U.S. EPA 1984).

1.3.1 Calibration Measurements

Calibration measurements are samples collected or measurements made in a known radon environment, such as a calibration chamber. Detectors requiring analysis, such as charcoal canisters, alpha track detectors, electret ion chambers, and radon progeny integrating samplers, are exposed in a calibration chamber and then analyzed. Instruments providing immediate results, such as continuous working level and radon monitors, should be operated in a chamber to establish individual instrument calibration factors.

Calibration measurements must be conducted to determine and verify the conversion factors used to derive the concentration results. These factors are determined normally for a range of concentrations and exposure times, and for a range of other exposure and/or analysis conditions pertinent to the particular device. Determination of these calibration factors is a necessary part of the laboratory analysis, and is the responsibility of the analysis laboratory. These calibration measurement procedures, including the frequency of tests and the number of devices to be tested, should be specified in the quality assurance program maintained by manufacturers and analysis laboratories.

Known exposure measurements or spiked samples consist of detectors that have been exposed to known concentrations in a radon calibration chamber. These detectors are labeled and submitted to the laboratory in the same manner as ordinary samples to preclude special processing. The results of these measurements are used to monitor the accuracy of the entire measurement system. Suppliers and analysis laboratories should provide for the blind introduction of spiked samples into their measurement processes and the monitoring of the results in their quality assurance programs. Providers of passive measurement devices should conduct spiked measurements at a rate of three

per 100 measurements, with a minimum of three per year and a maximum required of six per month. Providers of measurements with active devices are required to recalibrate their instruments at least once every 12 months. Participation in the EPA National RMP Program will not satisfy the need for annual calibration, as this Program is a performance test, not a calibration procedure.

1.3.2 Background Measurements

Background measurements are required both for continuous monitors and for passive detectors requiring laboratory analysis. Users of continuous monitors must perform sufficient instrument background measurements to establish a reliable instrument background and to act as a check on instrument operation.

Passive detectors requiring laboratory analysis require one type of background measurement made in the laboratory and another in the field. Suppliers and analysis laboratories should measure routinely the background of a statistically significant number of unexposed detectors from each batch or lot to establish the laboratory background for the batch and the entire measurement system. This laboratory blank value is subtracted routinely (by the laboratory) from the field sample results reported to the user, and should be made available to the users for quality assurance purposes. In addition to these background measurements, the organization performing the measurements should calculate the lower limit of detection (LLD) for its measurement system (Altshuler and Pasternack 1963, ANSI 1989, U.S. DOE 1990). This LLD is based on the detector and analysis system's background and can restrict the ability of some measurement systems to measure low concentrations.

Providers of passive detectors should employ field controls (called blanks) equal to approximately five percent of the detectors that are deployed, or 25 each month, whichever is smaller. These controls should be set aside from each detector shipment, kept sealed and in a low radon environment, labeled in the same manner as the field samples to preclude special processing, and returned to the analysis laboratory along with each shipment. These field blanks measure the background exposure that may accumulate during shipment and storage, and the results should be monitored and recorded. The recommended action to be taken if the concentrations measured by one or more of the field blanks is significantly greater than the LLD is dependent upon the type of detector and is discussed in the section for each method.

1.3.3 Duplicate (Collocated) Measurements

Duplicate measurements provide a check on the quality of the measurement result, and allow the user to make an estimate of the relative precision. Large precision errors may be caused by detector manufacture or improper data transcription or handling by suppliers, laboratories, or technicians performing placements. Precision error can be an important component of the overall error, so it is important that all users monitor

precision.

Duplicate measurements should be side-by-side measurements made in at least 10 percent of the total number of measurement locations, or 50 each month, whichever is smaller. The locations selected for duplication should be distributed systematically throughout the entire population of samples. Groups selling measurements to homeowners can do this by providing two measurements, instead of one, to a random selection of purchasers, with the measurements made side-by-side. As with spiked samples introduced into the system as blind measurements, the precision of duplicate measurements should be monitored and recorded in the quality assurance records. The analysis of data from duplicates should follow the methodology described by Goldin in section 5.3 of his report and plotted on range control charts (Goldin 1984, U.S. EPA 1984). If the precision estimated by the user is not within the precision expected of the measurement method, the problem should be reported to the analysis laboratory and the cause investigated.

1.3.4 Routine Instrument Performance Checks

Proper functioning of analysis equipment and operator usage require that the equipment and measurement system be subject to routine checks. Regular monitoring of equipment and operators is vital to ensure consistently accurate results. Performance checks of analysis equipment includes the frequent use of an instrument check source. In addition, important components of the device (such as a pump, battery, or electronics) should be checked regularly and the results noted in a log. Each user should develop methods for regularly monitoring (preferably daily) their measurement system, and for recording and reviewing results.

The EPA established the National RMP Program to enable participants to demonstrate their proficiency at measuring radon and radon decay product concentrations. One condition of successful participation in this Program is that the total error of any individual device (including both errors in precision and accuracy) be within ±25 percent of the "true" radon or radon decay product concentration at or above 4 pCi/L. For further information, please contact:

RMP Program Information Service
Research Triangle Institute
3040 Cornwallis Road-Building 7
P.O. Box 12194
Research Triangle Park, NC 27709-2194
(919-541-7131/FAX -7386).

Section 2: INDOOR RADON MEASUREMENT DEVICE PROTOCOLS

2.1 PROTOCOL FOR USING CONTINUOUS RADON MONITORS (CR) TO MEASURE INDOOR RADON CONCENTRATIONS

2.1.1 Purpose

This protocol provides guidance for using continuous radon monitors (CR) to measure indoor radon concentrations accurately and to obtain reproducible results. Adherence to this protocol will help ensure uniformity among measurement programs and allow valid comparison of results. Measurements made in accordance with this protocol will produce results representative of closed-building conditions. Measurements made under closed-building conditions have a smaller variability and are more reproducible than measurements made when the building conditions are not controlled. The investigator should also follow guidance provided by the EPA in "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c) or other appropriate EPA measurement guidance documents.

2.1.2 Scope

This protocol covers, in general terms, the sample collection and analysis method, the equipment needed, and the quality control objectives of measurements made with CRs. It is not meant to replace an instrument manual but, rather, provides guidelines to be incorporated into standard operating procedures by anyone providing measurement services. Questions about these guidelines should be directed to the U.S. Environmental Protection Agency, Office of Radiation Programs, Radon Division (ANR-464), Problem Assessment Branch, 401 M Street S.W., Washington, D.C. 20460.

2.1.3 Method

There are three general types of CR monitors covered by this protocol. In the first type, ambient air is sampled for radon in a scintillation cell after passing through a filter that removes radon decay products and dust. As the radon in the cell decays, the radon decay products plate out on the interior surface of the scintillation cell. Alpha particles produced by subsequent decays, or by the initial radon decay, strike the zinc sulfide coating on the inside of the scintillation cell, thereby producing scintillations. The scintillations are detected by a photomultiplier tube in the detector which generates electrical pulses. These pulses are processed by the detector electronics and the data are usually stored in the memory of the monitor where results are available for recall or transmission to a data logger or printer.

This type of CR monitor uses either a flow-through cell or a periodic-fill cell. In the flow-through cell, air is drawn continuously through the cell by a small pump. In the

periodic-fill cell, air is drawn into the cell once during each pre-selected time interval; then the scintillations are counted and the cycle repeated. A third variation operates by radon diffusion through a filter area with the radon concentration in the cell varying with the radon concentration in the ambient air, after a small diffusion time lag. The concentrations measured by all three variations of cells lag the ambient radon concentrations because of the inherent delay in the radon decay product disintegration process.

A second type of CR monitor operates as an ionization chamber. Radon in the ambient air diffuses into the chamber through a filtered area so that the radon concentration in the chamber follows the radon concentration in the ambient air with some small time lag. Within the chamber, alpha particles emitted during the decay of radon atoms produce bursts of ions which are recorded as individual electrical pulses for each disintegration. These pulses are processed by the monitor electronics; the number of pulses counted is displayed usually on the monitor, and the data are available usually for processing by an optional data logger/printer.

A third type of CR monitor functions by allowing ambient air to diffuse through a filter into a detection chamber. As the radon decays, the alpha particles are counted using a solid-state silicon detector. The measured radon concentration in the chamber follows the radon concentration in the ambient air by a small time lag.

2.1.4 Equipment

Equipment required depends on the type and model of CR monitor used. Aged air or nitrogen must be available for introduction into the CR monitor to measure the background count rate during calibration. For scintillation cell-type CRs, sealed scintillation cells with a measured low background should be available as spare cells.

2.1.5 Predeployment Considerations

The plans of the occupant during the proposed measurement period should be considered before deployment. The CR measurement should not be made if the occupant will be moving during the measurement period. Deployment should be delayed until the new occupant is settled in the house.

2.1.5.1 Pre-Sampling Testing. Before and after each measurement, the CR monitor should be tested carefully according to manufacturer's directions to:

- Verify that the correct input parameters and the unit's clock or timer are set properly; and
- Verify the operation of the pump. Flow rates within the range of the manufacturer's specifications are satisfactory.

After every 1,000 hours of operation of scintillation cell-type CRs, the background count rate should be checked by purging the unit with clean, aged air or nitrogen in accordance with the procedures identified in the operating manual for the instrument. In addition, the background count rate of all CR types should be monitored more frequently by operating the instrument in a low radon environment.

Participation in a laboratory intercomparison program should be conducted initially and at least once every 12 months thereafter, and after equipment repair, to verify that the conversion factor used by the CR monitor is accurate. This is done by comparing the unit's response to a known radon concentration. At this time, the correct operation of the pump should be verified. Participation in the EPA National Radon Measurement Proficiency (RMP) Program does not satisfy the need for annual calibration, as this Program is a performance test rather than an internal calibration.

2.1.6 Measurement Criteria

The reader should refer to Section 1.2.2 for the list of general conditions that must be met to ensure standardization of measurement conditions.

2.1.7 Deployment and Operation

2.1.7.1 Location Selection. The reader should refer to Section 1.2.3 for standard criteria that must be considered when choosing a measurement device location.

2.1.7.2 Operation. The CR monitor should be programmed to run continuously, recording periodically the radon concentration for at least 48 hours. Longer measurements may be required, depending on the CR type and radon level being measured. An increase in operating time decreases the uncertainty associated with using the measurement result to represent a longer-term average concentration.

Care should be taken to account for data that are produced before equilibrium conditions have been established in a flow-through cell. Generally, conditions stabilize after the first four hours. Measurements made prior to this time are low and should either be discarded or used to estimate radon concentrations using pre-established system constants (Busigin et al. 1979, Thomas 1972). If the first four hours of data from a 48-hour measurement are discarded, the remaining hours of data can be averaged and are sufficient to represent a two-day measurement.

2.1.8 Retrieval of Monitors

When the measurement is terminated, the operator should document the stop-date and -time and whether the closed-building conditions are still in effect.

2.1.9 Documentation

The reader should refer to Section 1.2.4 for the list of standard information that must be documented.

The serial numbers of the CR monitor, scintillation cells, and other equipment must also be recorded.

2.1.10 Results

2.1.10.1 Sensitivity. Most CR monitors are capable of a lower limit of detection (LLD [calculated using methods described by Altshuler and Pasternack 1963]) of 1.0 picoCurie per liter (pCi/L) or less.

2.1.10.2 Precision. Most CR monitors can achieve a coefficient of variation of less than 10 percent at 4 pCi/L or greater. An alternate measure of precision is a relative percent difference, defined as the difference between two duplicate measurements divided by their mean; note that these two measures of precision are not identical quantities. It is important that precision be monitored continuously over a range of radon concentrations and that a systematic and documented method for evaluating changes in precision be part of the operating procedures.

2.1.11 Quality Assurance

The quality assurance program for CR measurements includes four parts: (1) calibration, (2) background measurements, (3) duplicate measurements, and (4) routine instrument checks. The purpose of a quality assurance program is to identify the accuracy and precision of the measurements and to ensure that the measurements are not influenced by exposure from sources outside the environment to be measured. The quality assurance program should include the maintenance of control charts (Goldin 1984); general information is also available (Taylor 1987, U.S. EPA 1984).

2.1.11.1 Calibration. Every CR monitor should be calibrated in a radon calibration chamber before being put into service, and after any repairs or modifications. (Note that an inherent element in the calibration process is a thorough determination of the background count rate using clean, aged air or nitrogen.) Subsequent recalibrations and background checks should be done at least once every 12 months, with cross-checks to a recently calibrated instrument at least semiannually. All cells need individual calibration factors.

2.1.11.2 Background Measurements. After every 1,000 hours of operation of scintillation cell-type CRs (about every 20th 48-hour measurement), and whenever any type of CR is calibrated, the background should be checked by purging the monitor with clean, aged air or nitrogen. In addition, the background count rate should be monitored more

frequently by operating the instrument in a low radon environment. Cells which develop a high background after prolonged use should be reconditioned by the manufacturer.

2.1.11.3 Duplicate Measurements. When two or more CR monitors of the same type (e.g., scintillation cell, ionization chamber, or silicon detector types) are available, the precision of the measurements can be estimated by operating the monitors side-by-side. The analysis of duplicate results should follow the methodology described by Goldin (section 5.3 of Goldin 1984), by Taylor (Taylor 1987), or by the EPA (U.S. EPA 1984). Whatever procedures are used must be documented prior to beginning measurements. Consistent failure in duplicate agreement may indicate a problem in the measurement process and should be investigated.

2.1.11.4 Routine Instrument Checks. Proper operation of all radiation counting instruments requires that their response to a reference source be constant to within established limits. Therefore, counting equipment should be subject to routine checks to ensure proper operation. This is achieved by counting an instrument check cell (for scintillation cell-type CRs) prior to beginning each measurement. The count rate of the check source should be high enough to yield good counting statistics in a short time (for example, 1,000 to 10,000 counts per minute).

If a check source is unavailable or incompatible with the type of CR monitor being used, an informal intercomparison with another measurement method that has proven reliability (for example in the EPA National RMP Program) should be conducted at least every tenth measurement. In addition, it is important to check regularly all components of the equipment that affect the result, including battery and electronics, and to document these checks.

Pumps and flow meters should be checked routinely to ensure accuracy of volume measurements. This may be performed using a dry-gas meter or other flow measurement device of traceable accuracy.

2.2 PROTOCOL FOR USING ALPHA TRACK DETECTORS (AT or ATD) TO MEASURE INDOOR RADON CONCENTRATIONS

2.2.1 Purpose

This protocol provides guidance for using alpha track detectors (AT or ATD) to obtain accurate and reproducible measurements of indoor radon concentrations. Adherence to this protocol will help ensure uniformity among measurement programs and allow valid intercomparison of results. The investigator should also follow guidance provided by the EPA in "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c) or other appropriate EPA measurement guidance documents.

2.2.2 Scope

This protocol covers, in general terms, the equipment, procedures, and quality control objectives to be used in performing the measurements. It is not meant to replace an instrument manual but, rather, provides guidelines to be incorporated into standard operating procedures by anyone providing measurement services. Questions about these guidelines should be addressed to the U.S. Environmental Protection Agency, Office of Radiation Programs, Radon Division (ANR-464), Problem Assessment Branch, 401 M Street, S.W., Washington, D.C., 20460.

2.2.3 Method

An AT consists of a small piece of plastic or film enclosed in a container with a filter-covered opening or similar design for excluding radon decay products. Radon diffuses into the container and alpha particles emitted by the radon and its decay products strike the detector and produce submicroscopic damage tracks. At the end of the measurement period, the detectors are returned to a laboratory. Plastic detectors are placed in a caustic solution that accentuates the damage tracks so they can be counted using a microscope or an automated counting system. The number of tracks per unit area is correlated to the radon concentration in air, using a conversion factor derived from data generated at a calibration facility. The number of tracks per unit of analyzed detector area produced per unit of time (minus the background) is proportional to the radon concentration. AT detectors function as true integrators and measure the average concentration over the exposure period.

Many factors contribute to the variability of AT results, including differences in the detector response within and between batches of plastic, non-uniform plate-out of decay products inside the detector holder, differences in the number of background tracks, and variations in etching conditions. Since the variability in AT results decreases with the number of net tracks counted, counting more tracks over a larger area of the detector, particularly at low exposures, will reduce the uncertainty of the result.

2.2.4 Equipment

ATs are available from commercial suppliers. These suppliers offer contract services in which they provide the detector and subsequent analysis and reporting for a fixed price. Establishing an in-house capability to provide packaged detectors, a calibration program, and an analysis program would probably not be practical or economically advantageous for most users. Therefore, details for establishing the analytical aspects of an AT program are omitted from this protocol. Additional details concerning AT programs have been reviewed elsewhere (Fleischer et al. 1965, Lovett 1969).

Assuming ATs are obtained from a commercial supplier, the following equipment is needed to initiate a measurement:

- An AT in an individual, sealed container (such as an aluminized plastic bag) to prevent extraneous exposure before deployment;
- A means to attach the AT to its measurement location, if it is to be hung from the wall or ceiling;
- An instruction sheet for the occupant, a sample log sheet, and a shipping container (along with a prepaid mailing label, if appropriate);
- Manufacturer instructions for resealing the detector at the time of retrieval and prior to returning it to the supplier for analysis; and
- A data collection log, if appropriate.

2.2.5 Predeployment Considerations

The plans of the occupant during the proposed measurement period should be considered before deployment. The AT measurement should not be made if the occupant will be moving during the measurement period. Deployment should be delayed until the new occupant is settled in the house.

The AT should not be deployed if the user's schedule prohibits terminating the measurement at the appropriate time.

2.2.6 Measurement Criteria

The reader should refer to Section 1.2.2 for the list of general conditions that must be met to ensure standardization of measurement conditions.

A 12-month AT measurement provides information about radon concentrations in a building during an entire year, so the closed-building conditions do not have to be satisfied to perform a valid year-long measurement.

2.2.7 Deployment

2.2.7.1 Location Selection. The reader should refer to Section 1.2.3 for standard criteria that must be considered when choosing a measurement device location.

If the detector is installed during a site visit, the final site selected should be shown to the building occupant to be certain it is acceptable for the duration of the measurement period.

2.2.7.2 Timely Deployment. A group of ATs should be deployed into houses as soon as possible after delivery from the supplier. In order to minimize chances of high background exposures, users should not order more ATs than they can reasonably expect to install within the following few months. If the storage time exceeds more than a few months, the background exposures from a sample of the stored detectors should be assessed to determine if they are different from the background of detectors that are not stored for long periods. The supplier's instructions regarding storage and background determination should be followed. This background assessment of detectors stored for long periods is not necessary if the analysis laboratory measures routinely the background of stored detectors, and if the stored detectors remain tightly sealed.

The sampling period begins when the protective cover or bag is removed. The edge of the bag must be cut carefully, or the cover removed, so that it can be reused to reseal the detector at the end of the exposure period. The detector and the radon-proof container should be inspected to make sure that they are intact and have not been physically damaged in shipment or handling.

2.2.8 Retrieval of Detectors

At the end of the measurement period (usually 90 days for short-term tests and one year for long-term measurements), the detector should be inspected for damage or deviation from the conditions entered in the log book at the time of deployment. Any changes should be noted in the log book. The time and date of removal should be entered on the data form for the detector and in the log book, if used. The detector should then be resealed following the instructions provided by the supplier. After retrieval, the detectors should be stored in a low radon environment and returned as soon as possible to the analytical laboratory for processing. In many cases, attempts at resealing ATs have not been totally successful, resulting in some continued exposure of the detectors beyond the deployment period. This extra exposure could bias the results high if the detectors are held for a significant length of time prior to analysis.

2.2.9 Documentation

The reader should refer to Section 1.2.4 for the list of standard information that should be documented.

2.2.10 Analysis Requirements

2.2.10.1 Sensitivity. The lower limit of detection (LLD [calculated using methods described by Altshuler and Pasternack 1963]) is dependent upon the stability of the number of background tracks. Depending upon the system used, the background may be less variable if a greater area is analyzed. With present ATs, routine counting can achieve an LLD of 1 pCi/L-month, and an LLD of 0.2 pCi/L-month may be achieved by counting additional area.

2.2.10.2 Precision. The precision should be monitored using the results of the duplicate detectors described in Section 2.2.11.3 of this protocol, rather than a precision quoted by the manufacturer. The precision of an AT system is dependent upon the total number of tracks counted on the flank and test detector, and therefore the area of the detector that is analyzed. If few net tracks are counted, poor precision is obtained. Thus, it is important that the organization performing the measurement with an AT arranges for counting an adequate area or number of net tracks.

2.2.11 Quality Assurance

The quality assurance program for AT measurements involves five separate parts: (1) calibration, (2) known exposure measurements, (3) duplicate (collocated) detectors, (4) control detectors, and (5) routine instrument checks. The purpose of a quality assurance program is to identify the accuracy and precision of the measurements and to ensure that the measurements are not influenced by exposure from sources outside the environment to be measured. The quality assurance program should include the maintenance of control charts (Goldin 1984); general information is also available (Taylor 1987, U.S. EPA 1984).

2.2.11.1 Calibration. Every AT laboratory system should be calibrated in a radon calibration chamber at least once every 12 months. Determination of a calibration factor requires exposure of ATs to a known radon concentration in a radon exposure chamber. These calibration exposures are to be used to obtain or verify the conversion factor between net tracks per unit area and radon concentration. Participation in the EPA National Radon Measurement Proficiency Program does not satisfy the need for annual calibration, as this Program is a proficiency test rather than an internal calibration. The following guidance is provided to manufacturers and suppliers of AT services as minimum requirements in determining the calibration factor.

- ATs should be exposed in a radon chamber at several different radon concentrations or exposure levels similar to those found in the tested buildings (a minimum of three different concentrations).

- A minimum of 10 detectors should be exposed at each level.

- A calibration factor should be determined for each batch or sheet of detector material received from the material supplier. Alternatively, calibration factors may be established from several sheets, and these factors extended to detectors from sheets exhibiting similar sensitivities (within pre-established tolerance limits).

2.2.11.2 Known Exposure Measurements. Anyone providing measurement services with AT devices should submit ATs with known radon exposures (spiked samples) for analysis at a rate of three per 100 measurements, with a minimum of three per year and a maximum required of six per month. Known exposure (spiked) detectors should be labeled in the same manner as field detectors to ensure identical processing. The results of the spiked detector analyses should be monitored and recorded. Any significant deviation from the known concentration to which they were exposed should be investigated.

2.2.11.3 Duplicate (Collocated) Detectors. Anyone providing measurement services with AT devices should place duplicate detectors in enough houses to test the precision of the measurement. The number of duplicate detectors deployed should be approximately 10 percent of the number of detectors deployed each month or 50, whichever is smaller. The pair of detectors should be treated identically in every respect. They should be shipped, stored, opened, installed, removed, and processed together, and not identified as duplicates to the processing laboratory. The samples selected for duplication should be distributed systematically throughout the entire population of measurements. Groups selling measurements to homeowners can accomplish this by providing two detectors instead of one to a random selection of purchasers, with instructions to place the detectors side-by-side. Consideration should be given to providing some means to ensure that the duplicate devices are not separated during the measurement period. Data from duplicate detectors should be evaluated using the procedures described by Goldin (section 5.3 of Goldin 1984), by Taylor (Taylor 1987), or by the EPA (U.S. EPA 1984). Whatever procedures are used must be documented prior to beginning measurements. Consistent failure in duplicate agreement may indicate a problem in the measurement process and should be investigated.

2.2.11.4 Control Detectors

2.2.11.4.1 Laboratory Control Detectors. The laboratory background level for each batch of ATs should be established by each laboratory or supplier.

Suppliers should measure the background of a statistically significant number of unexposed ATs that have been processed according to their standard operating procedures. Normally, the analysis laboratory or supplier calculates the net readings (which are used to calculate the reported sample radon concentrations) by subtracting the laboratory blank values from the results obtained from the field detectors.

2.2.11.4.2 Field Control Detectors. Field control detectors must be a component of any AT measurement program. Field control ATs (field blanks) should consist of a minimum of five percent of the devices that are deployed every month or 25, whichever is smaller. Users should set these aside from each shipment, keep them sealed and in a low radon (less than 0.2 pCi/L) environment, label them in the same manner as the field ATs to assure identical processing, and send them back to the supplier with the field ATs for analysis. These control devices are necessary to measure the background exposure that accumulates during shipment and storage. The results should be monitored and recorded. If one or a few field blanks have concentrations significantly greater than the LLD established by the supplier, it may indicate defective packaging or handling. If the average value from the field control devices (field blanks) is significantly greater than the LLD established by the supplier, this average value should be subtracted from the individual values reported for the other devices in the exposure group.

It may be advisable to use three sets of detectors (pre-exposure, field, and post-exposure background) in order to allow the most thorough and complete evaluation of radon levels. For example, one group of detectors (pre-exposure detectors) may be earmarked for background measurement, and returned for processing immediately after the other detectors are deployed. The results from these detectors determine if the number of tracks acquired before deployment is significant and should be subtracted from the gross result. The second set of background detectors (post-exposure background detectors) are obtained just before the field monitors are to be collected, and are opened and kept in the same location as the returning field monitors for the same duration, and returned with them. Finally, this "post-exposure background" is subtracted from the field results, if found to be significant. In general, a value of 1 pCi/L or greater for any blank AT indicates a significant level that should be investigated, and potentially subtracted from the field AT results.

2.2.11.5 Routine Instrument Checks. Proper functioning of the analysis instruments and proper response by their operators require that the equipment be subject to routine checks. Daily or more frequent monitoring of equipment and operators is vital to ensuring consistently accurate results.

2.3 PROTOCOL FOR USING ELECTRET ION CHAMBER RADON DETECTORS (EC or ES, EL) TO MEASURE INDOOR RADON CONCENTRATIONS

2.3.1 Purpose

This protocol provides guidance for using electret ion chamber radon detectors (EC) to obtain accurate and reproducible measurements of indoor radon concentrations. Adherence to this protocol will help ensure uniformity among measurement programs and allow valid intercomparison of results. Measurements made in accordance with this protocol can produce either short-term or long-term measurements, depending upon the type of EC employed. The investigator should also follow guidance provided by the EPA in "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c) or other appropriate EPA measurement guidance documents.

2.3.2 Scope

This protocol covers, in general terms, the equipment, procedures, and quality control objectives to be used in performing the measurements. It is not meant to replace an instrument manual but, rather, provides guidelines to be incorporated into standard operating procedures by anyone providing measurement services. Questions about these guidelines should be addressed to the U.S. Environmental Protection Agency, Office of Radiation Programs, Radon Division, Problem Assessment Branch (ANR-464), 401 M Street, S.W., Washington, D.C., 20460.

2.3.3 Method

Short-term (ES) and long-term (EL) ECs have been described elsewhere (Kotrappa et al. 1988, 1990). They require no power, and function as true integrating detectors, measuring the average concentration during the measurement period.

The EC contains a charged electret (an electrostatically-charged disk of Teflon®) which collects ions formed in the chamber by radiation emitted from radon and radon decay products. When the device is exposed, radon diffuses into the chamber through filtered openings. Ions which are generated continuously by the decay of radon and radon decay products are drawn to the surface of the electret and reduce its surface voltage. The amount of voltage reduction is related directly to the average radon concentration and the duration of the exposure period. ECs can be deployed for exposure periods of two days (one day for research purposes) to 12 months, depending upon the thickness of the electret and the volume of the ion chamber chosen for use. These deployment periods are flexible, and valid measurements can be made with other deployment periods depending on the application.

The electret must be removed from the EC chamber and the electret voltage measured with a special surface voltmeter both before and after exposure. To determine the

average radon concentration during the exposure period, the difference between the initial and final voltages is divided first by a calibration factor and then by the number of exposure days. A background radon concentration equivalent of ambient gamma radiation is subtracted to compute radon concentration. Electret voltage measurements can be made in a laboratory or in the field.

2.3.4 Equipment

The following equipment is required to measure radon using the EC detection method:

- An EC of the type recommended for the anticipated exposure period and radon concentration (ES or EL);
- An instruction sheet for the user and a shipping container with a label for returning the detector(s) to the laboratory, if appropriate;
- A specially-built surface voltmeter for measuring electret voltages before and after exposure; and
- A data collection log.

2.3.5 Predeployment Considerations

The plans of the occupant during the proposed measurement period should be considered before deployment. The ES or EL measurement should not be made if the occupant will be moving during the measurement period. Deployment should be delayed until the new occupant is settled in the house.

The ES or EL should not be deployed if the user's schedule prohibits terminating the measurement at the appropriate time.

The ES or EL should be inspected prior to deployment to see that it has not been damaged during handling and shipping.

2.3.6 Measurement Criteria

The reader should refer to Section 1.2.2 for the list of general conditions that must be met to ensure standardization of measurement conditions.

A 12-month EL measurement provides information about radon concentrations during an entire year, so the closed-building conditions do not have to be satisfied to perform a valid year-long measurement.

2.3.7 Deployment

2.3.7.1 Location Selection. The reader should refer to Section 1.2.3 for standard criteria that must be considered when choosing a measurement device location.

2.3.7.2 Timely Deployment. Both ESs and ELs should be deployed as soon as possible after their initial voltage is measured. Until an ES or EL is deployed, an electret cover should remain in place over the electret to minimize voltage loss due to background radon and gamma radiation.

2.3.8 Retrieval of Detectors

The recommended deployment period for the very short-term ESs is two days (one day for research or special circumstances), two to seven days for the short-term ESs, and for the long-term ELs one to 12 months. If the occupant is terminating the sampling, the instructions should inform the occupant of when and how to terminate the sampling period. EC units integrate the radon (ion) signal permanently, so variations from these recommended measurement periods are acceptable to accommodate special circumstances as long as the final electret voltage for any measurement remains above 150 volts. In addition, the occupant also should be instructed to send the ES or EL to the laboratory as soon as possible, preferably within a few days following exposure termination.

At the end of the monitoring period, the ES or EL should be inspected for any deviation from the conditions described in the log book at the time of deployment. Any changes should be noted. The electret should be covered again using the mechanism provided.

2.3.9 Documentation

The reader should refer to Section 1.2.4 for the list of standard information that must be documented.

In addition, the serial number, type, and supplier of the chamber and electret, along with a code number or description which uniquely identifies customer, building, room, and sampling position, must be documented. If the temperature of the room in which the EC is analyzed after exposure is significantly different (more than 10°F) from the temperature of the room in which the EC was analyzed prior to exposure, those temperatures need to be recorded.

2.3.10 Analysis Requirements

In general, all ESs or ELs should be analyzed in the field or in the laboratory as soon as possible following removal from buildings. A background correction must be made to the radon concentration value obtained because electret ion chambers have a small

response to background gamma radiation. If the temperature at the time of analysis is significantly different (more than 10°F) than at the time when the pre-exposure voltage was determined, a temperature correction factor may be necessary (consult the manufacturer). It is therefore advisable to measure voltages after the temperatures of the reader and detector have stabilized to a room temperature in which both pre- and post-exposure voltages have been measured.

2.3.10.1 Sensitivity. For a seven-day exposure period using an ES, the lower level of detection (LLD), as defined by Thomas (Thomas 1971) as the concentration that can be measured with a 50 percent error, is about 0.2 pCi/L. For an EL, the LLD is about 0.3 pCi/L or less for a three-month measurement. Note that this definition of LLD is different from that for radiation counting instruments, as defined for other methods by Altshuler and Pasternack (Altshuler and Pasternack 1963).

2.3.10.2 Precision. Precision should be monitored by using the results of duplicate detector analyses described in Section 2.3.11.3 of this protocol. This method can produce duplicate measurements with a coefficient of variation of 10 percent or less at 4 pCi/L or greater. An alternate measure of precision is a relative percent difference, defined as the difference between two duplicate measurements divided by their mean; note that these two measures of precision are not identical quantities. It is important that precision be monitored continuously over a range of radon concentrations and that a systematic and documented method for evaluating changes in precision be part of the operating procedures.

2.3.11 Quality Assurance

The quality assurance program for measurements with ES or EL detectors includes five parts: (1) calibration, (2) known exposure detectors, (3) duplicate (collocated) detectors, (4) control detectors, and (5) routine instrument checks. The purpose of a quality assurance program is to assure and document the accuracy and precision of the measurements and that the measurements are not influenced by exposure from sources outside the environment to be measured.

2.3.11.1 Calibration. Every ES or EL detector system (detectors plus reader) should be calibrated in a radon calibration chamber at least once every 12 months. Initial calibration for the system is provided by the manufacturer. Determination of calibration factors for ES or EL detectors requires exposure of detectors to known concentrations of radon-222 in a radon exposure chamber. Since ESs and ELs are also sensitive to exposure to gamma radiation (see Section 2.3.11.4), a gamma exposure rate measurement in the test chamber is also required.

The following guidance is provided to manufacturers and suppliers of EC services as minimum requirements in determining the calibration factor:

- Detectors should be exposed in a radon chamber at several different radon concentrations or exposure levels similar to those found in the tested buildings (a minimum of three different concentrations).

- A minimum of 10 detectors should be exposed at each level.

- The period of exposure should be sufficient to allow the detector to achieve equilibrium with the chamber atmosphere.

2.3.11.2 Known Exposure Detectors. Anyone providing measurement services with ES or EL detectors should subject detectors with known radon exposures (spiked samples) for analysis at a rate of three per 100 measurements, with a minimum of three per year and a maximum required of six per month. Blind calibration detectors should be labeled in the same manner as the field detectors to ensure identical processing. The results of the spiked detector analysis should be monitored and recorded and any significant deviation from the known concentration to which they were exposed should be investigated.

2.3.11.3 Duplicate (Collocated) Detectors. Anyone providing measurement services with EC devices should place duplicate detectors in enough houses to test the precision of the measurement. The number of duplicate detectors deployed should be approximately 10 percent of the number of detectors deployed each month or 50, whichever is smaller. The duplicate devices should be shipped, stored, exposed, and analyzed under the same conditions, and not identified as duplicates to the processing laboratory. The samples selected for duplication should be distributed systematically throughout the entire population of samples. Groups selling measurement services to homeowners can accomplish this by providing two detectors instead of one to a random selection of purchasers, with instructions to place the detectors side-by-side. Consideration should be given to providing some means to ensure that the duplicate devices are not separated during the measurement period. The analysis of duplicate data should follow the methodology described by Goldin (section 5.3 of Goldin 1984), by Taylor (Taylor 1987), or by the EPA (U.S. EPA 1984). Whatever procedures are used must be documented prior to beginning measurements. Consistent failure in duplicate agreement may indicate a problem in the measurement process and should be investigated.

2.3.11.4 Control Detectors for Background Gamma Exposure and Electret Stability Monitoring. Electrets should exhibit very little loss in surface voltage due to internal electrical instabilities. Anyone providing measurement services with ES or EL detectors should set aside a minimum of five percent of the electrets or 10, whichever number is smaller, from each shipment and evaluate them for voltage drift. They should be kept covered with protective caps in a low radon environment and analyzed for voltage drift over a time period similar to the time period used for those deployed in homes. Any voltage loss found in the control electrets of more than one volt per week over a

three-week test period for ESs, or one volt per month over a three-month period for ELs, should be investigated.

ECs are sensitive to background gamma radiation. The equivalent radon signal in picoCuries per liter (pCi/L) per unit background radiation in microroentgens per hour (μR/hr) is determined by the manufacturer for three different types of EC chambers currently available. This is specific to the chamber and not to the electret used in the chamber. These parameters are 0.07, 0.087, and 0.12 for H, S, and L chambers, respectively. Depending upon the type of chamber employed in EC, one of these values must be multiplied by the gamma radiation level at the site (in μR/hr) and the product (in equivalent pCi/L) subtracted from the apparent radon concentration. The gamma radiation at the measurement site is usually taken from the EPA list of average background by State, as provided by the manufacturer. However, it can also be measured with an EC unit that is sealed in a radon-proof bag available from the manufacturer, or measured directly using appropriate radiation detection instruments. The latter step is necessary for accurate radon measurements at very low levels such as those encountered in the outdoor environment.

2.3.11.5 Routine Instrument Checks. Proper operation of the surface voltmeter should be monitored following the manufacturer's procedures for (1) zeroing the voltmeter, and (2) analyzing a reference electret. These checks should be conducted at least once a week while the voltmeter is in use.

2.4 PROTOCOL FOR USING ACTIVATED CHARCOAL ADSORPTION DEVICES (AC) TO MEASURE INDOOR RADON CONCENTRATIONS

2.4.1 Purpose

This protocol provides guidance for using activated charcoal adsorption devices (AC) to obtain accurate and reproducible measurements of indoor radon concentrations. As referred to in this document, ACs are those charcoal adsorption devices that are analyzed by gamma scintillation (including open-faced canisters, diffusion barrier canisters, and diffusion bags). Charcoal detectors analyzed by liquid scintillation are covered under a separate protocol (see Section 2.5). Adherence to this protocol will help ensure uniformity among measurement programs and allow valid intercomparison of results. Measurements made in accordance with this protocol will produce results representative of closed-building conditions. Measurements made under closed-building conditions have a smaller variability and are more reproducible than measurements made when the building conditions are not controlled. The investigator should also follow guidance provided by the EPA in "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c) or other appropriate EPA measurement guidance documents.

2.4.2 Scope

This protocol covers, in general terms, the sample collection and analysis method, the equipment needed, and the quality control objectives of measurements. It is not meant to replace an instrument manual but, rather, provides guidelines to be incorporated into standard operating procedures by anyone providing measurement services. Questions about these guidelines should be directed to the U.S. Environmental Protection Agency, Office of Radiation Programs, Radon Division (ANR-464), Problem Assessment Branch, 401 M Street, S.W., Washington, D.C., 20460.

2.4.3 Method

ACs are passive devices requiring no power to function. The passive nature of the activated charcoal allows continual adsorption and desorption of radon. During the measurement period (typically two to seven days), the adsorbed radon undergoes radioactive decay. Therefore, the technique does not integrate uniformly radon concentrations during the exposure period. As with all devices that store radon, the average concentration calculated using the mid-exposure time is subject to error if the ambient radon concentration varies substantially during the measurement period.

The AC technique is described in detail elsewhere (Cohen and Cohen 1983, George 1984, George and Weber 1990). A device used commonly by several groups consists of a circular, six- to 10-centimeter (cm) diameter container that is approximately 2.5 cm

deep and filled with 25 to 100 grams of activated charcoal. One side of the container is fitted with a screen that keeps the charcoal in but allows air to diffuse into the charcoal.

In some cases, the charcoal container has a diffusion barrier over the opening. For longer exposures, this barrier improves the uniformity of response to variations of radon concentration with time. Desiccant is also incorporated in some containers to reduce interference from moisture adsorption during longer exposures. Another variation of the charcoal container has charcoal packaged inside a sealed bag, allowing the radon to diffuse through the bag. All ACs are sealed with a radon-proof cover or outer container after preparation.

The measurement is initiated by removing the cover to allow radon-laden air to diffuse into the charcoal bed where the radon is adsorbed onto the charcoal. At the end of a measurement period, the device is resealed securely and returned to a laboratory for analysis.

At the laboratory, the ACs are analyzed for radon decay products by placing the charcoal, still in its container, directly on a gamma detector. Corrections may be needed to account for the reduced sensitivity of the charcoal due to adsorbed water. This correction may be done by weighing each detector when it is prepared and then reweighing it when it is returned to the laboratory for analysis. Any weight increase is attributed to water adsorbed on the charcoal. The weight of water gained is correlated to a correction factor, which is derived empirically by using a method discussed elsewhere (George 1984). This correction factor is used to correct the analytical results.

This correction is not needed if the configuration of the AC is modified to reduce significantly the adsorption of water and if the user has demonstrated experimentally that, over a wide range of humidities, there is a negligible change in the collection efficiency of the charcoal within the specified exposure period.

AC measurement systems are calibrated by analyzing detectors exposed to known concentrations of radon in a calibration facility.

2.4.4 Equipment

ACs made specifically for ambient radon-monitoring can be obtained from suppliers or can be manufactured using readily available components. Some charcoal canisters designed for use in respirators or in active air sampling may be adapted for use in ambient radon monitoring, as described elsewhere (Cohen and Cohen 1983, George 1984).

The following equipment is required to measure radon using ACs:

- A charcoal container(s) sealed with a protective cover;
- An instruction sheet and sampling data sheet for the occupant, and a shipping container (along with a prepaid mailing label, appropriate; and
- A data collection log.

Laboratory analysis of the exposed devices is performed using a sodium iodide gamma scintillation detector to count the gamma rays emitted by the radon decay products on the charcoal. The detector may be used in conjunction with a multi-channel gamma spectrometer or with a single-channel analyzer with the window set to include the appropriate gamma energy window. The detector system and detector geometry must be the same used to derive the calibration factors for the device.

2.4.5 Predeployment Considerations

The plans of the occupant during the proposed measurement period should be considered before deployment. The AC measurement should not be made if the occupant will be moving during the measurement period. Deployment should be delayed until the new occupant is settled in the house.

The devices should not be deployed if the occupant's schedule prohibits terminating the measurement at the time selected for sealing the device and returning it to the laboratory.

2.4.6 Measurement Criteria

The reader should refer to Section 1.2.2 for general conditions that must be adhered to in order to ensure standardization of measurement conditions.

2.4.7 Deployment

2.4.7.1 Location Selection. The reader should refer to Section 1.2.3 for standard criteria to use when choosing a measurement device location.

2.4.7.2 Timely Deployment. ACs should be deployed within the shelf life specified by the supplier. Until ACs are deployed, they should remain tightly sealed to maintain maximum sensitivity and low background.

For charcoal canisters, the sealing tape and protective cover should be removed from the canister to begin the sampling period. The cover and tape must be saved to reseal the canister at the end of the measurement. For diffusion bags, there is a radon-proof mailing container that is sealed at the end of the deployment period. This container may

be separate from the radon-proof packaging. The device should be inspected to see that it has not been damaged during handling and shipping. It should be intact, with no charcoal leakage. For canisters, the device should be placed with the open side up toward the air. Nothing, apart from the device, should impede air flow around it.

2.4.8 Retrieval of Detectors

The detectors should be deployed for a two- to seven-day measurement period as specified in the supplier's instructions. If the occupant is terminating the sampling, the instructions should inform the occupant of when to terminate the sampling period and should indicate that a deviation from the schedule may be acceptable if the time of termination is documented on the device. In addition, the occupant should also be instructed to send the device to the laboratory as soon as possible, preferably the day of termination. The analysis laboratory should be calibrated to permit accurate analysis of devices deployed for some reasonable time beyond the recommended sampling period. For example, a detector deployed for 24 hours beyond the recommended sampling time may not present an analysis problem to the measurement laboratory.

At the end of the monitoring period, the detector should be inspected for any deviation from the conditions described in the log book at the time of deployment. Any changes should be noted. The detector should be resealed using the original protective cover.

After the device is retrieved, it must be returned to the laboratory as soon as possible for analysis. The detector should be analyzed at least three hours after the end of sampling to allow for ingrowth of decay products.

2.4.9 Documentation

The reader should refer to Section 1.2.4 for the list of standard information that must be documented so that data interpretation and comparison can be made.

In addition, the test location temperature may need to be recorded, depending on the device configuration.

2.4.10 Analysis Requirements

ACs should be analyzed in the laboratory as soon as possible following removal from the houses. The maximum allowable delay time between the end of sampling and analysis will vary with the radon concentration and background experienced in each laboratory and should be evaluated, especially if sensitivity is of prime consideration. Corrections for the radon-222 decay during sampling, during the interval between sampling and counting, and during counting should be made. If the device does not have a moisture barrier, the detector should be weighed, and, if necessary, a correction should be applied

for the increase in weight due to moisture adsorbed. A description of the procedure used to derive the moisture correction factor is provided elsewhere (George 1984).

2.4.10.1 Sensitivity. For a two- to seven-day exposure period, the lower level of detection (LLD [calculated using methods described by Altshuler and Pasternack 1963]) should be 0.5 pCi/L or less. This LLD can normally be achieved with a counting time of up to 30 minutes. The LLD should be calculated using the results of the laboratory background determination that is described in Section 2.4.11.4.1 of this protocol.

2.4.10.2 Precision. Precision should be monitored using the results of the duplicate detector analyses described in this protocol (Section 2.4.11.3). This method can produce measurements with a coefficient of variation of 10 percent or less at 4 pCi/L or greater. An alternate measure of precision is a relative percent difference, defined as the difference between two duplicate measurements divided by their mean; note that these two measures of precision are not identical quantities. It is important that precision be monitored frequently over a range of radon concentrations and that a systematic and documented method for evaluating changes in precision be part of the operating procedures.

2.4.11 Quality Assurance

The quality assurance program for ACs includes five parts: (1) calibration, (2) known exposure detectors, (3) duplicate (collocated) detectors, (4) control detectors, and (5) routine instrument checks. The purpose of this program is to identify the accuracy and precision of the measurements and to assure that the measurements are not influenced by extraneous exposures. The quality assurance program should include the maintenance of control charts (section 5.3 of Goldin 1984); general information is also available (Taylor 1987, U.S. EPA 1984).

2.4.11.1 Calibration. Every AC system should be calibrated in a radon calibration chamber at least once every 12 months. Determination of calibration factors for ACs requires exposure of the detectors to known concentrations of radon-222 in a radon exposure chamber. The calibration factors depend on the exposure time and may also depend on the amount of water adsorbed by the charcoal container during exposure. These calibration factors should be determined using the procedures described previously (George 1984). Calibration factors should be determined for each AC measurement system (container type, amount of charcoal, gamma detector type, etc.).

2.4.11.2 Known Exposure Detectors. Anyone providing measurement services with AC detectors should submit charcoal detectors with known radon exposures (spiked samples) for analysis at a rate of three per 100 measurements, with a minimum of three per year and a maximum required of six per month. Known exposure (spiked) detectors should be labeled in the same manner as the field detectors to assure identical processing. The results of the spiked detector analysis should be monitored and

recorded and any significant deviation from the known concentration to which they were exposed should be investigated.

2.4.11.3 Duplicate (Collocated) Detectors. Anyone providing measurement services with AC devices should place duplicate detectors in enough houses to test the precision of the measurement. The number of duplicate detectors deployed should be approximately 10 percent of the number of detectors deployed each month or 50, whichever is smaller. The duplicate detectors should be shipped, stored, exposed, and analyzed under the same conditions, and not identified as duplicates to the processing laboratory. The locations selected to receive duplicates should be distributed systematically throughout the entire population of samples. Groups selling measurement services to homeowners can do this by providing two detectors instead of one to a random selection of purchasers, with instructions to place them side-by-side. Consideration should be given to providing some means to ensure that the duplicate detectors are not separated during the measurement period. Data from duplicate detectors should be evaluated using the procedures described by Goldin (Section 5.3 of Goldin 1984), by Taylor (Taylor 1987), or by the EPA (U.S. EPA 1984). Whatever procedures are used must be documented prior to beginning measurements. Consistent failure in duplicate agreement may indicate a problem in the measurement process and should be investigated.

2.4.11.4 Control Detectors

2.4.11.4.1 Laboratory Control Detectors. The laboratory background level for each batch of ACs should be established by each laboratory or supplier. Suppliers should measure the background of a statistically significant number of unexposed detectors that have been processed according to their standard operating procedures (laboratory blanks). Normally, the analysis laboratory or supplier calculates the net readings (which are used to calculate the reported sample radon concentrations) by subtracting the laboratory blank values from the results obtained from the field detectors.

2.4.11.4.2 Field Control Detectors. Field control detectors (field blanks) should consist of a minimum of five percent of the devices that are deployed every month or 25, whichever is smaller. Large users of ACs should set these aside from each shipment, keep them sealed and in a low radon (less than 0.2 pCi/L) environment, label them in the same manner as the field detectors to ensure identical processing, and send them back to the supplier with one shipment each month for analysis. These control devices measure the background exposure that may accumulate during shipment or storage, and results should be monitored and recorded. If one or a few of the field control detectors have concentrations significantly greater than the LLD established by the supplier it may indicate defective devices or poor procedures. If most of the controls have concentrations significantly greater than the LLD, the average value of the field controls should be

subtracted from the reported field detector concentrations and the supplier notified of a possible problem.

2.4.11.5 Routine Instrument Checks. Proper operation of all radiation counting instruments requires that their response to a reference source be constant to within established limits. Therefore, counting equipment should be subject to routine checks to ensure proper operation. This is achieved by counting an instrument check source at least once per day. The characteristics of the check source (i.e., geometry, type of radiation emitted, etc.) should, if possible, be similar to the samples to be analyzed. The count rate of the check source should be high enough to yield good counting statistics in a short time (for example, 1,000 to 10,000 counts per minute).

2.5 PROTOCOL FOR USING CHARCOAL LIQUID SCINTILLATION (LS) DEVICES TO MEASURE INDOOR RADON CONCENTRATIONS

2.5.1 Purpose

This protocol provides guidance for using charcoal liquid scintillation (LS) devices to obtain accurate and reproducible measurements of indoor radon concentrations. Adherence to this protocol will help ensure uniformity among measurement programs and allow valid intercomparison of results. Measurements made in accordance with this protocol will produce results representative of closed-building conditions. Measurements made under closed-building conditions have a smaller variability and are more reproducible than measurements made when the building conditions are not controlled. The investigator should also follow guidance provided by the EPA in "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c) or other appropriate EPA measurement guidance documents.

2.5.2 Scope

This protocol covers, in general terms, the equipment, procedures, and quality control objectives to be used in performing the measurements. It is not meant to replace an instrument manual but, rather, provides guidelines to be incorporated into standard operating procedures by anyone providing measurement services. Questions about these guidelines should be directed to the U.S. Environmental Protection Agency, Office of Radiation Programs, Radon Division (ANR-464), Problem Assessment Branch, 401 M Street, S.W., Washington, D.C., 20460.

2.5.3 Method

LS devices are passive detectors requiring no power to function. The passive nature of the activated charcoal allows continual adsorption and desorption of radon, and the adsorbed radon undergoes radioactive decay during the measurement period. Therefore, the technique does not integrate uniformly radon concentrations during the exposure period. As with all devices that store radon, the calculated average concentration is subject to error if the ambient radon concentration adsorbed during the first half of the sampling period is substantially higher or lower than the average over the period.

The LS technique is described elsewhere (Prichard and Marien 1985). Several companies now provide a type of LS device that is a capped, 20-ml liquid scintillation vial that is approximately 25 mm in diameter by 60 mm and contains one to three grams of charcoal (other designs are also feasible). In some cases, the vial contains a diffusion barrier over the charcoal which improves the uniformity of response of the device to variations of radon concentration with time, particularly for longer exposures. Some LS devices include a few grams of desiccant which reduces interference from moisture adsorption

by the charcoal (Perlman 1989). All LS devices are sealed with a radon-proof closure after preparation.

A measurement with the LS device is initiated by removing the radon-proof closure to allow radon-laden air to diffuse into the charcoal where the radon is adsorbed. At the end of the exposure (typically two to seven days), the device is resealed securely and returned to the laboratory for analysis.

At the laboratory, the devices are prepared for analysis by radon desorption techniques. This technique transfers reproducibly a major fraction of the radon adsorbed on the charcoal into a vial of liquid scintillation fluid. The vials of liquid scintillation fluid containing the dissolved radon are placed in a liquid scintillation counter and counted for a specified number of minutes (e.g., 10 minutes) or until the standard deviation of the count is acceptable (e.g., less than 10 percent).

2.5.4 Equipment

LS devices made specifically for ambient radon monitoring are supplied and analyzed by several laboratories.

The following equipment is required to measure radon with an LS device:

- LS devices properly sealed by the supplier;
- An instruction sheet for the occupant, and a shipping container (along with a prepaid mailing label, if appropriate; and
- A data collection log.

2.5.5 Predeployment Considerations

The plans of the occupant during the proposed measurement period should be considered before deployment. The LS measurement should not be made if the occupant will be moving during the measurement period. Deployment should be delayed until the new occupant is settled in the house.

The LS device should not be deployed if the occupant's schedule prohibits terminating the measurement at the time selected for closing the device and returning it to the laboratory.

2.5.6 Measurement Criteria

The reader should refer to Section 1.2.2 for the list of general conditions that must be met to ensure standardization of measurement conditions.

2.5.7 Deployment

2.5.7.1 Location Selection. The reader should refer to Section 1.2.3 for standard criteria that must be considered when choosing a measurement device location.

2.5.7.2 Timely Deployment. LS devices should be deployed into buildings within the shelf life specified by the supplier. Until they are deployed, they should remain tightly sealed to maintain low background.

The protective cap should be removed from the device to begin the sampling period. The cap must be saved to reseal the device at the end of the measurement. The device should be inspected to assure that it has not been damaged during handling and shipping. It should be intact, with no charcoal leakage. The device should also be placed with the open vial mouth up. Nothing should impede air flow around the device.

2.5.8 Retrieval of Devices

The device should be deployed for the measurement period (usually between two days and one week) specified in the instructions supplied by the analytical laboratory. If the occupant is terminating the sampling, the instructions should inform the occupant of when to terminate the sampling period and should indicate that the actual time of termination must be documented on the device. In addition, the occupant also should be instructed to send the device to the laboratory as soon as possible, preferably the day of sample termination. The analysis laboratory should be calibrated to permit accurate analysis of devices deployed for some reasonable time beyond the recommended sampling period. For example, a detector deployed for 24 hours beyond the recommended sampling time may not present an analysis problem to the measurement laboratory.

At the end of the monitoring period, the device should be inspected for any deviation from the conditions described in the log book at the time of deployment. Any changes should be noted. The device should be resealed using the original protective cap.

2.5.9 Documentation

The reader should refer to Section 1.2.4 for the list of standard information that must be documented so that data interpretation and comparison can be made.

2.5.10 Analysis Requirements

LS devices should be returned to the supplier's analysis laboratory as soon as possible following removal from the houses. The maximum allowable delay time between the end of sampling and analysis should not exceed the time specified by the supplier's instructions, especially if the radon concentration measured was expected to be low. Corrections for radon-222 decay during sampling, during the interval between sampling

and counting, and during counting, will be made by the analysis laboratory. The procedures followed by an individual supplier's analysis laboratory may include a correction for moisture as measured by weight gain if this is significant for their device configuration. Other correction or calibration factors applied by the analysis laboratory must include factors accounting for the transfer of radon from the charcoal to the scintillation fluid under rigorously controlled conditions, and for the counting efficiency achieved with the specified scintillation mixture and liquid scintillation counting system.

2.5.10.1 Sensitivity. The lower limit of detection (LLD [calculated using methods described by Altshuler and Pasternack 1963]) should be specified by individual suppliers for LS devices exposed and shipped according to their directions. It is estimated that LLDs of a few tenths of a picoCurie per liter (pCi/L) are achievable for some LS devices (Cohen 1988, Grodzins 1988, Perlman 1988, Prichard 1988). The LLD should be calculated using the results of the laboratory control devices discussed in Section 2.5.11.4.1 of this protocol.

2.5.10.2 Precision. Precision should be monitored and recorded periodically using the results of the duplicate device analyses described in Section 2.5.11.3 of this protocol. Measurements made with this method can produce duplicate results with a coefficient of variation of 10 percent or less at 4 pCi/L or greater. An alternate measure of precision is a relative percent difference, defined as the difference between two duplicate measurements divided by their mean; note that these two measures of precision are not identical quantities. It is important that precision be monitored frequently over a range of radon concentrations and that a systematic and documented method for evaluating changes in precision be part of the operating procedures.

2.5.11 Quality Assurance

The quality assurance program for an LS system includes five parts: (1) calibration, (2) known exposure devices, (3) duplicate (collocated) devices, (4) control devices, and (5) routine instrument checks. The purpose of a quality assurance program is to identify the accuracy and precision of the measurements and to ensure that the measurements are not influenced by exposure from sources outside the environment to be measured. The quality assurance program should include the maintenance of control charts (Goldin 1984); general information is also available (Taylor 1987, U.S. EPA 1984).

2.5.11.1 Calibration. Every LS laboratory system should be calibrated in a radon calibration chamber at least once every 12 months. Determination of calibration factors for LS devices requires exposure of calibration devices to known concentrations of radon-222 in a radon exposure chamber at carefully measured radon concentrations. The calibration factors depend on the exposure time and may also depend on the amount of water adsorbed by the device during exposure. Calibration factors should be determined for a range of different exposure times and, if appropriate, humidities.

2.5.11.2 Known Exposure Devices. Anyone providing measurement services with LS devices should submit devices with known radon exposures (spiked samples) for analysis at a rate of three per 100 measurements, with a minimum of three per year and a maximum required of six per month. Known exposure (spiked) devices should be labeled in the same manner as the field devices to ensure identical processing. The results of the spiked device analysis should be monitored and recorded, and any significant deviation from the known concentration to which they were exposed should be investigated.

2.5.11.3 Duplicate (Collocated) Devices. Anyone providing measurement services with LS devices should place duplicate detectors in enough houses to test the precision of the measurement. The number of duplicate detectors deployed should be approximately 10 percent of the number of detectors deployed each month or 50, whichever is smaller. Each pair of duplicate devices should be shipped, stored, exposed, and analyzed under the same conditions. The samples for duplication should be distributed systematically throughout the entire population of samples. Groups selling measurement services to homeowners can do this by providing two detectors instead of one to a random selection of purchasers with instructions to place them side-by-side. Consideration should be given to providing some means to ensure that the duplicate devices are not separated during the measurement period. Data from duplicate devices should be evaluated using procedures described by Goldin (section 5.3 of Goldin 1984), by Taylor (Taylor 1987), or by the EPA (U.S. EPA 1984). Whatever procedures are used must be documented prior to beginning measurements. Consistent failure in duplicate agreement may indicate a problem in the measurement process and should be investigated.

2.5.11.4 Control Devices

2.5.11.4.1 Laboratory Control Devices. The laboratory background level for each batch of LS devices should be established by each laboratory or supplier. Suppliers should measure the background of a statistically significant number of unexposed LS devices that have been processed according to their standard operating procedures (laboratory blanks). Normally, the analysis laboratory or supplier calculates the net readings (which are used to calculate the reported sample radon concentrations) by subtracting the laboratory blank values from the results obtained from the field detectors.

2.5.11.4.2 Field Control Devices. Field control devices (field blanks) should consist of a minimum of five percent of the devices that are deployed every month or 25, whichever is smaller. Large users of LS detectors should set these aside from each shipment, keep them sealed and in a low radon (less than 0.2 pCi/L) environment, label them in the same manner as the field devices, and send them back to the supplier with one shipment each month for analysis. These control devices measure the background exposure that may accumulate during shipment or storage, and the results should be monitored and recorded. If one or a few of

the field control detectors have concentrations significantly greater than the LLD established by the supplier, it may indicate defective devices or procedures. If most of the controls have concentrations significantly greater than the LLD, the average value at the field controls should be subtracted from the reported field device concentration and the supplier notified of a possible problem.

2.5.11.5 Routine Instrument Checks. Proper operation of all radiation counting instruments requires that their response to a reference source be constant to within established limits. Therefore, counting equipment should be subject to routine checks to ensure proper operation. This is achieved by counting an instrument check source at least once per day. The characteristics of the check source (i.e., type of radiation emitted) should, if possible, be similar to the samples to be analyzed. The count rate of the check source should be high enough to yield good counting statistics in a short time (for example, 1,000 to 10,000 counts per minute).

2.6 PROTOCOL FOR USING GRAB RADON SAMPLING (GB, GC, GS), PUMP/COLLAPSIBLE BAG DEVICES (PB), AND THREE-DAY INTEGRATING EVACUATED SCINTILLATION CELLS (SC) TO MEASURE INDOOR RADON CONCENTRATIONS

2.6.1 Purpose

This protocol provides guidance for three similar methods that measure indoor radon air concentrations: grab radon sampling techniques (GB, GC, GS), pumps with collapsible bags as devices (PB), and three-day integrating evacuated scintillation cells (SC). Adherence to this protocol will help obtain accurate and reproducible measurements, ensure uniformity among measurement programs, and allow valid comparisons of results. Measurements made in accordance with this protocol will produce results representative of closed-building conditions. Measurements made under closed-building conditions have a smaller variability and are more reproducible than measurements made when the building conditions are not controlled.

Results of grab sampling are influenced greatly by conditions that exist in the building during and for up to 12 hours prior to the measurement. It is therefore especially important when making grab measurements to conform to closed-building conditions for 12 hours before the measurement. Grab sampling techniques are not recommended for measurements made to determine the need for remedial action. The reader should also refer to the EPA guidance document entitled, "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c) or other appropriate EPA measurement guidance documents.

2.6.2 Scope

This protocol covers, in general terms, the equipment, procedures, and quality control objectives to be used in performing the measurements. It is not meant to replace an instrument manual but, rather, provides guidelines to be incorporated into standard operating procedures by anyone providing measurement services. Questions about these guidelines should be directed to the U.S. Environmental Protection Agency, Office of Radiation Programs, Radon Division (ANR-464), Problem Assessment Branch, 401 M Street, S.W., Washington, D.C. 20460.

2.6.3 Methods

2.6.3.1 Grab Radon Sampling Techniques. There are three grab radon sampling methods covered by this protocol. In the first method, known as grab radon/scintillation cell (GS), a sample of air is drawn into and sealed in a flask or cell that has a zinc sulfide phosphor coating on its interior surfaces. One surface of the cell is fitted with a clear window that is put in contact with a photomultiplier tube to count light pulses (scintillations) resulting from alpha disintegrations from the air sample interacting with the

zinc sulfide coating. The number of pulses is proportional to the radon concentration in the cell. The cell is counted about four hours after filling to allow the short-lived radon decay products to reach equilibrium with the radon. After the cells are placed in the counters, the counting system should be allowed to dark-adapt for two minutes. Correction factors (see Section 2.6.13, Exhibit 2-1) are applied to the counting results to compensate for decay during the time between collection and counting and for decay during counting if the counting time is long (> one hour). Supplementary information on this technique is provided in Section 2.6.13. In a variation of this method, used in some portable instruments, air is pumped continuously through a flow-through-type scintillation cell for just a few minutes. Alpha particles resulting from the decay of radon gas and decay products are counted as the gas is swept through.

A second grab method covered by this protocol, known as grab radon/activated charcoal (GC), uses air pumped through activated charcoal to collect the sample. A charcoal-filled cartridge is placed into a sampler and air is pumped through the carbon cartridge. The pump with a charcoal cartridge is not flow-dependent but must remain operational at the sampling location until the charcoal collects enough radon to be in equilibrium with the radon at the sampling location. A sampling duration of one hour has been found to be optimal for most systems. The cartridge must be weighed prior to and after sampling in order to correct for the reduced sensitivity of the charcoal due to adsorbed water. The cartridges are analyzed by placing them on a sodium iodide gamma scintillation system or a germanium gamma detector. The GC system must be calibrated by analyzing cartridges pumped with known concentrations of radon in a qualified facility.

The third grab method, known as grab radon pump/collapsible bag (GB), uses the same technology described in Section 2.6.3.2 for pump/collapsible bag devices (PB). The GB method covered in this section differs only in that the bag is filled over a much shorter collection period than in the PB method described below.

2.6.3.2 Pump/Collapsible Bag Devices (PB). One of the older and simpler methods of making an integrated measurement of the concentration of radon over a period of time is to collect a sample of ambient air in a radon-proof container over the desired sampling time period and measure the resulting radon concentration in the container.

One practical method is to use a small pump with a very low and uniform flow rate to pump ambient air into an inflatable and collapsible radon-proof bag (Sill 1977). After the desired sampling period (typically 24 hours), the concentration of radon in the bag can be analyzed by any of the standard methods such as the GS protocol (Section 2.6.3.1) using the appropriate radon decay correction factors (Section 2.6.13, Exhibit 2-1). For this method, the counting system should be allowed to dark-adapt for two minutes after the cells are placed in the counters. The main purpose of the collapsible bag is to avoid variation in pump flow rate due to build up of back pressure in a container. Bags that have been measured to have a very low loss of radon by diffusion through the bag have been made of laminated Mylar, aluminized laminated Mylar, and Tedlar®. The pump flow

rate is not critical as long as it is suitable for the size of the bag and the sample duration, but variation of the flow rate over the collection time period of the sample will affect the accuracy of the measurement. A number of suitable battery- and/or charger-operated pumps with controlled flow rates are available commercially.

Although this PB method accumulates radon over a period of time for subsequent analysis, it should not be considered a true integrating method. Radon peaks occurring early in the sampling period will leave less radon for analysis than the same size peak occurring toward the end of the sampling period.

2.6.3.3 Three-Day Integrating Evacuated Scintillation Cells (SC). This method typically uses Lucas-type scintillation cells that have been outfitted with a restricter valve attached to the main valve. Samples are collected by opening the valve on an evacuated cell. The restricter valve is set so that the cell fills from a 30-inch mercury (Hg) vacuum to about 80 percent of its capacity over a three-day period. At the end of the measurement period, the valve is closed and returned to the analysis laboratory. Since the volume of the cell is known, the exact volume of filtered air collected over the three-day measurement period can be calculated from the vacuum gauge reading at the end of the sampling period.

The sample is analyzed on an alpha scintillation counter. Prior to counting, the pressure in the cell is brought to one atmosphere by adding radon-free (aged) air so that the sample is analyzed under the same conditions that prevailed during calibration of the cell. To allow radon and radon decay products to grow into equilibrium and to allow any radon decay products that may have been collected to decay, the sample should be counted no sooner than four hours after the end of the measurement period. After the cells are placed in the counters, the counting system should be allowed to dark-adapt for two minutes.

During the three-day sampling period, some of the radon that has been collected decays. The midpoint of the sampling period cannot be used for the decay correction factor because the airflow into the cell is greater during the initial time of sampling. The fraction of radon that decays must therefore be calculated from the shape of a plot of percent fill versus time. This must be measured for each cell. This factor should be applied as a correction during data reduction.

Since this method accumulates radon over a period of time for subsequent analysis, it is not a true integrating method. Radon peaks occurring early in the sampling period will leave less radon for analysis than the same size peak occurring toward the end of the sampling period.

2.6.4 Equipment

2.6.4.1 Grab Radon Sampling Techniques

2.6.4.1.1 Grab Radon/Scintillation Cell Method (GS). The equipment needed for this method includes the following:

- A scintillation cell (flask) or cells to be filled at the site;
- A pump to flow air through the cell or to evacuate the cell (depending on the valve arrangement on the cell);
- A clock to measure time from collection to counting;
- A filter and filter holder to attach to the air inlet valve of the cell; and
- A data collection log.

The equipment required for analyzing the air sample includes the following:

- A photomultiplier tube and high-voltage assembly in a light-tight chamber;
- A scaler-timer for registering pulses from the photomultiplier tube assembly and timing the counting interval;
- A National Institute of Standards and Technology (NIST)-traceable alpha check source and scintillation disc;
- A calibration flask or cell;
- A vacuum pump and cell flushing apparatus; and
- Aged air or nitrogen for flushing counting cells.

2.6.4.1.2 Grab Radon/Activated Charcoal (GC). The equipment needed for this method includes the following:

- A charcoal cartridge with both apertures sealed with protective metallic or other impermeable covers;
- A pump to pull air through the cartridge;
- A data collection log;

- A sodium iodide gamma scintillation detector and analyzer; and
- An analytic scale capable of weighing small differences in weight (up to several grams) due to water adsorbed by the charcoal.

Laboratory analysis of the saturated charcoal cartridge is performed using a sodium iodide gamma scintillation detector to count the gamma rays emitted by the radon decay products adsorbed on the carbon. The detectors may be used in conjunction with a multi-channel gamma spectrometer or with a single-channel analyzer calibrated to include the appropriate gamma energies.

2.6.4.1.3 Grab Radon Pump/Collapsible Bag Sampling (GB). The equipment requirements for this method is similar to those for the PB method of Section 2.6.4.2.

2.6.4.2 Pump/Collapsible Bag Devices (PB). The following equipment is required to conduct measurements using the PB method:

- A pump with a suitable uniform flow rate. The materials of the pump should not absorb or off-gas any substantial amount of radon;
- A collapsible bag of tested, low radon-loss material; and
- A data collection log.

2.6.4.3 Three-Day Integrating Evacuated Scintillation Cells (SC). The following equipment is required to measure radon with an evacuated cell:

- An evacuated cell with the restricter valve and vacuum gauge prepared by the supplier;
- An instruction sheet and a shipping container (along with a prepaid mailing label, if appropriate; and
- A data collection log.

2.6.5 Predeployment Considerations

The plans of the occupant during the proposed measurement period should be considered before deployment. The measurement should not be made if the occupant will be moving during the measurement period. Deployment should be delayed until the new occupant is settled in the house.

The measurement devices should not be deployed if the occupant's schedule prohibits terminating the measurement at the time selected.

Prior to collection of the grab radon sample, proper operation of the counting equipment must be verified, and counter efficiency and background must be determined. In addition, a background for each cartridge or cell should be determined prior to sampling. This may be done using the procedures described in Section 2.6.13 for flask counting.

For highly accurate cell measurements, it is necessary to standardize cell pressure prior to counting because the path lengths of alpha particles are a function of air density. For example, a cell calibrated at sea level and used to count a sample collected at Grand Junction, Colorado (1,370 meters above sea level) would overestimate the radon activity of the sample by about nine percent (George 1983). This error probably approaches the maximum that would be encountered; therefore, it may not be necessary to make this correction if this error can be tolerated. Correction procedures are given elsewhere (George 1983).

2.6.6 Measurement Criteria

The reader should refer to Section 1.2.2 for the list of general conditions that must be met to ensure standardization of measurement conditions.

2.6.7 Deployment

2.6.7.1 Location Selection. The reader should refer to Section 1.2.3 for standard criteria that must be considered when choosing a measurement device location.

2.6.7.2 Sampling with GB, GC, and GS. All air samples drawn into scintillation cells or flasks must be filtered to remove radon decay products and other airborne radioactive particulates. The sampling hose should be short so as to draw room air (not hose air) into the cell. Filters may be reused many times as long as they remain undamaged and functional.

For collection of a sample using a single-valve cell (Lucas-type), the cell is evacuated to at least 25 inches of mercury, the filter is attached to the cell, and the valve is opened allowing the cell to fill with air. At least 10 seconds should be allowed for the cell to fill completely. To ensure a good vacuum at the time of sampling, the cell may be evacuated using a small hand-operated pump in the room being sampled. It is good practice to evacuate the cell at least five times, allowing it to fill completely with room air each time. The air to be sampled must flow through the filter each time. If it can be demonstrated that the cells and valves do not leak, it is acceptable to evacuate the cells in the laboratory and simply attach the filter and open the valve in the building to collect a sample.

To sample using the double-valve, flow-through type cell, the filter should be attached to the inlet valve and a suitable vacuum pump should be attached to the other valve. The pump may be motor-driven or hand-operated. To begin sampling, both valves should be opened and the pump operated to flow at least 10 complete air exchanges through the cell. The pump is then stopped and both valves are closed.

Sampling using the GC or GB method is accomplished by opening and attaching a prepared sealed cartridge or collapsible bag to the sampling pump. For charcoal cartridges, the pump should draw air through the cartridge at approximately the same rate as that used in calibrating the system. Sampling should continue until the charcoal collects enough radon to be in equilibrium with the radon at the sampling site. A one-hour sampling period is typical for most GC systems. For the GB method, the pump should have a known uniform flow rate and the system should be leak-proof.

2.6.7.3 Timely Deployment of SCs. SC devices should be deployed within the period specified by the supplier. Until they are deployed, they should remain tightly sealed to maintain maximum sensitivity and accuracy.

To deploy the SC device, the reading of the attached vacuum gauge must be recorded on the log sheet along with the start-date and -time for the sample. The sample collection is started by opening the main valve according to the supplier's instructions.

2.6.8 Retrieval of Devices

2.6.8.1 Grab Radon Sampling Techniques. All pertinent sampling information (discussed in Sections 1.2.4 and 2.6.7) should be recorded after completing the measurement. The detectors should be packaged carefully for return to the counting location so that the samples will not be lost due to breakage, valves being opened, or loss of cartridge integrity.

2.6.8.2 Three-Day Integrating Evacuated Scintillation Cells (SC). The SC device should be deployed for the measurement period specified in the instructions supplied by the analytical laboratory (typically three days). If the occupant is terminating the sampling, the instructions should inform the occupant of when and how to terminate the sampling period and should indicate that the actual time of termination must be documented on the data form. In addition, the vacuum gauge reading must be recorded on the data form after the sampling valve is closed. The occupant should also be instructed to send the device to the laboratory as soon as possible, preferably on the day of sample termination.

At the end of the monitoring period, the device should be inspected for any deviation from the conditions described in the log book at the time of deployment. Any changes should be noted.

2.6.9 Documentation

The reader should refer to Section 1.2.4 for the list of standard information that must be documented so that data interpretation and comparison can be made. In addition to this list, the following are method-specific details of documentation requirements.

- For GBs, GCs, and GSs, the serial numbers of cells, cartridges, bags, pumps, and counting equipment should also be recorded.
- For PBs, the serial numbers of bags, pumps, and equipment used for analysis of the radon concentration should also be recorded.
- For SCs, the start-time and stop-time vacuum gauge readings should also be recorded, along with the serial numbers of the cells and counting equipment.

2.6.10 Counting and Calculations

2.6.10.1 Grab Radon Sampling Techniques

2.6.10.1.1 Grab Radon/Scintillation Cell Sampling (GS). Cells should not be counted for at least four hours following the time of collection. Background and check sources should be counted as described in Section 2.6.13. The cell to be counted is placed on the photomultiplier tube, the cover placed over the cell, and the system allowed to dark-adapt. The cell may then be counted for a sufficient period to collect an adequate number of counts for good counting statistics in relation to the system background counts.

2.6.10.1.2 Grab Radon/Activated Charcoal Sampling (GC). Cartridges should not be analyzed for at least four hours after the end of sampling to allow for ingrowth of the radon decay products. Cartridges should then be analyzed in a laboratory following removal from the sampling location. The cartridge should be weighed, and if necessary, a correction should be applied for the increase in weight due to moisture adsorption. The maximum allowable delay time between the end of sampling and analysis will vary with the background experienced in each laboratory and should be evaluated, especially if sensitivity is of prime consideration. The cartridge should be analyzed on a calibrated sodium iodide gamma scintillation system or a germanium gamma detector.

2.6.10.1.3 Grab Radon Pump/Collapsible Bag Sampling (GB). After a four-hour waiting period, the concentration of radon in the bag can be analyzed by any of the standard methods including the GS method described above (Section 2.6.10.1.1).

2.6.10.1.4 Cell Flushing and Storage. After the cells have been counted and data are satisfactorily recorded, the cells must be flushed with aged air or nitrogen to remove the sample. Flow-through cells are flushed with at least 10 volume exchanges at a flow of about two liters per minute. Cells with single valves are evacuated and refilled with aged air or nitrogen at least five times. The cells are left filled with aged air or nitrogen and allowed to sit overnight before being counted for background. If an acceptable background is obtained, the cell is ready for reuse.

2.6.10.2 Pump/Collapsible Bag Devices (PB). If the radon concentration in the collapsible bag is to be analyzed on site, the appropriate grab radon sampling protocol (Section 2.6.10.1) should be followed.

If the radon concentration is to be measured by an analysis laboratory, the bag should be delivered to the laboratory as soon as possible following completion of sampling, especially if low concentrations are being measured.

2.6.10.3 Three-Day Integrating Evacuated Scintillation Cells (SC). SC devices should be returned to the supplier's analysis laboratory as soon as possible following removal from the buildings. The maximum allowable delay time between the end of sampling and analysis should not exceed the time specified by the supplier's instructions, especially if sensitivity is an important consideration. Corrections for the radon-222 decay during sampling, during the interval between sampling and counting, and during counting, will be made by the analysis laboratory.

2.6.11 Analysis Requirements

2.6.11.1 Sensitivity.

2.6.11.1.1 Grab Radon Sampling Techniques. The sensitivity of the GS method is dependent on the volume of the cell being used. However, sensitivities of 0.1 picoCuries per liter (pCi/L) are achievable (George 1980, George 1983). For the GC method, the lower limit of detection (LLD [calculated using methods described by Altshuler and Pasternack 1963]) should be 1.0 pCi/L or less. This can be achieved normally with a counting time of up to 30 minutes. The sensitivity of the GB method depends on the analysis method used.

2.6.11.1.2 Pump/Collapsible Bag Devices (PB). The LLD for a PB will depend on the method used to analyze the contents of the bag. If a GS method is used, an LLD of a few tenths of a pCi/L should be possible.

2.6.11.1.3 Three-Day Integrating Evacuated Scintillation Cells (SC). The LLD should be specified by individual suppliers for SC devices exposed and shipped

according to their directions. It is estimated that LLDs of a few tenths of a pCi/L are achievable with these devices.

2.6.11.2 Precision. The results of duplicates (collocated measurements) should be monitored and recorded using the results of the duplicate device analyses described in Section 2.6.12.3 of this protocol. These methods can produce duplicate measurements with a coefficient of variation of 10 percent or less at 4 pCi/L or greater. An alternate measure of precision is a relative percent difference, defined as the difference between two duplicate measurements divided by their mean; note that these two measures of precision are not identical quantities. It is important that precision be monitored frequently over a range of radon concentrations and that a systematic and documented method for evaluating changes in precision be part of the operating procedures.

2.6.12 Quality Assurance

The purpose of a quality assurance program is to identify the accuracy and precision of the measurements and to ensure that the measurements are not influenced by exposure from sources outside the intended structure. The quality assurance program should include the maintenance of control charts (Goldin 1984); general information is also available (Taylor 1987, U.S. EPA 1984).

This section describes five parts of a quality assurance program: (1) calibration of the system, (2) known exposure measurements, (3) duplicate (collocated) devices, (4) background measurements/control devices, and (5) routine instrument checks. Each type of method (GB, GC, GS, PB, and SC) requires some variation of all parts of the program.

2.6.12.1 Calibration

Every device should be calibrated in a radon calibration chamber before being put into service, and after any repairs or modifications. Subsequent recalibrations should be done once every 12 months, with cross-checks to a recently calibrated instrument at least semiannually.

2.6.12.1.1 Calibration Factors. Determination of calibration factors requires exposure of calibration devices to known concentrations of radon-222 in a radon exposure chamber at carefully measured radon concentrations. Since the cells are subject to shipping and handling, they should be recalibrated periodically at radon levels similar to those found in tested buildings. Scintillation counting systems used to count exposed cells should be either the system used to calibrate the cell or one calibrated against that system.

2.6.12.1.2 Cell Calibration. If a GS method of measuring the radon concentrations is used in the PB or GB methods, the following procedure on calibration should be followed.

The cell counting system consisting of the scaler, detector, and high-voltage supply must be calibrated. The correct high voltage is determined by increasing the high voltage by increments and plotting the resultant counts. This procedure is described elsewhere (George 1983). Each counting system should be calibrated in a radon calibration chamber before being put into service, and after any repairs or modifications. Subsequent recalibrations should be done once every 12 months, with cross-checks to a recently calibrated instrument at least semiannually. Also, a check source or calibration cell should be counted in each analysis system each day to demonstrate proper operation prior to counting any samples.

A separate calibration factor must be obtained for each cell in the counting system. This is done by filling each cell with radon of a known concentration and counting the cell to determine the conversion factor (in counts per minute per pCi). The known concentration of radon may be obtained from a radon calibration chamber or estimated from a bubbler tube containing a known concentration of radium. These calibration procedures are discussed in more detail elsewhere (Beckman 1975, George 1976, Lucas 1957).

2.6.12.1.3 Grab-Radon/Activated Charcoal (GC) Method Calibration. This method must be calibrated in a radon calibration chamber to establish a calibration factor for a specific cartridge model. Samples should be taken at different humidities and temperatures to establish correction factors. Calibration should be carried out at several flow rates and exposure times to verify the acceptable limits. Calibration factors must be established with the identical gamma counting system and counting geometry used in sampling.

2.6.12.2 Known Exposure Measurements. Anyone providing measurement services using these methods should submit devices with known radon exposures (spiked samples) for analysis at a rate of three per 100 measurements, with a minimum of three per year and a maximum required of six per month. Known exposure (spiked) devices should be labeled in the same manner as the field devices to assure identical processing. The results of the known exposure analyses should be monitored and recorded, and any significant deviation from the known concentration to which they were exposed should be investigated.

2.6.12.3 Duplicate (Collocated) Devices. Anyone providing measurement services with these methods should place duplicate devices in enough houses to test the precision of the measurement. The number of duplicate detectors deployed should be approximately 10 percent of the number of detectors deployed each month or 50, whichever is smaller.

To the greatest extent possible, care should be taken to ensure that the samples are duplicates, are taken in close proximity, and are away from drafts. The samples selected for duplication should be distributed systematically throughout the entire population of samples. The duplicate devices should be shipped, stored, exposed, and analyzed under the same conditions, and not identified as duplicates to the processing laboratory. Groups selling measurement services to homeowners can accomplish this by making two side-by-side measurements in a random selection of homes. Data from duplicate devices should be evaluated using the procedures described by Goldin (section 5.3 of Goldin 1984), by Taylor (Taylor 1987), or by the EPA (U.S. EPA 1984). Whatever procedures are used must be documented prior to beginning measurements. Consistent failure in duplicate agreement may indicate a problem in the measurement process and should be investigated.

2.6.12.4 Background Measurements/Control Devices

2.6.12.4.1 Background Measurements. A background count for each type of system is determined prior to measurement. When the GC method is used, the background of the charcoal should also be assessed routinely.

2.6.12.4.2 Laboratory Control Devices. The background level for each device should be established by each supplier. Suppliers should measure the background of each device before each use or periodically, with a frequency based on experience. In order to calculate the radon concentrations of the sample, the background should be subtracted from the field readings taken with that cell.

2.6.12.4.3 Field Control Devices. Field control devices (field blanks) should consist of a minimum of five percent of the devices that are deployed every month or 25, whichever is smaller. Users should set these aside from each shipment, keep them sealed and in a low radon (less than 0.2 pCi/L) environment, label them in the same manner as the field devices, and send them back to the supplier with one shipment each month for analyses. It may be clear to the analysis laboratory that these are blanks, however it is still important to conduct the analysis. For the SC method, careful initial and final readings of the vacuum gauges on the control cells and the cell background counts on analysis will be of some use in detecting an occasional leaking cell, but any background detected in a leaking cell is not relevant to the measured field sample concentrations.

2.6.12.5 Routine Instrument Checks. Proper operation of all radiation counting instruments requires that their response to a reference source be constant to within established limits. Therefore, counting equipment should be subject to routine checks to ensure proper operation. This is achieved by counting an instrument check source at least once per day. The characteristics of the check source (i.e., geometry, type of radiation emitted, etc.) should, if possible, be similar to the samples to be analyzed. The

count rate of the check source should be high enough to yield good counting statistics in a short time (for example, 1,000 to 10,000 counts per minute).

Pumps and flow meters should be checked routinely to ensure accuracy of volume measurements. This may be performed using a dry-gas meter or other flow measurement device of traceable accuracy.

2.6.13 Supplementary Information for the Grab Radon Sampling/ Scintillation Cell (GS) Method

2.6.13.1 Procedure. The procedure described below is that used by the EPA Office of Radiation Program in its field measurement programs. It is designed for measurements made using specific cell counters and their associated cells. Equipment is available from several suppliers, and it may be necessary to modify the procedure slightly to accommodate these differences. For example, the correct cell volume must be used in calculating the activity in the cell. The following is a general procedure for equipment used by the EPA:

(1) The cells to be used are flushed with aged air or nitrogen to remove traces of the previous sample. It may be necessary to store cells for 24 hours prior to reuse if the cell had contained a high activity sample. Each cell is placed in the counter, and allowed two minutes for the system to become dark-adapted. The background of the cell is then counted for ten minutes. Background data are recorded for each cell.

(2) At the survey site, the sample is collected by flowing air into the longer tube in the top of the double-valve cell for a period sufficient to allow 10 air exchanges. For the single-valve cells, it is only necessary to open the valve on the evacuated cells and allow 10 to 15 seconds for complete filling. Cells must be filled with air forced through a filter to prevent entry of airborne particulates.

(3) The filled cells must be allowed to equilibrate for four hours prior to counting. The cells should not be exposed to bright light prior to counting.

(4) The cells are placed in the counters, and the systems are allowed to dark-adapt for two minutes. The cells are then counted. Counting time will vary based on the activity in the cell; however, at least 1,000 counts is desirable to provide good statistics.

(5) The activity in the sample is calculated and corrected for ingrowth and decay as described below.

2.6.13.2 Calculation of Results. The radon concentration in pCi/L is determined using the following formula:

$$pCi/L = \frac{cpm(s) - cpm(bkg)}{E} \times \frac{C}{A} \times \frac{1}{V}$$

Where:

cpm(s)	=	Counts per minute for the sample
cpm(bkg)	=	Counts per minute for background
E	=	Efficiency of the system determined for each cell. For the cells used by the EPA, the factor is typically 4-5 cpm/pCi.
C	=	Radon correction factor for decay during counting (from Exhibit 2-1)
A	=	Radon correction factor for decay of radon from time of collection to start of counting (from Exhibit 2-1)
V	=	Volume of counting cell in liters (L).

2.6.13.3 Sample Calculation. The following sample calculation demonstrates the procedure for calculating results:

- Background count for system = 10 counts in 10 minutes, or 1 cpm
- Sample count for 120 minutes = 1200 counts, or 10 cpm
- System efficiency (E) from cell calibration. = 4.62 cpm/pCi
- Count time correction (C) for 120 minutes = 1.00757
- Delay time correction (A) for 4 hours = 0.97026
- Volume correction (V) for cell = 0.170 L

$$pCi/L = \frac{10 \text{ cpm} - 1 \text{ cpm}}{4.62 \text{ cpm/pCi}} \times \frac{1.00757}{0.97026} \times \frac{1}{0.170 \text{ L}} = 11.9$$

Exhibit 2-1

Radon Correction Factors

A = Correction for radon decay from time of collection to start of counting
C = Correction for radon decay during counting

	A			C
Time	Minutes	Hours	Days	Hours
0	1.00000	1.00000	1.00000	1.00000
1	0.99987	0.99248	0.83431	1.00378
2	0.99975	0.98502	0.69607	1.00757
3	0.99962	0.97761	0.58074	1.01136
4	0.99950	0.97026	0.48451	1.01517
5	0.99937	0.96296	0.40423	1.01899
6	0.99925	0.95572	0.33726	1.02281
7	0.99912	0.94854	0.26138	1.02665
8	0.99899	0.94140	0.23475	1.03050
9	0.99887	0.93432	0.19586	1.03435
10	0.99874	0.92730	0.16341	1.03821
11	0.99862	0.92033	0.13633	1.04209
12	0.99849	0.91340	0.11374	1.04597
13	0.99837	0.90654	0.09490	1.04986
14	0.99824	0.89972	0.07917	1.05377
15	0.99811	0.89295	0.06605	1.05768
16	0.99799	0.88624	0.05511	1.06160
17	0.99786	0.87958	0.04598	1.06553
18	0.99774	0.87296	0.03836	1.06947
19	0.99761	0.86640	0.03200	1.07342
20	0.99749	0.85988	0.02670	1.07738
21	0.99736	0.85342	0.02228	1.08135
22	0.99724	0.84700	0.01859	1.08532
23	0.99711	0.84063	0.01551	1.08931
24	0.99699	0.83431	0.01294	1.09331
25	0.99686	0.82803	0.01079	1.09732

Exhibit 2-1 (continued)

Radon Correction Factors

A = Correction for radon decay from time of collection to start of counting
C = Correction for radon decay during counting

Time	A			C
	Minutes	Hours	Days	Hours
26	0.99673	0.82181	0.00901	1.10133
27	0.99661	0.81563	0.00751	1.10536
28	0.99648	0.80950	0.00627	1.10939
29	0.99636	0.80341	0.00523	1.11344
30	0.99623	0.79737	0.00436	1.11749
31	0.99611	0.79137	0.00364	1.12155
32	0.99598	0.78542	0.00304	1.12562
33	0.99586	0.77951	0.00253	1.12971
34	0.99573	0.77365	0.00211	1.13380
35	0.99561	0.76784	0.00176	1.13790
36	0.99548	0.76206	0.00147	1.14201
37	0.99536	0.75633	0.00123	1.14613
38	0.99523	0.75064	0.00102	1.15026
39	0.99511	0.74500	0.00085	1.15440
40	0.99498	0.73940	0.00071	1.15854
41	0.99486	0.73384	0.00059	1.16270
42	0.99473	0.72832	0.00050	1.16687
43	0.99461	0.72284	0.00041	1.17105
44	0.99448	0.71741	0.00035	1.17523
45	0.99435	0.71201	0.00029	1.17943
46	0.99423	0.70666	0.00024	1.18363
47	0.99410	0.70134	0.00020	1.18784
48	0.99398	0.69607	0.00017	1.19207
49	0.99385	0.69084	0.00014	1.19630
50	0.99373	0.68564	0.00012	1.20054

Exhibit 2-1 (continued)

Radon Correction Factors

A = Correction for radon decay from time of collection to start of counting
C = Correction for radon decay during counting

Time	A			C
	Minutes	Hours	Days	Hours
51	0.99360	0.68049	0.00010	1.20479
52	0.99348	0.67537	0.00008	1.20905
53	0.99335	0.67029	0.00007	1.21332
54	0.99323	0.66525	0.00006	1.21760
55	0.99310	0.66025	0.00005	1.22189
56	0.99298	0.65528	0.00004	1.22619
57	0.99286	0.65036	0.00003	1.23050
58	0.99273	0.64547	0.00003	1.23481
59	0.99261	0.64061	0.00002	1.23914
60	0.99248	0.63579	0.00002	1.24347

2.7 INTERIM PROTOCOL FOR USING UNFILTERED TRACK DETECTION (UT) TO MEASURE INDOOR RADON CONCENTRATIONS

2.7.1 Purpose

This interim protocol provides guidance for using unfiltered track detection (UT) to obtain accurate and reproducible measurements of indoor radon concentrations. The Agency has not conducted large-scale field tests using the UT technique, and this interim protocol has been prepared with the assistance of researchers who have field experience with this method. As the EPA and others acquire more experience with this interim technique, the guidelines may be revised. Adherence to this protocol will help ensure uniformity among measurement programs and allow valid intercomparison of results. The investigator should also follow guidance provided by the EPA in "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c) or other appropriate EPA measurement guidance documents.

2.7.2 Scope

This protocol covers, in general terms, the equipment, procedures, and quality control objectives to be used in performing the measurements. It is not meant to replace an instrument manual but, rather, provides guidelines to be incorporated into standard operating procedures by anyone providing measurement services. Questions about these guidelines should be addressed to the U.S. Environmental Protection Agency, Office of Radiation Programs, Radon Division (ANR-464), Problem Assessment Branch, 401 M Street, S.W., Washington, D.C., 20460.

2.7.3 Method

A UT detector consists of a piece of cellulose nitrate film packaged in a shielded container. Alpha particles emitted by radon and its decay products in air strike the detector and produce submicroscopic damage tracks. Cellulose nitrate is sensitive to alpha energies between about 1.5 MeV and 4.8 MeV (Damkjaer 1986, Jonsson 1987). It is not sensitive to radon decay products that plate out on the detector since their energies are above 5 MeV. Because the device detects (with different sensitivities) both radon and radon decay products, the equilibrium ratio (calculated as [working level X 100] per pCi/L of radon) between radon decay products and radon can affect the device's ability to measure accurately the concentration of radon gas. While the effect may not be pronounced at values found typically in homes (estimated usually in the range from 20 to 60 percent [Nazaroff and Nero 1988]), the error becomes significant when extreme values are encountered. Based on the EPA specifications, devices of this type (which are produced by several manufacturers) can be operated over an equilibrium range of about 40 percent, with the midpoint value available from the manufacturer.

At the end of the measurement period, the detectors are returned to a laboratory for processing and analysis. Detectors are placed in a caustic solution that accentuates the damage tracks so they can be counted using a microscope or an automatic spark counter. The detector may be exposed on one or both sides. The number of tracks per unit area is correlated to the radon concentration in air, using a conversion factor derived from data generated at a calibration facility. This conversion factor may vary for different ranges of equilibrium ratio because of the contribution from radon or radon decay products. Within a predetermined range, the number of tracks produced per unit of analyzed detector area per unit of time is proportional to the radon concentration.

Several factors contribute to the variability of the UT measurement results, including equilibrium ratio, differences in the detector response within and between batches of film, detector placement, differences in the number of background tracks, variations in etching conditions, and type of readout mechanism. Since the variability in UT measurement results decreases as the number of net tracks counted increases, counting more tracks over a larger area of the detector will reduce the uncertainty of the result. Whereas a counting area of a few square millimeters is typical with the filtered alpha track detector, it is more common to count one or more square centimeters with the UT detector.

2.7.4 Equipment

UT detectors are available from commercial suppliers. These suppliers offer contract services in which they provide the detector and subsequent analysis and reporting for a unit price. Establishing an in-house capability to provide packaged detectors, a calibration program, and a readout program would probably not be practical or economically advantageous for most users. Therefore, details for establishing the analytical aspects of a UT program are omitted from this protocol.

Assuming that UT detectors are obtained from a commercial supplier, the following equipment is needed to initiate monitoring in a house:

- The UT detector packaged in an individual, shielded container to prevent extraneous exposure before deployment;
- An instruction sheet for the occupant, a sample log sheet, and a shipping container (along with a mailing label, if appropriate;
- At the time of retrieval, some means for sealing the detector prior to returning it to the supplier for analysis; and
- A data collection log, if appropriate.

2.7.5 Predeployment Considerations

The plans of the occupant during the proposed measurement period should be considered before deployment. The UT measurement should not be made if the occupant will be moving during the measurement period. Deployment should be delayed until the new occupant is settled in the house.

The UT detector should not be deployed if the user's schedule prohibits terminating the measurement at the appropriate time.

2.7.6 Measurement Criteria

The reader should refer to Section 1.2.2 for the list of general conditions that must be met to ensure standardization of measurement conditions.

2.7.7 Deployment

2.7.7.1 Location Selection. The reader should refer to Section 1.2.3 for standard criteria that must be considered when choosing a measurement device location.

If the detector is installed during a site visit, the final site selected should be shown to the building occupant to be certain it is acceptable for the duration of the measurement period.

2.7.7.2 Timely Deployment. A batch of UT detectors should be deployed into buildings as soon as possible after delivery from the supplier. To minimize chances of high background exposures, groups should not order more detectors than they can reasonably expect to install within the following few months. If the storage time exceeds more than a few months, the background exposures from a sample of the stored detectors should be assessed to determine if they are different from the background of detectors that are not stored for long periods. The supplier's instructions regarding storage and background determination should be followed. This background assessment of detectors stored for long periods is not necessary if the analysis laboratory measures routinely the background of stored detectors, and if the stored detectors remain tightly sealed.

The sampling period is initiated when the cellulose nitrate film is exposed. The detector should be inspected to ensure that it is intact and has not been physically damaged in shipment or handling.

2.7.8 Retrieval of Detectors

The device should be deployed for the measurement period specified in the instructions supplied by the analytical laboratory. If the occupant is terminating the

sampling, the instructions should inform the occupant of when to terminate the sampling period and should indicate that the actual time of termination must be documented on the device. In addition, the occupant also should be instructed to send the device to the laboratory as soon as possible, preferably the day of sample termination. The analysis system should be calibrated to permit accurate analysis of devices deployed for some reasonable time beyond the recommended sampling period.

At the end of the measurement period, the detector should be inspected for damage or deviation from the conditions entered in the log book at the time of deployment. Any changes should be noted in the log book. The date of removal is entered on the data form for the detector and in the log book. The detector is then resealed according to instructions supplied by the manufacturer. After retrieval, the detectors should be returned as soon as possible to the analytical laboratory for processing.

2.7.9 Documentation

The reader should refer to Section 1.2.4 for the list of standard information that must be documented so that data interpretation and comparison can be made.

2.7.10 Analysis Requirements

2.7.10.1 Sensitivity. The UT method permits analysis of large counting areas and thus can achieve high sensitivity. The lower limit of detection (LLD [calculated using methods described by Altshuler and Pasternack 1963]) and the precision of a UT system are, in part, dependent upon the total number of tracks counted. The number of tracks counted is dependent on the total area analyzed, the number of film emulsion sides exposed (one or two), the length of time of deployment, and the radon concentration being measured.

2.7.10.2 Precision. The precision should be monitored using the results of the duplicate detectors described in Section 2.7.11.3 of this protocol, rather than a precision quoted by the manufacturer. It is important that precision be monitored continuously over a range of radon concentrations and that a systematic and documented method for evaluating changes in precision be part of the operating procedures.

2.7.11 Quality Assurance

The quality assurance program for a UT system includes five parts: (1) calibration, (2) known exposure measurements, (3) duplicate (collocated) detectors, (4) control detectors, and (5) routine instrument checks. The purpose of a quality assurance program is to identify the accuracy and precision of the measurements and to ensure that the measurements are not influenced by exposure from sources outside the

environment to be measured. The quality assurance program should include the maintenance of control charts (Goldin 1984); general information is also available (Taylor 1987, U.S. EPA 1984).

2.7.11.1 Calibration. Every UT laboratory system should be calibrated in a radon calibration chamber at least once every 12 months. Determination of a calibration factor requires exposure of UT detectors to a known radon and decay product concentration in a radon exposure chamber. These calibration exposures are to be used to obtain or verify the conversion factor between net tracks per unit area and radon concentration. The following guidance is provided to manufacturers and suppliers of this device as minimum requirements in determining the calibration factor:

- UT detectors should be exposed in a radon chamber at several different radon and decay product concentrations similar to those expected in the tested buildings (a minimum of three different concentrations). Concentrations of radon decay products must be known in order to be included in the calculation of the calibration factor.

- A minimum of 10 detectors should be exposed at each level.

- A calibration factor should be determined for each batch of detector material received from the material supplier. Alternatively, calibration factors may be established from several sheets, and these factors extended to detectors from sheets exhibiting similar sensitivities (within pre-established tolerance limits).

- Altitude of the radon chamber must be known if located at more than 600 feet (200 meters) above sea level so that a correction can be included in the calculation of the calibration factor.

2.7.11.2 Known Exposure Measurements. Anyone providing measurement services with UT detectors should submit detectors with known radon and decay product exposures (spiked samples) for analysis at a rate of three per 100 measurements, with a minimum of three per year and a maximum required of six per month. Known exposure (spiked) detectors should be labeled in the same manner as field detectors to ensure identical processing. The results of the spiked detector analyses should be monitored and recorded. Any significant deviation from the known concentrations to which they were exposed should be investigated.

2.7.11.3 Duplicate (Collocated) Detectors. Anyone providing measurement services with UT devices should place duplicate detectors in enough houses to test the precision of the measurement. The number of duplicate detectors deployed should be approximately 10 percent of the number of detectors deployed each month or 50, whichever is smaller. The pair of detectors should be treated identically in every

respect. They should be shipped, stored, opened, installed, removed, and processed together, and not identified as duplicates to the processing laboratory. The samples selected for duplication should be distributed systematically throughout the entire population of measurements. Groups selling measurements to homeowners can do this by providing two detectors (instead of one) to a random selection of purchasers, with instructions to place the detectors side-by-side. Consideration should be given to providing some means to ensure that the duplicate devices are not separated during the measurement period. Data from duplicate detectors should be evaluated using the procedures described by Goldin (section 5.3 of Goldin 1984), by Taylor (Taylor 1987), or by the EPA (U.S. EPA 1984). Whatever procedures are used must be documented prior to beginning measurements. Consistent failure in duplicate agreement may indicate a problem in the measurement process and should be investigated.

2.7.11.4 Control Detectors

2.7.11.4.1 Laboratory Control Detectors. The laboratory background level for each batch of UT detectors should be established by each supplier. Suppliers should measure the background of a statistically significant number of unexposed detectors that have been processed according to their standard operating procedures. Normally, the analysis laboratory or supplier calculates the net readings (which are used to calculate the reported sample radon concentrations) by subtracting the laboratory blank values from the results obtained from the field detectors.

2.7.11.4.2 Field Control Detectors. Field control UT detectors (field blanks) should consist of a minimum of five percent of the devices that are deployed every month or 25, whichever is smaller. Users should set these aside from each shipment, keep them sealed and in a low radon (less than 0.2 pCi/L) environment, label them in the same manner as the field UT detectors to assure identical processing, and send them back to the supplier with the field UT detectors for analysis. These control devices are necessary to measure the background exposure that accumulates during shipment and storage. The results should be monitored and recorded. If one or a few field blanks have concentrations significantly greater than the LLD established by the supplier, it may indicate defective packaging or handling. If the average value from the field control devices (field blanks) is significantly greater than the LLD established by the supplier, this average value should be subtracted from the individual values reported for the other devices in the exposure group.

2.7.11.5 Routine Instrument Checks. Proper functioning of the analysis instruments and proper response by their operators require that the equipment be subject to routine checks. Daily or more frequent monitoring of equipment and operators is vital to ensuring consistently accurate results.

Section 3: INDOOR RADON DECAY PRODUCT MEASUREMENT DEVICE PROTOCOLS

3.1 PROTOCOL FOR USING CONTINUOUS WORKING LEVEL MONITORS (CW) TO MEASURE INDOOR RADON DECAY PRODUCT CONCENTRATIONS

3.1.1 Purpose

This protocol provides guidance for using continuous working level monitors (CW) to obtain accurate and reproducible measurements of indoor radon decay product concentrations. Adherence to this protocol will help ensure uniformity among measurement programs and allow valid intercomparison of results. Measurements made in accordance with this protocol will produce results representative of closed-building conditions. Measurements made under closed-building conditions have a smaller variability and are more reproducible than measurements made when the building conditions are not controlled. The investigator should also follow guidance provided by the EPA in "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c) or other appropriate EPA measurement guidance documents.

3.1.2 Scope

This protocol covers, in general terms, the sample collection and analysis method, the equipment needed, and the quality control objectives of measurements made with CW. It is not meant to replace an instrument manual but, rather, provides guidelines to be incorporated into standard operating procedures by anyone providing measurement services. Questions about these guidelines should be directed to the U.S. Environmental Protection Agency, Office of Radiation Programs, Radon Division (ANR-464), Problem Assessment Branch 401 M Street, S.W., Washington, D.C., 20460.

3.1.3 Method

The CW method samples the ambient air by filtering airborne particles as the air is drawn through a filter cartridge at a low flow rate of about 0.1 to one liter per minute. An alpha detector such as a diffused-junction or surface-barrier detector counts the alpha particles produced by the radon decay products as they decay on the filter. The detector is set normally to detect alpha particles with energies between two and eight MeV. The alpha particles emitted from the radon decay products radium A (Po-218) and radium C' (Po-214) are the significant contributors to the events that are measured by the detector. All CW detectors are capable of measuring individual radon and thoron decay products, while some can be adapted to measure the percentage of thoron decay products. The event count is directly proportional to the number of alpha particles emitted by the radon decay products on the filter. The unit contains typically a microprocessor that stores the

number of counts and elapsed time. The CW detector can be set to record the total counts registered over specified time periods. The unit must be calibrated in a calibration facility to convert count rate to Working Level (WL) values. This may be done initially by the manufacturer, and should be done periodically thereafter by the operator.

3.1.4 Equipment

In addition to the CW detector, equipment needed includes replacement filters, a readout or programming device (if not part of the detector), an alpha-emitting check source, and an air flow rate meter.

3.1.5 Predeployment Considerations

The plans of the occupant during the proposed measurement period should be considered before deployment. The CW measurement should not be made if the occupant will be moving during the measurement period. Deployment should be delayed until the new occupant is settled in the house.

The CW detector should not be deployed if the user's schedule prohibits terminating the measurement at the appropriate time.

3.1.5.1 Pre-Sampling Testing. The CW detector should be tested carefully before and after each measurement in order to:

- Verify that a new filter has been installed and the input parameters and clock are set properly;
- Measure the detector's efficiency with a check source such as Am-241 or Th-230 and ascertain that it compares well with the technical specifications for the unit; and
- Verify the operation of the pump.

When feasible, the unit should be checked after every fourth 48-hour measurement or week of operation to measure the background count rate using the procedures that are in the operating manual for the instrument.

In addition, participation in a laboratory intercomparison program should be conducted initially and at least once every 12 months thereafter, and after equipment repair, to verify that the conversion factor used by the microprocessor is accurate. This is done by comparing the unit's response to a known radon decay product concentration. At this time, the correct operation of the pump also should be verified by measuring the flow rate.

3.1.6 Measurement Criteria

The reader should refer to Section 1.2.2 for the list of general conditions that must be met to ensure standardization of measurement conditions.

3.1.7 Deployment and Operation

3.1.7.1 Location Selection. The reader should refer to Section 1.2.3 for standard criteria that must be considered when choosing a measurement device location.

3.1.7.2 Operation. The CW detector should be programmed to run continuously, recording the periodic integrated WL and, when possible, the total integrated average WL. The sampling period should be 48 hours, with a grace period of two hours (i.e., a sampling period of 46 hours is acceptable if conditions prohibit terminating sampling after exactly 48 hours). The longer the operating time, the smaller the uncertainty associated with using the measurement result to estimate a longer-term average concentration. The integrated average WL over the measurement period should be reported as the measurement result. If results are also reported in pCi/L, it should be stated that this approximate conversion is based on a 50 percent equilibrium ratio, which is typical of the home environment, and any individual environment may have a different relationship between radon and decay products.

3.1.8 Retrieval of Detectors

When the measurement is terminated, the operator should note the stop-date and -time and whether the standardized conditions are still in effect.

3.1.9 Documentation

The reader should refer to Section 1.2.4 for the list of standard information that must be documented so that data interpretation and comparison can be made.

In addition, the serial number of the CW detector and calibration factor used should be recorded.

3.1.10 Analysis Requirements

3.1.10.1 Sensitivity. All known commercially available CW detectors are capable of a lower limit of detection (LLD [calculated using methods described by Altshuler and Pasternack 1963]) of 0.01 WL or less.

3.1.10.2. Precision. Precision should be monitored and recorded using the results of side-by-side measurements described in Section 3.1.11.3 of this protocol. This method can produce duplicate measurements with a coefficient of variation of 10 percent or less

at 0.02 WL or greater. An alternate measure of precision is a relative percent difference, defined as the difference between two duplicate measurements divided by their mean; note that these two measures of precision are not identical quantities. It is important that precision be monitored frequently over a range of radon concentrations and that a systematic and documented method for evaluating changes in precision be part of the operating procedures.

3.1.11 Quality Assurance

The quality assurance program for a CW system includes four parts: (1) calibration and known exposures, (2) background measurements, (3) duplicate measurements, and (4) routine instrument checks. The purpose of a quality assurance program is to identify the accuracy and precision of the measurements and to ensure that the measurements are not influenced by exposure from sources outside the environment to be measured. The quality assurance program should include the maintenance of control charts (Goldin 1984); general information is also available (Taylor 1987, U.S. EPA 1984).

3.1.11.1 Calibration and Known Exposures. Every CW detector should be calibrated in a radon calibration chamber before being put into service, and after any repairs or modifications. Subsequent recalibrations should be done once every 12 months, with cross-checks to a recently calibrated instrument at least semiannually.

3.1.11.2 Background Measurements. Background count rate checks must be conducted after at least every 168 hours (fourth 48-hour measurement) of operation and whenever the unit is calibrated. The CW should be purged with clean, aged air or nitrogen in accordance with the procedures given in the instrument's operating manual. In addition, the background count rate may be monitored more frequently by operating the CW in a low radon environment.

3.1.11.3 Duplicate Measurements. When two or more CW detectors are available, the precision of the measurements can be estimated by operating the detectors side-by-side. The analysis of duplicate results should follow the methodology described by Goldin (section 5.3 in Goldin 1984), by Taylor (Taylor 1987), or by the EPA (U.S. EPA 1984). Whatever procedures are used must be documented prior to beginning measurements. Consistent failure in duplicate agreement may indicate a problem in the measurement process and should be investigated.

3.1.11.4 Routine Instrument Checks. Checks using an Am-241 or similar-energy alpha check source must be performed before and after each measurement. In addition, it is important to check regularly all components of the equipment that affect the result.

Pump and flow meters should be checked routinely to ensure accuracy of volume measurements. This may be performed using a dry-gas meter or other flow measurement device of traceable accuracy.

3.2 PROTOCOL FOR USING RADON PROGENY INTEGRATING SAMPLING UNITS (RPISU or RP) TO MEASURE INDOOR RADON DECAY PRODUCT CONCENTRATIONS

3.2.1 Purpose

This protocol provides guidance for using radon progeny integrating sampling units (RPISU or RP) to produce accurate and reproducible measurements of indoor radon decay product concentrations. Adherence to this procedure will help ensure uniformity in measurement programs and allow valid intercomparison of results. Measurements made in accordance with this protocol will produce results representative of closed-building conditions. Measurements made under closed-building conditions have a smaller variability and are more reproducible than measurements made when the building conditions are not controlled. The investigator should also follow guidance provided by the EPA in "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c) or other appropriate EPA measurement guidance documents.

3.2.2 Scope

This protocol covers, in general terms, the equipment, procedures, analysis, and quality control objectives for measurements made with RPs. It is not meant to replace an instrument manual but, rather, provides guidelines to be incorporated into standard operating procedures by anyone providing measurement services. Questions about these guidelines should be directed to the U.S. Environmental Protection Agency, Office of Radiation Programs, Radon Division (ANR-464), Problem-Assessment Branch, 401 M Street, S.W., Washington, D.C., 20460.

3.2.3 Method

3.2.3.1 Thermoluminescent Dosimeter (TLD) RP. There are three types of RPs. The TLD type contains an air sampling pump that draws a continuous, uniform flow of air through a detector assembly. The detector assembly includes a filter and at least two TLDs. One TLD measures the radiation emitted from radon decay products collected on the filter, and the other TLD is used for a background gamma correction. This RP is intended for a sampling period of 48 hours to a few weeks.

Analysis of the detector TLDs is performed in a laboratory using a TLD reader. Interpretation of the results of this measurement requires a calibration for the detector and the analysis system based on exposures to known concentrations of radon decay products.

3.2.3.2 Alpha Track Detector (ATD) RP. A second type of RP consists of an air sampling pump and an ATD assembly. The air sampling pump draws a continuous, uniform flow

of air through a filter in the detector assembly where the radon decay products are deposited. Opposite to the side of the filter where the radon decay products are deposited is a cylinder with three collimating cylindrical holes. Alpha particles emitted from the radon decay products on the filter pass through the collimating holes and through different thicknesses of energy-absorbing film before impinging on a disc of alpha track detecting plastic film (LR-115 or CR-39). Analysis of the number of alpha particle tracks in each of the three sectors of the film allows the determination of the number of alpha particles derived from radium A (Po-218) and radium C' (Po-214). This feature allows the determination of the equilibrium factor for the radon decay products. This type of RP is intended for a sampling period of about 48 hours to a few weeks.

Etching and counting of the alpha track assembly is carried out by mailing the detector film to the analysis laboratory. Interpretation of the results of this measurement requires a calibration for the detector and the analysis system based on exposure to known concentrations of radon decay products.

3.2.3.3 Electret RP. The electret RP is similar in operation to the TLD-type RP, except that the TLD is replaced with an electret. The current model of this device contains a one-liter-per-minute constant air flow pump and collects the decay products on a 11.4 cm^2 filter. As the radon decay products that are collected on the filter decay, negatively charged ions generated by alpha particle radiation are collected on a positively-charged electret, thereby reducing its surface voltage. This reduction has been demonstrated to be proportional to the radon decay product concentration. For more general information on electrets, the reader should refer to Section 2.3.

RPs are true integrating instruments if the pump flow rate is uniform throughout the sampling period. The electret must be removed from the chamber and the electret voltage measured with a special surface voltmeter both before and after exposure. To determine the average radon concentration during the exposure period, the difference between the initial and final voltages is divided first by a calibration factor and then by the number of exposure days. A background radon concentration equivalent of ambient gamma radiation is subtracted to compute radon concentration. Electret voltage measurements can be made in a laboratory or in the field.

3.2.4 Equipment

The three types of RP sampling systems include a sampling pump and the detector assembly. Sampling with the TLD-type RP requires either a fresh detector assembly or fresh TLD chips to be inserted in the detector assembly. Using the electret-type RP requires a sufficient charge on the electret. Sampling with the ATD-type RP requires a fresh detector disc (LR-115 or CR-39). An air flow rate meter should be available for checking flow rates with the RP, and spare filters should be available as replacements as needed.

3.2.5 Predeployment Considerations

The plans of the occupant during the proposed measurement period should be considered before deployment. The RP measurement should not be made if the occupant will be moving during the measurement period. Deployment should be delayed until the new occupant is settled in the house.

The RPISU should not be deployed if the user's schedule prohibits terminating the measurement at the appropriate time.

Prior to installation in the building, the pump should be checked to ensure that it is operable and capable of maintaining a uniform flow through the detector assembly. Extra pump assemblies should be available during deployment in case a problem is encountered.

Arrangements should be made with the occupant of the building to ensure that entry into the building is possible at the time of installation, and to determine availability of a suitable electrical outlet near the sampling area in the selected room.

3.2.6 Measurement Criteria

The reader should refer to Section 1.2.2 for the list of general conditions that must be met to ensure standardization of measurement conditions.

3.2.7 Deployment and Operation

3.2.7.1 Location Selection. The reader should refer to Section 1.2.3 for standard criteria that must be considered when choosing a measurement device location.

In addition, the air intake (sampling head) should be placed at least 50 centimeters (20 inches) above the floor and at least 10 centimeters (four inches) from surfaces that may obstruct flow.

3.2.7.2 Operation. The RP should be installed and, if possible, the air flow rate checked with a calibrated flow meter. The location, date, starting time, running-time meter reading, and flow rate should be recorded on the detector assembly envelope and in a log. The RP should be observed for a few minutes after initiating measurements to ensure continued operation. The occupants should also be informed about the RP and requested that they report any problems or pump shut-down. The occupants should be aware of the length of time the RP will be operated, and an appointment should be arranged to retrieve the unit. The criteria for the standardized measurement conditions (Section 1.2.2) should also be told to the occupants.

The sampling period should be at least 48 hours, and may need to be longer, depending on the type of RP head. A longer operating time decreases the uncertainty associated with the measurement result.

3.2.8 Retrieval of Devices

Prior to pump shut-down, the flow rate should be measured with a calibrated flow meter (if possible) and the unit should be observed briefly to ensure that it is operating properly. The detector assembly or detector film should be removed for processing and the date, time, running-time meter reading, and flow rate should be recorded both on the envelope and in a log book. The filter should be checked for holes or dust loading and any other observed conditions that might affect the measurement. If TLDs or film discs are to be removed from the detector assembly, removal should be delayed for at least three hours after sampling is completed to allow for decay and registration of radon decay products on the filter.

3.2.9 Documentation

The reader should refer to Section 1.2.4 for the list of standard information that must be documented so that data interpretation and comparison can be made.

In addition, the serial numbers of the RPs, TLDs, film discs, or electrets must be recorded.

3.2.10 Analysis Requirements

Analysis of the film from the ATD-type RPs requires an analysis laboratory equipped to etch and count alpha track film.

Analysis of TLD-type RPs requires a TLD reader. The TLD reader is an instrument that heats the TLDs at a uniform and reproducible rate and measures simultaneously the light emitted by the thermoluminescent material. The readout process is controlled carefully, with the detector purged with nitrogen to prevent spurious emissions. Prior to analyzing the RPISU dosimeters, the TLD reader should be tested periodically using dosimeters exposed to a known level of alpha or gamma radiation. TLDs are prepared for reuse by cleaning and annealing at the prescribed temperature in an oven.

Analysis of the electret-type RPs requires a specially-built surface voltmeter for measuring electret voltages before and after exposure. For more information on analysis requirements, the reader should refer to Section 2.3.10 (Electret Ion Chamber Radon Detectors) of the Radon Measurement Device Protocols.

3.2.10.1 Sensitivity. The lower limit of detection (LLD [calculated using methods described by Altshuler and Pasternack 1963]) should be specified by individual suppliers for RP detectors exposed according to their directions. The LLD will depend upon the

length of the exposure and the background of the detector for materials used. The LLD should be calculated using the results of the laboratory control devices.

3.2.10.2 Precision. Precision should be monitored and recorded using the results of the duplicate detector analyses described in Section 3.2.11.3. This method may achieve a coefficient of variation of 10 percent at radon decay product concentrations of 0.02 WL or greater. An alternate measure of precision is a relative percent difference, defined as the difference between two duplicate measurements divided by their mean; note that these two measures of precision are not identical quantities. It is important that precision be monitored continuously over a range of radon concentrations and that a systematic and documented method for evaluating changes in precision be part of the operating procedures.

3.2.11 Quality Assurance

The quality assurance program for an RP system includes five parts: (1) calibration, (2) known exposure detectors, (3) duplicate (collocated) detectors, (4) control detectors, and (5) routine instrument checks. The purpose of a quality assurance program is to identify the accuracy and precision of the measurements and to ensure that the measurements are not influenced by exposure from sources outside the environment to be measured. The quality assurance program should include the maintenance of control charts (Goldin 1984); general information is also available (Taylor 1987, U.S. EPA 1984).

Users of electret-type RPs should follow the quality assurance guidance given for electret ion chamber devices in Section 2.3 of this document.

3.2.11.1 Calibration. Every RP should be calibrated in a radon calibration chamber before being put into service, and after any repairs or modifications. Subsequent recalibrations should be done once every 12 months, with cross-checks to a recently calibrated instrument at least semiannually. Calibration of RPs requires exposure in a controlled radon-exposure chamber where the radon decay product concentration is known during the exposure period. The detector must be exposed in the chamber using the normal operating flow rate for the RP sampling pumps. Calibration should include exposure of a minimum of four detectors exposed at different radon decay product concentrations representative of the range found in routine measurements. The relationship of TLD reader units or etched track reader units to working level (WL) for a given sample volume and the standard error associated with this measurement should be determined. Calibration of the RPs also includes testing to ensure accuracy of the flow rate measurement.

3.2.11.2 Known Exposure Devices. Anyone providing measurement services with RP devices should submit detectors with known decay product exposures (spiked samples) for analysis at a rate of three per 100 measurements, with a minimum of three per year and a maximum required of six per month. Known exposure detectors should be labeled

in the same manner as the field detectors to assure blind processing. The results of the known exposure detector analysis should be monitored and recorded, and any significant deviation from the known concentration to which they were exposed should be investigated.

3.2.11.3 Duplicate (Collocated) Detectors. Anyone providing measurement services with RP devices should place duplicate detectors in enough houses to test the precision of the measurement. The number of duplicate detectors deployed should be approximately 10 percent of the number of detectors deployed each month or 50, whichever is smaller. The duplicate detectors should be shipped, stored, exposed, and analyzed under the same conditions. The samples selected for duplication should be distributed systematically throughout the entire population of samples. Groups selling measurement services to homeowners can do this by making two side-by-side measurements in a random selection of homes. Data from duplicate detectors should be evaluated using the procedures described by Goldin (section 5.3 in Goldin 1984), by Taylor (Taylor 1987), or by the EPA (U.S. EPA 1984). Whatever procedures are used must be documented prior to beginning measurements. Consistent failure in duplicate agreement may indicate a problem in the measurement process and should be investigated.

3.2.11.4 Control Detectors. TLD-type RPs use a TLD that is shielded from the gamma radiation emitted by the material on the filter. This TLD is incorporated in the detector assembly to measure the environmental gamma exposure of the sampling detector. The two TLDs are processed identically and the environmental gamma exposure is subtracted from the sample reading. Electret-type RPs also require an environmental gamma background correction.

3.2.11.4.1 Laboratory Control Detectors. The laboratory background level for each batch of assembled TLDs should be established by each supplier. Suppliers should measure the background of a statistically significant number of unexposed thermoluminescent assemblies that have been processed according to their standard operating procedures. To calculate the net readings used to calculate the reported sample radon concentrations, the analysis laboratory subtracts this laboratory blank value from the results obtained from the field detectors.

Similarly, the laboratory background level for each batch of ATD-type RPs should be established by each supplier of these detectors. Suppliers should measure the background of a statistically significant number of unexposed detector films that have been processed according to their standard operating procedures. The analysis laboratory will subtract this laboratory blank value from the results obtained from the field detectors before calculating the final result.

Users of electret-type RPs should follow similar control detector procedures discussed in section 2.3.11.1.

3.2.11.4.2 Field Control Detectors (Blanks). Field control detectors (field blanks) should consist of a minimum of five percent of the detectors deployed each month or 25, whichever is smaller. Users should set these aside from each shipment, keep them sealed, label them in the same manner as the field detectors, and, where applicable, send them back to the analysis laboratory as blind controls with one shipment each month. These field blank detectors measure the background exposure that may accumulate during shipment or storage. The results should be monitored and recorded. If one or a few of the field blanks have concentrations significantly greater than the LLD established by the supplier, it may indicate defective material or procedures. If the average value from the background control detectors (field blanks) is significantly greater than the LLD established by the supplier, this average value should be subtracted from the individual values reported for the other detectors in the exposure group. The cause for the elevated field blank readings should then be investigated.

3.2.11.5 Routine Instrument Checks. Proper operation of all analysis equipment requires that their response to a reference source be constant to within established limits. Therefore, analysis equipment should be subject to routine checks to ensure proper operation. This is achieved by counting an instrument check source at least once per day during operation.

Pumps and flow meters should be checked routinely to ensure accuracy of volume measurements. This may be performed using a dry-gas meter or other flow measurement device of traceable accuracy.

3.3 PROTOCOL FOR USING GRAB SAMPLING-WORKING LEVEL (GW) TO MEASURE INDOOR RADON DECAY PRODUCT CONCENTRATIONS

3.3.1 Purpose

This protocol provides guidance for using the grab sampling-working level (GW) technique to provide accurate and reproducible measurements of indoor radon decay product concentrations. Adherence to this protocol will help ensure uniformity among measurement programs and allow valid intercomparison of results. Measurements made in accordance with this procedure will produce results representative of closed-building conditions. Measurements made under closed-building conditions have a smaller variability and are more reproducible than measurements made when the building conditions are not controlled.

The results of the GW method are influenced greatly by conditions that exist in the building during and for up to 12 hours prior to the measurement. It is therefore especially important when making grab measurements to conform to the closed-building conditions for 12 hours before the measurement. Grab sampling techniques are not recommended for measurements made to determine the need for remedial action. The investigator should also follow guidance provided by the EPA in "Protocols for Radon and Radon Decay Product Measurements in Homes" (U.S. EPA 1992c) or other appropriate EPA measurement guidance documents.

3.3.2 Scope

This procedure covers, in general terms, the equipment, procedures, and quality control objectives to be used in performing the measurements. It is not meant to replace an instrument manual but, rather, provides guidelines to be incorporated into standard operating procedures by anyone providing measurement services. Questions about these guidelines should be directed to the U.S. Environmental Protection Agency, Office of Radiation Programs, Radon Division (ANR-464), Problem Assessment Branch, 401 M Street, S.W., Washington, D.C., 20460.

3.3.3 Method

Grab sampling measurements of radon decay product concentrations in air are performed by collecting the decay products from a known volume of air on a filter and by counting the activity on the filter during or following collection. Several methods for performing such measurements have been developed and have been described previously (George 1980). Comparable results may be obtained using all these methods. This procedure, however, will describe two methods that have been used most widely with good results. These are the Kusnetz procedure and the modified Tsivoglou procedure.

The Kusnetz procedure (ANSI 1973, Kusnetz 1956) may be used to obtain results in working levels (WL) when the concentration of individual decay products is unimportant. Decay products from up to 100 liters of air are collected on a filter in a five-minute sampling period. The total alpha activity on the filter is counted at any time between 40 and 90 minutes after the end of sampling. Counting can be done using a scintillation-type counter to obtain gross alpha counts for the selected period. Counts from the filter are converted to disintegrations using the appropriate counter efficiency. The disintegrations from the decay products collected from the known volume of air may be converted into WLs using the appropriate "Kusnetz factor" (see Section 3.4.11, Exhibit 3-1) for the counting time used.

The Tsivoglou procedure (Tsivoglou et al. 1953), as modified by Thomas (Thomas 1972), may be used to determine WL and the concentration of the individual radon decay products. Sampling is the same as that used for the Kusnetz procedure; however, the filter is counted three separate times following collection. The filter is counted between the interval of two to five minutes, six to 20 minutes, and 21 to 30 minutes, following completion of sampling. Count results are used in a series of equations to calculate concentrations of the three radon decay products and WL. These equations and an example calculation appear in Section 3.4.11.

3.3.4 Equipment

Equipment required for radon decay product concentration determination by GW consists of the following items:

- An air sampling pump capable of maintaining a flow rate of two to 25 liters per minute through the selected filter. The flow rate should not vary significantly during the sampling period;
- A filter holder (with adapters for attachment) to accept a 25- or 47-mm diameter, 0.8-micron membrane or glass fiber filter;
- A calibrated air flow measurement device to determine the air flow through the filter during sampling;
- A stopwatch or timer for accurate timing of sampling and counting;
- A scintillation counter and a zinc sulfide scintillation disc;
- A National Institute of Standards and Technology (NIST)-traceable alpha calibration source to determine counter efficiency; and
- A data collection log.

3.3.5 Predeployment Considerations

The plans of the occupant during the proposed measurement period should be considered before deployment. The GW measurement should not be made if the occupant will be moving during the measurement period. Deployment should be delayed until the new occupant is settled in the house.

The GW device should not be deployed if the user's schedule prohibits terminating the measurement at the appropriate time.

3.3.5.1 Premeasurement Testing

Prior to collection of the sample, proper operation of the equipment must be verified, and the counter efficiency and background must be determined. This is especially critical for the Tsivoglou procedure, in which the sample counting must begin two minutes following the end of sampling.

The air pump, filter assembly, and flow meter must be tested to ensure that there are no leaks in the system. The scintillation counter must be operated with the scintillation tray (where applicable) and scintillation disc in place to determine background for the counting system. Also, the counter must be operated with an NIST-traceable alpha calibration source in place of a filter in the counting location to determine system counting efficiency. Both the system background and system efficiency are used in the calculation of results from the actual sample.

3.3.6 Measurement Criteria

The reader should refer to Section 1.2.2 for the list of general conditions that must be met to ensure standardization of measurement conditions.

3.3.7 Deployment

3.3.7.1 Location in Room. The reader should refer to Section 1.2.3 for standard criteria that must be considered when choosing a measurement device location.

3.3.7.2 Sampling. A new filter should be placed in the filter holder prior to entering the building. Care should be taken to avoid puncturing the filter and to avoid leakage. The sampling is initiated by starting the pump and the clock simultaneously. The air flow rate should be noted and recorded in a log book. The time the sampling was begun should also be recorded. The sampling period should be five minutes, and the time from the beginning of sampling to the time of counting must be recorded precisely.

3.3.8 Documentation

The reader should refer to Section 1.2.4 for the list of standard information that must be documented so that data interpretation and comparison can be made.

3.3.9 Analysis Requirements

Analysis may be done using the Kusnetz procedure (ANSI 1973, Kusnetz 1956), the modified Tsivoglou procedure (Thomas 1972, Tsivoglou et al. 1953), or other procedures described elsewhere (George 1980). If the Tsivoglou procedure is used, the counting must be started two minutes following the end of sampling. Analysis using the Kusnetz procedure must be performed between 40 and 90 minutes following the end of sampling. A counting time of 10 minutes during this period is usually used. The reader should refer to Sections 3.3.3 and 3.3.11 for more information.

The filter from the holder must be removed using forceps, and placed carefully facing the scintillation phosphor. The side of the filter on which the decay products were collected must face the phosphor disc. The chamber containing the filter and disc should be closed and allowed to dark-adapt prior to starting counting. For the Tsivoglou method, this procedure of placing the filter in the counting position must be done quickly, since the first of the three counts must begin two minutes following the end of sampling. If the counter used has been shown to be slow to dark-adapt, the counting should be done in a darkened environment. Additional details on the procedure and calculations are available (Kusnetz 1956, Thomas 1972, Tsivoglou et al. 1953).

3.3.9.1 Sensitivity. For a five-minute sampling period (10 to 20 liters of air) on a 25-mm filter, the lower limit of detection (LLD [calculated using methods described by Altshuler and Pasternack 1963]) using the Kusnetz or modified Tsivoglou counting procedure can be approximately 0.0005 WL (George 1980).

3.3.9.2 Precision. Precision should be monitored using the results of duplicate measurements (refer to Section 3.4.10.2). Sources of error in the procedure may result from inaccuracies in measuring the volume of air sampled, characteristics of the filter used, and measurement of the amount of radioactivity on the filter. The method can produce duplicate measurements with a coefficient of variation of 10 percent or less at 0.02 WL or greater. An alternate measure of precision is a relative percent difference, defined as the difference between two duplicate measurements divided by their mean; note that these two measures of precision are not identical quantities. It is important that precision be monitored continuously over a range of radon concentrations and that a systematic and documented method for evaluating changes in precision be part of the operating procedures.

3.3.10 Quality Assurance

The quality assurance program for a GW system includes three parts: (1) calibration of the system, (2) duplicate measurements, and (3) routine instrument checks. The purpose of a quality assurance program is to identify the accuracy and precision of the measurements and to ensure that the measurements are not influenced by exposure from sources outside the environment to be measured. The quality assurance program should include the maintenance of control charts (Goldin 1984); general information is also available (Taylor 1987, U.S. EPA 1984).

3.3.10.1 Calibration. Pumps and flow meters used to sample air must be calibrated routinely to ensure accuracy of volume measurements. This may be performed using a dry-gas meter or other flow measurement device of traceable accuracy.

Every GW device should be calibrated in a radon (decay product) calibration chamber before being put into service, and after any repairs or modifications. Subsequent recalibrations should be done once every 12 months, with cross-checks to a recently calibrated instrument at least semiannually. Grab measurements should be made in a calibration chamber with known radon decay product concentrations to verify the calibration factor. These measurements should also be used to test the collection efficiency and self-absorption of the filter material being used for sampling. A change in the filter material being used requires that the new material be checked for collection efficiency in a calibration chamber.

3.3.10.2 Duplicate Measurements. Anyone providing measurement services with GW devices should place duplicate detectors in enough houses to test the precision of the measurement. The number of duplicate detectors deployed should be approximately 10 percent of the number of detectors deployed each month or 50, whichever is smaller. To the greatest extent possible, care should be taken to ensure that the samples are duplicates. The filter heads should be relatively close to each other and away from drafts. Care should also be taken to ensure that one filter is not in the discharge air stream of the other sampler. The measurements selected for duplication should be distributed systematically throughout the entire population of measurements. Data from duplicate samples should be evaluated using the procedures described by Goldin (section 5.3 of Goldin 1984), by Taylor (Taylor 1987), or by the EPA (U.S. EPA 1984). Whatever procedures are used must be documented prior to beginning measurements. Consistent failure in duplicate agreement may indicate a problem in the measurement process and should be investigated.

3.3.10.3 Routine Instrument Checks. Proper operation of all radiation counting instruments requires that their response to a reference source be constant to within established limits. Therefore, counting equipment should be subject to routine checks to ensure proper operation. This is achieved by counting an instrument check source at least once per day. The characteristics of the check source (i.e., geometry, type of

radiation emitted, etc.) should, if possible, be similar to the samples to be analyzed. The count rate of the check source should be high enough to yield good counting statistics in a short time (for example, 1,000 to 10,000 counts per minute).

The radiological counters should have calibration checks run daily to determine counter efficiency. This is particularly important for portable counters taken into the field that may be subject to rugged use and temperature extremes. These checks are made using an NIST-traceable alpha calibration source such as Am-241. In addition, the system background count rate should be assessed regularly.

Pumps and flow meters should be checked routinely to ensure accuracy of volume measurements. This may be performed using a dry-gas meter or other flow measurement device of traceable accuracy.

3.3.11 Supplementary Information for the Grab Sampling-Working Level (GW) Method

3.3.11.1 Sample Collection. Two commonly used methods are described below. There are several other methods reported in the literature. Sampling using these methods requires collection of radon decay products on a filter, and measuring the alpha activity of the sample with a calibrated detector at time intervals that are specific for each method.

The filter is installed in the filter holder assembly and attached to the pump. The pump is then operated for exactly five minutes, pulling air through the filter. Starting time and air flow rate should be recorded. The pump is stopped at the end of the five-minute sampling time. At this time, the stopwatch should be started or reset.

3.3.11.2 Sample Counting. Sample counting for two different techniques is described below.

3.3.11.2.1 Modified Tsivoglou Technique (Thomas 1972, Tsivoglou et al. 1953). The filter is transferred carefully from the filter holder assembly to the detector. The collection side of the filter is oriented toward the face of the detector.

The counter is operated for the following time intervals (after sampling has stopped): two to five minutes, six to 20 minutes, and 21 to 30 minutes. The total counts for each time period are then recorded.

3.3.11.2.2 Kusnetz Technique (Kusnetz 1956). The filter is transferred carefully from the filter holder assembly to the detector. The collection side of the filter is oriented toward the face of the detector.

The counter is operated over any 10-minute time interval between 40 minutes and 90 minutes after sampling starts. The total counts for the sample and the time (in minutes after sampling) at the midpoint of the 10-minute time interval are then recorded.

3.3.11.3 Data Analysis. Data analysis for the two different techniques is described below.

3.3.11.3.1 Modified Tsivoglou Technique. The concentration, in picoCuries per liter (pCi/L), of each of the radon decay products (Po-218, Pb-214, and Po-214) can be determined by using the following calculations:

$$C_2 = \frac{1}{FE}(0.16921\ G_1 - 0.08213\ G_2 + 0.07765\ G_3 - 0.5608\ R)$$

$$C_3 = \frac{1}{FE}(0.001108\ G_1 - 0.02052\ G_2 + 0.04904\ G_3 - 0.1577\ R)$$

$$C_4 = \frac{1}{FE}(-0.02236\ G_1 + 0.03310\ G_2 - 0.03766\ G_3 - 0.05720\ R)$$

It is important to note that the constants in these equations are based on a 3.04-minute half-life of Po-218. The working level (WL) associated with these concentrations can then be calculated using the following relationship:

$$WL = (1.028 \times 10^{-3} \times C_2 + 5.07 \times 10^{-3} \times C_3 + 3.728 \times 10^{-3} \times C_4)$$

Where:

C_2 = concentration of Po-218 (RaA) in pCi/L;

C_3 = concentration of Pb-214 (RaB) in pCi/L;

C_4 = concentration of Po-214 (RaC') in pCi/L;

F = sampling flow rate in liters per minute (Lpm);

E = counter efficiency in counts per minute/disintegrations per minute (cpm/dpm);

G_1 = gross alpha counts for the time interval of two to five minutes;

G_2 = gross alpha counts for the time interval of six to 20 minutes;

G_3 = gross alpha counts for the time interval of 21 to 30 minutes; and

R = background counting rate in cpm.

Reference: (Thomas 1972).

3.3.11.3.2 Kusnetz Technique. WL is calculated as follows:

$$WL = \frac{C}{K_t V E}$$

Where:

C = sample cpm - background cpm;
K_t = factor determined from Exhibit 3-1 (PHS 1957) for time from end of collection to midpoint of counting;
V = total sample air volume in liters [calculated as flow rate (L/m) x sample time (m)]; and
E = counter efficiency in cpm/dpm.

Exhibit 3-1

Kusnetz Factors
(Public Health Service 1957)

Time	K_t
40	150
42	146
44	142
46	138
48	134
50	130
52	[illegible]
54	122
56	118
58	114
60	110
62	106
64	102
66	98
68	94
70	90
72	87
74	84
76	82
78	78
80	75
82	73
84	69
86	66
88	63
90	60

3.3.11.4 Sample Problems

3.3.11.4.1 Sample Problem for the Modified Tsivoglou Technique

Given:

F = sampling flow rate = 3.5 Lpm
E = counting efficiency = 0.47 cpm/dpm
G_1 = 880
G_2 = 2660
G_3 = 1460
R = 0.5

Calculate:

$$C_2 = \frac{1}{3.5 \times 0.47}(0.16921 \times 880 - 0.08213 \times 2660 + 0.07765 \times 1460 - 0.05608 \times 0.5)$$

$C_2 = 26.8$ pCi/L

$$C_3 = \frac{1}{3.5 \times 0.47}(0.001108 \times 880 - 0.02052 \times 2660 + 0.04904 \times 1460 - 0.1577 \times 0.5)$$

$C_3 = 10.9$ pCi/L

$$C_4 = \frac{1}{3.5 \times 0.47}(-0.02236 \times 880 + 0.03310 \times 2660 - 0.03766 \times 1460 - 0.05720 \times 0.5)$$

$C_4 = 8.1$ pCi/L

$WL = (1.028 \times 10^{-3} \times 26.8 + 5.07 \times 10^{-3} \times 10.9 + 3.728 \times 10^{-3} \times 8.1)$

$WL = 0.11$

3.3.11.4.2 Sample Problem for the Kusnetz Technique

Background count = 3 counts in 5 minutes, or 0.6 cpm

Standard count = 5,985 counts in 5 minutes, or 1,197 cpm

$$\text{Efficiency} = \frac{1197 \text{ cpm} - 0.6 \text{ cpm}}{2430 \text{ dpm}} = 0.49 \text{ (known source of 2439 dpm)}$$

Sample volume = 4.4 liter/minute x 5 minutes = 22 liters

Sample count at 45 minutes (time from end of sampling period to start of counting period) = 560 counts in 10 minutes, or 56 cpm

K_t at 50 minutes (from Exhibit 3-1) = 130

$$WL = \frac{56 \text{ cpm} - 0.6 \text{ cpm}}{130 \times 22 \text{ L} \times 0.49}$$

WL = 0.04

GLOSSARY

Accuracy: The degree of agreement of a measurement (X) with an accepted reference or true value (T); usually expressed as the difference between the two values (X - T), or the difference as a percentage of the reference or true value (100[X - T]/T), and sometimes expressed as a ratio (X/T).

Active radon/radon decay product measurement device: A radon or radon decay product measurement system which uses a sampling device, detector, and measurement system integrated as a complete unit or as separate, but portable, components. Active devices include continuous radon monitors, continuous working level monitors, and grab radon gas and grab working level measurement systems, but does not include devices such as electret ion chamber devices, activated carbon or other adsorbent systems, or alpha track devices.

Alpha particle: Two neutrons and two protons bound as a single particle that is emitted from the nucleus of certain radioactive isotopes in the process of decay.

Background count rate: The counting rate obtained on a given instrument with a background counting sample. Typical reference background counting samples are:

- Empty planchet: for G-M detectors, internal proportional counters, low background beta counters, alpha spectrometers.
- Scintillation vial containing scintillant and sample known to contain no radioactivity: for liquid scintillation counters.
- Container filled with distilled water: for gamma spectrometers.

Background measurements: Measurements made with either active instruments exposed to a radon-free gas, such as aged air or nitrogen, or for passive detectors by analyzing unexposed detectors. Results are subtracted from the actual field measurements before calculating the reported concentration. Background levels may be due to electronic noise of the analysis system, leakage of radon into the detector, detector response to gamma radiation, or other causes.

Background radiation: Radiation arising from radioactive material other than that under consideration. Background radiation due to cosmic rays and natural radioactivity is always present; background radiation may also be due to the presence of radioactive substances in building materials.

Bias: A systematic (consistent) error in test results. Bias can exist between test results and the true value (absolute bias, or lack of accuracy), or between results from different sources (relative bias). For example, if different laboratories analyze a homogeneous and stable blind sample, the relative biases among the laboratories would be measured by the differences existing among the results from the different laboratories. However, if the true value of the blind sample were known, the absolute bias or lack of accuracy from the true value would be known for each laboratory. See **Systematic error.**

Blank sample: A control sample in which the detector is unexposed and submitted for analysis. Often used to determine detector background values.

Blind spikes: Detectors exposed to known radon or decay product concentrations and submitted for analysis without being labelled as such. Used to evaluate the accuracy of the measurement.

Calibrate: To determine the response or reading of an instrument relative to a series of known values over the range of the instrument; results are used to develop correction or calibration factors.

Check source: A radioactive source, not necessarily calibrated, which is used to confirm the continuing satisfactory operation of an instrument.

Coefficient of variation (COV), relative standard deviation (RSD): A measure of precision, calculated as the standard deviation (s or σ) of a set of values divided by the average (X_{ave} or μ), and usually multiplied by 100 to be expressed as a percentage.

$$\text{COV} = \text{RSD} = \frac{s}{X_{ave}} \times 100 \text{ for a sample,}$$

or

$$COV' = RSD' = \frac{\sigma}{\mu} \times 100 \text{ for a population.}$$

See Relative percent difference.

Curie (Ci): A standard measurement for radioactivity, specifically the rate of decay for a gram of radium – 37 billion decays per second. A unit of radioactivity equal to 3.7×10^{10} disintegrations per second.

Duplicate measurements: Two measurements made concurrently and in the same location, or side-by-side. Used to evaluate the precision of the measurement method.

Electron: An elementary constituent of an atom that orbits the nucleus and has a negative charge. Beta decay is radioactive decay in which an electron is emitted from a nucleus.

Electron volt (eV): One eV is equivalent to the energy gained by an electron in passing through a potential difference of one volt. One unit of energy = 1.6×10^{-12} ergs = 1.6×10^{-19} joules; 1 MeV = 10^6 eV.

Equilibrium, radioactive: A state in which the formation of atoms by decay of a parent radioactive isotope is equal to its rate of disintegration by radioactive decay.

Equilibrium ratio, radioactive: The total concentration of radon decay products (RDPs) present divided by the concentration that would exist if the RDPs were in radioactive equilibrium with the radon gas concentration which is present. At equilibrium (i.e., at an equilibrium ratio of 1.0), 1 WL of RDPs would be present when the radon concentration was 100 pCi/L. The ratio is never 1.0 in a house. Due to ventilation and plate-out, the RDPs never reach equilibrium in a house environment. A commonly assumed equilibrium ratio is 0.5 (i.e., the progeny are halfway toward equilibrium), in which case 1 WL corresponds to 200 pCi/L. However, equilibrium ratios vary with time and location, and ratios of 0.3 to 0.7 are commonly observed. Large buildings, including schools, often contain equilibrium ratios less than 0.5.

Exposure time: The length of time a specific mail-in device must be in contact with radon or radon decay products to get an accurate radon measurement. Also called exposure period, exposure parameters, or duration of exposure.

Gamma radiation: Short-wavelength electromagnetic radiation of nuclear origin, with energies between 10 keV to 9 MeV.

Integrating device: A device that measures a single average concentration value over a period of time. Also called a time integrating device.

Ion: An electrically charged atom in which the number of electrons does not equal the number of protons.

Ionization: The process whereby a neutral atom or molecule becomes negatively or positively charged by acquiring or losing an electron.

Ionizing radiation: Any type of radiation capable of producing ionization in materials it contacts; includes high-energy charged particles such as alpha and beta rays, and nonparticulate radiation such as gamma rays and X-rays. In contrast to wave radiation (e.g., visible light and radio waves) in which waves do not ionize adjacent atoms as they move.

Lower limit of detection (LLD): The smallest amount of sample activity which will yield a net count for which there is confidence at a predetermined level that activity is present. For a five percent probability of concluding falsely that activity is present, the LLD is approximately equal to 4.65 times the standard deviation of the background counts (assuming large numbers of counts where Gaussian statistics can be used [ANSI 1989, Pasternack and Harley 1971, U.S. DOE 1990]).

Passive radon/radon decay product measurement device: A radon or radon decay product measurement system in which the sampling device, detector, and measurement system do not function as a complete, integrated unit. Passive devices include electret ion chamber devices, activated carbon or other adsorbent systems, or alpha track devices, but does not include continuous radon/radon decay product monitors, or grab radon/radon decay product measurement systems.

PicoCurie (pCi): One pCi is one trillionth of a Curie, 0.037 disintegrations per second, or 2.22 disintegrations per minute.

PicoCurie per liter (pCi/L): A unit of radioactivity corresponding to one decay every 27 seconds in a volume of one liter, or 0.037 decays per second in every liter of air.

Pooled estimate of variance: An estimate of precision derived from different sets of duplicates, calculated as follows:

$$S_{dp}^2 = \frac{S_{d1}^2 (n_1 - 1) + S_{d2}^2 (n_2 - 1)}{(n_1 - 1) + (n_2 - 1)}$$

where:

S^2dp = pooled variance;
S^2d1 = variance observed with the first group of detectors or equipment;
S^2d2 = variance observed with the second group of detectors or equipment;
n_1 = sample size of the first group of detectors or equipment; and
n_2 = sample size of the second group of detectors or equipment.

Precision: A measure of mutual agreement among individual measurements of the same property, usually under prescribed and similar conditions. Most desirably expressed in terms of the standard deviation, but can be expressed in terms of the variance, pooled estimate of variance, range, relative percent difference, or other statistic.

Quality assurance: A complete program designed to produce results which are valid, scientifically defensible, and of known precision, bias, and accuracy. Includes planning, documentation, and quality control activities.

Quality control: The system of activities to ensure a quality product, including measurements made to ensure and monitor data quality. Includes calibrations, duplicate, blank, and spiked measurements, interlaboratory comparisons, and audits.

Radon (Rn): A colorless, odorless, naturally occurring, radioactive, inert, gaseous element formed by radioactive decay of radium (Ra) atoms. The atomic number is 86. Although other isotopes of radon occur in nature, radon in indoor air is almost exclusively Rn-222.

Radon chamber: An airtight enclosure in which operators can induce and control different levels of radon gas and radon decay products. Volume is such that samples can be taken without affecting the levels of either radon or its decay products within the chamber.

Random error: Variations of repeated measurements that are random in nature and not predictable individually. The causes of random error are assumed to be

indeterminate or nonassignable. The distribution of random errors is assumed generally to be normal (Gaussian).

Range: The difference between the maximum and minimum values of a set of values. When the number of values is small (i.e., eight or less), the range is a relatively sensitive (efficient) measure of variability. As the number of values increases above eight, the efficiency of the range (as an estimator of the variability) decreases rapidly. The range, or difference between two paired values, is of particular importance in air pollution measurement, since in many situations duplicate measurements are performed as part of the quality assurance program.

Relative percent difference (RPD): A measure of precision, calculated by:

$$R_{d\%} = \frac{|X_1 - X_2|}{X_{ave}} \times 100$$

where:

X_1 = concentration observed with the first detector or equipment;
X_2 = concentration observed with the second detector, equipment, or absolute value; and
X_{ave} = average concentration = ((X1 + X2) / 2)

The relative percent difference (RPD) and coefficient of variation (COV) provide a measure of precision, but they are not equal. Below are example duplicate radon results and the corresponding values of relative percent difference and coefficient of variation:

Rn1 (pCi/L)	Rn2 (pCi/L)	RPD (%)	COV (%)
8	9	12	8
13	15	14	10
17	20	16	11
26	30	14	10
7.5	10	29	20

See Coefficient of variation (COV).

Relative standard deviation: See Coefficient of variation.

Spiked measurements, or known exposure measurements: Quality control measurements in which the detector or instrument is exposed to a known concentration and submitted for analysis. Used to evaluate accuracy.

Standard deviation (s): A measure of the scatter of several sample values around their average. For a sample, the standard deviation (s) is the positive square root of the sample variance:

$$s = \frac{\sqrt{\sum_{i=1}^{n} (X_i - X_{ave})^2}}{\sqrt{n-1}}$$

For a finite population, the standard deviation (s) is:

$$\sigma = \frac{\sqrt{\sum_{i=1}^{N} (X_i - \mu)^2}}{\sqrt{N}}$$

where μ is the true arithmetic mean of the population and N is the number of values in the population. The property of the standard deviation that makes it most practically meaningful is that it is in the same units as the observed variable X. For example, the upper 95% probability limit on differences between two values is 2.77 times the sample standard deviation.

Standard operating procedure: A written document which details an operation, analysis, or action whose mechanisms are prescribed thoroughly and which is commonly accepted as the method for performing certain routine or repetitive tasks.

Statistical control chart, Shewhart control chart: A graphical chart with statistical control limits and plotted values (for some applications in chronological order) of some measured parameter for a series of samples. Use of the charts provides a visual display of the pattern of the data, enabling the early detection of time trends and shifts in level. For maximum usefulness in control, such charts should be plotted in a timely manner (i.e., as soon as the data are available).

Statistical control chart limits: The limits on control charts that have been derived by statistical analysis and are used as criteria for action, or for judging whether a set of data does or does not indicate lack of control. On a means control chart, the warning level may be two standard deviations above and below the mean, and the control limit may be three standard deviations above and below the mean.

Systematic error: The condition of a consistent deviation of the results of a measurement process from the reference or known level. The cause for the deviation, or bias, may be known or unknown, but is considered "assignable" (i.e., if the cause is unknown, it should be possible to determine the cause). See **Bias**.

Time integrated sampling: Sampling conducted over a specific time period (e.g., from two days to a year or more) producing results representative of the average value for that period.

Uncertainty: The estimated bounds of the deviation from the mean value, expressed generally as a percentage of the mean value. Taken ordinarily as the sum of (1) the random errors (errors of precision) at the 95% confidence level, and (2) the estimated upper bound of the systematic error (errors of accuracy).

Variance: Mathematically, the sample variance is the sum of squares of the differences between the individual values of a set and the arithmetic average of the set, divided by one less than the number of values:

$$s^2 = \frac{\sum_{i=1}^{n} (X_i - X_{ave})^2}{n - 1}$$

For a finite population, the variance σ^2 is the sum of squares of deviations from the arithmetic mean, divided by the number of values in the population:

$$\sigma^2 = \frac{\sum_{i=1}^{N} (X_i - \mu)^2}{N}$$

where μ is the true arithmetic mean of the population.

Working level (WL): Any combination of short-lived radon decay products in one liter of air that will result in the ultimate emission of 1.3×10^5 MeV of potential alpha energy. This number was chosen because it is approximately the alpha energy released from the decay products in equilibrium with 100 pCi of Ra-222. Exposures are measured in working level months (WLM).

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APPENDIX E

FIELD AUDIT FORM

Appendix E. Field Audit Form

Field Personnel

Auditor: _____ Project Manager: _____
Date: _____ Site Health & Safety Officer: _____
Location: _____ Field Staff: _____
Project: _____
Activity: _____

Health and Safety

Personal Protection Equipment: _____

Incidents: _____

Responses: _____

Noncompliance with Plan: _____

Monitoring Procedures

Sampling Procedure Noncompliance: _____

Field Parameter Measurement Noncompliance: _____

Decontamination Procedure Noncompliance: _____

Field Documentation Noncompliance: _____

Label Noncompliance: _____

Chain-of-Custody/Sample-Analysis-Request: _____

Noncompliance: _____

Preservation Noncompliance: _____

Completeness

Field Duplicate (1/10):

Field Blank (1/10):

Equipment Blank (1/10):

Trip Blank (1/cooler):

MS/MSD (1pair/20):

Noncompliances with Plan:

Auditor, Company, Date

General Notes

APPENDIX F

LABORATORY GUIDELINES

F-1. TIER I AND II LABORATORY PERFORMANCE GUIDELINES

F-2. TIER III AND IV LABORATORY PERFORMANCE GUIDELINES

APPENDIX F-1

TIER I AND II LABORATORY PERFORMANCE GUIDELINES

Appendix F-1
Tier I and II Laboratory Performance Guidelines

Communication: Trihydro requests that the laboratory notifies the project contact in the event of any non-conformances with the data. In general, all communication between the laboratory and Trihydro regarding problems or exceptions that may affect the data result for submitted samples will be directed to the specified project manager or the secondary point of contact. Notification by e-mail is acceptable and preferred, but a follow-up phone call is appreciated. In addition, the Trihydro project team should know the status and quality of the data at every stage of the process. Trihydro would appreciate prompt notification of any problems regarding the analysis of the samples or the generation of the final data report. Specifically, Trihydro requests that the point of contact be immediately notified of any of the following problems:

- Missing or incomplete chain-of-custody documents or custody seals
- Missing or damaged sample containers
- Switched, missing, or illegible sample container labels
- Sample temperatures outside of the method acceptable range of 2.0° to 6.0˚C (if applicable)
- Inadequate sample volume(s) to perform the required analyses and/or quality control tests
- Inadequate sample preservations
- Presence of headspace (bubbles greater than 6 millimeters in diameter) in VOA vials (holding time reduced to 7 days)
- Samples received outside of holding times or too close to the holding times for the laboratory to complete the analyses within the required timeframe
- Any other physical conditions relating to the samples which might adversely affect the final quality of the analytical results

Bottle Orders: Trihydro requests that the laboratory check bottle orders against the required analyte list prior to shipping to the project site. The field team requires a list that indicates which bottles are required for each analysis. For safety reasons, sample containers made of clear glass must be manufactured to the highest strength standard ("33 Expansion" or equivalent), and documentation must be provided for bottles that have an equivalent safety design. Additionally, adequate packing material to prevent sample breakage or scratching during shipping must be provided.

Analyses: Trihydro requests that the laboratory report only those constituents requested in the agreed upon laboratory quote. Trihydro requests that the laboratory report data using the lowest dilution feasible for each individual analyte and that the laboratory only reports the final sample result for each analyte. If the laboratory instrument is unable to meet the required reporting limit for any reason other than those previously discussed with the project manager or during the bid process, please notify the Trihydro project contact. During the analysis of the samples, the laboratory will immediately notify the project contact of problems, which may include highly buffered samples that will compromise data integrity, missed holding times (including method holding times), problems with the samples that will prevent the laboratory from meeting the requirements specified in the agreed upon laboratory quote, and significant failures of quality control checks that require re-extraction and/or reanalysis of any sample outside of holding time. The laboratory should report full spike lists equal to the requested constituents for both Laboratory Control Samples and Matrix Spikes. **Soils should be reported dry-weight for most projects. Please verify.**

Reporting: Trihydro requests that for large sampling events, the laboratory report approximately 20 samples per data set in order to minimize data validation costs. In addition, Trihydro requests that a complete and signed data set be provided by the laboratory in either a Portable Document Format (PDF) (preferred) and/or hard copy (mailed to Trihydro) within the turnaround time specified in the laboratory quote. Laboratory reports should include, at a minimum, the following elements (where applicable to the analytical method):

a. A complete Case Narrative or laboratory notes that address major and minor exceptions relating to analysis of the data set
b. Sample data and quality control (QC) data including QC limits
c. Batch information for samples and QC data for each analysis
d. Dilution information for each sample and analyte
e. Notation of all collection, receipt, preparation/extraction, and analyses dates and times
f. All QC data as required by the method, including, but not limited to:
    i. Method Blank Results
    ii. Matrix Spike/Matrix Spike Duplicate Samples, percent recoveries, relative percent differences, QC limits, and parent samples
    iii. Laboratory Control Samples/Laboratory Control Sample Duplicates percent recoveries and RPD results
    iv. Laboratory duplicate RPD results
    v. Calibration data (if included in the standard report)
    vi. Surrogate Recoveries and QC limits for each sample
g. Signed chain-of-custody forms
h. Sample Receipt Checklist (or equivalent)
i. Definitions of laboratory qualifiers used

For electronic deliverables (EDDs), Trihydro requests that reports be issued in an electronic format acceptable to Trihydro's database (guidelines and example file are available). **Trihydro expects that the laboratory will ensure that EDDs and hard copy report values are identical and that similar QC measures are applied to the EDD and hard copy data reports.** In addition, Trihydro expects that the laboratory will be responsible for correcting any deficiencies or inaccuracies in either the electronic or hard copy versions of the data report in the time-frame specified by the contract.

APPENDIX F-2

TIER III AND IV LABORATORY PERFORMANCE GUIDELINES

Appendix F-2
Tier III and IV Laboratory Performance Guidelines

Communication: Trihydro requests that the laboratory notify the project contact in the event of any non-conformances with the data. In general, all communication between the laboratory and Trihydro regarding problems or exceptions that may affect the data result for submitted samples will be directed to the specified project manager or the secondary point of contact. Notification by e-mail is acceptable and preferred but a follow-up phone call is appreciated. In addition, the Trihydro project team should know the status and quality of the data at every stage of the process. Trihydro would appreciate prompt notification of any problems regarding the analysis of the samples or the generation of the final data report. Specifically, Trihydro requests that the point of contact be immediately notified of any of the following problems:

- Missing or incomplete chain-of-custody documents or custody seals
- Missing or damaged sample containers
- Switched, missing, or illegible sample container labels
- Sample temperatures outside of the method acceptable range of 2.0 to 6.0˚C (if applicable)
- Presence of headspace (bubbles greater than 6 millimeters in diameter) in VOA vials (holding time reduced to 7 days)
- Inadequate sample volume to perform the required analyses and/or quality control tests
- Inadequate sample preservation
- If samples are received outside of holding times or too close to the holding times for the laboratory to complete the analyses within the required timeframe
- Any other physical conditions relating to the samples which might adversely affect the final quality of the analytical results

Bottle Orders: Trihydro requests that the laboratory check bottle orders against the required analyte list prior to shipping to the project site. The field team requires a list that indicates which bottles are required for each analysis. For safety reasons, sample containers made of clear glass must be manufactured to the highest strength standard ("33 Expansion" or equivalent), and documentation must be provided for bottles that have an equivalent safety design. Additionally, adequate packing material to prevent sample breakage or scratching during shipping must be provided.

Analyses: Trihydro requests that the laboratory report only those constituents requested in the agreed upon laboratory quote. Trihydro requests that the laboratory report data using the lowest dilution feasible for each individual analyte. If the laboratory instrument is unable to meet the required reporting limit for any reason other than those previously discussed with the project manager or specified during the bid process, please notify the Trihydro project contact. During the analysis of the samples, the laboratory will immediately notify the project contact of problems which may include highly buffered samples that will compromise data integrity, missed holding times, internal standard recoveries below 50%, problems with the samples that will prevent the laboratory from meeting the requirements specified in the agreed upon laboratory quote, or significant failures of QC data that require re-extraction and/or reanalysis of any sample outside of holding time. The laboratory should report full spike lists equal to the requested constituents for both Laboratory Control Samples and Matrix Spikes. **Soils should be reported dry-weight for most projects. Please verify.**

Reporting: Trihydro requests that for large sampling events, the laboratory report approximately 20 samples per data set in order to minimize data validation costs. In addition, Trihydro requests that a complete and signed data set be provided by the laboratory in either a Portable Document Format (PDF) (preferred) and/or hard copy (mailed to Trihydro) within the turnaround time specified in the laboratory quote. Laboratory reports should include, at a minimum, the following elements (where applicable to the analytical method):

a. A complete Case Narrative that addresses major and minor exceptions relating to analysis of the data set
b. Sample data and quality control (QC) data including QC limits
c. Batch information for samples and QC data for each analysis
d. Dilution information for each sample and analyte
e. Notation of all collection, receipt, preparation/extraction, and analyses dates and times
f. All QC data as required by the method including, but not limited to:
    i. Method Blank results
    ii. Matrix Spike/Matrix Spike Duplicate Samples, percent recoveries, relative percent differences, QC limits and parent samples
    iii. Laboratory Control Samples/Laboratory Control Sample Duplicates percent recoveries and RPD results
    iv. Serial dilution data
    v. Laboratory duplicate RPD results.
    vi. Internal standard data (where applicable)
    vii. Calibration, instrument tunes, and other instrument performance data
    viii. Raw data applicable to the samples
    ix. Surrogate recoveries and QC limits for each sample
g. Signed chain-of-custody forms
h. Sample Receipt Checklist (or equivalent)
i. Definitions of laboratory qualifiers used
j. Contract Laboratory Program (CLP) or CLP-like forms (compiled in one location within the report)

For electronic deliverables (EDDs), Trihydro requests that reports be issued in an electronic format acceptable to the Trihydro's database (guidelines and example file are available). **Trihydro expects that the laboratory will ensure that EDDs and hard copy report values are identical and that similar QC measures are applied to the EDD and hard copy data reports.** In addition, Trihydro expects that the laboratory will be responsible for correcting any deficiencies or inaccuracies in either the electronic or hard copy versions of the data report in the time-frame specified by the contract.

APPENDIX G

DATA VALIDATION TEMPLATE

G-1. TIER II DATA VALIDATION REPORT SUMMARY

G-2. TIER III DATA VALIDATION REPORT SUMMARY

APPENDIX G-1

TIER II DATA VALIDATION REPORT SUMMARY

Appendix G-1
Tier II Data Validation Report Summary

Client:	Laboratory:
Project Name:	Sample Matrix:
Project Number:	Sample Start Date:
Date Validated:	Sample End Date:
Parameters Included: ▪ ▪ ▪ ▪	
Laboratory Project ID:	
Data Validator:	
Reviewer:	

DATA EVALUATION CRITERIA SUMMARY

A Tier II Data Validation was performed by Trihydro Corporation's Chemical Data Evaluation Services Group on the analytical data report package generated by _____ evaluating samples from the _____ site located in _____.

Precision, accuracy, method compliance, and completeness of this data package were assessed during this data review. Precision was determined by evaluating the calculated relative percent difference (RPD) values from:

- Field duplicate pairs
- Laboratory duplicate pairs
- Matrix spike (MS) and matrix spike duplicate (MSD) pairs
- Laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) pairs

Laboratory accuracy was established by reviewing the demonstrated percent recoveries (%R) of the following items to verify that data are not biased.

- MS/MSD samples
- LCS/LCSD samples
- Organic system monitoring compounds (surrogates)

Field accuracy was established by collecting and analyzing the following samples to monitor for possible ambient or cross contamination during sampling and transportation.

- Trip blanks
- Field blanks
- Equipment blanks

Tier II Data Validation Report Summary

Method compliance was established by reviewing sample integrity, holding times, detection limits, surrogate recoveries, laboratory blanks, initial and continuing calibrations (where applicable), and the LCS/LCSD percent recoveries against method-specific requirements.

Completeness was evaluated by determining the overall ratio of the number of samples and analyses planned versus the number of samples with valid analyses. Determination of completeness included a review of the chain-of-custody (CoC), laboratory analytical methods, and other laboratory and field documents associated with this analytical data set.

SAMPLE NUMBERS TABLE

Client Sample ID	Laboratory Sample Number

Tier II Data Validation Report Summary

The laboratory data were reviewed to evaluate compliance with the methods and the quality of the reported data. Assessment of CoC completeness is included in Item 3 of the Data Validation Checklist. A check mark (✓) indicates that the referenced validation criteria were deemed acceptable, whereas a crossed circle (⊗) indicates validation criteria for which the data have been qualified by the data validator. An empty circle (○) indicates that the specified criterion does not apply to the reviewed data. Details are noted in the tables below.

Validation Criteria

- ✓ Data Completeness
- ✓ CoC Documentation (Item 3)
- ✓ Holding Times and Preservation (Items 6 and 7)
- ✓ Initial and Continuing Calibrations (Items 9 and 10)
- ✓ Laboratory Blanks (Items 11 and 12)
- ✓ MS/MSD (Items 13 and 14)
- ✓ LCS/LCSD (Items 15 and 16)
- ✓ System Monitoring Compounds (i.e., Surrogates) (Item 17)
- ✓ Field, Equipment, and Trip Blanks (Items 18 and 19)
- ✓ Field Duplicates (Items 20 and 21)
- ✓ Laboratory Duplicates (Item 22)
- ✓ Data Relationships (Item 23)

Guidance References

Chemical data validation was conducted in accordance with the United States Environmental Protection Agency (USEPA) Contract Laboratory Program (CLP) National Functional Guidelines for the analyses listed below, or by the appropriate method if not covered in the National Functional Guidelines.

- Data for organic analyses were evaluated according to validation criteria set forth in the USEPA CLP National Functional Guidelines for Organic Superfund Methods Data Review, document number EPA-540-R-2017-002, January 2017 with additional reference to the USEPA CLP National Functional Guidelines for Organic Data Review, document number EPA 540/R-99/008, October 1999.
- Data for inorganic analyses were evaluated according to validation criteria set forth in the USEPA CLP National Functional Guidelines for Inorganic Superfund Methods Data Review, document number EPA-540-R-2017-001, January 2017 with additional reference to the USEPA CLP National Functional Guidelines for Inorganic Data Review, document number EPA 540-R-04-004, October 2004.
- Review of field duplicates was conducted according to the USEPA New England Environmental Data Review Supplement for Region 1 Data Review Elements and Superfund Specific Guidance/Procedures, EQADR-Supplement1, June 2018.
- The USEPA CLP National Functional Guidelines for High Resolution Superfund Methods Data Review, document number EPA-542-B-16-001, April 2016, was referenced for review of chlorinated dibenzodioxins (CDD) and chlorinated dibenzofurans (CDF) or chlorinated biphenyl congeners (CBC), as applicable.

Tier II Data Validation Report Summary

- Air and vapor data for samples collected in canisters and analyzed by EPA organics Method TO-15 were reviewed with reference to the USEPA Hazardous Waste Support Section, Analysis of Volatile Organic Compounds in Air Contained in Canisters by Method TO-15, SOP NO. HW-31, Revision 6, June 2014.
- Radiochemistry data were evaluated following criteria defined in USEPA Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP), document number EPA 402-B-04-001A, July 2004 and American Nuclear Society Standard 41.5-2012 (ANS 2012). Changes to data validation procedures for radiological analyses may be made at the discretion of the data validator and will be documented in the data validation reports.
- Trihydro Data Validation Variance Documentation, February 2019.
- Project-specific Quality Assurance Project Plans (QAPP) data validation requirements, as applicable.

OVERALL DATA PACKAGE ASSESSMENT

Based on a data validation review, the data are acceptable as delivered. Data qualified by the laboratory are discussed in Item 2 of the Validation Criteria Checklist.

The purpose of validating data and assigning qualifiers is to assist in proper data interpretation. Data that are not qualified meet the site data quality objectives. If values are assigned qualifiers other than an R (rejected, data not usable), the data may be used for site evaluation; however, consideration should be given to the reasons for qualification when interpreting sample concentrations. Data points that are assigned an R qualifier should not be used for site evaluation purposes.

If applicable, text was identified in **bold font** in the Validation Criteria Checklist to indicate that further action and/or qualification of the data were required. Data may have been qualified with J data flags by the laboratory if the result was greater than or equal to the method detection limit (MDL) but less than the reporting limit (RL). These laboratory-applied J flags were preserved, if present, and included in the Data Qualification Summary table at the end of this report. If applicable, data validation qualifiers were added for the items noted with crossed circles in the Validation Criteria section above. Please see the Data Qualification Summary table at the end of this report for a complete list of samples and analytes qualified.

If data would be qualified with more than one flag, one qualifier was assigned based on the severity; however, all reasons for qualification were retained. Data that would be qualified with both J+ and J- flags were evaluated based on validation criteria and assigned the appropriate flag.

Data qualifiers used during this validation are included in the following table.

Flag Code	Flag Definition
J	Estimated concentration or result
J+	The result is an estimated concentration, but may be biased high (This code is not applicable to the data validation of radiological analyses.)
J-	The result is an estimated concentration, but may be biased low (This code is not applicable to the data validation of radiological analyses.)
UJ	Estimated reporting limit (This code is not applicable to the data validation of radiological analyses.)
U	Evaluated to be undetected at the reporting limit or for radiological analyses the analyte result is less than the critical value
JB	Estimated concentration due to blank contamination (This code is not applicable to the data validation of radiological analyses.)

R	Rejected, data not usable
NJ	Tentative identification and estimated concentration
Q	A reported combined standard uncertainty, which exceeds the project's required method uncertainty. This qualifier will only be used for radiological analyses data validation.

Data Completeness

The analyses were performed as requested on the CoC records. The associated samples were received by the laboratory and analyzed properly unless otherwise noted in the Criteria Checklist below. The complete data package consisted of _____ data points excluding blank samples. No data points were rejected. The data completeness measure for this data package is calculated to be 100% and is acceptable. ***This form may be edited to meet the requirements of the analytical method and data validation guidelines. The template will serve as an example.***

VALIDATION CRITERIA CHECKLIST	
1. Was the report free of non-conformances identified by the laboratory?	Yes
Comments:	
2. Were the data free of data qualification flags and/or notes used by the laboratory? If no, define.	Yes
Comments:	
3. Were sample CoC forms and custody procedures complete?	Yes
Comments:	
4. Were detection limits or minimum detectable concentration in accordance with the quality assurance project plan (QAPP), permit, or method, required minimum detectable concentration, or indicated as acceptable?	Yes
Comments:	
5. Was the measured uncertainty provided where applicable? If so, was it in accordance with uncertainty requested?	Yes
Comments:	
6. Were the reported analytical methods and constituents in compliance with the QAPP, permit, or CoC?	Yes
Comments:	
7. Were samples received in good condition within method-specified requirements?	Yes
Comments:	
8. Were samples extracted/digested and analyzed within method-specified or technical holding times?	Yes
Comments:	
9. Were reported units appropriate for the sample matrix/matrices and analytical method(s)? Specify if wet or dry units were used for soil.	Yes
Comments:	
10. Did the laboratory provide any specific initial and/or continuing calibration results?	Yes
Comments:	
11. If initial and/or continuing calibration results were provided, were the results within acceptable limits?	Yes
Comments:	
12. Was the total number of laboratory blank samples prepared equal to at least 5% of the total number of samples or analyzed as required by the method?	Yes
Comments:	
13. Were target analytes reported as not detected in the laboratory blanks?	Yes
Comments:	

VALIDATION CRITERIA CHECKLIST	
14. Was the total number of MS samples prepared equal to at least 5% of the total number of samples or analyzed as required by the method? Comments:	Yes
15. For MS/MSDs prepared from project samples, were percent recoveries and RPDs within data validation or laboratory quality control (QC) limits? Comments:	Yes
16. Was the total number of LCSs analyzed equal to at least 5% of the total number of samples or analyzed as required by the method? Comments:	Yes
17. Were LCS/LCSD percent recoveries and LCS/LCSD RPDs within data validation or laboratory QC limits? Comments:	Yes
18. Were surrogate recoveries within laboratory QC limits? Comments:	Yes
19. Were the number of trip blank, field blank, and/or equipment blank samples collected equal to at least 10% of the total number of samples or as required by the project guidelines, QAPP, SAP, or permit? Comments:	Yes
20. Were target analytes reported as not detected in the trip blank, field blank, and/or equipment blank samples? Comments:	Yes
21. Was the number of field duplicates collected equal to at least 10% of the total number of samples or as required by the project guidelines, QAPP, SAP, or permit? Comments:	Yes
22. Were field duplicate RPD values within data validation QC limits (soil 0-50%, water 0-30%, or air 0-25%)? Comments:	Yes
23. For laboratory duplicates prepared from project samples, were RPDs within laboratory QC limits? Comments:	Yes
24. Were the following data relationships realistic and acceptable? • Target analytes were reported by more than one method (e.g., 8260/8270, EPH/8270) and the results were in agreement? Comments: • Both total and dissolved metals analyses were performed and the total metals results were greater than or equal to the dissolved metals results? Comments:	Yes Yes

FIELD DUPLICATE SUMMARY

Client Sample ID: Field Duplicate Sample ID:				
Method	**Analyte**	**Laboratory Result (units)**	**Duplicate Result (units)**	**Relative Percent Difference (RPD)**

Field duplicate RPD control limits are not to exceed 30% for water, 50% for soil, or 25% for air or vapor as established by USEPA New England Environmental Data Review Supplement for Regional Data Review Elements and Superfund Specific Guidance/Procedures, EQADR-Supplement0, April 2013.

DL – Indicates that the analyte was detected in one of the duplicate samples and was undetected in the other sample, and therefore an RPD could not be calculated. Data were not qualified since the detection was within two times the reporting limit. Non-detected results are indicated above with the applicable reporting limit as ND (RL).

+/-RL – Indicates that the detections in both of the samples were within two times the reporting limit. Qualification of data was not required.

DATA QUALIFICATION SUMMARY

Data qualifiers were not applied as a result of this validation.

Abbreviation	Reason

Analyte	Method	Field Sample ID	Lab Sample ID	Result	Limit	Units	Reviewer Qualifier	DV Flag Reasons

APPENDIX G-2

TIER III/IV DATA VALIDATION REPORT SUMMARY

Appendix G-1
Tier II Data Validation Report Summary

Client:	Laboratory:
Project Name:	Sample Matrix:
Project Number:	Sample Start Date:
Date Validated:	Sample End Date:
Parameters Included: ▪ ▪ ▪ ▪	
Laboratory Project ID:	
Data Validator:	
Reviewer:	

DATA EVALUATION CRITERIA SUMMARY

A Tier II Data Validation was performed by Trihydro Corporation's Chemical Data Evaluation Services Group on the analytical data report package generated by _____ evaluating samples from the _____ site located in _____.

Precision, accuracy, method compliance, and completeness of this data package were assessed during this data review. Precision was determined by evaluating the calculated relative percent difference (RPD) values from:

- Field duplicate pairs
- Laboratory duplicate pairs
- Matrix spike (MS) and matrix spike duplicate (MSD) pairs
- Laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) pairs

Laboratory accuracy was established by reviewing the demonstrated percent recoveries (%R) of the following items to verify that data are not biased.

- MS/MSD samples
- LCS/LCSD samples
- Organic system monitoring compounds (surrogates)

Field accuracy was established by collecting and analyzing the following samples to monitor for possible ambient or cross contamination during sampling and transportation.

- Trip blanks
- Field blanks
- Equipment blanks

Tier II Data Validation Report Summary

Method compliance was established by reviewing sample integrity, holding times, detection limits, surrogate recoveries, laboratory blanks, initial and continuing calibrations (where applicable), and the LCS/LCSD percent recoveries against method-specific requirements.

Completeness was evaluated by determining the overall ratio of the number of samples and analyses planned versus the number of samples with valid analyses. Determination of completeness included a review of the chain-of-custody (CoC), laboratory analytical methods, and other laboratory and field documents associated with this analytical data set.

SAMPLE NUMBERS TABLE

Client Sample ID	Laboratory Sample Number

Tier II Data Validation Report Summary

The laboratory data were reviewed to evaluate compliance with the methods and the quality of the reported data. Assessment of CoC completeness is included in Item 3 of the Data Validation Checklist. A check mark (✓) indicates that the referenced validation criteria were deemed acceptable, whereas a crossed circle (⊗) indicates validation criteria for which the data have been qualified by the data validator. An empty circle (○) indicates that the specified criterion does not apply to the reviewed data. Details are noted in the tables below.

Validation Criteria

- ✓ Data Completeness
- ✓ CoC Documentation (Item 3)
- ✓ Holding Times and Preservation (Items 6 and 7)
- ✓ Initial and Continuing Calibrations (Items 9 and 10)
- ✓ Laboratory Blanks (Items 11 and 12)
- ✓ MS/MSD (Items 13 and 14)
- ✓ LCS/LCSD (Items 15 and 16)
- ✓ System Monitoring Compounds (i.e., Surrogates) (Item 17)
- ✓ Field, Equipment, and Trip Blanks (Items 18 and 19)
- ✓ Field Duplicates (Items 20 and 21)
- ✓ Laboratory Duplicates (Item 22)
- ✓ Data Relationships (Item 23)

Guidance References

Chemical data validation was conducted in accordance with the United States Environmental Protection Agency (USEPA) Contract Laboratory Program (CLP) National Functional Guidelines for the analyses listed below, or by the appropriate method if not covered in the National Functional Guidelines.

- Data for organic analyses were evaluated according to validation criteria set forth in the USEPA CLP National Functional Guidelines for Organic Superfund Methods Data Review, document number EPA-540-R-2017-002, January 2017 with additional reference to the USEPA CLP National Functional Guidelines for Organic Data Review, document number EPA 540/R-99/008, October 1999.
- Data for inorganic analyses were evaluated according to validation criteria set forth in the USEPA CLP National Functional Guidelines for Inorganic Superfund Methods Data Review, document number EPA-540-R-2017-001, January 2017 with additional reference to the USEPA CLP National Functional Guidelines for Inorganic Data Review, document number EPA 540-R-04-004, October 2004.
- Review of field duplicates was conducted according to the USEPA New England Environmental Data Review Supplement for Region 1 Data Review Elements and Superfund Specific Guidance/Procedures, EQADR-Supplement1, June 2018.
- The USEPA CLP National Functional Guidelines for High Resolution Superfund Methods Data Review, document number EPA-542-B-16-001, April 2016, was referenced for review of chlorinated dibenzodioxins (CDD) and chlorinated dibenzofurans (CDF) or chlorinated biphenyl congeners (CBC), as applicable.

Tier II Data Validation Report Summary

- Air and vapor data for samples collected in canisters and analyzed by EPA organics Method TO-15 were reviewed with reference to the USEPA Hazardous Waste Support Section, Analysis of Volatile Organic Compounds in Air Contained in Canisters by Method TO-15, SOP NO. HW-31, Revision 6, June 2014.
- Radiochemistry data were evaluated following criteria defined in USEPA Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP), document number EPA 402-B-04-001A, July 2004 and American Nuclear Society Standard 41.5-2012 (ANS 2012). Changes to data validation procedures for radiological analyses may be made at the discretion of the data validator and will be documented in the data validation reports.
- Trihydro Data Validation Variance Documentation, February 2019.
- Project-specific Quality Assurance Project Plans (QAPP) data validation requirements, as applicable.

OVERALL DATA PACKAGE ASSESSMENT

Based on a data validation review, the data are acceptable as delivered. Data qualified by the laboratory are discussed in Item 2 of the Validation Criteria Checklist.

The purpose of validating data and assigning qualifiers is to assist in proper data interpretation. Data that are not qualified meet the site data quality objectives. If values are assigned qualifiers other than an R (rejected, data not usable), the data may be used for site evaluation; however, consideration should be given to the reasons for qualification when interpreting sample concentrations. Data points that are assigned an R qualifier should not be used for site evaluation purposes.

If applicable, text was identified in **bold font** in the Validation Criteria Checklist to indicate that further action and/or qualification of the data were required. Data may have been qualified with J data flags by the laboratory if the result was greater than or equal to the method detection limit (MDL) but less than the reporting limit (RL). These laboratory-applied J flags were preserved, if present, and included in the Data Qualification Summary table at the end of this report. If applicable, data validation qualifiers were added for the items noted with crossed circles in the Validation Criteria section above. Please see the Data Qualification Summary table at the end of this report for a complete list of samples and analytes qualified.

If data would be qualified with more than one flag, one qualifier was assigned based on the severity; however, all reasons for qualification were retained. Data that would be qualified with both J+ and J- flags were evaluated based on validation criteria and assigned the appropriate flag.

Tier II Data Validation Report Summary

Data qualifiers used during this validation are included in the following table.

Flag Code	Flag Definition
J	Estimated concentration or result
J+	The result is an estimated concentration, but may be biased high (This code is not applicable to the data validation of radiological analyses.)
J-	The result is an estimated concentration, but may be biased low (This code is not applicable to the data validation of radiological analyses.)
UJ	Estimated reporting limit (This code is not applicable to the data validation of radiological analyses.)
U	Evaluated to be undetected at the reporting limit or for radiological analyses the analyte result is less than the critical value
JB	Estimated concentration due to blank contamination (This code is not applicable to the data validation of radiological analyses.)
R	Rejected, data not usable
NJ	Tentative identification and estimated concentration
Q	A reported combined standard uncertainty, which exceeds the project's required method uncertainty. This qualifier will only be used for radiological analyses data validation.

Data Completeness

The analyses were performed as requested on the CoC records. The associated samples were received by the laboratory and analyzed properly unless otherwise noted in the Criteria Checklist below. The complete data package consisted of _____ data points excluding blank samples. No data points were rejected. The data completeness measure for this data package is calculated to be 100% and is acceptable. ***This form may be edited to meet the requirements of the analytical method and data validation guidelines. The template will serve as an example.***

VALIDATION CRITERIA CHECKLIST	
1. Was the report free of non-conformances identified by the laboratory?	Yes
Comments:	
2. Were the data free of data qualification flags and/or notes used by the laboratory? If no, define.	Yes
Comments:	
3. Were sample CoC forms and custody procedures complete?	Yes
Comments:	
4. Were detection limits or minimum detectable concentration in accordance with the quality assurance project plan (QAPP), permit, or method, required minimum detectable concentration, or indicated as acceptable?	Yes
Comments:	
5. Was the measured uncertainty provided where applicable? If so, was it in accordance with uncertainty requested?	Yes
Comments:	
6. Were the reported analytical methods and constituents in compliance with the QAPP, permit, or CoC?	Yes
Comments:	
7. Were samples received in good condition within method-specified requirements?	Yes
Comments:	
8. Were samples extracted/digested and analyzed within method-specified or technical holding times?	Yes
Comments:	
9. Were reported units appropriate for the sample matrix/matrices and analytical method(s)? Specify if wet or dry units were used for soil.	Yes
Comments:	
10. Did the laboratory provide any specific initial and/or continuing calibration results?	Yes
Comments:	
11. If initial and/or continuing calibration results were provided, were the results within acceptable limits?	Yes
Comments:	
12. Was the total number of laboratory blank samples prepared equal to at least 5% of the total number of samples or analyzed as required by the method?	Yes
Comments:	
13. Were target analytes reported as not detected in the laboratory blanks?	Yes
Comments:	

VALIDATION CRITERIA CHECKLIST	
14. Was the total number of MS samples prepared equal to at least 5% of the total number of samples or analyzed as required by the method? Comments:	Yes
15. For MS/MSDs prepared from project samples, were percent recoveries and RPDs within data validation or laboratory quality control (QC) limits? Comments:	Yes
16. Was the total number of LCSs analyzed equal to at least 5% of the total number of samples or analyzed as required by the method? Comments:	Yes
17. Were LCS/LCSD percent recoveries and LCS/LCSD RPDs within data validation or laboratory QC limits? Comments:	Yes
18. Were surrogate recoveries within laboratory QC limits? Comments:	Yes
19. Were the number of trip blank, field blank, and/or equipment blank samples collected equal to at least 10% of the total number of samples or as required by the project guidelines, QAPP, SAP, or permit? Comments:	Yes
20. Were target analytes reported as not detected in the trip blank, field blank, and/or equipment blank samples? Comments:	Yes
21. Was the number of field duplicates collected equal to at least 10% of the total number of samples or as required by the project guidelines, QAPP, SAP, or permit? Comments:	Yes
22. Were field duplicate RPD values within data validation QC limits (soil 0-50%, water 0-30%, or air 0-25%)? Comments:	Yes
23. For laboratory duplicates prepared from project samples, were RPDs within laboratory QC limits? Comments:	Yes
24. Were the following data relationships realistic and acceptable? • Target analytes were reported by more than one method (e.g., 8260/8270, EPH/8270) and the results were in agreement? Comments: • Both total and dissolved metals analyses were performed and the total metals results were greater than or equal to the dissolved metals results? Comments:	Yes Yes

FIELD DUPLICATE SUMMARY

Client Sample ID: Field Duplicate Sample ID:				
Method	**Analyte**	**Laboratory Result (units)**	**Duplicate Result (units)**	**Relative Percent Difference (RPD)**

Field duplicate RPD control limits are not to exceed 30% for water, 50% for soil, or 25% for air or vapor as established by USEPA New England Environmental Data Review Supplement for Regional Data Review Elements and Superfund Specific Guidance/Procedures, EQADR-Supplement0, April 2013.

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DATA QUALIFICATION SUMMARY

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Abbreviation	Reason

Analyte	Method	Field Sample ID	Lab Sample ID	Result	Limit	Units	Reviewer Qualifier	DV Flag Reasons