QUALITY ASSURANCE PROJECT PLAN

WEST LAKE LANDFILL SUPERFUND SITE OPERABLE UNIT 1

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The United States Environmental Protection Agency Region VII

Prepared on Behalf of:

The West Lake Landfill OU-1 Respondents

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LIST OF ACRONYMS

ACRONYM	Definition
>	greater than
<	less than
ARAR	Applicable or Relevant and Appropriate Requirements
ASAOC	Administrative Settlement Agreement and Order of Consent
ASTM	American Society for Testing and Materials
B2005GS	below the 2005 ground surface
bss	below sediment surface
CAR	Corrective Action Report
CCM	contamination concern map
CDC	Centers for Disease Control
CDF	cumulative distribution function
CPM	counts per minute
CSM	Conceptual Site Model
CSU	combined standard uncertainty
DI	design investigation
DIWP	Design Investigation Work Plan
DoD	Department of Defense
DOE	Department of Energy
DMP	Data Management Plan
DQI	Data Quality Indicator
DQO	Data Quality Objective
DU	Decision Unit
EMSI	Engineering Management Support, Inc.
FFS	Final Feasibility Study
FSP	Field Sampling Plan
GC/ECD	gas chromatograph/electron capture detector
GS/MS	gas chromatograph/mass spectrometer
GSMO	geostatistical modeling objective
H2SO4	sulfuric acid
HNO3	nitric acid
IC	ion chromatography
IK*	indicator kriging*[2]
IDQTF	Intergovernmental Data Quality Task Force
LBSR	leached barium sulfate residue
LCL	Lower Confidence Limit
LCS/LCSD	laboratory control sample/laboratory control sample duplicate
µg/L	microgram(s) per liter
m^2	square meters
MDC	minimum detectable concentration
MDL	method detection limit
MDNR	Missouri Department of Natural Resources
mg/L	milligram(s) per liter
mL	milliliter(s)
MPC	measure performance criteria
MS/MSD	matrix spike/matrix spike duplicate
MSW	municipal solid waste
NCC	non-combustible cover
NEP	non-exceedance probability
NRC	Nuclear Regulatory Commission
OU	Operable Unit
%R	Percent Recovery
PAL	Project Action Limit
PCB	polychlorinated biphenyl
pCi/g	picocurie/gram
PM	Project Manager
PSQ	Principle Study Question
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RA	Remedial Action
RCRA	Resource Conservation and Recovery Act
RER	relative error ratio
RD	Remedial Design
RIM	radiologically impacted material[1]
RL	reporting limits
ROC	radionuclides of concern
RODA	Record of Decision Amendment
RPD	relative percent difference
RPM	Remedial Project Manager
SDWS	Standard Deviation to Warrant Sampling
SOP	standard operating procedure
SOW	Statement of Work
SSP&A	S.S. Papadopolus & Associates
SVOC	semivolatile organic compound

TCLP	Toxicity Characteristic Leaching Procedure
UCL	Upper Confidence Limit
UFP-QAPP	Uniform Federal Policy for Quality Assurance Project Plan
UMTRCA	Uranium Mill Tailings Radiation Act
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
UU/UE	Unlimited Use/Unrestricted Exposure
VSP	Visual Sampling Plan
VOC	volatile organic compound

[1] RIM is defined in Section 5.5 of Part II of the RODA and pertains to concentrations of radium, thorium, and uranium isotopes. As stated in the RODA, RIM will be identified as waste material containing combined radium (radium-226 plus radium-228) or combined thorium (thorium-230 plus thorium-232) at levels greater than 7.9 picocuries per gram.

[2] Indicator Kriging* for this project is completed as Ordinary Kriging on a set of probabilities as defining by CDF development. While typically IK suggests the data are strictly binary for this project the definition of IK* includes other probabilities between 0 and 1.

EXECUTIVE SUMMARY

ES.1 Introduction

The United States Environmental Protection Agency (USEPA) signed a Record of Decision Amendment (RODA) for Operable Unit (OU) 1 of the West Lake Landfill Site (Superfund Site ID # MOD079900932) in September 2018. The selected amended remedy in the RODA primarily includes partial excavation and off-site disposal of radiologically impacted material (RIM) followed by installation of a final cover system, with the objective of preventing direct contact or radiation exposure from the contaminated media at OU-1 of the West Lake Landfill Superfund Site (the Site), including protection of groundwater by limiting infiltration and thus leaching of contaminants.

USEPA and the Respondents have agreed to the conditions under which the Respondents will design the selected amended remedy in the RODA, as set forth in the Third Amendment to the Administrative Settlement Agreement and Order of Consent (ASAOC) and associated Statement of Work (USEPA Docket No. VII-93-F-0005). The selected amended remedy in the RODA includes:

- Partial excavation of RIM from Radiological Areas 1 and 2 of OU-1 and disposal at an off-site facility;
- Excavation of radiologically impacted soil from the Buffer Zone and/or Lot 2A2 sufficient to reduce concentrations of radionuclides to allow for unrestricted use of the property;
- Installation of a landfill cover over Radiological Areas 1 and 2;
- Design, installation, and management of maintenance/monitoring systems for surface water, groundwater and gas;
- Long-term operation, maintenance and monitoring; and
- Implementation of institutional controls.

Several remedial investigations have been completed in OU-1 areas. Additional investigations are to be conducted during Remedial Design (RD) to support the design of the selected amended remedy. This Quality Assurance Project Plan (QAPP) has been prepared on behalf of the West Lake Landfill OU-1 Respondents Bridgeton Landfill, LLC, Cotter Corporation (N.S.L), and the U.S. Department of Energy (Respondents). This QAPP has been prepared to support the RD investigation. It has been prepared in accordance with the Uniform Federal Policy Quality Assurance Project Plan (UFP-QAPP) procedures laid out in *USEPA Requirements for Quality Assurance Project Plans*, QA/R-5, EPA/240/B-01/003 (Mar. 2001, reissued May 2006); *Guidance for Quality Assurance Project Plans*, QA/G-5, EPA/240/R 02/009 (Dec. 2002); and *Uniform Federal Policy for Quality Assurance Project Plans*, Parts 1-3, EPA/505/B-04/900A though 900C (Mar. 2005).

This QAPP has been developed utilizing the optimized format developed by the Intergovernmental Data Quality Task Force (IDQTF), a working group made up of representatives from the USEPA, the Department of Defense (DoD), and the Department of Energy (DOE). In 2010, the IDQTF established a subgroup to make recommendations for optimizing the worksheets. The optimization effort was performed with the following objectives:

1. Eliminate redundancy of information contained in certain worksheets;
2. Increase the ease of worksheet population, review, and use;
3. Clarify and promote the use of the systematic planning process and the implementation of a graded approach; and
4. Promote consistency in the use of quality assurance/quality control (QA/QC) terminology and procedures among the Federal agencies.

The following QAPP presents information in this optimized format.

Worksheet #1 and #2: Title and Approval Page

1.1 Project Identifying Information

Document Title:	Quality Assurance Project Plan West Lake Landfill Superfund Site Operable Unit 1
Project Name and Site Location:	West Lake Landfill, 13570 St. Charles Rock Road Bridgeton, Missouri
Prepared for:	OU-1 Respondents
Prepared by:	Parsons, Ameriphysics, GEL Laboratories
Document Version	0
Revision Number:	3
Revision Date:	October 9, 2020

Relevant plans and reports from previous investigations are described in Worksheets #10 and #13.

1.2 Signatures

The following signatures indicate the representatives of the subject organizations have reviewed this QAPP and concur with its implementation as written.

Christine Jump, USEPA-Regional Project Manager	Jump, Christine Digitally signed by Jump, Christine Date: 2020.09.16 15:25:15 -05'00'	Date
Diane Harris, USEPA R7 QA Manager	DIANE HARRIS Digitally signed by DIANE HARRIS Date: 2020.09.17 12:01:14 -05'00'	Date
Paul Rosasco, Engineering Management Support, Inc. OU-1 Project Coordinator		9/11/2020
Raymond D'Hollander, Parsons Project Manager		9/11/2020
Tom Hansen, Ameriphysics QA Officer		9/11/2020
Maryanne Kosciewicz, Parsons Senior QA Chemist		9/11/2020

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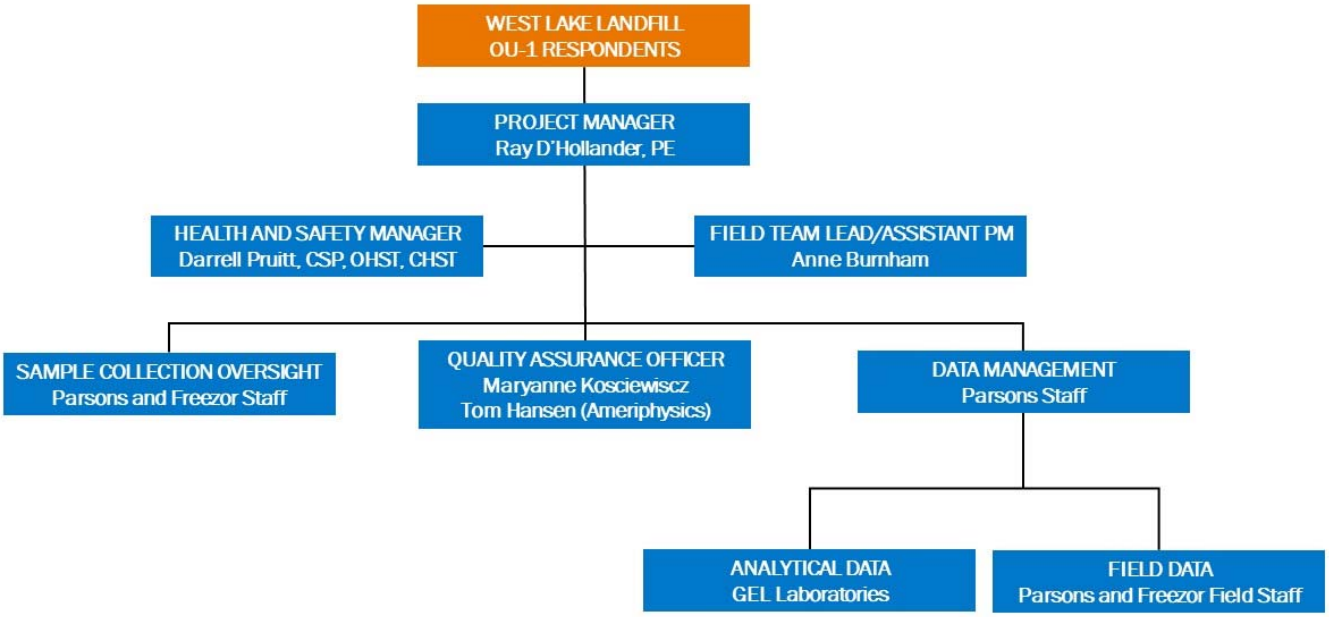
Worksheets #3 and #5: Project Organization & QAPP Distribution

The QAPP will be distributed to members of the project shown in the organization chart below as well as to the United States Environmental Protection Agency (USEPA) and Missouri Department of Natural Resources (MDNR). The Parsons Project Manager (PM), or his delegate (i.e., the Assistant PM) shall be responsible for the distribution of a modified QAPP, as necessary, when modifications are made and approved following USEPA review. They shall also have the responsibility for proper document control of the QAPP versions. The QAPP will be maintained by those staff, who are based in Syracuse, New York. Both a hard and electronic copy will be locally maintained at the Site during the Design Investigation field activities.



Worksheet #4, 7, & 8: Personnel, Qualifications and Sign-off Sheet

Key Project Personnel

Project Tile/Role	Name/Organization	Contract Information (phone/email)	Experience	Signature/Date
Project Manager	Chris Jump, USEPA	913-551-7141/ Jump.Chris@epa.gov	Remedial Project Manager (RPM) responsible for Superfund investigations and remediation including consistency of project work with the requirements of USEPA orders, guidance and policies and for coordination of USEPA and other agency reviews of project submittals	
Project Coordinator	Paul Rosasco, Engineering Management Support, Inc. (EMSI)	303-808-7227/ paulrosasco@esmidenever.com	B. Sc. Geology and M. Eng. Engineering Geology. P.E. CO and WA with 43 years professional experience including 38 years of experience with Superfund investigations and removal and remedial actions	
Parsons Project Manager	Raymond D'Hollander, P.E., Parsons	315-552-9683/ Ray.dhollander@parsons.com	B.Sc. Civil & Environmental Engineering, M.Eng. Civil Engineering (Geotechnical), Professional Engineer (MO), Licensed Environmental Professional (CT), 38 years of experience	
Assistant Project Manager, Field Team Lead	Anne L. Burnham, Parsons	315-552-9775/ anne.burnham@parsons.com	B.S. Biology and Environmental Studies, M.S. Ecology/ 5 years of industry experience	
Project Chemist, QA Officer	Maryanne Kosciewicz, Parsons	315-552-9703/ maryanne.kosciewicz@parsons.com	B.S. Chemistry B.S. Mathematics 31 years of industry experience	
QA Officer, Ameriphysics	Thomas Hansen, Ameriphysics	800-563-7497/ tom@ameriphysics.com	Ph.D. Public Health Masters, Health Physics B.S. Radiation Protection Certified Health Physicist 30 years of experience	

Other Project Personnel

Project Tile/Role	Name/Organization	Contract Information (phone/email)	Experience	Signature/Date
Chief Operating Officer	Carey Bocklet, GEL Laboratories	843-556-8171x4429/ carey.bocklet@gel.com	B.S., Chemical Engineering; M.S., Business Administration/ With GEL 30 years	
Project Manager	Brielle Luthman, GEL Laboratories	843-769-7371/ team.luthman@gel.com	B.S., Biology/ With GEL 5 years	
Quality Systems Director	Bob Pullano, GEL Laboratories	843-556-8171x4414	B.S. Marine Science and Biology With GEL 31 Years	

Worksheet #6: Communication Pathways

Communication Driver	Organization	Role	Procedure
Regulatory agency interface	Parsons/EMSI	Parsons PM/Assistant PM/Project Coordinator	Provides project updates regarding project/field activities as requested/as needed to USEPA/MDNR.
Field progress reports	Parsons	Field Team Lead	Documents progress reports daily and submits for distribution. Daily reports will be submitted within 24-hours of work completion or whenever possible to the Parsons PM and EMSI.
Stop work due to safety issues	Parsons	Field Team Lead	Field Team Lead notifies Parsons PM verbally and/or via e-mail as soon as possible after work stoppage. Parsons PM follows notifications to others (i.e., respondents, USEPA) as detailed in the Project Health Environment and Safety Plan.
Stop work due to emergencies/ unanticipated events	Parsons	Field Team Lead	Follows protocols laid out in current Emergency Response Plan and Health and Safety Plan. Field Team Lead notifies Parsons PM and/or via e-mail as soon as possible after work stoppage. Parsons PM follows notifications to others (i.e., respondents, USEPA) as detailed in the relevant plan.
QAPP changes prior to fieldwork	Parsons/Ameriphysics	QA Officer	Follows change and review and approval process; communicates directly as needed (verbally and/or in writing) and submits field changes for discussion; does not implement change until approval is granted by USEPA; consults with other personnel as needed.
QAPP changes during fieldwork	Parsons/Ameriphysics	QA Officer	Changes will be noted and, within 24 hours the Field Team Lead will submit a change request form to the PM and Quality Assurance (QA) Officer for review. Following review and approval, the PM will submit the change to USEPA via email.

Communication Driver	Organization	Role	Procedure
Field corrective actions	Parsons	Project Manager	The need for field corrective actions will be determined by the Parsons PM, and/or contractor technical personnel. The contractor technical personnel will notify the Parsons PM of any needed field corrective actions and the Parsons PM will respond within 24 hours. Field corrections will be documented and included in the Design Investigation Report, as necessary.
Field non-conformance	Parsons	Field Team Lead	Within 24 hours of non-conformance, non-conformance will be documented and information supplied to the Parsons PM and QA Officer for review. Any response actions that result from review of the non-conformance (i.e., a corrective actions) will be documented as such.
Sample receipt variances and laboratory quality control (QC) variances	Laboratory	Laboratory Project Manager	Applicable Laboratory PM will notify Parsons data management, QA Officer and PM/Assistant PM verbally and/or in writing. All sample receipt variances will be communicated within 24 hours of sample receipt.
Analytical corrective actions and Data Validation corrective actions	Parsons and Laboratory	QA Officer/Laboratory PM	The need for corrective actions for analytical and data validation issues will be determined by Parsons and laboratory when/if error occurs during the analysis or noticed during data review or validation stage. Corrective action report will be included in the associated data package. Parsons will notify project team of any non-conformance laboratory issues if errors cause rejected data or re-analysis cannot be performed due to holding time. Any non-conformance laboratory issues will be documented in the site-specific report.
Reporting Data Validation Issues	Laboratory /Parsons/Ameriphysics	Laboratory PM/Parsons and Ameriphysics QA Officers	All completeness and data issues will be addressed with the laboratory directly, verbally and/or in writing immediately in case the team is still in the field and samples can be recollected. The validated laboratory data package will be due within approximately 28 calendar days of sample receipt. Data validator will validate laboratory data

Communication Driver	Organization	Role	Procedure
			package with analytical results. Validated data will be managed as described in the Data Management Plan (DMP). Data will be provided to USEPA, clients and other approved parties as needed.

Worksheet #9: Project Planning Session Summary

Date of planning session: Ongoing; includes preparation meetings and meetings with regulators. Includes meetings on the following dates: September 18-19, 2019, October 23-24, 2019, November 18-19, 2019, December 3-5, 2019, January 14-15, 2020, February 18-20, 2020. Additional planning sessions for the Design Investigation Work Plan (DIWP) and development of that and its associated documents occurred from July 24-August 4, 2020.

Location: Kansas City, Kansas or Bridgeton, Missouri

Purpose: Discuss various investigation and design topics, upcoming deliverables

Participants: Various; representatives participating on behalf of USEPA, MDNR, EMSI), Bridgeton Landfill, LLC, Cotter Corporation (N.S.L.), Parsons, Feezor Engineering, Ameriphysics. Below is a list of general participants; meetings may have had additional participants dependent upon the topic of discussion for the given planning session.

Name	Organization	Title/Role	Email/Phone
Christine Jump	USEPA	Remedial Project Manager	Jump.Chris@epa.gov
Tom Mahler	USEPA	Remedial Project Manager	Mahler.tom@epa.gov
Lynn Juett	USEPA	USEPA Region Executive Review	Juett.lynn@epa.gov 913-551-7883
Diana Engeman	USEPA	USEPA Region Executive Review	Engeman.diana@epa.gov 913-551-7746
Ryan Seabaugh	MDNR	MDNR Reviewer	Ryan.seabaugh@dnr.mo.gov 573-751-8628
Paul Rosasco	EMSI	Project Coordinator	paulrosasco@emsidenver.com 303-808-7227
Ray D'Hollander	Parsons	Project Manager	ray.dhollander@parsons.com 315-552-9683
Paul Roth	Parsons	Assistant Project Manager	Paul.Roth@parsons.com 315-552-9726
Anne Burnham	Parsons	Assistant Project Manager	Anne.burnham@parsons.com 315-552-9775
Victoria Warren	Participating on behalf of Bridgeton Landfill, LLC	Director, Hydrogeology and Superfund	vwarren@republicservices.com 317-335-9550
Joe Benco	Participating on behalf of Bridgeton Landfill, LLC	Vice President, Engineering & Environmental Management	JBenco@republicservices.com
Scott Sklenar	Participating on behalf of Cotter Corporation (N.S.L.)	Environmental Manager	scott.sklenar@exeloncorp.com 267-533-1885
Tom Hansen	Ameriphysics	Health Physicist	tom@ameriphysics.com 800-563-7497

Name	Organization	Title/Role	Email/Phone
Paul Jones	Ameriphysics	GM Radiological Programs	pjones@ameriphysics.com 865-591-8632
Dan Feezor	Feezor Engineering	Principal Engineer	dfeezor@feezorengineering.com 217-836-8842

Notes/Comments: Notes from each of the meetings between the client group, Parsons, and the relevant agencies (which at any given meeting included representatives from USEPA, MDNR and U.S. Army Corps of Engineers [USACE]) were distributed to meeting attendees. Meeting materials are maintained by Parsons. They are not included herein due to size.

Consensus decisions made: Noted in meeting summaries.

Action Items: Noted in meeting summaries.

Action	Responsible Party	Due Date

Worksheet #10: Conceptual Site Model

A detailed site history is provided by the 2018 Remedial Investigation Addendum (RIA), and the objective of this worksheet is not to repeat that information. Rather, the concise summary below focuses on elements of the Conceptual Site Model (CSM) that are important to an understanding of data gaps to be resolved as a means of informing data quality objective (DQO) development. Further details related to Site conditions, maps/aerial photographs, and other specifics on Site information are included throughout the Field Sampling Plan (FSP). The conceptual model is informed by the 2018 RIA and 2018 Record of Decision Amendment (RODA), which describe a municipal solid waste (MSW) landfill that received materials containing low-level radionuclides in 1973 when soil mixed with leached barium sulfate residues (LBSR) was disposed of at the landfill and reportedly used as daily, intermediate cover. Based on the presence of radiologically impacted material (RIM) at the ground surface, USEPA has assumed that material may also have been used as final cover for landfilling operations. These early landfilling activities (prior to 1974) were not subject to state permitting (although they were still subject to an authorization issued by the county), and the portion of the landfill property where these activities occurred has been referred to as the "unregulated landfill." Since this time, the radioactive materials have become intermixed with other wastes in the landfill including refuse, debris, fill materials, and quarry spoils.

The Site has been the subject of numerous investigations, monitoring, and sampling activities over the course of more than 40 years, and has been studied by local, state and federal agencies including the USEPA, USACE, U.S. Geologic Survey, Nuclear Regulatory Commission (NRC), Agency for Toxic Substance and Disease Registry, MDNR, Missouri Department of Health and Senior Services, and the St. Louis County Department of Public Health. Sampling and analysis of the Site has included four overland radiation surveys; 314 soil borings, hand augers, and gamma cone penetration testing soundings; analysis of approximately 500 soil/waste samples; and sampling and analysis of other media, including radon, air/dust, surface water/stormwater, sediment, and groundwater. A complete list of the various reports prepared for or potentially related to Operable Unit (OU)-1 are presented in Section 2 of the RIA.

Radiologically impacted materials have been found in two areas at the Site, designated as Radiological Area 1 and Area 2 of OU-1. Area 1, which encompasses approximately 17.6 acres, is located immediately to the southwest of the landfill entrance. Area 2 encompasses approximately 41.8 acres and is located in the northwestern part of the landfill property. The total waste volume deposited is estimated to be 1,031,000 cubic yards in Area 1 (note: this volume includes the above-grade portion of the Bridgeton Landfill that extends out over the southern portion of Area 1) and 1,443,000 cubic yards in Area 2. Adjacent properties that, although not used for waste disposal, are known to contain radionuclides in soil as a result of transport of radionuclides by surficial processes from OU-1. These properties include the Buffer Zone and Lot 2A2 of the Crossroads Industrial Park. Accordingly, they are included as part of the Site.

The primary method for identifying occurrences of RIM has been via the results of laboratory analyses of soil/waste samples. These analytical data are considered direct measurements of potential RIM occurrences. These direct measurements are referred to a "hard" data in the RIA and elsewhere. Indirect data, or "soft" data, potentially indicative of or helpful in identifying RIM include overland gamma survey results, downhole gamma logging, and radon flux measurements. Specifically, RIM occurrences in Areas 1 and 2 were identified with hard and soft data from the following:

- Data obtained by NRC investigation (RMC 1982);
- OU-1 RI investigations (McLaren/Hart 1996h and EMSI 2000);
- USEPA split samples obtained during the OU-1 RI investigations (McLaren/Hart 1996f);

- Phase 1 Investigations (EMSI et al. 2016b);
- Additional Characterization Investigation (EMSI 2015e);
- USEPA split samples obtained during the Additional Characterization Investigation;
- Samples analyzed in conjunction with EPA's pyrolysis and radon attenuation studies (TetraTech 2016a);
- Additional testing conducted by Cotter (Arcadis 2015);
- USEPA's verification testing of the Cotter samples; and
- Surface soil samples obtained in conjunction with construction of the non-combustible cover (NCC).

The occurrences of RIM at the Site have been identified to consist primarily of radionuclides in the uranium 238 (U-238) decay series. Radionuclides from the uranium-235 (U-235) and thorium-232 (Th-232) decay series are also present above mean background concentrations, although at a lesser frequency and lower activity levels. Due to the nature of the activities that generated the RIM (processing uranium feed material for the production of uranium chemicals for the Manhattan Engineering District and the AEC), long-lived radionuclides are not in equilibrium with their long-lived progeny (e.g., thorium-230 [Th-230] is not in secular equilibrium with either U-238 or uranium-234 [U-234], and radium-226 [Ra-226] is not in secular equilibrium with Th-230).The radionuclides involved are gamma, beta, and alpha emitters, with the latter being recognized as difficult to detect and quantify in environmental media with field equipment. This document includes discussion of how alpha emitters will be addressed in field screening. This is important to the design investigation because alpha-emitting Th-230 is a principal constituent of concern from the U-238 series, and existing data demonstrate Th-230 to be present at much higher concentrations than either uranium or radium.

- Considering all of the previous investigations conducted, a total of 177 soil borings from which soil samples were historically collected for laboratory analyses have been drilled in Areas 1 and 2, including 84 soil borings in Area 1 (4.8 borings per acre) and 88 soil borings and 5 hand auger borings drilled in Area 2 (2.2 borings per acre). From these, a total of nearly 500 investigative (i.e., exclusive of duplicate and other QA/QC samples) soil samples have been obtained and submitted for laboratory analyses for radium, thorium and uranium isotopes. These analyses reflect hard data and includes:
- 159 samples during the OU-1 RI field investigations;
- 74 samples during the Phase 1C investigation;
- 42 samples during the Phase 1D investigation;
- 58 samples and 10 USEPA split samples during the Additional Characterization of Areas 1 and 2 investigation;
- 6 samples collected by USEPA from existing core material or the ground surface for the pyrolysis/radon emanation study;
- 34 (non-duplicate) samples as part of the additional work performed by Cotter plus 12 samples re-analyzed by USEPA; and
- 129 surface soil samples collected and analyzed in conjunction with construction of the NCC.

RIM has been identified in multiple irregular areas and volumes, and such occurrences are consistent with the use of soil materials containing radionuclides as cover material which would have been placed primarily on inclined, irregular surfaces of the working face of the refuse. Moreover, the distribution of the RIM within the landfilled areas has been impacted by both natural and anthropogenic processes, such as the initial placement and the subsequent 40-plus years of decomposition, consolidation, and differential settlement of the MSW over time. Consequently, the RIM is not present as a laterally continuous layer, but is now interspersed within separate areas and intervals of MSW such that RIM cannot be easily distinguished from the surrounding MSW and native soil matrix within which it is found. RIM was previously present at the ground surface in 1.15 acres of Area 1; however, the surface RIM is now entirely covered by either a NCC installed in 2016, inert fill that was placed in 2007-2008, or an asphalt parking lot that was installed sometime after 1978. RIM was previously present at the ground surface in 9.46 acres of Area 2, of which all is currently covered by the NCC or inert fill. Consequently, RIM is expected to be present at the surface or in the subsurface beneath approximately 8.4 acres of Area 1 and

an estimated 26.8 acres of Area 2, and the total volumes of RIM in Areas 1 and 2 are estimated to be approximately 58,700 cubic yards and 251,000 cubic yards, respectively.

The areal extent of RIM in Areas 1 and 2 have been estimated with geostatistics in support of the RIA and the evaluation of potential remedial alternatives for the Final Feasibility Study (FFS). Specifically, the extent of RIM within OU-1 Areas 1 and 2 was estimated in three dimensions (3D) using indicator kriging at multiple activity concentration thresholds. While the indicator kriging method is commonly used to identify regions of the subsurface that exhibit properties that exceed one or more defined threshold activity criterion, as described in 2017 by S.S. Papadopulos & Associates (SSP&A), there is significant uncertainty associated with the estimated extent and volume of RIM in Areas 1 and 2. Furthermore, SSP&A (2017) indicate that these estimates are more likely to be biased low than be biased high and therefore underestimate the actual volume of RIM in Areas 1 and 2. Contributing to such uncertainty is that the geostatistical analysis relies on soft data for predicting RIM occurrences when hard data are not available, and this requires an assumption that the soft data exhibit a correlation with the hard data. Moreover, the analysis focused on the utility of existing gamma emission data for inferring the presence and concentration of radium and thorium in the absence of alpha emission data when the concentration of the most predominant constituent of concern, Th-230, is not directly quantified via gamma measurements.

The Remedy set forth in the RODA will partially remove RIM by excavating certain material from the Areas 1 and 2 of OU-1 that contains combined radium or combined thorium activities greater than 52.9 picocuries per gram (pCi/g) that is located generally within 12 feet of the 2005 topographic surface. Following excavation, the remedy requires the construction of an engineered cover meeting Uranium Mill Tailings Radiation Act (UMTRCA) standards (as described in the RODA) over portions of the Site where RIM remains. Data gaps related to defining the extent of RIM (combined radium or combined thorium above 7.9 pCi/g), and thus the extent of the engineered cover (or "UMTRCA cap"), are addressed in the DIWP and later worksheets of this QAPP. Optimization of RIM removal above and below the 12-foot target depth (excavation as deep as 20 feet or as shallow as 8 feet) will be performed during the Remedial Design (RD) based on criteria set forth in Section 12.0 of the RODA and as summarized in Step 1 of **Worksheet #11** of this QAPP. Removal of radioactively impacted soils above background from Lot 2A2 and portions of the Buffer Zone is also planned to allow for unlimited exposure and unrestricted use, which prevents the need for institutional controls on these properties. Thus, the Remedy depends on being able to reliably predict the occurrences of RIM and the areal extent of such.

Data gaps and uncertainties that are expected be addressed by the current DI include: (1) the location and volume of RIM greater than 52.9 pCi/g between the current surface and a depth of 20 feet below the 2005 ground surface (B2005GS) sufficient to reasonably determine an optimized excavation; (2) the specific locations of RIM significantly above 52.9 pCi/g between 12 feet and 20 feet B2005GS to reasonably determine an optimized excavation; (3) the specific locations of RIM that appear to be isolated from larger occurrences of RIM between 8 feet and 12 feet below the ground surface sufficient to be accounted for in the optimized excavation; (4) the specific vertical intervals of RIM that have been estimated from prior borings; (5) the preliminary model predictions; (6) soft and hard data correlations/thorium detection capability; (7) boundaries of Area 1 and Area 2 related either to the extent of waste (with regard to the purposes of cap design) or in some cases the extent of RIM; (8) radionuclide occurrences in sediments located below the current surface (below the top 6 inches) of drainage areas surrounding OU-1; (9) the current location of RIM on the Buffer Zone and Lot 2A2; (10) representative radionuclide background concentrations; and (11) constituent information needed for designing a treatment system for leachate and contact water.

Data gaps associated with potential radiological impacts to on-Site or Site-adjacent drainage areas, including the Northern Water Body and Earth City Flood Control Channel, will be addressed during the Design Investigation (DI). Sediment sampling will be performed to further define the nature and extent of potential radiological impacts as discussed in Section 3.2.5 of the DIWP.

Worksheet #11: Project/Data Quality Objectives

"USEPA provides an explanation and details about the DQO process in EPA QA/g-4 - EPA/240/B-06/001 (February 2006): "The DQO Process is a series of logical steps that guides managers or staff to a plan for the resource-effective acquisition of environmental data. It is both flexible and iterative, and applies to both decision-making (e.g., compliance/non-compliance with a standard) and estimation (e.g., ascertaining the mean concentration level of a contaminant). The DQO Process is used to establish performance and acceptance criteria, which serve as the basis for designing a plan for collecting data of sufficient quality and quantity to support the goals of the study. Use of the DQO Process leads to efficient and effective expenditure of resources; consensus on the type, quality, and quantity of data needed to meet the project goal; and the full documentation of actions taken during the development of the project."

This **Worksheet #11** outlines the steps taken to identify the relevant study goals and associated data quality criteria/objectives to guide the development of an investigation plan that provides the necessary data to satisfy these objectives.

Step 1. State the Problem

Outputs of this Step
• A concise description of the problem, • A conceptual model of the environmental problem to be investigated with a preliminary, determination of the type of data needed and how it will be used, • A list of the planning team members and identification of the decision maker, and • A summary of available resources and relevant deadlines for data collection.

Describing the problem. Data are needed to design and implement the Remedy set forth in the RODA, West Lake Landfill Site, Bridgeton, Missouri OU-1, dated September 27, 2018.

The scope of the Remedy is summarized in the Statement of Work (SOW) for OU-1 dated April 2019. That summary is repeated here, to provide the complexity of the challenge:

(a) Excavation and stockpiling of overburden in OU-1 Radiological Areas 1 and 2 to access the RIM;
(b) Excavation of RIM from the Areas 1 and 2 of OU-1 that contains combined radium or combined thorium activities greater than 52.9 pCi/g that is located generally within 12 feet of the 2005 topographic surface. Optimization of RIM removal above and below the 12-foot target depth (excavation as deep as 20 feet or as shallow as 8 feet) will be performed during the RD based on criteria set forth in Section 12.0 of the RODA and summarized below:
    - If RIM greater than 52.9 pCi/g occurs between 12 and 20 feet below the surface, then evaluate and excavate where necessary to achieve long-term effectiveness and permanence objective;
    - There is a priority on focusing the excavation on the higher activity occurrences of RIM. Therefore, the USEPA expects the areas between 12 and 16 feet will be excavated if they are greater than 1,000 pCi/g;
    - The USEPA also expects to focus the excavation in the areas between 16 to 20 feet on the higher activity occurrences of RIM (greater than 1,000 pCi/g) if it doesn't add significant excavation of non-RIM waste;
    - Data show that isolated pockets of RIM between 8 and 12 feet only occur in a limited number of areas; and
    - Not excavating isolated pockets of RIM between 8 and 12 feet will minimize the short-term impacts by reducing the volume of overburden and setback.

(c) Excavation of radiologically impacted soil from the Buffer Zone and/or Lot 2A2 sufficient to reduce concentrations of radionuclides to background in order to allow for unlimited use and unrestricted exposure (UU/UE);
(d) Loading and transport of the RIM and radiologically impacted soil for disposal at an off-site permitted disposal facility;
(e) Regrading of the remaining solid waste materials within Areas 1 and 2 to meet the minimum (5%) and maximum (25%) slope criteria;
(f) Installation of a landfill cover over Areas 1 and 2 designed to meet the Resource Conservation and Recovery Act (RCRA) hazardous waste design criteria, municipal waste landfill regulations, and Uranium Mill Tailings Radiation Control Act (UMTRCA) performance and longevity standards;
(g) Design, installation, and maintenance of surface water runoff controls;
(h) Groundwater monitoring;
(i) Landfill gas and radon monitoring and control, in accordance with applicable or relevant and appropriate requirements (ARARs), as defined by the Design Criteria Report and 30% Design Report;
(j) Institutional controls (ICs) to prevent land uses that are inconsistent with a closed landfill containing radiological materials; and
(k) Long-term surveillance and maintenance of the landfill cover in Areas 1 and 2 and other remedial components.

A large amount of Site data has been collected through various investigations over the years, and the boundaries of an excavation conforming to the Remedy are predicted by a geostatistical model using such data. There are some uncertainties and limitations associated with the existing data set that impact the existing model's ability to accurately predict occurrences of RIM sufficient to design the optimized excavation portion of the remedy. There are uncertainties and limitations to be considered for an optimized excavation per the RODA which include:

- Estimation of where the RIM is >52.9 pCi/g;
- Estimation of activities, in particular, higher levels of activity between 12-20 feet B2005GS; and
- Estimation of activity and distribution of isolated pockets of RIM >52.9 pCi/g deeper than 8 feet B2005GS. These areas are mostly contiguous with areas where thorium was estimated, but not radium.

The uncertainties that are related to the above bullets include the ability to collect samples and the accuracy and precision of analyses for activity concentrations with laboratory instrumentation, the ability to estimate activity with gamma instruments (particularly thorium at low concentrations), and uncertainty in the estimation processes within the geostatistical model and related to the depth interval from which samples have been collected. Settlement related to depth intervals is also a concern, and is discussed in Section 2.2 of the DIWP rather than within this QAPP.

The term "isolated pockets" is used in the RODA to describe certain infrequent occurrences of RIM between 8 and 12-feet that may be left in place to reduce the volume of the excavation, provided the estimated activities associated with such pockets is removed from deeper locations elsewhere, with a preference for high activity areas. This term is important throughout the following narrative.

The Remedy includes installation of a landfill cover over Areas 1 and 2. There is uncertainty related to the boundary of waste in these areas. Sampling is planned near the physical boundaries of Areas 1 and 2 to confirm the waste boundaries, and step-out borings will be performed in instances where the planned borings do not confirm such boundaries. The boundary of waste is needed to develop the toe design of the landfill cover, including stormwater management. The excavations inside the landfill boundaries will also require management of surface water and contact water. The chemical nature of the leachate that may be present inside the landfill which can mix with contact water requiring treatment prior to discharge, and potential temporal variations in whether or not leachate is present within the proposed excavation depths, both require evaluation.

Establishing the planning team. The planning team includes the OU-1 Respondents, the design prime contractor (Parsons), and design subcontractors (Feezor Engineering, Inc. and Ameriphysics, LLC). Designs are approved by the lead regulatory agency, USEPA Region 7, and USEPA is supported by MDNR and assisted by subcontractors of its own.

Identifying available resources, constraints, and deadlines. The short-term effectiveness of the Remedy is decreased when materials in Area 1 and Area 2 are unnecessarily excavated or excavations remain open for unnecessary periods, increasing risk. Such decreased effectiveness is the direct result of increasing risk to remediation workers, off-site workers, and residents; generating odors; creating potential bird attractants; and increasing truck traffic. In order to reduce the short-term impacts described above, a limited number of the isolated pockets of RIM that would otherwise be excavated between 8- and 12-feet may be left in place.

In a surface assessment of residual radioactivity, measurements are easily accessible and comprehensive scans provide a safety net regarding whether a Decision Unit (DU) complies with criterion. In the subsurface, however, issues of inaccessibility, lack of comprehensive scans, and an increase in media complexity present major challenges. Thus, any study design of the subsurface may be complicated by the following concerns of internal validity:

- Statistical hypothesis testing assumes that the samples come from the same population. That is, there is nothing fundamentally different occurring that would imply sampling has occurred over two populations. In the subsurface, this may not be the case. Different depth layers may be characterized by changes in soil type, density, moisture content, chemistry, etc. Therefore, it is inconceivable that if N samples are required for the presumably homogenous surface, that N samples would suffice for the subsurface under an assumption of complete homogeneity.
- The greatest difficulty comes from the fact that investigators cannot completely scan the subsurface. The lack of comprehensive coverage so easily gained at the surface presents a real obstacle in determining activity levels at depth. For gamma emitters, such as Ra-226 and Ra-228, scanning boreholes is possible; however, it is difficult to specify a geometry for the source term, thereby limiting the interpretation of count data in terms of activity levels and location.

These limitations are described in greater detail in NUREG/CR-7021, *A Subsurface Decision Model for Supporting Environmental Compliance*, which recommends a geospatial modeling and decision framework for conducting subsurface confirmation surveys at residually radioactive sites. The framework relies on USEPA's Triad approach for managing decision-making at complex hazardous waste sites, and in particular, Triad's emphasis on the contributions of all available information, including expertise, modeling, multiple forms of data, and relevant computer technologies to assist with clarifying and mitigating decision uncertainties. At the heart of the subsurface framework is a particular implementation of the conceptual site model called the contamination concern map (CCM). The CCM is analogous to the Site's geostatistical model, developed during the FFS and RODA periods (SSP&A) and then carried forward through the Preliminary Excavation Plan and in the DIWP and relevant appendices.

The subsurface framework described in NUREG/CR-7021 is characterized by different phases that depict how the subsurface analysis moves from a very qualitative beginning to a more quantitative conclusion. Consequently, the RD for this project includes a geostatistical model for pre-delineating excavation boundaries. Substantial sampling and analysis have already been accomplished to develop the model, and the data recovered during these activities are valuable to the current study. Additional sampling is proposed in the DIWP to improve the existing geostatistical model. The final boundaries of excavation will be confirmed within DUs no larger than 2,000 square meters (m^2) including confirmation sampling.

The estimated 1,000-year non-discounted cost to execute the Remedy is $412,000,000 per the RODA. The costs for the Remedy are based on excavation of the volume of RIM and non-RIM wastes associated with a strict depth

of 12 feet B2005GS and concentration criteria of 52.9 pCi/g or greater combined radium and combined thorium. Because the Remedy allows for flexibility in the depth of excavation as a means of reducing short term public and environmental impacts, optimization of the excavation during RD could also reduce the total excavation volume and thus the construction schedule and completion cost. Although cost is not a constraint, it is desirable to accomplish the Remedy in a cost-effective manner. Such cost effectiveness is emphasized by the RODA, which states in part that the design will seek to minimize the total volume of landfill waste to be excavated, while maintaining long-term protectiveness and permanence without significantly altering the cost.

All deliverables and tasks required by the SOW must be submitted or completed by the deadlines or within the time durations listed in the RD Schedule set forth in the SOW, unless otherwise approved by USEPA.

Step 2. Identify the Goals of the Study

Outputs of this Step
• A well-defined principal study question, • A listing of alternative outcomes or actions as a result of addressing the principal study questions, • For decision problems, a list of decision statements that address the study question, and • For estimation problems, a list of estimation statements that address the study question.

Step 2 of the DQO process involves identifying the key questions that the study attempts to address, along with alternative actions or outcomes that may result based on the answers to these key questions. The principal study question (PSQ) helps focus the search for information that will address the study problem, and therefore, should be stated as specifically as possible. PSQs also help identify key unknown conditions or unresolved issues that will lead to finding a solution to the problem. The answer to the PSQ provides the basis for deciding on a proper course of action to solve a decision problem or provide the missing information needed to make an accurate estimate on an estimation problem.

USEPA's guidance on systematic planning using the DQO process recommends that planners should initially concentrate on specifying one principal study question and expand consideration to other issues and questions later in the DQO process. Nonetheless, the Remedy is such that it presents five unique study problems as presented in **Table 11-1**. Three of these problems are decision problems and two are estimating problems.

TABLE 11-1 PRINCIPAL STUDY QUESTIONS, ALTERNATIVE ACTIONS, AND DECISION STATEMENTS

Principal Study Questions (PSQs)	Alternative Actions / Estimation Statement
PSQ-1. What is the spatial and depth distribution of RIM within Area 1 and Area 2 as related to the design of the excavation and extent of the landfill cap? (Estimate)	A. Estimate the location and volume of RIM greater than 52.9 pCi/g between the current surface and a depth of 20 feet B2005GS sufficient to reasonably determine an optimized excavation. B. Estimate the specific locations of RIM significantly above 52.9 pCi/g between 12 feet and 20 feet B2005GS to reasonably determine an optimized excavation. C. Estimate the specific locations of RIM that appear to be isolated from larger occurrences of RIM between 8 feet and 12 feet B2005GS sufficient to be accounted for in the optimized excavation. D. Estimate the uncertainty in the vertical intervals of RIM that have been estimated from the original RI. E. Evaluate the preliminary model predictions. F. Estimate the boundaries of Area 1 and Area 2 related to cap design and the extent of RIM.
PSQ-2. Do radionuclide concentrations in the Buffer Zone and Lot 2A2 exceed background? (Decision)	A. Yes, take action(s) that will lead to reducing concentration to background. B. No, allow for unlimited use and unrestricted exposure.
PSQ-3. What are the radionuclide impacts as a result of migration from OU-1 in sediments of drainage areas and the northwest, or NW, surface water body (Estimate)	▪ Estimate the concentrations of radionuclides in sediments in drainage areas and the NW surface water body.

PSQ-4	What are the concentrations of constituents in leachate that are important to treatment design in Areas 1 and 2? (Estimate)	▪ Estimate the concentrations of constituents that are present to support decisions related to the need for and the design of a treatment system.

Estimation/Decision Statements	
PSQ-1:	Estimate the spatial and depth distribution of RIM within Areas 1 and 2 such that the remedy can be designed.
PSQ-2:	Determine whether or not concentrations of radionuclides in Buffer Zone and Lot 2A2 DUs are statistically greater than background.
PSQ-3:	Estimate radionuclide concentrations in drainage areas and the NW surface water body.
PSQ-4:	Estimate baseline concentrations of constituents that are important to leachate treatment system design.

Once a list of alternative actions is compiled for a decision problem, this list and the principal study question are brought together to arrive at one or more decision statements that express choices to be made among alternative actions. The estimation and decision statements are shown in **Table 11-1**.

Step 3. Identify Information Inputs

Outputs of this Step
• Lists of environmental characteristics that will resolve the decision or estimate and potential sources for the desired information inputs, • Information on the number of variables that will need to be collected, • The type of information needed to meet performance or acceptance criteria, and • Information on the performance of appropriate sampling and analysis methods.

This section will discuss the types and sources of information needed to resolve the PSQs, whether new data collection is necessary, the information basis the planning team will use for establishing appropriate analysis approaches and performance or acceptance criteria, and whether appropriate sampling and analysis methodology exists to properly measure environmental characteristics for addressing the problem.

PSQ-1

The spatial distribution of concentrations of total radium and total thorium in pCi/g are needed, where the former is informed by the radioisotopes Ra-226 (via Bi-214) and Ra-228 (via Ac-228) and the latter by the radioisotopes Th-230 and Th-232. Data gaps will be resolved with a new data collection effort; however, the estimate relies in part on previously collected data. Data contributing to the estimate are obtained via: 1) laboratory analysis of soil or soil-like material via alpha and gamma spectroscopy (i.e., "hard" data), 2) inference from alpha and gamma detections made with radiological field instruments (i.e., "soft" data), 3) the most recent version of the Site geostatistical model, and 4) surveying of the boring locations and recording depth of sample collection/gamma measurements.

Samples related to PSQ-1 will be obtained by drilling into the mass to target depths specified in the DIWP and FSP. A considerable amount of radionuclide-specific data has already been collected using methods similar to what are proposed by the FSP. These historic data are valuable to the current study when they are of sufficient quality according to the QAPP.

PSQ-2

The RODA considers radiological impacts in broader terms in the Buffer Zone and Lot 2A2 where PSQ-2 is concerned. **Table 11-2** lists the radionuclides that are important to PSQ-2 and nuclide properties from International Commission on Radiological Protection Publication 107, *Nuclear Decay Data for Dosimetric Calculations*, including half-life, decay mode and fraction, and energy emitted per nuclear transformation.

TABLE 11-2 RADIONUCLIDES OF CONCERN AND PROPERTIES OF DECAY

Nuclide	Half-Life[1]	Decay Mode[2] (Fraction)	Energy Emitted (MeV/transformation)			
			Alpha	Electron	Photon	Total
Uranium Series						
U-238	4.468E+9 y	A (1.00) SF (5.5E-07)	4.2584	0.0092	0.0014	4.2691
Th-234	24.10 d	B- (1.00)	-	0.0622	0.0105	0.0728
Pa-234	6.70 h	B- (1.00)	-	0.4037	1.4718	1.8755
U-234	2.455E+5 y	A (1.00)	4.8430	0.0137	0.0020	4.8587
Th-230	7.538E+4 y	A (1.00)	4.7538	0.0146	0.0018	4.7702

Nuclide	Half-Life[1]	Decay Mode[2] (Fraction)	Energy Emitted (MeV/transformation)			
			Alpha	Electron	Photon	Total
Ra-226	1600 y	A (1.00)	4.8603	0.0039	0.0074	4.8716
Pb-214	26.8 m	B- (1.00)	-	0.2948	0.2533	0.5481
Bi-214	19.9 m	B- (1.00) A (2.1E-4)	0.0012	0.6631	1.4793	2.1436
Pb-210	22.20 y	B- (1.00) A (1.9E-8)	<0.0001	0.0404	0.0053	0.0457
Actinium Series						
U-235	7.04E+8 y	A (1.00)	4.4693	0.0530	0.1669	4.6891
Th-231	25.52 h	B- (1.00)	-	0.1622	0.0269	0.1891
Pa-231	3.276E+4 y	A (1.00)	5.0592	0.0538	0.0450	5.1580
Ac-227	21.772 y	B- (0.99) A (0.01)	0.0693	0.0150	0.0011	0.0853
Th-227	18.68 d	A (1.00)	5.9883	0.0755	0.1317	6.1955
Ra-223	11.43 d	A (1.00)	5.7702	0.0781	0.1413	5.9895
Pb-211	36.1 m	B- (1.00)	-	0.4543	0.0644	0.5187
Bi-211	2.14 m	A (1.00) B- (2.8E-3)	6.6757	0.0100	0.0473	6.7330
Thorium Series						
Th-232	1.405E+10 y	A (1.00)	4.0688	0.0126	0.0015	4.0829
Ra-228	5.75 y	B- (1.00)	-	0.0132	0.0031	0.0163
Ac-228	6.15 h	B- (1.00)	-	0.4495	0.8671	1.3166
Th-228	1.9116 y	A (1.00)	5.4956	0.0210	0.0036	5.5202
Ra-224	3.66 d	A (1.00)	5.7766	0.0023	0.0104	5.7893
Pb-212	10.64 h	B- (1.00)	-	0.1766	0.1450	0.3217
Bi-212	60.55 m	B- (0.64) A (0.36)	2.2164	0.5046	0.1038	2.8247
Tl-208	3.053 m	B- (1.00)	-	0.6113	3.3603	3.9716

[1] Key to half-life: h is hours, m is minutes, d is days, and y is years
[2] Key to decay mode: A is alpha, B- is beta minus, SF is spontaneous fission

In the cases of radionuclides of concern (ROCs) with half-lives greater than 25 days, the radionuclides are reasonably detected with laboratory equipment via their alpha and/or gamma emissions at concentrations of 1 pCi/g or below in soil-like material. The same is not true of all ROCs with half-lives of 25 days or less, but these radionuclides may be assumed to be in equilibrium with their closest long-lived predecessor. Ra-226 and Ra-228 are quantified via their progeny, Bi-214 and Ac-228, respectively. Th-234, Pb-210, Pb-212, Bi-212, and Tl-208 will be quantified using their own energy lines.

Samples related to PSQ-2 will be collected from the Buffer Zone and Lot 2A2 via hand-auger from 0 to 6 inches and 6 to 12 inches below any gravel fill/recycled asphalt cover regardless of when it was placed.

PSQ-3

Similar to PSQ-1, PSQ-3 is concerned with the spatial distribution of concentrations of total radium and total thorium in pCi/g. A new data collection effort is planned that will examine such concentrations in sediment samples.

PSQ-4

PSQ-4 is concerned with characterization of concentrations of constituents in leachate. The specific analytes and corresponding methods and detection limits are detailed in the FSP and in the applicable worksheets of the QAPP. The parameters were selected based on likely permit discharge requirements, expected potential constituents, and treatment considerations. The base list of inorganic and organic parameters comes from Appendix I of 10 CSR 80.3 as likely MSW leachate constituents. Total phenols and total toxic organics are added to this as a check of potential elevated levels of less soluble organic compounds that are in Appendix II. Radiological compounds are also included due to their potential presence. Various parameters were added that are not otherwise required in Appendix I but could significantly impact water treatment during the Remedial Action (RA), such as iron, potassium, dissolved and suspended solids, oil and grease, chemical and biological demand, and pH (field and laboratory, temperature (field and laboratory), and UV transmittance.

Step 4. Define the Boundaries of the Study

Outputs of this Step
• Definition of the target population with detailed descriptions of geographic limits (spatial boundaries), • Detailed descriptions of what constitutes a sampling unit, • Time frame appropriate for collecting data and making the decision or estimate, together with those practical constraints that may interfere with data collection, and • The appropriate scale for decision making or estimation.

PSQ-1

The OU-1 boundary is generally defined by the distribution of RIM. The RIA (EMSI 2018) concludes that the presence of radionuclides within Area 1 are generally contained by physical boundaries:

- The Site access road located to the northwest, which is underlain by native material, precluded disposal of RIM.
- The landfill property boundary to the northeast abuts St. Charles Rock Road, which existed prior to disposal of RIM at the Site.
- Buildings (transfer station, asphalt plant, and former cement plant) are located to the southwest, which are underlain by native material based on review of historical boring/geologic logs.
- The outer boundary of the below-grade portion of the North Quarry, which did not begin accepting waste until 1979, abuts Area 1 to the southeast.

The OU-1 boundary of Area 2 is similarly confined:

- The landfill property boundary to the northeast is adjacent to St. Charles Rock Road, which existed prior to disposal of RIM at the Site.
- The landfill property boundary to northwest and west abuts the Crossroads Industrial Park, which is not considered to have been subject to waste disposal. The presence of radionuclides within Lot 2A2 of the Crossroads Industrial Park is due to historical erosion/runoff as discussed in PSQ-2.
- The landfill property boundary to the southwest abuts Old St. Charles Rock Road, which existed prior to disposal of RIM at the Site.
- The south and southeastern edges of Area 2 are bounded by the Inactive Sanitary Landfill and the Closed Demolition Landfill. Site operations for both the Inactive Sanitary Landfill and Closed Demolition Landfill occurred coincidently with landfilling in Area 2, however a 1977 fly-over gamma survey performed by EG&G "did not detect elevated levels of radioactivity in either this area [the Closed Demolition Landfill] or that portion of the Inactive Sanitary Landfill that was in operation at the same time that wastes were being disposed in Areas 1 and 2" (EMSI 2018).

The boundaries listed above provide the most current estimate of the Area 1 and Area 2 boundaries. The investigation proposed in the DIWP and presented in this QAPP for the perimeter borings will provide data to confirm boundaries for the RD. Estimates related to excavation design are focused on the 0- to 20-foot depth B2005GS of Areas 1 and 2. Although the Site boundaries reflecting Areas 1 and 2 have been previously estimated (EMSI 2018), additional data collection is proposed to determine the extent of RIM and waste for the purpose of confirming the OU-1 boundaries and placement of the engineered cover required by the RODA.

In terms of constraints, random or systematic sampling may have a low probability of identifying small areas of elevated radiological activity. For this reason, scanning surveys are typically performed before sampling at sites impacted by surface radioactivity, where the term "scanning" is used to describe the process of moving portable radiation detectors across a suspect surface with the intent of locating radionuclide contamination. A matter complicating data collection in Areas 1 and 2 is that the surface of potential radioactivity is covered and even a

few centimeters of cover can make field screening non-representative. Specifically, because RIM is buried in Areas 1 and 2, surface scans may not be representative of subsurface or near-surface radioactivity, respectively. The concern over representativeness can be lessened by increasing sampling frequency; however, subsurface sampling is time consuming and costly.

Another practical limitation of subsurface examinations is that sample recovery is not always possible. The drilling and augering processes are sometimes unsuccessful, due to poor recovery or refusal. Poor recovery describes a situation where the sampling tool is unable to collect a representative soil sample due to method limitations and/or subsurface conditions, while the term "refusal" refers to the inability of the sampling equipment to be advanced to the targeted sampling interval due to encountered buried debris or rock sufficiently larger than the sampling apparatus diameter that it blocks the sampling equipment. Poor recovery and refusal have been observed during prior investigations at this Site and may occur during the DI because of the physical characteristics that are expected from buried waste material at a landfill. Some or all of a sample may also fall out of the sample tool as it is withdrawn from the borehole, or the spatial coordinates of the sample may represent a void space. Because field personnel cannot view what is happening inside the borehole, it is impossible to know for certain what factor(s) are leading to poor recovery. Consequently, when the quantity of material recovered is sufficient for analysis, it is analyzed as though it is a complete sample. Incomplete samples, due to refusal or insufficient recovery, are recorded as such, but multiple attempts to obtain the same sample should not be made because the sample eventually recovered may not be representative.

PSQ-2

PSQ-2 relates to the Buffer Zone and Lot 2A2. The spatial boundaries for this PSQ are not easily recognized. The two areas are separated by fence, but the properties are not completely enclosed by fencing along their other boundaries. Further information pertaining to the Buffer Zone and Lot 2A2 boundaries is provided in the RIA (EMSI 2018). Unlike Areas 1 and 2 where radioactive material is known to have been buried, burials did not occur in either the Buffer Zone or Lot 2A2. Instead, residual radioactivity is believed to be the result of erosion of surficial soils and subsequent transport of radionuclides via stormwater runoff from the northwest-facing slope of an Area 2 landfill berm, as discussed in Section 6.7 of the RIA. This event occurred prior to the establishment of vegetation on the landfill slope, following completion of the landfilling activities in Area 2. Additional details can be found in the RIA. Consequently, PSQ-2 is concerned with surface radioactivity; however, soil surface in this instance is not the same as ground surface. These areas are known to have been covered by gravel and other gravel-like material after it was discovered that RIM material had migrated from Area 2 (EMSI 2018). Furthermore, prior to the application of a gravel cover, surface soils were disturbed due to anthropogenic activities (grading and regrading), therefore it is not certain that radionuclide impacts would be constrained to the 6 inches of soil directly underlying gravel/asphalt cover. Consequently, soil samples will be collected from the 0 – 6 inch and 6 – 12-inch depths (as measured below the reworked gravel and/or asphalt interface), and soils will be screened with a radiological detector. In the event that radionuclide impacts are observed from 6 – 12 inches, additional soils will be collected and analyzed until a clean interval is observed. Further sampling details and the decision units related to PSQ-2 are described in the DIWP and are shown in Figures 11 and 12 of that document.

PSQ-2 involves comparisons against background radioactivity, which means that data are also needed from a background reference area. Four areas have been designated background reference units. The areas designated as background reference units are described in the DIWP, and shown on Figure 12 of the DIWP.

PSQ-3

This estimate is concerned with historical impacts to drainage areas and the NW Surface Water Body, where a historical impact is indicated by the presence of total radium or total thorium in a concentration exceeding 7.9 pCi/g. As described in the DIWP, the potential exists for radionuclides associated with the Site to have been

transported from Areas 1 and 2 during rain events and deposited in drainage areas adjacent to the Site. Based on an analysis of surface flow patterns presented in the RIA most, if not all, of the surficial runoff from Area 1 and runoff from the southeastern portion of Area 2 ultimately flows into the Northern Surface Water Body (also referred to as the North Surface Water Impoundment). A review of historical aerial imagery was performed during the RI and concluded that "the North Surface Water Body did not exist in 1941 but does appear on the 1953 aerial photograph" (EMSI 2018). The RIA also states that the "perimeter of the North Surface Water Body has been inspected by the OU-1 Respondents, Bridgeton Landfill and EPA and no outlet structure or points of discharge from the North Surface Water body were identified," (EMSI 2018). Based on this information, the extent of potential Site-derived radiological impacts due to erosion of surficial RIM in Area 1 and from the southeastern portion of Area 2 are presumed topographically constrained to the perimeter drainage ditch conveying runoff to the impoundment, and the North Surface Water Body itself.

Deposition within the North Surface Water body must have begun at some point following the formation of this feature, between 1941 and 1953, and likely continues into the present day. Sediment samples will be collected within the North Surface Water Body to measure the thickness of overlying sediment, which will then be used to calculate a range of possible deposition rates. A bathymetric survey will be performed to identify depositional features (outwash fans, ripples) and/or erosional features (channels, runnels) in the sediment surface which may be used to shift proposed sample locations.

Surficial runoff from the southwestern region of Area 2 flows down the western landfill slope and onto the Buffer Zone. According to the RIA, surficial runoff ponds "unless sufficient water accumulates such that the water reaches the western portion of the Buffer Zone where it can flow overland onto the southwest portions of Lots 2A2 and 2A1, and from there into a culvert that conveys stormwater to the large Earth City stormwater basin located adjacent to Area 2 and the AAA Trailer property," (EMSI 2018).

Sediment samples have previously been collected from the northeast perimeter drainage ditch that feeds into the North Surface Water Body, as well as from the influent and effluent ends of the culvert that feeds into the Earth City stormwater basin. During the DI, historical sediment locations will be resampled and additional sediment samples will be collected from sediments within the North Surface Water Body itself, as described in the DIWP, baring practical limitations that may impact ability of site crews to collect data such as water depth and unsafe access to the ponded areas.

PSQ-4

This estimate is concerned with establishing baseline concentrations of constituents in leachate within Areas 1 and 2. These data will be used to evaluate the characteristics of potential leachate that may be present within Areas 1 and 2 and to estimate the characteristics and treatment requirements of water that may come into contact with waste / RIM (contact water). As described in the DIWP, leachate monitoring wells will be installed in two proposed locations in Area 1 and five proposed locations within or adjacent to Area 2. These wells will be used to collect liquid level measurements on a monthly basis and to collect liquid samples for field tests and/or laboratory analysis. The fact that such wells are examined monthly reflects possible temporal concerns resulting from seasonal changes in precipitation, runoff, and infiltration volume. The presence, or lack thereof, of leachate may vary throughout the year. It is anticipated that one sample of leachate will be obtained from each of the seven standpipe wells, but the timing of that collection may vary depending on availability of sufficient volume for sampling. It is anticipated that the spatial variability of the leachate characteristics will be greater than the temporal variability because different areas of the Site received different waste and cover materials; therefore, the analytical chemistry focus is on obtaining samples from different locations.

Step 5. Develop the Analytic Approach

Outputs of this Step
• Identification of the population parameters most relevant for making inferences and conclusions on the target population, • For decision problems, an "if…then…" theoretical decision rule based upon a chosen Action Level, and • For estimation problems, the specification of the estimator to be used.

The expected outputs of this step are captured on **Table 11-3** for all PSQs and are collectively called the study's analytic approach. Note that according to USEPA 2006, Action Levels should be specified for decision problems and may be relevant to estimating problems.

TABLE 11-3 ANALYTIC APPROACH

Question	Estimating Statement*	Parameter of Interest	Action Level(s)	Decision/Estimating Rules
PSQ-1	A,E	1) Total radium (Ra-226 + Ra-228) 2) Total thorium (Th-230 + Th-232) 3) Non-exceedance probability	For 1) and 2), 52.9 pCi/g For 3), 0.5	For 1) and 2), when the estimated parameter is less than or equal to (≤) the Action Level within Site boundaries from 0-20 feet, then that portion of the Site does not need to be considered for excavation, otherwise it does. For 3), when the estimated parameter is < Action Level, it is assumed there is a 50% probability that the material is greater than (>) 52.9 pCi/g, otherwise it is assumed there is a 50% probability the material is less than 52.9 pCi/g.
	B	4) Total radium (Ra-226 + Ra-228) 5) Total thorium (Th-230 + Th-232)	N/A	Estimate total activity from 0-16' when RIM > 52.9 pCi/g.
	C	6) See A and B above	See A and B above	See A and B above
	D	7) Average settlement for individual borings 8) Vertical distribution of settlement	N/A	For 7), compare recent survey locations to historical locations to identify differences and average over the estimated thickness of waste at each location.

Question	Estimating Statement*	Parameter of Interest	Action Level(s)	Decision/Estimating Rules
				For 8), compare significant gamma intervals in historical surveys to gamma intervals in recent surveys to estimate the amount of settlement that has occurred.
	F	9) Total radium 10) Total thorium	7.9 pCi/g	When the estimated parameter is > Action Level in a perimeter boring, additional data are needed to confirm the boundary of waste; otherwise, additional data are not needed.
PSQ-2	N/A	1) Mean U-238, U-234, Th-230, Ra-226, and Pb-210 2) Mean U-235, Pa-231, and Ac-227 3) Mean Th-232, Ra-228, and Th-228	Estimate of the mean of background concentration	If the difference between the mean concentration in a DU and the background mean is statistically significant, then action is needed; otherwise, no action is required and allow for unlimited use and unrestricted exposure.
PSQ-3	N/A	1) Total radium 2) Total thorium	7.9 pCi/g	When estimated parameter is > Action Level, determine if corrective actions are needed, and if so, develop appropriate alternative actions.
PSQ-4	N/A	Constituents as noted in the FSP	N/A at this stage as monitoring is intended to gather data solely for purposes of considering design alternatives	Estimate range of characteristics of leachate over time that may be present within Areas 1 and 2 to aid in evaluation of treatment requirements of water that may come into contact with waste / RIM (contact water)

* PSQ-1 only with identifiers A through F correspond to Estimating Statements for PSQ-1 from Step 2 of this worksheet.
N/A – not applicable

Step 6. Specify Performance or Acceptance Criteria

Outputs of this Step
• For decisions, the decision maker's tolerable decision error rates based on the consequences of making an incorrect decision, and • For estimates, specify performance metrics and acceptable levels of uncertainty.

PSQ-1

PSQ-1 (including estimate statements A-F) involves several categories of estimation processes, Therefore in Step 6 this PSQ is separated into three components: (1) quantitative point data (i.e. hard data), (2) field scanning data (i.e. soft data) which are processed in order to be used quantitatively, and (3) spatial/depth interpolations of both hard and soft data. Separating these estimation tool improves the ability of specifying performance metrics and acceptable levels of uncertainty. These three components are explained for Step 6 as follows:

Hard Data (used to resolve estimating statements A-F)

Quantitative point estimates of total thorium and total radium are calculated from isotopic detections of Th-230, Th-232, Ra-226 (via Bi-214), and Ra-228 (via Ac-228) in individual samples. The thorium and radium constituents are well quantified at concentrations below the lowest Action Level for PSQ-1 with laboratory analyses that measure radioactive emissions via alpha and gamma spectrometry, respectively. The data are continuous, and the range of possible results for each radionuclide in a sample varies from negative values below the detection sensitivity of the counting system (measured in MDC) to as high as one or more orders of magnitude above Action Levels based on historic data. When the laboratory reports activity concentrations of one of the radionuclides leading to the calculation of total thorium or radium, it will also report the radionuclide-specific uncertainty and MDC where the former is calculated at the 95% confidence level (1.96-sigma). For the calculation of combined radium, uncertainty will be calculated for the sum of two variables that may not be independent, e.g., $1.96\sqrt{\sigma_X{}^2 + \sigma_Y{}^2 + \sigma_{XY}}$, where Ra-226 and Ra-228 are represented by x and y, respectively. The covariance term σ_{XY} will be computed given the current data set. The same calculation will be performed for combined thorium (Th-230 and Th-232). For comparison against Action Levels and for purposes of RD and total activity determination, the concentrations of combined radium and combined thorium calculated from individual isotope results from laboratory samples are accepted as true values when the individual analyses meet the measurement performance criteria specified in Worksheet #12.

In the case of composite samples that are used to resolve estimating statement F, results close to the Action Level (i.e., within the summation of uncertainties reported by the laboratory) are important. When results are close but below the Action Level, individual one-foot samples will be analyzed from the core-run that the composite sample represents, and actions will be based on the results observed. When results from composites are close but above Action Levels, individual one-foot samples from the core-run may be analyzed at the discretion of the PM, and in such cases actions will be based on the results observed.

The acceptance criteria for composite sample field duplicates is detailed in Worksheet #12.

Soft Data (used to resolve estimating statements A-F)

The investigation allows for inclusion of field measurement instruments as a means of estimating extent and activity of RIM > 52.9 pCi/g. Field data are collected in units of counts or count rate (e.g., counts per minute) depending on whether the instrument is used as a scaler or a ratemeter, respectively. The data collected are continuous, and the expected range is from 300 to 2,000,000 counts per minute. Quantitative comparisons against Action Levels are possible in the absence of true point estimates when field data are normalized, and examined with a regression that integrates the relationship between field data and laboratory data. That is, a

relatively large number of counts (or high count rate) observed at a specific location are likely to be associated with total activity above the Action Level than are relatively fewer counts at the same location; and statistics can be used to estimate the probability that an observed number of counts predicts total thorium or radium activity above an Action Level. For comparison against Action Levels and for purposes of Remedy Design and total activity determination, the concentrations inferred with properly calibrated and functioning field instruments expected to be used, but it is accepted that they estimate values of total thorium and radium activity with a higher level of uncertainty. This uncertainty is accepted as discussed in the next paragraph. Concepts that are important to investigations that rely on count data are critical level (L_C) and detection level (L_D) where the former is the net count in a zero-mean count distribution having a probability (α) of being exceeded and the latter is the number of mean net counts for which the number of counts are almost always certain to exceed L_C *for* a given value of β. It is common practice to set α and β to 0.05 when calculating L_C and L_D which means there is a 5% probability of committing a Type I error (false positive detection) and a 5% probability of incorrectly concluding that that no activity is present when it is indeed present (Type II error).

In order to further specify performance metrics and acceptable levels of uncertainty related to soft data, the following process is provided. There are two uses of the data in this process: (1) estimate of the probability of exceeding a threshold and (2) activity calculations to complete excavation optimization. Each is described below:

1) For estimating the extent of RIM, the standard error is used to transform the data into probabilities, which therefore incorporates the uncertainty into the process. It is acknowledged that if the standard error of the regression is pragmatically adjusted, then the uncertainty may not be sufficiently accounted for. Appendix E of the DIWP explains these processes which factor uncertainty into the estimates of probability. In other words, the estimate of probability (i.e. indicator value) incorporates the uncertainty: for example, an estimate of a non-exceedance criteria of 0.7 is a 70% likelihood of being below the threshold of 52.9 pCi/g. In this example 70% likelihood is a mathematical function of standard error (i.e. uncertainty). The section below in Step 6 and Appendix E of the DIWP provides further performance metrics and acceptable levels of uncertainty as related to estimating the extent of RIM based on a spatial/depth interpolation algorithm.
2) A separate model has been proposed to estimate the activity of RIM within locations that are equal to or greater than 52.9 pCi/g for the purposes of the excavation design. The proposed ordinary kriging model estimates a concentration of combined radium and combined thorium, rather than a non-exceedance probability, directly from soft data regressions. As a result, the uncertainty of these regressions will be considered differently than in #1 above. It is expected that this uncertainty may be derived, subject to USEPA approval, from the Upper Confidence Limit (UCL) and Lower Confidence Limit (LCL) of these regressions. The final approach to considering the uncertainty of an activity estimate, including the uncertainty from any the soft data used for the estimate, will be included in the Revised Excavation Plan.

   It should be noted that:
   - The activity model has only been used to provide estimates within the delineated extent of RIM >52.9 pCi/g as well as approximately 1000 pCi/g as needed to develop an optimized excavation plan.
   - The activity estimates are not intended to reflect or evaluate the risk profile of the Site.

<u>Spatial/Depth Interpolation (used to resolve estimating statements A-E)</u>

In the absence of exhaustive quantitative or semi-quantitative data, geostatistics software allows for interpolation to estimate values for locations between those for quantitative or semi-quantitative results. The software provides a method of constructing new data points within the range of known data points as a means of predicting whether or not an Action Level is exceeded. These predictions are not environmental data

collections in the usual sense; rather, they rely on the data collections described in the immediately preceding paragraphs. Detailed descriptions of the updated and future geostatistical processes and modeling are provided in Appendix E of the DIWP rather than in this document.

A process for highlighting regions to target for sampling, based on standard deviation and RIM non-exceedance probability (NEP), was developed in response to Comment #17 of the USEPA's Comments on the 3/30/2020 draft of the DIWP and is further explained in Section 4.2.2 of the DIWP Appendix E. This process statistically combined the standard deviation with indicator kriging (IK*[1]) indicator values into a metric for confidence levels as related to NEP. As such, areas of the model can be queried to demonstrate where additional samples might be useful in reducing standard deviation and achieving said confidence level. This process uses a metric termed Standard Deviation to Warrant Sampling (SDWS) and provides relevance to evaluating acceptable levels of uncertainty and determining if sufficient samples are being proposed. A thorough evaluation in Appendix E of the DIWP describes the process of scenario development evaluation of several types of SDWS confidence levels as a means for evaluating NEP confidence levels. Based on the information and analyses provided in this Appendix E, an acceptable confidence level of 70% for NEP < 0.5 (inside RIM > 52.9 pCi/g) and 60% confidence level for NEP > 0.5 (outside RIM > 52.9 pCi/g) was selected for further evaluation and modeling. These confidence intervals are considered acceptable because:

- When Type I error confidence level is less than Type II error, there is more emphasis towards over-excavation rather than under-excavation (when outside RIM >52.9 pCi/g), yet there is recognition that because the RODA (USEPA, 2018) requires optimizing the excavation, limiting over-excavation is important;
- This project is a subsurface investigation of a landfill, and inherently includes a level of uncertainty by which excessive sampling will not overcome (NRC 2012); and
- Confirmation sampling will verify the excavation limits.

Using the 70% confidence level and 60% confidence level, as described above, the model was re-run with the proposed boring plan and SDWS fields were re-processed with new model output. This is shown in Appendix E Figure E-11d insets A and B, which provides maps of spatial extent of SDWS in the existing model and an updated model using the proposed borings with artificial data. In Appendix E Figure E-11d Inset B it can be observed with the proposed boring plan that there is one area of significant SDWS in the middle of Area 2, southwest of proposed borings A2-SB001 and A2-SB016. As a following step (outlined in the workflow provided in Appendix E), two additional borings were added to the model with artificial data to determine if the SDWS is sufficiently lowered. Appendix E Figure E-11d inset C provides the SDWS model output after the inclusion of the additional borings, which shows all remaining SDWS areas (with the exception of a few minor polygons) have been removed. Therefore, the analysis indicated that the previously proposed borings, with two additional borings focused on remaining SDWS areas, is sufficient to meet SDWS at the 70% confidence level for NEP < 0.5 (inside RIM > 52.9 pCi/g) and 60% confidence level for NEP > 0.5 (outside RIM > 52.9 pCi/g).

PSQ-2

For decision problems such as PSQ-2, the probability of making decision errors can be controlled by adopting a scientific approach called hypothesis testing. In this approach, the survey results are used to select between one condition of the environment (the null hypothesis, H_0) and an alternative condition (the alternate hypothesis, H_a). The null hypothesis is treated like a baseline condition that is assumed to be true in the absence of strong evidence to the contrary. Acceptance or rejection of the null hypothesis depends upon whether or not the particular survey results are consistent with the hypothesis. A decision error occurs when the decision maker

[1] IK* Indicator Kriging for this project is completed as ordinary kriging on a set of probability's as defining by cumulative distribution function (CDF) development. While IK typically suggests the data are strictly binary for this project, the definition of IK* includes other probabilities between 0 and 1.

rejects the null hypothesis when it is true, or accepts the null hypothesis when it is false. These two types of decision errors are classified as Type I and Type II decision errors. **Figure 11-1** represents the null hypotheses and corresponding Type I and Type II decision errors for PSQ-2.

H_0: The mean activity in the DU is indistinguishable from the mean in background			
		Decision	
		Reject H_0 (Mean in the DU exceeds background)	Accept H_0 (Mean in the DU is indistinguishable from background)
TRUE CONDITION OF DU	Exceeds background	(No decision error)	Incorrectly release the DU (Type II)
	Indistinguishable	Incorrectly conclude the DU is contaminated (Type I)	(No decision error)

FIGURE 11-1 REPRESENTATION OF DECISION ERRORS FOR PSQ-2

A Type I decision error occurs when the null hypothesis is rejected when it is true and is sometimes referred to as a false positive error. The probability of making a Type I decision error, or the level of significance, is denoted by alpha (α). Alpha reflects the amount of evidence a decision maker would like to see before abandoning the null hypothesis and is also referred to as the size of the test.

A Type II decision error occurs when the null hypothesis is accepted when it is false. This is sometimes referred to as a false negative error. The probability of making a Type II decision error is denoted by beta (β). The term (1- β) is the probability of rejecting the null hypothesis when it is false and is also referred to as the power of the test.

The relationship between α and β impacts survey design. In general, increasing α decreases β and vice versa, holding all other variables constant. Increasing the number of measurements typically results in a decrease in both α and β. The number of measurements that will produce the desired values of α and β can be estimated from α, β, the Action Level, and the estimated variance of the distribution of the parameter of interest.

For PSQ-2, decision-error-rate limits for α and β are set at 0.05, meaning a 5% probability of making a Type I or Type II error is acceptable.

PSQ-3

PSQ-3 is an estimating question. Sediment samples from drainage areas and the NW surface water body will be used to make point estimates of total thorium and total radium concentration to determine historical impacts. Hard data and their associated laboratory uncertainty, as described above for PSQ-1, are accepted as true values of total thorium and radium activity at the locations from where such samples are obtained when the individual analyses meet the measurement performance criteria specified in Worksheet #12.

PSQ-4

Similar to PSQs #1 and #3, laboratory analytical results and their associated uncertainty are accepted as true values of the parameters, as such results are intended to represent and are used to explore the characteristics of leachate within Areas 1 and 2 as a means of evaluating possible treatment options and for determining if additional data collections are necessary. In addition, the individual analyses must meet the performance criteria specified in Worksheet #12.

Step 7. Develop the Detailed Plan for Obtaining Data

Outputs of this Step
• The most resource-effective design for the study that is expected to achieve the DQOs

The SOW describes a set of interconnected deliverables where the DI is concerned. These deliverables include: a DIWP that evaluates and summarizes existing data and describes additional data needs; an FSP that describes media to be sampled, contaminants, or parameters for which sampling will be conducted, sample locations (including boring locations and sample depths), and number of samples; a DMP that describes the site-wide approach to the collected data; and a QAPP that addresses sample analysis and data handling and other QA/QC requirements. Consequently, except in the case of PSQ-2, the sampling design for the remaining PSQs is conveyed in other documents associated with the DI as shown in **Table 11-4**.

TABLE 11-4 PLAN FOR OBTAINING DATA

PSQ	Estimating/Decision Statement	Sampling Design	Sample Selection
PSQ-1	A. Estimate the location and volume of RIM > 52.9 pCi/g between the current surface and a depth of 20 feet B2005GS sufficient to reasonably determine an optimized excavation.	DIWP 3.1 – 3.2.2.4	FSP 2.4.3
	B. Estimate the specific locations of RIM significantly > 52.9 pCi/g between 12 feet and 20 feet B2005GS to reasonably determine an optimized excavation.	DIWP 3.1 – 3.2.2.4 and Appendix E	FSP 2.4.3
	C. Estimate the specific locations of RIM that appear to be isolated from larger occurrences of RIM between 8 feet and 12 feet below the ground surface sufficient to be accounted for in the optimized excavation.	DIWP 3.1 – 3.2.2.4	FSP 2.4.3
	D. Estimate the uncertainty in the vertical intervals of RIM that have been estimated from the original RI.	DIWP 2.2	FSP 2.4.3
	E. Evaluate the preliminary model predictions.	DIWP 3.1 – 3.2.2.4	FSP 2.4.3
	F. Estimate the boundaries of Area 1 and Area 2 related to cap design and the extent of RIM	DIWP 3.2.1 and 3.2.3	FSP 2.2 and 2.3
PSQ-2	Determine whether or not concentrations of radionuclides in Buffer Zone and Lot 2A2 DUs are statistically greater than background.	DIWP 3.2.4 and the narrative following this table	FSP 2.4.2.1 and 2.4.2.2
PSQ-3	Estimate radionuclide concentrations in drainage areas and the NW surface water body.	DIWP 3.2.5	FSP 2.4.4
PSQ-4	Estimate baseline concentrations of constituents that are important to leachate treatment system design.	DIWP 3.3.3	DIWP 3.3.3 and FSP 2.6.3

It is expected that the sample design for PSQ-2 may serve as confirmation sampling in the Buffer Zone and Lot 2A2 as required by Section 12.2.4 of the RODA when such sampling leads to a decision that unlimited use and unrestricted exposure of a DU is warranted. Consequently, the sampling design proposed by **Table 11-4** and described in the corresponding sections of the DIWP and FSP are further evaluated herein in terms of its to appropriateness to serve in this capacity. Specifically, the number of samples that are proposed is examined in the paragraphs that follow.

Visual Sampling Plan (VSP) is a software tool that supports the development of a defensible sampling plan based on statistical sampling theory and the statistical analysis of sample results to support confident decision making. VSP is developed by Pacific Northwest National Laboratory with support from USEPA and other federal entities including the Department of Energy (DOE), Department of Defense (DoD), Department of Homeland Security, and Centers for Disease Control (CDC). VSP version 7.15 is used to evaluate the suitability of the proposed numbers of samples in the Buffer Zone, Lot 2A2, and the background reference area.

PSQ-2 asks, "Are radionuclide concentrations in the Buffer Zone and Lot 2A2 statistically greater than background?" This question is answered by sampling DUs in the Buffer Zone and Lot 2A2 and reference units comprising a background reference area and then 1) testing the equivalency of means between individual DUs and the background reference area with an appropriate statistical test based on the population distributions; 2) determining if the 75th quantiles of the two distributions are equivalent with the quantile test; and 3) via additional characterization in a DU when warranted based on professional judgement. The testing of populations will include tests of assumptions of normality, homogeneity of variance, and consideration of influence of outliers and censoring (non-detects). The assumptions of the statistical tests, procedures for implementation, and alternate procedures when assumptions are not met are described in greater detail in Worksheet #37.

In its list of features for meeting sampling goals, VSP contains a tool called "Compare Average to Reference Average." When the MARSSIM application of VSP is used, and the code is asked to calculate the number of samples for analyte-by-analyte comparisons (rather than unity), a minimum of 14 samples are required when the following design parameters are used as shown in **Figure 11-2**:

- Null hypothesis: The DU is acceptable (true mean ≤ Action level) until proven otherwise.
- False rejection rate (α) and LBGR: Provide at least 95% confidence that it is concluded that the DU is acceptable if the true median is no greater than 0.5 units above the true reference median. Note that VSP accepts inputs in fields called "units"; thus, a LBGR of 0.5 units is the equivalent of 0.5 x background.
- Upper bound of the gray region and false acceptance rate (β): If the true median is 0.5 units above (i.e., 0.5 units below) the true reference median (i.e., 0.5 x background), then no more than 5% chance of incorrectly accepting the null hypothesis.
- The estimated standard deviation due to sampling and analytical variability is limited to 0.5 units (i.e., 0.5 x background).
- The minimum number of samples, *n*, is increased by 20% to account for to account for uncertainty in the calculated value of *n*.

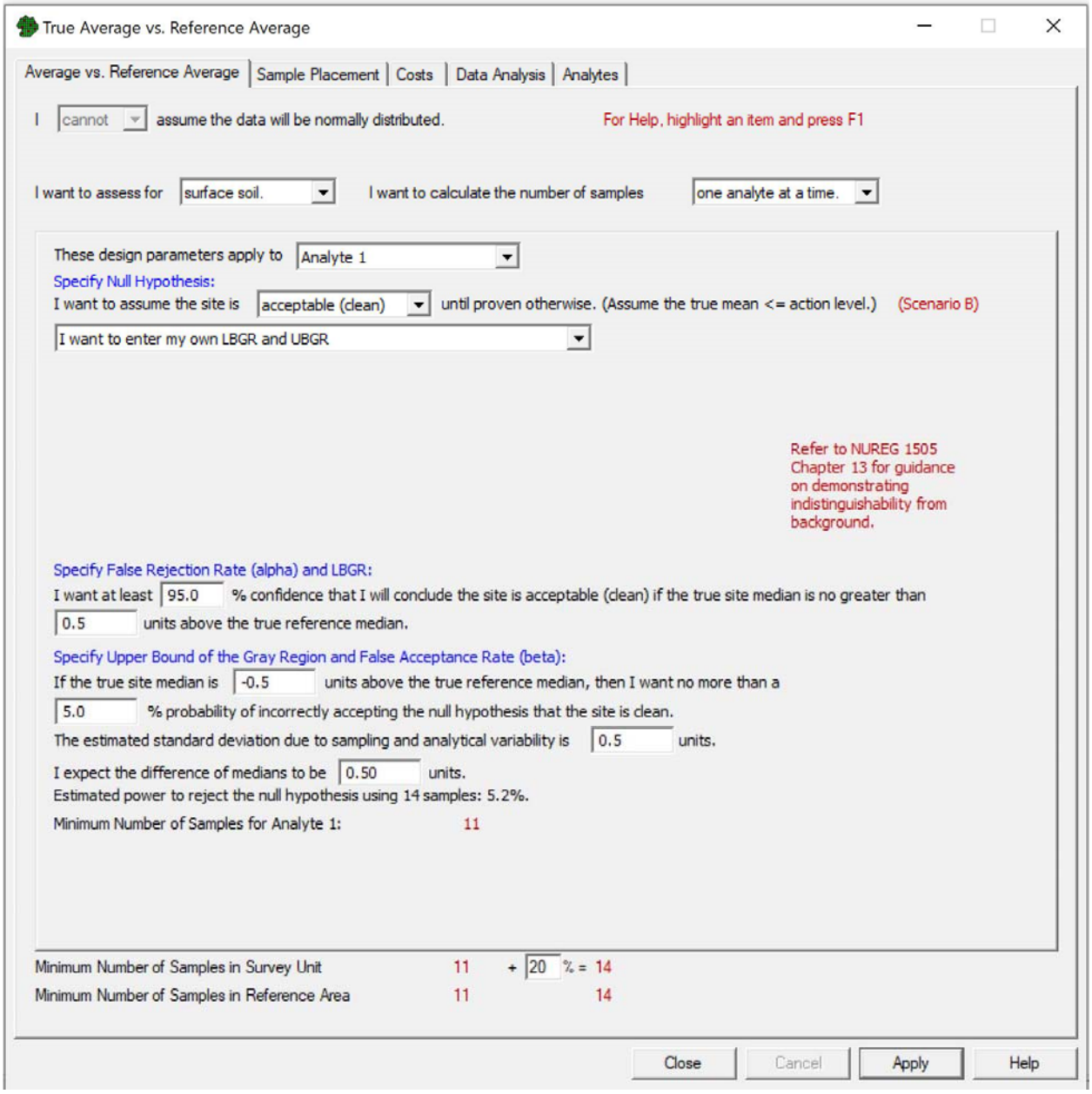


FIGURE 11-2 VSP OUTPUT FOR PSQ-2

Although the intent of the hypothesis test for PSQ-2 is to compare the mean of radionuclides in decision units to background, the MARSSIM application of VSP does not allow the data to be assumed to be normally distributed. Thus, VSP relies on the median statistic rather than the mean to conservatively calculate same size (i.e., a larger number of samples is returned than had the mean been used). Consequently, we can conclude that the minimum number of samples planned per DU (14 samples) is acceptable based on acceptable Type I and Type II decision error rates and a conservative estimate of standard deviation because it reflects the largest number of samples that are required regardless of whether the data are normally distributed or not. Note that in application, normality will be tested as described previously and in Worksheet #37 and the appropriate statistic will be used for decision making.

The gridded spacing between sample locations in the Buffer Zone and Lot 2A2 was calculated as $L = \sqrt{A/n}$; where "L" is equal to the space between sampling locations, "A" is the area of the survey unit, and "*n*" is the sample size (*n* =14 samples per survey unit). For instance, where A = 2,000m^2 and *n* = 14, grid spacing (L) is equal to 12m. Borings were placed L distance from the random-start point due north, south, east, and west, and the process was repeated at each successive point until a survey unit boundary was encountered.

Radiological investigations involving statistical comparisons against background typically require at least as many samples in the background reference area as in the DUs. In order to determine a statistically valid background concentrations for the Buffer Zone and Lot 2A2, a total of 120 background samples from 60 locations are planned from four reference units comprising the Background Reference Area. Four reference units are adjacent to the Bridgeton Landfill and are expected to demonstrate characteristics similar to the Buffer Zone and Lot 2A2. In application, 15 sample locations are randomly located in each reference unit and two samples, one 0- to 6-inches deep and one 6- to 12-inches deep, are recovered from each location using techniques and controls explained in the FSP. Samples from the two depth intervals are planned so that any between-strata variability (e.g., due to anthropogenic factors) can be observed and assessed. When such samples do not indicate between-depth impacts, data from 0-6 inch samples will be used to determine the mean radionuclide concentration and uncertainty. If between-strata variability is observed in background samples, the data from DUs will be compared separately against the two depth intervals. Four background reference units and corresponding random-generated sample locations are shown on Figure 7A of the DIWP.

Worksheet 11 References

Crumbling, D. 2002. *Using the TRIAD approach to improve the cost-effectiveness of hazardous waste site cleanups.* U.S. Environmental Protection Agency. doi:EPA-542-R-01-016.

NRC. 2012. *A Subserface Decision Model For Supporting Environmental Compliance.* Office of Nuclear Regulatory Research. doi:NUREG/CR-7021.

Worksheet #12: Measurement Performance Criteria

The tables below summarize the quantitative measurement performance criteria (MPC) that has been established for the sampling tasks to be conducted for this project. The quality of the sampling procedures and laboratory results will be evaluated for compliance with DQOs through a review in accordance with the procedures described in **Worksheet #37**. The results will be summarized in a data usability report. Sample collection procedures and analytical methods/standard operating procedures (SOPs) are summarized in **Worksheet #21** and **Worksheet #23**, respectively. All analyses will be performed by GEL Laboratories.

Matrix: Leachate and Waste

Analytical Group or Method: Volatile organic compounds (VOCs)/SW8260C (leachate) and Toxicity Characteristic Leaching Procedure (TCLP) VOCs/SW1311, SW8260C (waste characterization)

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates (VOCs only)	Relative percent difference (RPD) ≤ 30% when VOCs are detected in both samples ≥ sample-specific reporting limit (RL)
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates	RPD ≤ 20%
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	70-130%R
Analytical Accuracy/Bias (matrix interference)	Matrix Spike/Matrix Spike Duplicates (MS/MSD)	70-130%R
Overall accuracy/bias (contamination)	Laboratory Blanks/Equipment Blanks/Trip Blanks	No target analyte concentrations ≥ RL
Sensitivity	Reporting Limit (RL) verification sample (spiked at RL)	Recovery within ±25% of RL
Completeness	>90% Usability	Data Completeness Check

Matrix: Waste

Analytical Group or Method: TCLP semivolatile organic compounds (SVOCs)/SW1311, SW8270D (waste characterization)

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates (LCSDs)	RPD ≤ 30%
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples (LCSs)	See table below
Overall accuracy/bias (contamination)	Laboratory Blanks	No target analyte concentrations ≥ RL
Sensitivity	RL verification sample (spiked at RL)	Recovery within ±25% of RL
Completeness	>90% Usability	Data Completeness Check

Analyte	LCS % Recovery
m,p-Cresols	30-130
o-Cresol	30-130
1,4-Dichlorobenzene	30-130
2,4-Dinitrotoluene	30-130
2,4,5-Trichlorophenol	30-130
2,4,6-Trichlorophenol	30-130
Hexachlorobenzene	52-108
Hexachlorobutadiene	33-91
Hexachloroethane	33-91
Nitrobenzene	51-110
Pentachlorophenol	48-121
Pyridine	25-81

Matrix: Waste

Analytical Group or Method: Polychlorinated biphenyls (PCBs)/SW8082A (waste characterization)

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates	RPD ≤ 30%
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	See table below
Analytical Accuracy/Bias (matrix interference)	Matrix Spike/Matrix Spike Duplicates	See table below
Overall accuracy/bias (contamination)	Laboratory Blanks	No target analyte concentrations ≥ RL
Sensitivity	RL verification sample (spiked at RL)	Recovery within ±25% of RL
Completeness	>90% Usability	Data Completeness Check

Analyte	LCS % Recovery	MS/MSD % Recovery
Aroclor-1016	50-102	29-125
Aroclor-1221	50-150	50-150
Aroclor-1232	50-150	50-150
Aroclor-1242	50-150	50-150
Aroclor-1248	50-150	50-150
Aroclor-1254	32-125	50-150
Aroclor-1260	53-115	32-129
Aroclor-1262	50-150	50-150
Aroclor-1268	50-150	50-150

Matrix: Waste

Analytical Group or Method: TCLP Pesticides/SW1311, SW8081B (waste characterization)

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates	RPD ≤ 30%
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	See table below
Overall accuracy/bias (contamination)	Laboratory Blanks	No target analyte concentrations ≥ RL
Sensitivity	RL verification sample (spiked at RL)	Recovery within ±25% of RL
Completeness	>90% Usability	Data Completeness Check

Analyte	LCS % Recovery
Chlordane	49-136
Endrin	39-138
Heptachlor	43-123
Heptachlor epoxide	47-128
gamma-BHC (Lindane)	46-130
Methoxychlor	51-135
Toxaphene	52-105

Matrix: Waste

Analytical Group or Method: TCLP Herbicides/SW1311, SW8151A (waste characterization)

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates	RPD ≤ 30%
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	See table below
Overall accuracy/bias (contamination)	Laboratory Blanks	No target analyte concentrations ≥ RL
Sensitivity	RL verification sample (spiked at RL)	Recovery within ±25% of RL
Completeness	>90% Usability	Data Completeness Check

Analyte	LCS % Recovery
2,4-D	58-138
2,4,5-TP (Silvex)	63-137

Matrix: Leachate

Analytical Group or Method: Metals (including mercury)/SW6020A, SW7470A

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	RPD ≤ 30% when metals are detected in both samples ≥ sample-specific RL
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates	RPD ≤ 20%
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	85-115%R 85-115%R (Mercury)
Analytical Accuracy/Bias (matrix interference)	Matrix Spike Duplicates	75-125%R 85-115%R (Mercury)
Overall accuracy/bias (contamination)	Laboratory Blanks/Equipment Blanks	No target analyte concentrations ≥ RL
Sensitivity	RL verification sample (spiked at RL)	Recovery within ±25% of RL
Completeness	>90% Usability	Data Completeness Check

Matrix: Waste

Analytical Group or Method: TCLP Metals (including TCLP mercury)/SW1311, SW6010C, SW7470A (waste characterization)

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates	RPD ≤ 20%
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	85-115%R 85-115%R (Mercury)
Overall accuracy/bias (contamination)	Laboratory Blanks	No target analyte concentrations ≥ RL
Sensitivity	RL verification sample (spiked at RL)	Recovery within ±25% of RL
Completeness	>90% Usability	Data Completeness Check

Matrix: Leachate and Soil

Analytical Group or Method: Radionuclides/Refer to **Worksheet #23**

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	RPD ≤ 30% (water), 50% (soil) if >5* MDC, or relative error ratio (RER) </= 3 if <5*MDC
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates/Matrix Spike Duplicates (where applicable)	If activity<5*MDC, then RPD is 100% or less or RER</=3 (see note below). If activity>5*MDC, then RPD is 20% or less.
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples Chemical Tracer Yields Carrier Yields	75-125% Recovery (%R) (see note below) 15-125% R (see note below) 25-125%R (see note below)
Analytical Accuracy/Bias (matrix interference)	Matrix Spike/Matrix Spike Duplicates (where applicable)	75-125%R (see note below)
Overall accuracy/bias (contamination)	Laboratory Blanks/Equipment Blanks	Target analyte concentrations <1.65 times combined standard uncertainty (CSU)
Sensitivity	MDC Determination	MDC<1/10 Action Level
Completeness	>90% Usability	Data Completeness Check

Note: This information was provided by the laboratory.

Matrix: Leachate

Analytical Group or Method: General Chemistry/Refer to **Worksheet #19/30**

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Overall Precision	Field Duplicates	RPD ≤ 30%
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates	Refer to SOP in Worksheet #23
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Refer to SOP in Worksheet #23
Analytical Accuracy/Bias (matrix interference)	Matrix Spike Duplicates	Refer to SOP in Worksheet #23
Overall accuracy/bias (contamination)	Laboratory Blanks/Equipment Blanks	No target analyte concentrations ≥ RL
Sensitivity	RL verification sample (spiked at RL)	Recovery within ±25% of RL
Completeness	>90% Usability	Data Completeness Check

Matrix: Waste

Analytical Group or Method: Ignitability, Corrosivity, and Reactive Cyanide/Reactive Sulfide/SW1030, SW9045, SW9012/SW9034

Data Quality Indicator (DQI)	QC sample or measurement performance activity	Measurement Performance Criteria
Analytical Precision (laboratory)	Laboratory Control Sample Duplicates	Refer to SOP in Worksheet #23
Analytical Accuracy/Bias (laboratory)	Laboratory Control Samples	Refer to SOP in Worksheet #23
Overall accuracy/bias (contamination)	Laboratory Blanks	Refer to SOP in Worksheet #23
Sensitivity	RL verification sample (spiked at RL)	Refer to SOP in Worksheet #23
Completeness	>90% Usability	Data Completeness Check

Measurement Performance Criteria For Field Related Tasks

Field operations for this project involve multiple elements as detailed in the FSP and in **Worksheets 17** and **21**.

Definable Feature of Work (Data Type)	Data Quality Indicator(s)	Performance Criteria	Activity to Assess Measurement
Alpha Radiological Scan	Accuracy	Response to a source of known activity +/- 20% of originally obtained measurement.	Response check before use each day. In the case of multiple shifts, response check is per shift. Response check at the end of each day or shift that the instrument is used.
Beta Radiological Scan	Accuracy	Response to a source of known activity +/- 20% of originally obtained measurement.	Response check before use each day. In the case of multiple shifts, response check is per shift. Response check at the end of each day or shift that the instrument is used.
Gamma Radiological Scan	Accuracy	Response to a source of known activity +/- 20% of originally obtained measurement.	Response check before use each day. In the case of multiple shifts, response check is per shift. Response check at the end of each day or shift that the instrument is used.
VOC Field Screening	Accuracy	Instrument (PID) must detect concentrations within 0.2 parts per million of true value.	Daily two-point calibration using 100 parts per million isobutylene span gas and 0.0 (ambient air) zero gas.
Water Quality Parameters	Accuracy	Instrument must detect parameters within decision making thresholds (stabilization thresholds discussed in FSP)	Daily calibration
Survey Equipment	Accuracy	Instrument must be within calibration standards per the manufacturer	Daily calibration

Worksheet #13: Secondary Data Uses and Limitations

Data type	Source(s)	Data uses relative to current project	Factors affecting the reliability of data and limitations on data use
Site Meteorological Data: 15-min wind speed and direction, air temperature, barometric pressure, daily precipitation	On-site weather station(s) (plus National Weather Service data from Lambert-St. Louis Int'l Airport 6/2017-7/2017)	Estimations of seasonal fluctuations in storm water runoff	Data available since 5/26/2015. Communication errors or maintenance downtime resulted in occasional data gaps requiring data acquisition from nearby but off-site station (Lambert-St. Louis Int'l Airport).
OU-1 Subsurface Soil Radiological Laboratory Data	Previous investigations conducted 1982 (NRC), 1995 (McLaren/Hart), 1997 (EMSI), 2014-2015 (FEI et al), 2015 (SSPA, Cotter), & USEPA splits, 2018 RI Addendum (EMSI)	Support estimate of RIM extent and location of DIWP borings	For all data sets: Evaluations of differential settlement effects on sampling depths at each borehole location Conversion of surveyed ground surface elevations For 1982 investigation: Data uncertainties due to lack of reported details regarding sample collection methods and depths, descriptions of materials sampled, drilled depths, hole locations/elevations, lack of Th & Ra-228 analyses, data reporting errors, and potential errors during translation of borehole locations from generalized report figures For 1995 investigation: Sampling depth uncertainties due to inaccurate collection procedures,

Data type	Source(s)	Data uses relative to current project	Factors affecting the reliability of data and limitations on data use
			material displacement due to borehole sloughing, wall "smear", and flowing sands Inconsistencies in Th-230 analyses/results Potential for biased-high results For 2014-2015 investigations: Sampling depth uncertainties due to material displacement in core runs of less than 100% recovery and borehole sloughing
OU-1 Subsurface Soil Radiological Field Screening Data	Open borehole gamma scans performed 1982, 1995, 2014, & 2015, and recovered core alpha/gamma scans performed 2014 & 2015	Support estimate of RIM extent and location of DIWP borings	For all screening data sets associated with recovered core (2014/2015): Evaluations of differential settlement effects on screening depths at each borehole location Conversion of surveyed ground surface elevations Core screening depth uncertainties due to material displacement in core runs of less than 100% recovery and borehole sloughing Ability to accurately detect / estimate pci/g from gamma
OU-1 Subsurface Soil General Chemistry Data	Previous investigations conducted 1995 (McLaren/Hart), 2014-2015 (FEI et al), & 2015 (SSPA, Cotter)	For reference	For all data sets: Evaluations of differential settlement effects on sampling depths at each borehole location

Data type	Source(s)	Data uses relative to current project	Factors affecting the reliability of data and limitations on data use
			Conversion of surveyed ground surface elevations For 1995 investigation: Sampling depth uncertainties due to inaccurate collection procedures, material displacement due to borehole sloughing, wall "smear", and flowing sands For 2014-2015 investigations: Sampling depth uncertainties due to material displacement in core runs of less than 100% recovery and borehole sloughing
OU-1 Surface Soil General Chemistry Data	Previous investigation conducted 1995 (McLaren/Hart)	For reference	No known limitations
Overland Gamma Survey Data	Previous investigations conducted 1982 (NRC), 1995 (McLaren/Hart), 2014-2015 (FEI et al), & NCC work	Support location of DIWP borings	No known limitations
Radiological Laboratory Data for OU-1 Sediments	Previous investigations conducted 1997 (EMSI), during NCC work, & USEPA split sampling	For reference	No known limitations
Stormwater Data: samples collected when flow present	12 outfalls monitored following >0.10-in events	Assessments of site baseline	No known limitations
Aerial Photography	Appendix O, 2018 RI Addendum (EMSI)	Support location of DIWP borings	Decreased resolution with age
OU-1 Waste/Cover Thickness	2018 RI Addendum (EMSI)	Support excavation design and overburden estimates	No known limitations

Worksheet #14 and #16: Project Tasks & Schedule

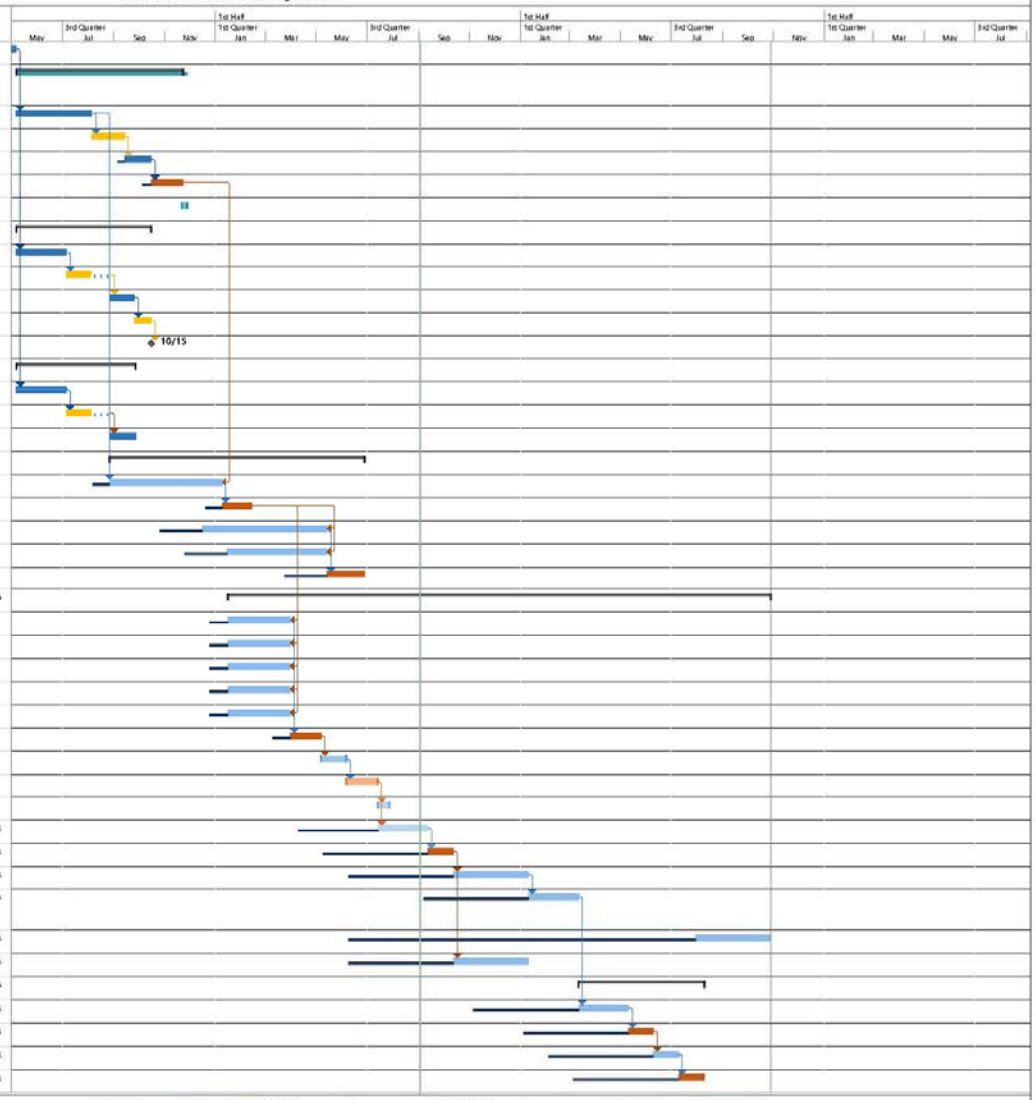
The below Gantt Chart details the current schedule for deliverables, as detailed in the SOW and the Administrative Settlement Agreement and Order on Consent (ASAOC). The schedule show below is for activities/deliverables through the approval of the DIWP. Responsibilities for each item fall to either the Respondents or USEPA. Key dates include:

- Final DIWP due to USEPA for Review and Approval on September 11 , 2020
- USEPA to approve Final DIWP October 12, 2020

Further detail can be found on the following page. The schedule is subject to change based on actual dates of delivery of documents to USEPA/actual dates of comments and approvals of documents by USEPA. The Parsons PM is responsible for overseeing the project tasks and schedule on behalf of the Respondents for those activities, while the USEPA Remedial Project Manager is responsible for those activities for which USEPA is responsible.

WEST LAKE
Statement of Work - Remedial Design Schedule

ID	Task Mode	Task Name	Duration	Start	Finish	Predecessors	Finish Variance
1		3rd Amendment to AOC	112 days	Tue 1/15/19	Mon 5/6/19		0 days
2		**RD Work Plan & Design Criteria Report**	**200 days**	**Tue 5/7/19**	**Fri 11/22/19**		**18 days**
3		Draft RDWP & Design Criteria Re	91 days	Tue 5/7/19	Mon 8/5/19	1	0 days
4		*EPA review RDWP/DCR*	*38 days*	*Tue 8/6/19*	*Fri 9/13/19*	3	9 days
5		Final RDWP/DCR	32 days	Sat 9/14/19	Tue 10/15/19	4	11 days
6		*EPA approve RDWP/DCR*	*38 days*	Wed 10/16/19	Fri 11/22/19	5	18 days
7		*RDWP PE sealed*	4 days	Thu 11/21/19	Wed 11/27/19		0 days
8		**Emergency Response Plan**	**162 days**	**Tue 5/7/19**	**Tue 10/15/19**		**71 days**
9		Draft ERP	60 days	Tue 5/7/19	Fri 7/5/19	1	0 days
10		*EPA Review and Approval*	*30 days*	Sat 7/6/19	Tue 8/27/19	9	22 days
11		Resubmit ERP	29 edays	Tue 8/27/19	Wed 9/25/19	10	0 days
12		*EPA Review and Approval*	20 edays	Wed 9/25/19	Tue 10/15/19	11	0 days
13		*EPA Approved ERP with Commer*	0 edays	Tue 10/15/19	Tue 10/15/19	12	0 days
14		**Site Management Plan**	**143 days**	**Tue 5/7/19**	**Thu 9/26/19**		**52 days**
15		Draft SMP	60 days	Tue 5/7/19	Fri 7/5/19	1	0 days
16		*EPA Review and Approval*	*30 days*	Sat 7/6/19	Tue 8/27/19	15	22 days
17		Resubmit SMP	30 edays	Tue 8/27/19	Thu 9/26/19	16	0 days
18		**Preliminary (30%) Design**	**306 days**	**Tue 8/27/19**	**Sat 6/27/20**		**51 days**
19		Preliminary Excavation Plan	135 days	Tue 8/27/19	Wed 1/8/20	6FF+47 days, 3	20 days
20		*EPA Review and Approval*	*38 days*	Thu 1/9/20	Thu 2/13/20	19	21 days
21		Draft 30%	150 days	Mon 12/16/19	Wed 5/13/20	20FF+90 days	51 days
22		LTODP	120 days	Wed 1/15/20	Wed 5/13/20	20FF+90 days	51 days
23		*EPA review*	*45 days*	*Thu 5/14/20*	*Sat 6/27/20*	21	51 days
24		**Design Investigation Work Plan**	**852 days**	**Thu 1/16/20**	**Thu 10/28/21**		**357 days**
25		Draft DIWP	75 days	Thu 1/16/20	Mon 3/30/20	20FF+46 days	21 days
26		Field Sampling Plan	75 days	Thu 1/16/20	Mon 3/30/20	20FF+46 days	21 days
27		Quality Assurance Project Plan	75 days	Thu 1/16/20	Mon 3/30/20	20FF+46 days	21 days
28		Health & Safety Plan	75 days	Thu 1/16/20	Mon 3/30/20	20FF+46 days	21 days
29		Data Management Plan	75 days	Thu 1/16/20	Mon 3/30/20	20FF+46 days	21 days
30		*EPA review*	*37 days*	*Tue 3/31/20*	*Wed 5/6/20*	25	28 days
31		Resubmit DIWP	30 days	Wed 5/6/20	Fri 6/5/20	30	0 days
32		*EPA review*	38 days	*Sat 6/6/20*	*Mon 7/13/20*	31	0 days
33		Submit DIWP 1.2.1 and Fig 5	14 days	Tue 7/14/20	Mon 7/27/20	32	0 days
34		Final DIWP	60 days	Tue 7/14/20	Fri 9/11/20	32	126 days
35		*EPA Approve DIWP*	*31 days*	*Sat 9/12/20*	*Mon 10/12/20*	34	126 days
36		Field Investigation	90 days	Tue 10/13/20	Sun 1/10/21	35	126 days
37		Laboratory analysis/data validation	60 days	Mon 1/11/21	Thu 3/11/21	36	126 days
38		Wildlife Hazard Mitigation Plan	90 days	Sat 7/31/21	Thu 10/28/21		416 days
39		Site Wide Monitoring Plan	90 days	Tue 10/13/20	Sun 1/10/21	35	125 days
40		**Design Investigation Report**	**151 days**	**Fri 3/12/21**	**Mon 8/9/21**		**126 days**
41		Draft DIR	60 days	Fri 3/12/21	Mon 5/10/21	37	126 days
42		*EPA review*	*30 days*	*Tue 5/11/21*	*Wed 6/9/21*	41	126 days
43		Final Design Invest. Report	30 days	Thu 6/10/21	Fri 7/9/21	42	126 days
44		*EPA Approve Design Invest Repo*	*31 days*	Sat 7/10/21	Mon 8/9/21	43	126 days



Date: Thu 9/3/20

Task | Split | Milestone | Summary | Project Summary | Inactive Task | Inactive Milestone | Inactive Summary | Manual Task | Duration-only | Manual Summary Rollup | Manual Summary | Start-only | Finish-only | External Tasks | External Milestone | Deadline | Progress | Manual Progress | Slippage

West Lake SOW RD Schedule 07 22 2020 with detailed slippage 5-6-19 AOC baseline-30 day DIWP 3 ...

Worksheet #15: Project Action Limits and Laboratory Specific Detection/Quantitation Limits

This worksheet provides the parameters to be analyzed and their associated quantitation limits or RLs and method detection limits (MDLs) to satisfy the overall DQOs. The Project Action Limits (PALs), as referenced in the DQOs on **Worksheet #11**, are also included as applicable. Field sampling SOPs are detailed on **Worksheet #21**.

Matrix: Leachate

Analytical Group: VOCs

Analytical Method: SW8260C

Analyte	Project Action Limit (PAL)[1]	Reporting Limit (RL) µg/L[2]	Method Detection Limit (MDL) µg/L
Acetone	–	10	3
Acrylonitrile	–	10	3
Benzene	–	2	0.3
Bromochloromethane	–	2	0.3
Bromodichloromethane	–	2	0.3
Bromoform	–	2	0.3
Bromomethane	–	2	0.3
2-Butanone	–	10	3
Carbon Disulfide	–	10	1.6
Carbon Tetrachloride	–	2	0.3
Chlorobenzene	–	2	0.3

Analyte	Project Action Limit (PAL)[1]	Reporting Limit (RL) µg/L[2]	Method Detection Limit (MDL) µg/L
Chloroethane	–	2	0.3
Chloroform	–	2	0.3
Chloromethane	–	2	0.3
Dibromochloromethane	–	2	0.3
Dibromomethane	–	2	0.3
1,2-Dibromo-3-chloropropane	–	2	0.5
1,2-Dibromoethane	–	2	0.3
1,2-Dichlorobenzene	–	2	0.3
1,4-Dichlorobenzene	–	2	0.3
trans-1,4-Dichloro-2-butene	–	10	1.5
Dichlorodifluoromethane	–	2	0.3
1,1-Dichloroethane	–	2	0.3
1,2-Dichloroethane	–	2	0.3
1,1-Dichloroethene	–	2	0.3
cis-1,2-Dichloroethene	–	2	0.3
trans-1,2-Dichloroethene	–	2	0.3
1,2-Dichloropropane	–	2	0.3
cis-1,3-Dichloropropene	–	2	0.3
trans-1,3-Dichloropropene	–	2	0.3
Ethylbenzene	–	2	0.3
2-Hexanone	–	10	3
Iodomethane	–	10	3
Isopropylbenzene	–	2	0.3

Analyte	Project Action Limit (PAL)[1]	Reporting Limit (RL) µg/L[2]	Method Detection Limit (MDL) µg/L
Methylene Chloride	–	5	1.6
4-Methyl-2-pentanone	–	10	3
Methyl-tert-butyl ether	–	2	0.3
Styrene	–	2	0.3
1,1,1,2-Tetrachloroethane	–	2	0.3
1,1,2,2-Tetrachloroethane	–	2	0.3
Tetrachloroethene	–	2	0.3
Toluene	–	2	0.3
1,1,1-Trichloroethane	–	2	0.3
1,1,2-Trichloroethane	–	2	0.3
Trichloroethene	–	2	0.3
Trichlorofluoromethane	–	2	0.3
1,2,3-Trichloropropane	–	2	0.3
Vinyl Acetate	–	5	1.6
Vinyl Chloride	–	2	0.3
Xylenes, Total	–	6	0.3

[1] Not applicable at this stage.
[2] µg/L – micrograms per liter

Matrix: Waste

Analytical Group: TCLP VOCs

Analytical Method: SW1311/SW8260C

Analyte	Project Action Limit (PAL)[1] mg/L[2]	Reporting Limit (RL) mg/L	Method Detection Limit (MDL) mg/L
1,1-Dichloroethylene	0.7	0.02	0.003
1,2-Dichloroethane	0.5	0.02	0.003
2-Butanone	200	0.1	0.03
Benzene	0.5	0.02	0.003
Carbon tetrachloride	0.5	0.02	0.003
Chlorobenzene	100	0.02	0.003
Chloroform	6	0.02	0.003
Tetrachloroethylene	0.7	0.02	0.003
Trichloroethylene	0.5	0.02	0.003
Vinyl chloride	0.2	0.02	0.003

[1] *Federal Register*, June 29, 1990.
[2] mg/L – milligrams per liter

Matrix: Waste

Analytical Group: TCLP SVOCs

Analytical Method: SW1311/SW8270D

Analyte	Project Action Limit (PAL)[1] mg/L	Reporting Limit (RL) mg/L	Method Detection Limit (MDL) mg/L
m,p-Cresols	200[2]	0.05	0.0185
o-Cresol	200[2]	0.05	0.015
1,4-Dichlorobenzene	7.5	0.05	0.015
2,4-Dinitrotoluene	0.13	0.05	0.015
2,4,5-Trichlorophenol	400	0.05	0.015
2,4,6-Trichlorophenol	2	0.05	0.015
Hexachlorobenzene	0.13	0.05	0.015
Hexachlorobutadiene	0.5	0.05	0.015
Hexachloroethane	3	0.05	0.015
Nitrobenzene	2	0.05	0.015
Pentachlorophenol	100	0.05	0.015
Pyridine	5	0.05	0.015

[1] *Federal Register*, June 29, 1990.
[2] If o-, m-, and p-Cresol concentrations cannot be d fferentiated, the total cresol concentration is used. The regulatory level for total cresol is 200 mg/L.
mg/L – milligrams per liter

Matrix: Waste

Analytical Group: PCBs

Analytical Method: SW8082A

Analyte	Project Action Limit (PAL)[1]	Reporting Limit (RL) µg/L	Method Detection Limit (MDL) µg/L
Aroclor-1016	-	0.1	0.0333
Aroclor-1221	-	0.1	0.0333
Aroclor-1232	-	0.1	0.0333
Aroclor-1242	-	0.1	0.0333
Aroclor-1248	-	0.1	0.0333
Aroclor-1254	-	0.1	0.0333
Aroclor-1260	-	0.1	0.0333
Aroclor-1262	-	0.1	0.0333
Aroclor-1268	-	0.1	0.0333
Aroclor-Total	-	0.1	0.0333

[1] Not applicable; samples collected for waste characterization. Limits vary by waste facility.
µg/L – micrograms per liter

Matrix: Waste

Analytical Group: TCLP Pesticides

Analytical Method: SW1311/SW8081A

Analyte	Project Action Limit (PAL)[1] mg/L	Reporting Limit (RL) mg/L	Method Detection Limit (MDL) mg/L
Chlordane	0.03	0.0025	0.000765
Endrin	0.02	0.0004	0.0001
Heptachlor	0.008	0.0002	0.0000665
Heptachlor epoxide	0.008	0.0002	0.0000665
gamma-BHC (Lindane)	0.4	0.0002	0.0000665
Methoxychlor	10	0.002	0.0005
Toxaphene	0.5	0.005	0.0015

[1] *Federal Register*, June 29, 1990.
mg/L – milligrams per liter

Matrix: Waste

Analytical Group: TCLP Herbicides

Analytical Method: SW1311/SW8151A

Analyte	Project Action Limit (PAL)[1] mg/L	Reporting Limit (RL) mg/L	Method Detection Limit (MDL) mg/L
2,4-D	10	0.05	0.016666
2,4,5-TP (Silvex)	1	0.05	0.016666

[1] *Federal Register*, June 29, 1990.
mg/L – milligrams per liter

Matrix: Leachate

Analytical Group: Metals (including Mercury)

Analytical Method: SW6020A/SW7470A

Analyte	Project Action Limit (PAL)[1]	Reporting Limit (RL) µg/L	Method Detection Limit (MDL) µg/L
Antimony	–	3	1
Arsenic	–	5	1.7
Barium	–	4	0.6
Beryllium	–	0.5	0.2
Boron	–	15	7.5
Cadmium	–	1	0.3
Calcium	–	200	80
Chromium	–	10	3
Cobalt	–	1	0.1
Copper	–	2	0.35
Iron		100	33
Lead	–	2	0.5
Magnesium	–	30	10
Manganese	–	5	1
Mercury	–	0.2	0.067
Nickel	–	2	0.5
Potassium	–	300	80
Selenium	–	5	2
Silver	–	1	0.4
Sodium	–	250	80
Thallium	–	2	0.6
Vanadium	–	20	4.5
Zinc	–	20	3.5

[1] Not applicable at this stage.
µg/L – micrograms per liter

Matrix: Waste

Analytical Group: TCLP Metals (including TCLP Mercury)

Analytical Method: SW1311/SW6010C/SW7470A

Analyte	Project Action Limit (PAL)[1] mg/L	Reporting Limit (RL) mg/L	Method Detection Limit (MDL) mg/L
Arsenic	5	0.05	0.017
Barium	100	0.04	0.006
Cadmium	1	0.01	0.003
Chromium	5	0.1	0.03
Lead	5	0.02	0.005
Mercury	0.2	0.002	0.00067
Selenium	1	0.05	0.02
Silver	5	0.01	0.004

[1] *Federal Register*, June 29, 1990.
mg/L – milligrams per liter

Matrix: Leachate

Analytical Group: Radionuclides

Analytical Method: Refer to **Worksheet #23**

Analyte	Project Action Limit (PAL)[1]	Minimum Detectable Concentration (MDC) pCi/L
Uranium-233/234	–	1
Uranium-235/236	–	1
Uranium-238	–	1
Thorium-228	–	1
Thorium-230	–	1
Thorium-232	–	1
Radium-228	–	3
Radium-226	–	2
Tritium	–	700
Gross Alpha	–	5
Gross Beta	–	5

[1] Not applicable at this stage.
pCi/L - picocuries per l ter

Matrix: Soil

Analytical Group: Radionuclides

Analytical Method: Refer to **Worksheet #23**

Analyte	Project Action Limit (PAL)[1]	Minimum Detectable Concentration (MDC) pCi/g
Uranium-233/234	–	0.1
Uranium-235/236	–	0.1
Uranium-238	–	0.1
Thorium-228	–	0.1
Thorium-230	–	0.1
Thorium-232	–	0.1
Thorium-234	–	3
Radium-228	–	0.2
Radium-226	–	0.1
Lead-210	–	5
Lead-212	–	0.1
Lead-214	–	0.2
Bismuth-212	–	1
Bismuth-214	–	0.2
Thallium-208	–	0.1
Potassium-40	–	5
Actinium-228	–	0.5
Protactinium-231	–	1.5

[1] See Worksheet 11 and the DIWP for specific levels for the different groupings of sample locations (i.e., Areas 1 and 2, Buffer Zone/Lot 2A2).
pCi/g - picocuries per gram

Matrix: Leachate

Analytical Group: General Chemistry

Analytical Method: Refer to **Worksheet #19/#30**

Analyte	Project Action Limit (PAL)[1]	Reporting Limit (RL) mg/L	Method Detection Limit (MDL) mg/L
Alkalinity, Total as $CaCO_3$	--	2	0.725
Ammonia as N	--	0.05	0.017
BOD	--	2	1
COD	--	20	8.952
Chloride	--	0.2	0.067
Fluoride	--	0.1	0.033
Sulfate	--	0.4	0.133
Hardness, Total	--	2	1
Nitrate+Nitrite as N	--	0.05	0.017
Phosphorus, Total	--	0.05	0.02
TDS	--	14	3.4
TSS	--	5	1.14
TOC	--	1	0.33
Total Phenols	--	0.005	0.001667
Oil and Grease	--	5	1.4

[1] Not applicable at this stage.

Matrix: Waste

Analytical Group: Ignitability, Corrosivity, and Reactive Cyanide/Reactive Sulfide

Analytical Method: SW1030/SW9045/SW9012/SW9034

Analyte	Project Action Limit (PAL)[1]	Reporting Limit (RL)	Method Detection Limit (MDL)
Ignitability	_	>140 degrees F	
Corrosivity (pH)	_	0.1 SU	0.01 SU
Reactive Cyanide (Total)	_	0.005 mg/L	0.00167 mg/L
Reactive Sulfide (Acid Volatile Sulfides)	_	2.5 mg/L	1 mg/L

[1] Not applicable; samples collected for waste characterization. Limits vary by waste facility.
SU – standard unit
mg/L – milligrams per liter

Matrix: Sediment

Analytical Group: Radionuclides

Analytical Method: Refer to **Worksheet #23**

Analyte	Project Action Limit (PAL)[1]	Minimum Detectable Concentration (MDC) pCi/g
Uranium-234	–	0.1
Uranium-235	–	0.1
Uranium-238	–	0.1
Thorium-230	–	0.1
Thorium-232	–	0.1
Thorium-234	–	3
Radium-228	–	0.2
Radium-226	–	0.1
Lead-210	–	5
Lead-212	–	0.1
Lead-214	–	0.2
Bismuth-214	–	0.2
Thallium-208	–	0.1
Potassium-40	–	5
Actinium-228	–	0.5
Protactinium-231	–	1.5

Worksheet #17: Sampling Design and Rationale

The goal of the DI is to collect additional data to support the design and implementation of the selected remedy, which includes further characterizing RIM greater than 52.9 pCi/g as related to the geostatistical modeling objectives (GSMOs). The boundaries of Areas 1 and 2, as well as the Buffer Zone and Lot 2A2, have been studied in historical investigations, as summarized in the DIWP. The data discussed below are currently expected to be collected in Summer 2020, barring any continued restrictions resulting from the COVID-19 pandemic that impact the ability to schedule or conduct the necessary field work.

The data needs of the geostatistical model are primarily based on radium and thorium, either measured from laboratory analytical data or estimated from gamma readings collected in the field. Borings are proposed to target portions of Areas 1 and 2 where data gaps exist in the prior data sets, or where model uncertainty was unacceptable based on historical boring density and sample collection intervals. Furthermore, a significant number of samples will be collected randomly (see FSP) to decrease uncertainty and sampling bias.

The sampling strategy for these objectives serves to improve overall data density, as well as target specific areas of the Site where the model uncertainty is high, as described in the DIWP and Appendix E. These strategies are discussed in depth in the DIWP and FSP, but generally samples will be collected from target gamma count ranges identified during boring installation. Laboratory analytical data, combined with field readings in targeted (40,000 – 500,000 counts per minute [cpm]) gamma count ranges, will serve to bolster the existing data set where the radium, thorium and gamma correlations are weakest.

In some areas, identification of RIM to be excavated at the Site is expected to be based primarily on thorium occurrences above 52.9 pCi/g. Depending upon the associated radium levels, thorium activities near 52.9 pCi/g may not effectively be detected by field gamma reading techniques. In addition, there are specific areas of the Site where thorium occurrences at depth are interpreted from modeling based on surface analytical samples correlated with field and downhole gamma data. A subset of borings has been proposed with systematic (20 meter) grid spacing to increase model resolution in these thorium-driven excavation areas. Additionally, random samples will be collected from 4-foot core runs within interior borings whenever field gamma readings are not present within the target gamma range.

In areas of the Site where RIM greater than 52.9 pCi/g is expected to consist predominantly of radium and thorium, or radium only, less boring and sample density is required, based on the ability of field gamma detectors to detect radium at the activities typically encountered at the Site.

In areas of the Site where RIM greater than 52.9 pCi/g is expected to be present deeper than the prescribed excavation depth, laboratory analytical samples will be collected from 16 to 20 feet in order to increase data resolution in areas where RIM may be removed at greater depth to achieve the total activity removal at the Site.

In addition to the data needs of the geostatistical model, there are other general design investigation objectives to further the design and implementation of the selected RA, such as delineating the extent of waste/RIM along the perimeter of Area 1 and Area 2 and determining if radionuclide concentrations in the Buffer Zone and Lot 2A2 exceed background.

The Buffer Zone and Lot 2A2 are distinct parcels adjacent to but outside of the landfill boundary, where it is believed that historical rainfall and surficial runoff may have transported radionuclides from Area 2 of the West Lake Landfill and deposited it in the surface soils of these parcels. For evaluation purposes, each of these parcels was divided into contiguous survey units, each of approximately 2,000 m^2 area. The division into survey units reflected a balance between proximity to potential contamination and minimizing spatial extremities within each

survey unit. There are eight survey units for Lot 2A2 and three survey units for the Buffer Zone. Within each survey unit 14 sample locations were selected based on random-start systematic sampling on a square grid. The grid spacing, L, is approximately 12m, calculated as $\sqrt{A/N}$, where A is the area of the survey unit and N is the number of samples (14). The random start location was determined for each of the x and y coordinates in each survey unit independently using the pseudo-random number generator function rand() in Microsoft Excel to generate a number between 0 and 1, and multiplying that random number by the range between the minimum and maximum of coordinates in each survey unit, e.g., $X_1 = X_{min} + rand() * (X_{max} - X_{min})$. The remaining sampling points were then multiples of the grid spacing distance L that fell within the survey unit. In situations where only 13 grid points fit within a survey unit, an additional random sampling point was added to meet the target of 14.

In the Buffer Zone and Lot 2A2 it is expected, based on historical data, that areas of potential radiologically impacted soils were disturbed by anthropogenic activities, including grading, stockpiling, and regrading of surficial soils throughout the Buffer Zone and Lot 2A2. Because the effect of anthropogenic activities on the distribution of radiologically-impacted soils is unclear, samples will be collected from 0 – 12 inches below the base of gravel/recycled asphalt fill that was placed to improve surface conditions for the parking of trailers. Additionally, if impacts are observed within the 6 – 12-inch sampling via radiological field screening, soil samples will be screened and collected from deeper intervals.

In order to evaluate a background concentration for the Buffer Zone and Lot 2A2, a background reference area comprised of four reference units was established. Reference units were selected to represent conditions at the Site prior to impact by radiological contamination. These areas are approximately 2,000 m^2 in area, and 15 sample locations (with alternate sampling locations) within each reference area were randomly selected. Alternate locations were selected in the case that randomly-selected sample locations may be positioned in areas that are unsuitable for sampling due to the presence of pavement, trees, or some other feature. Laboratory analytical samples will be collected from each location from 0 to 6 and 6 to 12 inches below grade.

Previous investigations have identified the risk of potential impacts to site drainage areas via transportation and deposition of radionuclides by surface runoff during precipitation events. Sediment samples will be collected from locations in, and adjacent to, the Northern Surface Water Body and from the banks of Earth City Flood Control Channel in order to evaluate the presence of radionuclides above background, if any, in these areas. The depth of deposition for site-related sediments is unknown, therefore sediment will be collected from a minimum of 0 – 24 inches below sediment surface (bss). Sediment will be screened using field radiological detectors. In the event that an elevated radiological response is measured in a 24-inch bss interval, deeper sediments will be collected and screened. A minimum of two analytical samples will be collected from each sediment sampling location: one from the 0 – 6 inches, and a second from 6 – 12 inches, and a third from 12 – 24 inches. Sediment samples will be biased within these intervals from areas exhibiting the highest radiological response. If necessary, an additional sediment sample will be collected from the deepest interval exhibiting an elevated radiological response during field screening to delineate potential impacts.

In addition to collecting sediment samples for radiological parameter laboratory analysis, a bathymetric survey of the NW Body will be performed to identify distinct depositional/erosion features, as discussed in the DIWP, which may result in modification of proposed sediment sampling locations.

For proposed borings and sample locations, exact location will ultimately be determined based on field conditions. Small adjustments (i.e., within a 25-foot radius) may be needed to avoid obstacles such as underground or overhead utilities; efforts will be made to identify such obstacles prior to drilling. In the case of the Buffer Zone, Lot 2A2, and the reference (background) areas, similar small adjustments may be necessary based on field conditions. Soil cores/samples from borings will be archived, so in the event that a laboratory analytical sample from a specified interval cannot be collected, the soil archives will be evaluated based on appearance and field scanning for suitability for sample collection while considering the design or geostatistical modeling objective the boring was to fulfill. The Field Team Lead will assess situations where laboratory analytical

samples cannot be obtained from a specified depth interval and, if necessary, discuss these scenarios with the PM and evaluate alternative sample collection strategies on a case by case basis.

Situations precluding the collection of samples from specified depth intervals may include poor recovery, recovery of non-soil-like debris that is unsuitable for specified data purpose (e.g., wood, concrete, plastic, etc.), or refusal. These are common occurrences associated with subsurface drilling. The methods outlined in the DIWP and FSP aim to minimize the effects of these occurrences, but when poor recovery, unsuitable materials and/or refusal are encountered during the investigation, the Field Team Lead will make the decision to relocate the boring/sample interval based on discussions with the PM.

Data will also be collected to characterize the liquid levels within the potential excavation footprint and evaluate the characteristics of potential leachate that may be present, and estimate characteristics/treatment requirements of water that may contact waste/RIM to aid in design evaluations. Standpipe wells will be used to collect potential leachate in Areas 1 and 2 as described in the DIWP and FSP, and will be gauged monthly for one year to evaluate liquid volumes and seasonal variability within the proposed excavation.

Worksheet #18: Sampling Locations and Methods

Area 1 and Area 2 Sample Locations and Methods

Soil samples will be obtained from Areas 1 and 2 via sonic or hollow-stem auger drilling techniques using the soil sampling methods described in the FSP. Generally, soils obtained from Areas 1 and 2 during the design investigation will be described and scanned with radiological detectors and laboratory samples will be collected from prescribed intervals and analyzed for various parameters as described in the FSP. Proposed borings will also be logged using a downhole gamma detector. **Tables 1 and 2 of the FSP** provide the location and expected depth of proposed borings and the data to be collected from each boring. In addition to these samples, field QC samples will be collected as presented in **Worksheet #20**.

The target depths and sampling intervals for proposed borings listed in the table B2005GS. Prior to the start of drilling operations at the Site, a sitewide topographic survey will be performed as described in Section 3.6 of the DIWP. Following the topographic survey, proposed target depths will be adjusted from feet B2005GS to feet below grade (as well as feet amsl) using the approaches described in Section 2.2.2 of the DIWP. In summary, the 2005 ground surface will be defined through consideration of the following:

1. Areas of NCC placement – Pre-construction ground surface elevations (i.e., base of NCC geotextile) will be used as the basis to measure the depth at which 4-foot core runs will begin.
2. Undisturbed Vegetated Areas – The ground surface (below vegetation) at these areas is presumed to be equivalent to the 2005 ground surface, therefore 4-foot core runs will be performed beginning from the current day ground surface.
3. Areas of inert fill placement – The 2005 ground surface was calculated through photogrammetric analysis. This surface will be compared to the new 2020 ground surface elevation to calculate a correction factor to determine the depth at which 4-foot core runs will begin.

Buffer Zone and Lot 2A2 Sample Locations and Methods

Radiologically Impacted Soils within the Buffer Zone and Lot 2A2

Surficial soil samples will be collected from the Buffer Zone and Lot 2A2 via hand-auger or direct push using the sampling methods described in the FSP. Generally, soils obtained from the Buffer Zone and Lot 2A2 during the design investigation will be described and scanned with radiological detectors and laboratory samples will be collected from depth intervals below gravel/asphalt layers, and to be analyzed for parameters as described in the FSP. **Table 3 of the FSP** shows the location and expected sampling interval and the data to be collected from each boring. In addition to these samples, field QC samples will be collected as presented in **Worksheet #20**.

Background Study for the Buffer Zone and Lot 2A2

Surficial soil samples will be collected from the Buffer Zone and Lot 2A2 via hand-auger or direct push using the sampling methods described in the FSP. Generally, soils obtained from the Buffer Zone and Lot 2A2 during the DI will be described and scanned with radiological detectors and laboratory samples will be collected from depth intervals below ground surface, as described in the FSP. **Table 4 of the FSP** shows the location and expected sampling interval and the data to be collected from each location. In addition to these samples, field QC samples will be collected as presented in **Worksheet #20**.

The possibility exists that the randomly-selected sample locations may be positioned in areas that are unsuitable for sampling due to the presence of pavement, trees, or some other feature. In the event that proposed locations are unsuitable for sampling, alternate sample locations for each reference unit are shown in **Table 4 of the FSP**. Additional background reference units have been identified in the event that primary reference units cannot be accessed. If samples are collected in these locations, they will be sampled and analyzed in accordance with the FSP, as with primary reference locations. In addition to these samples, field QC samples will be collected as presented in **Worksheet #20**.

Drainage Areas Sediment Sample Locations and Methods

Potential Radiological Impacts to Site Drainage Areas

Sediment samples will be collected from locations in and around the NW Surface Water Body, adjacent to the Earth City Flood Control Channel, and from Site drainage features, such as the perimeter drainage ditch, via hand-auger and water-based sampling methods described in the FSP. Generally, soils obtained from Site drainage areas during the design investigation will be described and scanned with radiological detectors, and laboratory samples will be collected from depth intervals below sediment surface, and analyzed for parameters as described in the FSP. Table 5 of the FSP shows the location and expected sampling interval and the data to be collected from each boring. In addition to these samples, field QC samples will be collected as presented in Worksheet #20.

Worksheet #19 & 30: Sample Containers, Preservation, and Hold-Times

This worksheet summarizes the analytical methods for each sampling matrix, including the required sample volume, containers, preservation, and holding time requirements. Details concerning sampling handling are included in **Worksheets #26 and 27.** All samples will be packed in ice and delivered to GEL Laboratories located in Charleston, South Carolina, via UPS or FedEx next day delivery. Since the State of Missouri does not have an accreditation program for environmental laboratories, GEL is National Environmental Laboratory Accreditation Conference (NELAC) certified and accredited through the State of Utah Department of Health Environmental Laboratory Certification Program to conduct all analyses for the West Lake project.

Analyte/ Analyte Group	Matrix	Method/ SOP	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
VOCs	Leachate	SW8260C GL-OA-E-038	10/31/2020	3, 40-mL VOA vials w/ PTFE-faced silicone septum	4 ± 2°C	7 days	7 days	28 days
TCLP VOCs	Waste	SW1311/SW8260C GL-OA-E-038	10/31/2020	2, 4 oz Jar	4 ± 2°C	14 days	14 days	28 days
TCLP SVOCs	Waste	SW1311/SW3510 / SW8270D GL-OA-E-009	10/31/2020	2, 4 oz Jar	4 ± 2°C	14 days	7 (extract) / 40 days	28 days
PCBs	Waste	SW3541A/SW8082A GL-OA-E-040	10/31/2020	2, 4 oz Jar	4 ± 2°C	365 days	40 days	28 days
TCLP Pesticides	Waste	SW1311/SW3535A/ SW8081B GL-OA-E-041	10/31/2020	2, 4 oz Jar	4 ± 2°C	14 days	7 (extract) / 40 days	28 days

Analyte/ Analyte Group	Matrix	Method/ SOP	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
TCLP Herbicides	Waste	SW1311/SW8151 A GL-OA-E-011	10/31/2020	2, 4 oz Jar	4 ± 2°C	14 days	7 (extract) / 40 days	28 days
Metals (except Mercury)	Leachate	SW3005A/SW6020A GL-MA-E-014	10/31/2020	1, 250 milliliter (mL) Polyethylene	4 ± 2°C Nitric acid (HNO3) to pH<2	180 days	180 days	28 days
TCLP Metals (except Mercury)	Waste	SW1311/SW3010A/SW6020A GL-MA-E-014	10/31/2020	1, 4 oz Jar	4 ± 2°C	180 days	180 days	28 days
Mercury	Leachate	SW7470A GL-MA-E-010	10/31/2020	1, 250 mL Polyethylene	4 ± 2°C HNO3 to pH<2	28 days	28 days	28 days
Mercury	Waste	SW1311/SW7470A GL-MA-E-010	10/31/2020	1, 4 oz Jar	4 ± 2°C	28 days	28 days	28 days
Radionuclides	Leachate	See Worksheet #23	10/31/2020	2, 1 L Polyethylene	4 ± 2°C HNO3 to pH<2 (except Tritium)	180 days	180 days	28 days
Radionuclides	Soil	See Worksheet #23	10/31/2020	1, L Jar	4 ± 2°C	180 days	180 days	28 days
Alkalinity, Total as CaCO3	Leachate	USEPA 310.1	10/31/2020	1, 250 mL Polyethylene	4 ± 2°C	14 days	14 days	28 days
Ammonia as N	Leachate	SM4500-NH3G	10/31/2020	1, 250 mL Polyethylene	4 ± 2°C Sulfuric acid (H2SO4) to pH<2	28 days	28 days	28 days

Analyte/ Analyte Group	Matrix	Method/ SOP	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Chemical Oxygen Demand (COD)	Leachate	USEPA 410.4	10/31/2020	1, 250 mL Polyethylene	4 ± 2°C H2SO4 to pH<2	28 days	28 days	28 days
Biochemical Oxygen Demand (BOD)	Leachate	SM5210B	10/31/2020	1, 1 L Polyethylene	4 ± 2°C	48 hours	48 hours	28 days
Chloride, Fluoride, Sulfate	Leachate	SW9056	10/31/2020	1, 250 mL Polyethylene	4 ± 2°C	28 days	28 days	28 days
Hardness, Total	Leachate	SM2340	10/31/2020	1, 250 mL Polyethylene	4 ± 2°C HNO3 to pH<2	180 days	180 days	28 days
Nitrate+Nitrite as N	Leachate	USEPA 353.2	10/31/2020	1, 125 mL Polyethylene	4 ± 2°C H2SO4 to pH<2	28 days	28 days	28 days
Phosphorus, Total	Leachate	USEPA 365.41	10/31/2020	1, 250 mL Polyethylene	4 ± 2°C H2SO4 to pH<2	28 days	28 days	28 days
TDS	Leachate	SM2540 C	10/31/2020	1, 250 mL Polyethylene	4 ± 2°C	7 days	7 days	28 days
TSS	Leachate	SM2540D	10/31/2020	1, 1 L Polyethylene	4 ± 2°C	7 days	7 days	28 days
TOC	Leachate	SM5310C	10/31/2020	3, 40-mL VOA vials w/ PTFE-faced silicone septum	4 ± 2°C H2SO4 to pH<2	28 days	28 days	28 days
Total Phenols	Leachate	SW9066	10/31/2020	2, 250 mL Amber Glass	4 ± 2°C H2SO4 to pH<2	28 days	28 days	28 days

Analyte/ Analyte Group	Matrix	Method/ SOP	Accreditation Expiration Date	Container(s) (number, size & type per sample)	Preservation	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Oil and Grease	Leachate	USEPA 1664	10/31/2020	2, 1 L Amber Glass	4 ± 2°C HCl to pH<2	28 days	28 days	28 days
Ignitability	Waste	SW1020	10/31/2020	1, 4 oz jar	4 ± 2°C	None	None	28 days
Corrosivity (pH)	Waste	SW9045	10/31/2020	1, 4 oz jar	4 ± 2°C	Immediately	Immediately	28 days
Reactive Cyanide as Total Cyanide	Waste	SW9012	10/31/2020	1, 4 oz jar	4 ± 2°C	14 days	14 days	28 days
Reactive Sulfide as Acid Volatile Sulfides	Waste	SW9034	10/31/2020	1, 4 oz jar	4 ± 2°C	28 days	28 days	28 days

Worksheet #20: Field QC Summary

Matrix	Analyte/ Analytical Group	Field Samples	Field Duplicates	Matrix Spikes	Matrix Spike Duplicates	Field Blanks	Equipment Blanks	Trip Blanks	Other	Total # analyses
Soil[1]	Radionuclides (non BZ/Lot 2A2)	2350	25 [3]	108	108	0	0	0	N/A	2591
Soil[1]	Radionuclides (BZ/Lot 2A2 and Reference Areas)	446	23	23	23	0	23	0	N/A	538
Sediment	Radionuclides (Drainage Areas)	51	2	2	2	0	2	0	N/A	59
Leachate	Radionuclides	7	0	1	1	0	1	0	0	10
	Metals	7	0	1	1	0	1	0	0	10
	VOCs	7	0	1	1	0	1	7[2]	0	17
	TSS/TDS	7	0	1	1	0	1	0	0	10
	Tritium	7	0	1	1	0	1	0	0	10
	Ammonia	7	0	1	1	0	1	0	0	10
	BOD	7	0	1	1	0	1	0	0	10
	Oil/Grease	7	0	1	1	0	1	0	0	10
	Phenol	7	0	1	1	0	1	0	0	10
	Iron	7	0	1	1	0	1	0	0	10
	Manganese	7	0	1	1	0	1	0	0	10

Matrix	Analyte/ Analytical Group	Field Samples	Field Duplicates	Matrix Spikes	Matrix Spike Duplicates	Field Blanks	Equipment Blanks	Trip Blanks	Other	Total # analyses
Waste Characteriz-ation	Radionuclides	35	0	0	0	0	0	0	0	35
	Paint Filter	35	0	0	0	0	0	0	0	35
	pH	35	0	0	0	0	0	0	0	35
	Cyanide screen	35	0	0	0	0	0	0	0	35
	Sulfides Screen	35	0	0	0	0	0	0	0	35
	TCLP Metals plus Hg	35	0	0	0	0	0	0	0	35
	TCLP VOCs/SVOCs	35	0	0	0	0	0	0	0	35
	TCLP Total Pesticides	35	0	0	0	0	0	0	0	35
	TCLP Total Herbicides	35	0	0	0	0	0	0	0	35
	PCBs	35	0	0	0	0	0	0	0	35

[1] Equipment Blanks may be added at a frequency of one blank per 20 field samples if disposable sampling equipment is not used.

[2] Estimated. One trip blank shipped to laboratory per sample cooler containing VOC samples.

[3] Field duplicates will not be collected from interior or perimeter borings. Replicate samples will be collected from each perimeter boring proposed within waste.

Worksheet #21: Field SOPs

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
FSP Section 2.2.1 Drilling Methods	Section 2.2.1.1 – Direct Push Drilling and Sampling	Parsons and FEI	Macrocore sampler	N	Reference American Society for Testing and Materials (ASTM) D6282
FSP Section 2.2.1 Drilling Methods	Section 2.2.1.2 – Sonic Drilling and Sampling	Parsons and FEI	Core sampler	N	Reference ASTM D6914
FSP Section 2.2.1 Drilling Methods	Section 2.2.1.3 – Hollow Stem Auger Drilling	Parsons and FEI	Split-spoon (see below)	N	Reference ASTM D6151/D6151M
FSP Section 2.3 Subsurface Measurements	Section 2.3.1 - Standard Penetration Testing	Parsons and FEI	Split-spoon sampler	N	Reference ASTM D1586
FSP Section 2.3 Subsurface Measurements	Section 2.3.2 - Downhole Gamma Logging	Parsons, FEI, and Ameriphysics	Model 44-10 (2-inch x 2-inch sodium iodide) coupled with Ludlum Model 2221 or equivalent *	Y	Refer to FSP and Radiation Control Procedures
FSP Section 2.3 Subsurface Measurements	Section 2.3.3 – Field Density Measurements	Parsons	Split-spoon or sonic core samplers	Y	Refer to FSP for apparatus assembly and measurement procedure
FSP Section 2.4 Soil Sampling	Section 2.4.2 – Surface Sampling	Parsons and FEI	Disposable trowel	Y	Refer to FSP for collection procedure
FSP Section 2.4 Soil Sampling	Section 2.4.3 – Subsurface Sampling	Parsons and FEI	Samples collected via split-spoons or sonic core sampler	Y	Refer to FSP for collection procedure

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
FSP Section 2.4 Soil Sampling	Section 2.4.4 – Sediment Sampling	Parsons and FEI	Disposable trowel	Y	Refer to FSP for collection procedure
FSP Section 2.6 Water Sampling and Hydrologic Measurements	Section 2.6.1 – Leachate Sampling	Parsons and FEI	Dedicated bladder pump, peristaltic pump, or disposable bailer (as necessary)	Y	Refer to FSP for collection procedure
FSP Section 2.6 Water Sampling and Hydrologic Measurements	Section 2.6.2 – Surface Water Sampling	Parsons and FEI	Dedicated sample cup and/or peristaltic pump	Y	Refer to FSP for collection methods and procedures
FSP Section 2.6 – Water Sampling and Hydrologic Measurements	Section 2.6.5 – Hydraulic Conductivity Testing	Parsons and FEI	Field measurements using pressure transducers and water level probe	Y	Refer to FSP for test method and procedure
FSP Section 2.8 Decontamination	Section 2.8 – Decontamination	Parsons and FEI	Applies to personnel, and all non-disposable and non-dedicated equipment	Y	Refer to FSP and RSP for procedure

*Each Model 44-10 will only be used with a ratemeter/scaler to which it is calibrated.

Worksheet #22: Field Equipment Calibration, Maintenance, Testing, and Inspection

Field Equipment	Activity	SOP Reference	Title or position of responsible person	Frequency	Acceptance Criteria	Corrective Action
Water Quality Meter (e.g., Horiba U-52)	Parameter Calibration	FSP Section 2.7.3	Field Team Lead	Daily/prior to use	Per Manufacturer Standards	Per Manufacturer Standards
Radiation detector (alpha, beta, gamma)	Calibration	FSP Section 2.7.1	Radiation Control Supervisor	Annually	Per Manufacturer Standards	Per Manufacturer Standards
	Integrity and Performance Check	Ameriphysics RCP 4-3	Radiation Control Supervisor	Daily before use and at the end of each day the instrument is used. In the case of multiple shifts, daily checks are performed per shift.	+/- 20% of setup (i.e., originally observed) values	Per RCP 4-3
Organic Vapor Meters	Span and Zero Gas Calibration	FSP Section 2.7.2	Field Team Lead	Daily	Per Manufacturer Standards	Per Manufacturer Standards
Survey equipment	Topographical survey	NA	Surveyor, MO licensed	Daily	Per Manufacturers' Standards Correction	Per Manufacturer Standards

Worksheet #23: Analytical Standard Operating Procedures

The applicable SOPs to be used for the analysis of samples collected during the investigation are listed in the below table. The laboratory SOP references were provided by GEL Laboratories and are presented in **Attachment 1** to this QAPP.

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project? Y/N
GL-OA-E-038	Volatile Organic Compounds (VOC) by Gas Chromatograph/Mass Spectrometer (GC/MS), Sep. 2019, Rev. 28, 8260B, 8260C, 8260D	Definitive	Leachate/VOCs (SW8260C) Waste/TCLP VOCs (SW1311/SW8260C)	GC/MS	N
GL-OA-E-039	Closed-System Purge-and-Trap Collection and Extraction: Volatile Organics in Soil and Waste Samples, Sep. 2018, Rev. 13, 5035A	Definitive	Leachate/VOCs (SW8260C) Waste/TCLP VOCs (SW1311/SW8260C)	Low-level, closed-system purge and trap	N
GL-LB-E-006	Toxicity Characteristic Leaching Procedure Preparation, Jan. 2018, Rev 22, 1311	Definitive	Waste/TCLP VOCs (SW1311/SW8260C)	ZHE	N
GL-OA-E-009	Analysis of Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Dec. 2019, Rev. 45, 8270D, 8270E	Definitive	Waste/TCLP SVOCs (SW1311/SW8270D)	GC/MS	N

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project? Y/N
GL-OA-E-066	Automated Soxhlet Extraction, Aug. 2018, Rev. 18, 3541	Definitive	Waste/TCLP SVOCs (SW1311/SW8270D) Waste/PCBs (SW8082A) Waste/TCLP Pesticides (SW1311/SW8081B)	Automated Soxhlet	N
GL-OA-E-013	Extraction of Semivolatile and Nonvolatile Organic Compounds from Groundwater, Wastewater, and Other Aqueous Samples, Oct. 2019, Rev. 34, 3510C	Definitive	Waste/TCLP SVOCs (SW1311/SW8270D)	Separatory Liquid-Liquid	N
GL-LB-E-006	Toxicity Characteristic Leaching Procedure Preparation, Jan. 2018, Rev 22, 1311	Definitive	Waste/TCLP SVOCs (SW1311/SW8270D) Waste/TCLP Pesticides (SW1311/SW8081B) Waste/TCLP Herbicides (SW1311/SW8151A) Waste/TCLP Metals (SW1311/SW6010C/SW7470A)	Rotating Agitation Apparatus	N
GL-OA-E-040	Polychlorinated Biphenyls, 8082A, Jan. 2018, Rev. 25.	Definitive	Waste/PCBs (SW8082A)	GC/Electron Capture Detector (ECD)	N
GL-OA-E-041	Organochlorine Pesticides and Chlorinated Hydrocarbons, Mar. 2019, Rev. 20, 8081A, 8081B	Definitive	Waste/TCLP Pesticides (SW1311/SW8081B)	GC/ECD	N
GL-OA-E-045	Polychlorinated Biphenyls, 8082A, Jan. 2018, Rev. 25.	Definitive	Waste/PCBs (SW8082A) Waste/TCLP Pesticides (SW1311/SW8081B)	Activated Copper	N
GL-OA-E-047	Gel Permeation Cleanup of Solvent Extracts, Aug. 2012, Rev. 4, 3640A	Definitive	Waste/TCLP Pesticides (SW1311/SW8081B)	Gel Permeation Cleanup	N

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project? Y/N
GL-OA-E-049	Silica Gel Cleanup Using Solid Phase Silica Gel Extraction Cartridges, April 2016, Rev. 6, 3630C	Definitive	Waste/TCLP Pesticides (SW1311/SW8081B)	Extraction Cartridge	N
GL-OA-E-070	Solid-Phase Extraction, 3535A, Dec. 2019, Rev 11	Definitive	Waste/PCBs (SW8082A) Waste/TCLP Pesticides (SW1311/SW8081B)	Solid Phase Extraction	N
GL-OA-E-011	Analysis of Chlorophenoxy Acid Herbicides by ECD, July 2019, Rev. 25, 8151A	Definitive	Waste/TCLP Herbicides (SW1311/SW8151A)	GC/ECD	N
GL-OA-E-015	The Extraction of Herbicides from Groundwater, Wastewater and Other Aqueous Samples, Oct. 2019, Rev. 20, 8151A	Definitive	Waste/TCLP Herbicides (SW1311/SW8151A)	Separatory Liquid-Liquid	N
GL-OA-E-027	The Extraction of Herbicides from Soil and Sludge Samples, Mar. 2019, Rev. 17, 8151A	Definitive	Waste/TCLP Herbicides (SW1311/SW8151A)	Sonication	N
GL-MA-E-014	Determination of Metals by ICP-MS, July 2019, Rev. 33, 6020A, 6020B	Definitive	Leachate/Metals (SW6020A)	Inductively Coupled Plasma Mass Spectrometry	N
GL-MA-E-008	Acid Digestion of Total Recoverable or Dissolved Metals in Surface and Groundwater Samples for Analysis by ICP or ICP-MS, Oct. 2017, Rev. 19, 3010A	Definitive	Leachate/Metals (SW6020A)	Hot Block	N
GL-MA-E-009	Acid Digestion of Sediments, Sludges, and Soils, Dec. 2019, Rev. 29, 3050B	Definitive	Waste/TCLP Metals (SW1311/SW6010C)	Hot Block	N

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project? Y/N
GL-MA-E-010	Mercury Analysis Using the Perkin Elmer Automated Mercury Analyzer, Oct. 2019, Rev. 38, 7470A, 7471B	Definitive	Leachate/Mercury (SW7470A) Waste/TCLP Mercury (SW1311/SW7470A)	Cold Vapor Atomic Absorption	N
GL-RAD-A-001	The Determination of Gross Alpha And Gross Non-Volatile Beta in Water, Revision 20	Screening	Leachate/RAD (USEPA 900.0)	Gas Flow Proportional	N
GL-RAD-A-001B	The Determination of Gross Alpha And Gross Non-Volatile Beta in Soil, Filters, Solid Matrices And Direct Count Air Filters, Revision 20	Screening	Soil/RAD (USEPA 900.0)	Gas Flow Proportional	N
GL-RAD-A-002	The Determination of Tritium, Revision 23	Definitive	Leachate/RAD (USEPA 906.0)	Liquid Scintillation	N
GL-RAD-A-008	The Determination of Radium-226, Revision 15	Definitive	Leachate/RAD (USEPA 903.1)	Ludlum Lucas Cell	N
GL-RAD-A-009	The Determination of Radium-228 in Water and Solids, Revision 17	Definitive	Leachate/RAD (USEPA 904.1)	Gas Flow Proportional	N
GL-RAD-A-011	The Isotopic Determination of Americium, Curium, Plutonium, and Uranium, Revision 27	Definitive	Leachate/RAD (DOE EML U-02) Soil/RAD (DOE EML U-02)	Alpha Spectrometer	N

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project? Y/N
GL-RAD-A-013	The Determination of Gamma Isotopes, Revision 27	Definitive	Leachate/RAD (DOE EML 4.5.2.3) Various Gamma Isotopes Soil/RAD (DOE EML 4.5.2.3) Soil/RAD (USEPA 901.1) Various Gamma Isotopes Including Ra-226 and Ra-228 (Note: Ingrow for 20 days for Ra-226 determination.)	Gamma Spectrometer	N
GL-RAD-A-038	The Isotopic Determination of Thorium, Revision 18	Definitive	Leachate/RAD Soil/RAD (DOE EML Th-01)	Alpha Spectrometer	N
GL-LB-E-029	Standard Operating Procedure For Laboratory Sub-Sampling, Revision 0	Definitive	Soil/RAD	Scoop	N
GL-GC-E-001	Total Dissolved Solids, Oct. 2019, Rev 16	Definitive	Leachate/General Chemistry (SM2540C)	Balance	N
GL-GC-E-008	pH, Dec. 2017, Rev. 23	Definitive	Leachate/General Chemistry (SW9045)	Electrode	N
GL-GC-E-010	Paint Filter Test, May 2013, Rev. 10	Definitive	Leachate/General Chemistry (SW9095B)	Paint Filter	N
GL-GC-E-012	Total Suspended Solids, Oct. 2019, Rev. 16	Definitive	Leachate/General Chemistry (SM2540D)	Balance	N
GL-GC-E-033	Alkalinity: Total, Bicarbonate, Carbonate, Hydroxide, and Phenolphthalein, Aug. 2016, Rev. 13	Definitive	Leachate/General Chemistry (USEPA 310.1)	Buret	N
GL-GC-E-045	Biochemical Oxygen Demand (BOD), Aug. 2019, Rev. 27	Definitive	Leachate/General Chemistry (SM5210B)	D.O. Meter	N

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project? Y/N
GL-GC-E-061	Chemical Oxygen Demand (COD) - Digestion Reactor Method, Aug. 2019, Rev. 21	Definitive	Leachate/General Chemistry (USEPA 410.4)	Vis Spec	N
GL-GC-E-082	Acid-Soluble Sulfides, Oct. 2017, Rev. 13	Definitive	Leachate/General Chemistry (SW9034)	Buret	N
GL-GC-E-086	Ion Chromatography (IC), Jul. 2019, Rev. 27	Definitive	Leachate/General Chemistry (SW9056)	IC	N
GL-GC-E-093	Total, Total Inorganic, and Total Organic Carbon (TOC) Using the OI Analytical Model 1010 TOC Analyzer, Aug. 2019, Rev. 16	Definitive	Leachate/General Chemistry (SM5310C)	TOC Analyzer	N
GL-GC-E-094	N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM, Non-Polar Material) in Aqueous Matrices, Aug. 2019, Rev. 18	Definitive	Leachate/General Chemistry (USEPA 1664)	Balance	N
GL-GC-E-095	Cyanide Analysis by Lachat QuikChem 8000 FIA, Mar. 2018, Rev. 22	Definitive	Leachate/General Chemistry (SW9012)	Lachat	N
GL-GC-E-100	Total Hardness by Titration, July 2019, Rev. 8	Definitive	Leachate/General Chemistry (SM2340)	Buret	N
GL-GC-E-102	Total Recoverable Phenol by the Lachat QuikChem FIA+ 8000 Series, Aug.	Definitive	Leachate/General Chemistry (SW9066)	Lachat	N
GL-GC-E-103	Total Phosphorus By The Lachat Quickchem FIA + 8000 Series Instrument, Nov. 2017, Rev. 11	Definitive	Leachate/General Chemistry (USEPA 365.4)	Lachat	N

SOP #	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project? Y/N
GL-GC-E-106	Ammonia Determination by the Lachat Quickchem FIA +8000 Series, Nov. 2017, Rev. 10	Definitive	Leachate/General Chemistry (SM4500)	Lachat	N
GL-GC-E-128	Nitrate/Nitrite (NO3+NO2) Analysis Using the Lachat QuikChem FIA+ 8000 Series Instrument, Nov. 2017, Rev. 10	Definitive	Leachate/General Chemistry (USEPA 353.2)	Lachat	N

Worksheet #24: Analytical Instrument Calibration

The Analytical Instrument Calibration Table and the specific analytical method SOP references are provided in **Attachment 1** of this QAPP.

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
GC/MS	Initial Calibration (ICAL)–five-point ICAL	Initial calibration prior to sample analysis	%RSD (relative standard deviation) <20% all compounds, Relative Response Factor meet method criteria	Repeat calibration	Analyst	GL-OA-E-038 GL-OA-E-009
GC/MS	Second Source Calibration Verification	Once after each initial calibration	Value of second source for all analytes within ±30% of expected	Rerun ICV one time, second failure requires recalibration	Analyst	GL-OA-E-038 GL-OA-E-009
GC/MS	Calibration Verification (CV)	Daily, before sample analysis, and every 12 hours of analysis time	+/-20%D criteria for all analytes	Re-inject CV; if passes rerun previous 10 samples and continue run; if 2nd CV fails, recalibrate	Analyst	GL-OA-E-038 GL-OA-E-009
GC/ECD	Initial Calibration (ICAL) – five-point ICAL	Initial calibration prior to sample analysis	RSD for each analyte <20%	Repeat calibration	Analyst	GL-OA-E-011 GL-OA-E-040 GL-OA-E-041

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
GC/ECD	Second Source Calibration Verification	Once after each initial calibration	Value of second source for all analytes within ± 20% of expected value (initial source)	Rerun ICV one time, second failure requires recalibration	Analyst	GL-OA-E-011 GL-OA-E-040 GL-OA-E-041
GC/ECD	Calibration Verification (Initial [ICV] and continuing [CCV])	ICV: Daily, before sample analysis; CCV: After every 12 hours of analysis time and at the end of the analysis sequence	All analytes within ± 20% of expected value from the ICAL	Re-inject CCV; if passes rerun previous 10 samples and continue run; if 2nd CCV fails, recalibrate	Analyst	GL-OA-E-011 GL-OA-E-040 GL-OA-E-041
ICP/MS	Initial Calibration (ICAL)–minimum one high standard and a calibration blank	Daily initial calibration prior to sample analysis	3 standards and a blank. Correlation Coefficient of ≥ 0.998	Recalibrate	Analyst	GL-MA-E-014
ICP/MS	Second Source Calibration Verification (ICV)	Once after each initial calibration, prior to sample analysis	Value of second source for all analyte(s) within ± 10% of expected	Recalibrate	Analyst	GL-MA-E-014
ICP/MS	Continuing Calibration Verification (CCV)	After every 10 samples and at the end of the analysis sequence	All analytes within + 10% of expected value	Recalibrate – rerun 10 samples previous to failed CCV	Analyst	GL-MA-E-014
CVAA	Initial Calibration (ICAL)	Daily initial calibration prior to sample analysis	Correlation coefficient R>=0.995 for linear regression	Recalibrate	Analyst	GL-MA-E-010

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
CVAA	Second Source Calibration Verification (ICV)	Once after each initial calibration, prior to sample analysis	Value of second source for all analyte(s) within ± 10% of expected value (second source)	Recalibrate	Analyst	GL-MA-E-010
CVAA	Continuing Calibration Verification (CCV)	After every 10 samples and at the end of the analysis sequence.	All analytes within + 20% of expected value	Recalibrate – rerun 10 samples previous to failed CCV.	Analyst	GL-MA-E-010
Gamma Spectroscopy	Initial: multi-point (8-12 isotopes across energy range) for each geometry	Initially and as required per method	For the energy calibration, the absolute value of the difference must be less than 1.0 and for the FWHM calibration, the absolute value of the difference must be less than 0.5. Verification source counted must be within 10% of known values for all isotopes.	Re-run initial calibration verification (ICV). Corrective action for out-of-control data might require instrument maintenance, re-analysis, using a new spike mix, or a more complex set of actions.	Laboratory Analyst / Group Leader or Designee	GL-RAD-I-001 GL-RAD-I-012

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
Gamma Spectroscopy	Continuing: multi-point	Daily	Peak centroid energy ± 2 keV Peak centroid channel ± 4 channels FWHM based on manufacturers specifications Activity 10% of known or 3sigma	Immediately rerun check. If the check fails again, mark the detector out of service and make a note in the instrument logbook. The instrument can be returned to service following a successful instrument check.	Laboratory Analyst / Group Leader or Designee	GL-RAD-I-001 GL-RAD-I-012
Gas Flow Proportional Counters	Initial: multi-point	Initially and as required per method	Verification result ± 25% of known value	If the calibration fails a second time, create new calibration sources and re-perform initial calibration.	Laboratory Analyst / Group Leader or Designee	GL-RAD-I-006 GL-RAD-I-016 GL-RAD-I-015 GL-RAD-I-021 GL-RAD-I-012

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
Gas Flow Proportional Counters	Continuing calibration verification (CCV) Count: multipoint	Daily	Alpha/Beta check sources ± 3s	Immediately rerun. If the check fails a second time the instrument is locked out of service and the cause investigated. The instrument status board will be updated to reflect the lockout, the appropriate lockout sign will be placed on the front of the instrument and a logbook entry will be made. The instrument can be returned to service following a successful instrument check.	Laboratory Analyst / Group Leader or Designee	GL-RAD-I-006 GL-RAD-I-016 GL-RAD-I-015 GL-RAD-I-021 GL-RAD-I-012
Ludlum Lucas Cell Counter	Initial: multi-point	Initially and as required per method	Standard deviation < 10% of cell constant average Verification result ± 25% of known value	Re-run ICV. If the check fails a second time, create new calibration sources and re-perform initial calibration.	Laboratory Analyst / Group Leader or Designee	GL-RAD-I-007 GL-RAD-I-012 GL-RAD-A-008

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
Ludlum Lucas Cell Counter	CCV Count: single point	Daily	± 3s	Immediately rerun. If the instrument fails the check, mark the instrument out of service and make a logbook entry. The instrument may be returned to service following a successful daily instrument check.	Laboratory Analyst / Group Leader or Designee	GL-RAD-I-007 GL-RAD-I-012 GL-RAD-A-008
Alpha Spectrometer	Initial: multi-point	Initially and then monthly	Energy Calibration Offset: 2300-2450 kiloelectron volt (keV) Energy Calibration Slope: 4.7-5.3 keV/channel Constant full width at half maximum (FWHM): 3-25 channels Average Efficiency: 3s standard deviation	The status board will be updated to reflect the "out of service" condition for that instrument and a logbook entry will be made. The condition will be investigated and the instrument may be returned to service following a successful instrument calibration.	Laboratory Analyst / Group Leader or Designee	GL-RAD-I-009 GL-RAD-I-012

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
Alpha Spectrometer	Continuing: single point	Daily	FWHM 1-35 keV Peak centroid ± 15 channels of mean Peak energy ± 50 keV of mean Count rate ± 3% of mean	The failed check should be immediately rerun. If the check fails a second time the instrument is locked out of service and the cause will be investigated. The instrument status board will be updated to reflect the lockout condition and a logbook entry will be made. The instrument will returned to service following a successful instrument check.	Laboratory Analyst / Group Leader or Designee	GL-RAD-I-009 GL-RAD-I-012
Liquid Scintillation Counter	Initial: multi-point (quench curve)	Initially and as required per method	Verification result ± 10% of known value	If the calibration fails a second time, create new calibration sources and re-perform initial calibration.	Laboratory Analyst / Group Leader or Designee	GL-RAD-I-004 GL-RAD-I-014 GL-RAD-I-017 GL-RAD-I-012
Liquid Scintillation Counter	Continuing calibration verification (CCV) Count: multipoint	Daily	4C, 3H, and background standards.	Immediately rerun. If the instrument fails the check, mark the instrument out of service and make a logbook entry. The instrument may be returned to service following two successful daily instrument checks.	Laboratory Analyst / Group Leader or Designee	GL-RAD-I-004 GL-RAD-I-014 GL-RAD-I-017 GL-RAD-I-012

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
Lachat	ICAL – Minimum of a 6-point calibration curve plus a blank is prepared	Prior to sample analysis	Linear regression correlation coefficient greater than or equal to 0.995	Investigate source of problem; recalibrate	Laboratory Analyst / Group Leader or Designee	GL-GC-E-095 GL-GC-E-102 GL-GC-E-103 GL-GC-E-106 GL-GC-E-128
Lachat	ICV	Once after each ICAL prior to beginning a sample run	90-110%R	If the ICV fails high, report samples that are <RL; redigest, recalibrate, and/or reanalyze other samples	Laboratory Analyst / Group Leader or Designee	GL-GC-E-095 GL-GC-E-102 GL-GC-E-103 GL-GC-E-106 GL-GC-E-128
Lachat	CCV	One after every 10 samples	90-110%R	If the CCV fails high, report samples that are <RL; redigest, recalibrate, and/or reanalyze other samples back to last acceptable CCV recovery	Laboratory Analyst / Group Leader or Designee	GL-GC-E-095 GL-GC-E-102 GL-GC-E-103 GL-GC-E-106 GL-GC-E-128
IC	ICAL – A minimum of a 5-point calibration is prepared.	Prior to sample analysis	Linear regression correlation coefficient greater than or equal to 0.995	Correct problem and rerun calibration	Laboratory Analyst / Group Leader or Designee	GL-GC-E-086
IC	ICV	Once after each ICAL prior to sample analysis	90-110%R	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL.	Laboratory Analyst / Group Leader or Designee	GL-GC-E-086

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
IC	CCV	After every 10 samples and at the end of the sequence	90-110%R	Correct problem and rerun calibration verification. If that fails, repeat ICAL. Reanalyze all samples since the last successful calibration verification.	Laboratory Analyst / Group Leader or Designee	GL-GC-E-086
TOC Analyzer	ICAL – A minimum of a 5-point calibration is prepared.	Initially when the daily CCV does not pass but no longer than every 3 months.	Linear regression correlation coefficient greater than or equal to 0.995	Recalibrate and/or perform necessary equipment maintenance. Check calibration standards.	Laboratory Analyst / Group Leader or Designee	GL-GC-E-093
TOC Analyzer	ICV	Once after each ICAL prior to beginning a sample run.	90-110%R	If the ICV fails high, report samples that are <RL; redigest, recalibrate, and/or reanalyze other samples	Laboratory Analyst / Group Leader or Designee	GL-GC-E-093
TOC Analyzer	CCV	Every 10 samples and at the end of the run.	90-110%R	If the CCV fails high, report samples that are <RL; redigest, recalibrate, and/or reanalyze other samples back to last acceptable CCV recovery	Laboratory Analyst / Group Leader or Designee	GL-GC-E-093

Worksheet #25: Analytical Instrument and Equipment Maintenance, Testing, and Inspection

This worksheet provides information on analytical instruments and equipment, maintenance, testing, and inspection. To ensure that the analytical instruments and equipment are available and in working order when needed, all laboratory analytical equipment will undergo maintenance and testing procedure in accordance with the laboratory SOPs provided in **Attachment 1** of this QAPP.

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Title/position responsible for corrective action	Reference
GC/MS	Daily items may include septa replacement, injection port items, solvent replenishment, instrument tuning adjustment, etc.	VOCs, TCLP VOCs TCLP SVOCs	Instrument resolving power, GC performance, and isomer specificity are monitored daily.	Maintenance is ongoing and performed as needed. Preventative maintenance such as septa replacement and solvent replenishment is performed daily.	Successful daily instrument calibration per requirements.	Documentation of item addressed is located in the instruments maintenance logbook. All instrument maintenance items are recorded.	Analyst	GL-OA-E-009 GL-OA-E-038
GC/ECD	Daily items may include septa replacement, injection port items, solvent replenishment, etc.	PCBs TCLP Pest TCLP Herb	Instrument resolving power, GC performance, and isomer specificity are monitored daily.	Maintenance is ongoing and performed as needed. Preventative maintenance such as septa replacement and solvent replenishment is performed daily.	Successful daily instrument calibration per requirements.	Documentation of item addressed is located in the instruments maintenance logbook. All instrument maintenance items are recorded.	Analyst	GL-OA-E-011 GL-OA-E-040 GL-OA-E-041

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Title/position responsible for corrective action	Reference
ICP-MS	Maintenance specified in SOP	Metals TCLP Metal	Torch, nebulizer, spray chamber, pump tubing	Maintenance is ongoing and performed as needed	Successful daily instrument calibration per requirements.	Documentation of item addressed is located in the instruments maintenance logbook. All instrument maintenance items are recorded.	Analyst	GL-MA-E-014
CVAA	Maintenance specified in SOP	Mercury TCLP Mercury	Tubing, sample probe, optical cell	Maintenance is ongoing and performed as needed	Successful daily instrument calibration per requirements.	Documentation of item addressed is located in the instruments maintenance logbook. All instrument maintenance items are recorded.	Analyst	GL-MA-E-010
Gamma Spectroscopy	Liquid Nitrogen fill	See Worksheet #23	NA	Weekly	NA	NA	Analyst	GL-RAD-I-010
Gas Flow Proportional Counter	Sample Shelf Cleaning	See Worksheet #23	NA	Weekly	NA	NA	Analyst	GL-RAD-I-010
Ludlum Lucas Cell Counter	Photomultiplier tube cleaning	See Worksheet #23	NA	Weekly	NA	NA	Analyst	GL-RAD-I-010

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Title/position responsible for corrective action	Reference
Alpha Spectrometer	Vacuum Pump Oil replacement	See Worksheet #23	NA	semi-annually	NA	NA	Analyst	GL-RAD-I-010
Alpha Spectrometer	Filter cleaning on the air intake of the instrument cabinet	See Worksheet #23	NA	quarterly	NA	NA	Analyst	GL-RAD-I-010
Liquid Scintillation Counter	Sample Changer Cleaning	See Worksheet #23	NA	As needed	NA	NA	Analyst	GL-RAD-I-010
Lachat	Change pump tubing monthly, replace capillary tubing, clean valves and flow cells	Total Phenolics, total Phosphorous, Ammonia, Nitrate-Nitrite	Pump tubing, capillary tubing, reagent bottles, manifolds	Daily	Acceptable calibration or CCV	Correct problem and repeat calibration of CCV.	Analyst	GL-GC-E-095 GL-GC-E-102 GL-GC-E-103 GL-GC-E-106 GL-GC-E-128
TOC analyzer	Check level of dilution water, auto sampler rinse water and phosphoric acid vessel and fill as needed. Replace oxygen cylinder.	TOC	Tubing, sample boat, syringe, humidifier, rinse reservoir, phosphoric acid vessel, oxygen pressure	Prior to initial calibration and as necessary	Acceptable calibration or CCV	Correct problem and repeat calibration of CCV.	Analyst	GL-GC-E-093

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Title/position responsible for corrective action	Reference
IC	Check regenerate pump tubing and replace as needed. Clean or regenerate column as needed. Replace analytical column or guard column as needed. Change suppressor as needed.	Chloride, Fluoride, Sulfate	Tubing, column, suppressor	Prior to initial calibration and as necessary	Passing ICAL or CCV	Correct problem and repeat calibration of CCV.	Analyst	GL-GC-E-086

Worksheet #26 & 27: Sample Handling, Custody, and Disposal

Sample handling, custody, packaging, and shipping are described in the FSP and DMP. All samples will be shipped via FedEx or UPS next day delivery to:

GEL Laboratories
2040 Savage Road
Charleston, SC 29407

Activity	Organization and title or position of person responsible for the activity	SOP reference
Sample labeling	Parsons, Field Team	Refer to DMP and FSP
Chain-of-custody form completion	Parsons, Field Team	Refer to FSP
Packaging	Parsons, Field Team	Refer to FSP
Shipping coordination	Parsons, Field Team	Refer to FSP
Sample receipt, inspection, & log-in	GEL Laboratories, Sample Receipt Dept.	GL-SR-E-001
Sample custody and storage	GEL Laboratories	GL-SR-E-001
Sample disposal	GEL Laboratories **Samples are to be held indefinitely until authorized for disposal.**	GL-SR-E-001

Worksheet #28: Analytical Quality Control and Corrective Action

The tables in this worksheet describe the requirements for laboratory analysis of QC samples (e.g., laboratory control samples, method blanks, matrix spikes, etc.) for each analytical method used. The tables below detail the QC sample frequency, method/SOP QC acceptance criteria, corrective actions to be taken in the event analyses do not meet the acceptance criteria and the person(s) responsible for implementing corrective actions, and measurement performance criteria.

Matrix: Leachate and Waste

Analytical Group: VOCs, TCLP VOCs

Analytical Method/SOP: SW8260C/GL-OA-E-038; SW1311, SW8260C/GL-LB-E-006, GL-OA-E-038

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Internal Standards	Every field sample and QC samples	RT within ±30 seconds from RT of initial calibration midpoint standard; area counts within -50% to +100% of initial calibration midpoint standard	Correct problem, then reanalyze affected samples	Laboratory Manager/ Analyst	RT within ±30 seconds and area count within -50% to 100%
Method Blank	One per prep batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater). No laboratory common	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater). No laboratory common contaminants detected greater than RL.

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
		contaminants detected greater than RL.			
Tumble blank (TCLP only)	One per tumble batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).
MS/MSD	One MS/MSD pair per preparation batch per matrix	LCS limits; RPD less than 20% between MS and MSD	Identify problem; if not related to matrix interference, reanalyze MS/MSD and all associated batch samples	Laboratory Manager/ Analyst	LCS limits; RPD less than 20% between MS and MSD
LCS/LCSD	One LCS or LCS/LCSD pair per preparation batch per matrix	70-130%R; RPD less than 20% between LCS and LCSD	Correct problem, then reanalyze the LCS and all associated batch samples	Laboratory Manager/ Analyst	70-130%R; RPD less than 20% between LCS and LCSD
Surrogate standards	Every field sample and QC sample	Surrogate recovery criteria specified in Worksheet #12	Correct problem, then reanalyze all affected samples	Laboratory Manager/ Analyst	Surrogate recovery criteria specified in Worksheet #12
MDL Study	Initial setup, once per 12-month period or	Detection limits established will be below the RLs	Correct problem, then repeat the MDL study	Laboratory Manager/ Analyst	Follow requirements from 40CFR 136 Appendix B

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
	quarterly MDL verification				
RL Study	Annually and quarterly RL verification	RL greater than MDL and within calibration range. Laboratory procedure for establishing the RL will empirically demonstrate precision and bias at the RL.	Correct problem, then repeat the RL study.	Laboratory Manager/ Analyst	Recovery within established limits.

Matrix: Waste

Analytical Group: TCLP SVOCs

Analytical Method/SOP: SW1311, SW8270D/GL-LB-E-006, GL-OA-E-009

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Internal Standards	Every field sample and QC samples	RT within ±30 seconds from RT of initial calibration midpoint standard; area counts within -50% to +100% of initial calibration midpoint standard	Correct problem, then reanalyze affected samples	Laboratory Manager/ Analyst	RT within ±30 seconds and area count within -50% to 100%
Method Blank	One per prep batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater). No laboratory common contaminants detected greater than RL.	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater). No laboratory common contaminants detected greater than RL.
Tumble blank (TCLP only)	One per tumble batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
MS/MSD	One MS/MSD pair per preparation batch per matrix	Recovery limits specified in Worksheet #12; RPD less than 30% between MS and MSD	Identify problem; if not related to matrix interference, reanalyze MS/MSD and all associated batch samples	Laboratory Manager/ Analyst	Recovery limits specified in Worksheet #12; RPD less than 30% between MS and MSD
LCS/LCSD	One LCS or LCS/LCSD pair per preparation batch per matrix	Recovery limits specified in Worksheet #12; RPD less than 30% between LCS and LCSD	Correct problem, then reanalyze the LCS and all associated batch samples	Laboratory Manager/ Analyst	Recovery limits specified in Worksheet #12; RPD less than 30% between LCS and LCSD
Surrogate standards	Every field sample and QC sample	Surrogate recovery criteria specified in Worksheet #12	Correct problem, then reanalyze all affected samples	Laboratory Manager/ Analyst	Surrogate recovery criteria specified in Worksheet #12
MDL Study	Initial setup, once per 12-month period or quarterly MDL verification	Detection limits established will be below the RLs	Correct problem, then repeat the MDL study	Laboratory Manager/ Analyst	Follow requirements from 40CFR 136 Appendix B
RL Study	Annually and quarterly RL verification	RL greater than MDL and within calibration range. Laboratory procedure for establishing the RL will empirically demonstrate precision and bias at the RL	Correct problem, then repeat the RL study	Laboratory Manager/ Analyst	Recovery within established limits

Matrix: Waste

Analytical Group: PCBs

Analytical Method/SOP: SW8082A/GL-OA-E-040

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Method Blank	One per prep batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).
MS/MSD	One MS/MSD pair per preparation batch per matrix	Recovery limits specified in Worksheet #12; RPD less than 20% between MS and MSD	Identify problem; if not related to matrix interference, reanalyze MS/MSD and all associated batch samples	Laboratory Manager/ Analyst	Recovery limits specified in Worksheet #12; RPD less than 20% between MS and MSD
LCS/LCSD	One LCS or LCS/LCSD pair per preparation batch per matrix	Recovery limits specified in Worksheet #12; RPD less than 20% between LCS and LCSD	Correct problem, then reanalyze the LCS and all associated batch samples	Laboratory Manager/ Analyst	Recovery limits specified in Worksheet #12; RPD less than 20% between LCS and LCSD
Surrogate standards	Every field sample and QC sample	Surrogate recovery criteria specified in Worksheet #12	Correct problem, then reanalyze all affected samples	Laboratory Manager/ Analyst	Surrogate recovery criteria specified in Worksheet #12
MDL Study	Initial setup, once per 12-month period or quarterly MDL verification	Detection limits established will be below the RLs	Correct problem, then repeat the MDL study	Laboratory Manager/ Analyst	Follow requirements from 40CFR 136 Appendix B

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
RL Study	Annually and quarterly RL verification	RL greater than MDL and within calibration range. Laboratory procedure for establishing the RL will empirically demonstrate precision and bias at the RL.	Correct problem, then repeat the RL study.	Laboratory Manager/ Analyst	Recovery within established limits.

Matrix: Waste

Analytical Group: TCLP Pesticides

Analytical Method/SOP: SW1311, SW8081B/GL-LB-E-006, GL-OA-E-041

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Method Blank	One per prep batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).
Tumble blank (TCLP only)	One per tumble batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).
MS/MSD	One MS/MSD pair per preparation batch per matrix	Recovery limits specified in Worksheet #12; RPD less than 30% between MS and MSD	Identify problem; if not related to matrix interference, reanalyze MS/MSD and all associated batch samples	Laboratory Manager/ Analyst	Recovery limits specified in Worksheet #12; RPD less than 30% between MS and MSD
LCS/LCSD	One LCS or LCS/LCSD pair per preparation batch per matrix	Recovery limits specified in Worksheet #12; RPD less than 30% between LCS and LCSD	Correct problem, then reanalyze the LCS and all associated batch samples	Laboratory Manager/ Analyst	Recovery limits specified in Worksheet #12; RPD less than 30% between LCS and LCSD

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Surrogate standards	Every field sample and QC sample	Surrogate recovery criteria specified in Worksheet #12	Correct problem, then reanalyze all affected samples	Laboratory Manager/ Analyst	Surrogate recovery criteria specified in Worksheet #12
MDL Study	Initial setup, once per 12-month period or quarterly MDL verification	Detection limits established will be below the RLs	Correct problem, then repeat the MDL study	Laboratory Manager/ Analyst	Follow requirements from 40CFR 136 Appendix B
RL Study	Annually and quarterly RL verification	RL greater than MDL and within calibration range. Laboratory procedure for establishing the RL will empirically demonstrate precision and bias at the RL.	Correct problem, then repeat the RL study.	Laboratory Manager/ Analyst	Recovery within established limits.
PEM	DDT and Endrin Breakdown	≤15% for DDT and Endrin	Clean and start over (cannot proceed with sample analysis). The DQI would be exceeding the limit of 15%.	Laboratory Manager/ Analyst	≤15% for DDT and Endrin

Matrix: Waste

Analytical Group: TCLP Herbicides

Analytical Method/SOP: SW1311, SW8151A/GL-LB-E-006, GL-OA-E-011

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Method Blank	One per prep batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).
Tumble blank (TCLP only)	One per tumble batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).
MS/MSD	One MS/MSD pair per preparation batch per matrix	Recovery limits specified in Worksheet #12; RPD less than 30% between MS and MSD	Identify problem; if not related to matrix interference, reanalyze MS/MSD and all associated batch samples	Laboratory Manager/ Analyst	Recovery limits specified in Worksheet #12; RPD less than 30% between MS and MSD
LCS/LCSD	One LCS or LCS/LCSD pair per preparation batch per matrix	Recovery limits specified in Worksheet #12; RPD less than 30% between LCS and LCSD	Correct problem, then reanalyze the LCS and all associated batch samples	Laboratory Manager/ Analyst	Recovery limits specified in Worksheet #12; RPD less than 30% between LCS and LCSD

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Surrogate standards	Every field sample and QC sample	Surrogate recovery criteria specified in Worksheet #12	Correct problem, then reanalyze all affected samples	Laboratory Manager/ Analyst	Surrogate recovery criteria specified in Worksheet #12
MDL Study	Initial setup, once per 12-month period or quarterly MDL verification	Detection limits established will be below the RLs	Correct problem, then repeat the MDL study	Laboratory Manager/ Analyst	Follow requirements from 40CFR 136 Appendix B
RL Study	Annually and quarterly RL verification	RL greater than MDL and within calibration range. Laboratory procedure for establishing the RL will empirically demonstrate precision and bias at the RL.	Correct problem, then repeat the RL study.	Laboratory Manager/ Analyst	Recovery within established limits.

Matrix: Leachate and Waste

Analytical Group: Metals, TCLP Metals

Analytical Method/SOP: SW6020A/GL-MA-E-014; SW1311, SW6010C/GL-LB-E-006, GL-OA-E-014

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Method Blank	One per prep batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).
Tumble blank (TCLP only)	One per tumble batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).
MS/MSD or Laboratory Duplicate	One per preparation batch per matrix	75-125%R; RPD<20 between MS and MSD or laboratory duplicate	Identify problem; if not related to matrix interference, reanalyze MS/MSD and all associated batch samples	Laboratory Manager/ Analyst	75-125%R; RPD<20 between MS and MSD or laboratory duplicate
LCS/LCSD	One LCS or LCS/LCSD pair per preparation batch per matrix	85-115%R	Correct problem, then reanalyze the LCS and all associated batch samples	Laboratory Manager/ Analyst	85-115%R

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Calibration Blank	Before beginning a sample run, after every 10 samples, and at end of the analysis sequence	No analytes detected > RL	Any sample associated with a blank that fails the criteria checks will be reprocessed in a subsequent preparation batch, except when the sample analysis resulted in a non-detect. If no sample volume remains for reprocessing, the results will be reported with appropriate data qualifying codes.	Laboratory Manager/ Analyst	No analytes detected > RL
Serial Dilution	Each new sample matrix	1:5 dilution must agree within ±10% of original determination.	Perform post-digestion spike if serial dilution does not meet criteria	Laboratory Manager/ Analyst	1:5 dilution must agree within ±10% of original determination.
Post-Digestion Spike	When serial dilution or matrix spike fails	80-120%R	Reanalyze post-digestion spike.	Laboratory Manager/ Analyst	80-120%R
MDL Study	Initial setup, once per 12-month period or quarterly MDL verification	Detection limits established will be below the RLs	Correct problem, then repeat the MDL study	Laboratory Manager/ Analyst	Follow requirements from 40CFR 136 Appendix B

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
RL Study	Annually and quarterly RL verification	RL greater than MDL and within calibration range. Laboratory procedure for establishing the RL will empirically demonstrate precision and bias at the RL.	Correct problem, then repeat the RL study.	Laboratory Manager/ Analyst	Recovery within established limits.

Matrix: Leachate and Waste

Analytical Group: Mercury, TCLP Mercury

Analytical Method/SOP: SW7470A/GL-MA-E-010; SW1311, SW7470A/GL-LB-E-006, GL-OA-E-010

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Method Blank	One per prep batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).
Tumble blank (TCLP only)	One per tumble batch	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).	Correct problem, then reanalyze method blank and all samples processed with the contaminated blank	Laboratory Manager/ Analyst	No target analytes detected greater than one-half RL and 1/10 the amount measured in any sample or 1/10 regulatory limit (whichever is greater).
MS/MSD or Laboratory Duplicate	One per preparation batch per matrix	85-115%R; RPD<20 between MS and MSD or laboratory duplicate	Identify problem; if not related to matrix interference, reanalyze MS/MSD and all associated batch samples	Laboratory Manager/ Analyst	85-115%R
LCS/LCSD	One LCS or LCS/LCSD pair per preparation batch per matrix	85-115%R	Correct problem, then reanalyze the LCS and all associated batch samples	Laboratory Manager/ Analyst	85-115%R

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Calibration Blank	Before beginning a sample run, after every 10 samples, and at end of the analysis sequence	No analytes detected > RL	Any sample associated with a blank that fails the criteria checks will be reprocessed in a subsequent preparation batch, except when the sample analysis resulted in a non-detect. If no sample volume remains for reprocessing, the results will be reported with appropriate data qualifying codes.	Laboratory Manager/ Analyst	No analytes detected > RL
MDL Study	Initial setup, once per 12-month period or quarterly MDL verification	Detection limits established will be below the RLs	Correct problem, then repeat the MDL study	Laboratory Manager/ Analyst	Follow requirements from 40CFR 136 Appendix B
RL Study	Annually and quarterly RL verification	RL greater than MDL and within calibration range. Laboratory procedure for establishing the RL will empirically demonstrate precision and bias at the RL.	Correct problem, then repeat the RL study.	Laboratory Manager/ Analyst	Recovery within established limits.

Matrix: Leachate, Soil, and Waste

Analytical Group: Radionuclides

Analytical Method/SOP: See **Worksheet #23**

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Method Blank	One per 20 samples or analytical batch	Result < RL or less than 5% associated sample activity.	Narrate, recount, reanalyze batch	Analyst	Result < RL or less than 5% associated sample activity.
LCS	One per 20 samples or analytical batch	75-125%R	Narrate, recount, reanalyze batch	Analyst	75-125%R
Laboratory Duplicate	One per 20 samples or analytical batch	activity<5*MDC, then RPD is 100% or less. If activity>5*MDC, then RPD is 20% or less or RER</=3	Narrate, recount, reanalyze batch	Analyst	activity<5*MDC, then RPD is 100% or less. If activity >5*MDC, then RPD is 20% or less or RER</=3
Matrix Spike (where applicable)	One per 20 samples or analytical batch for analytical methods that do not employ tracer or carrier	75-125%R	Narrate, recount, reanalyze batch	Analyst	75-125%R
Tracers	All field and QC samples	Tracer recoveries 15% -125%.	Re-prep; notify client; qualify or narrate why condition is acceptable.	Analyst	Tracer recoveries 15% -125%.
Stable Carriers	All field and QC samples	Carrier recoveries 25% -125%.	Re-prep; notify client; qualify or narrate why condition is acceptable.	Analyst	Carrier recoveries 25% - 125%.

Matrix: Leachate

Analytical Group: General Chemistry

Analytical Method/SOP: See **Worksheet #23**

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Project-Specific MPC
Method Blank (where applicable)	One per 20 samples or analytical batch	No target analytes > RL	Narrate, correct, and/or reanalyze batch as necessary	Analyst	Refer to SOP listed in Worksheet #23
LCS (where applicable)	One per 20 samples or analytical batch	Refer to SOP listed in Worksheet #23	Investigate source of problem, narrate, correct, and/or reanalyze batch as necessary.	Analyst	Refer to SOP listed in Worksheet #23
Laboratory Duplicate (where applicable)	One per 20 samples or analytical batch	Refer to SOP listed in Worksheet #23	Investigate source of problem, narrate, correct, and/or reanalyze parent sample as necessary.	Analyst	Refer to SOP listed in Worksheet #23
Matrix Spike (where applicable)	One per 20 samples or analytical batch	Refer to SOP listed in Worksheet #23	Investigate source of problem, narrate, correct, and/or reanalyze parent sample as necessary.	Analyst	Refer to SOP listed in Worksheet #23

Worksheet #29: Project Documents and Records

All final document files, including reports, figures, and tables will be submitted in electronic format.

Sample Collection and Field Records			
Record	**Generation**	**Verification**	**Storage location/archival**
Field logbook or data collection sheets	Field Task Leader (Anne L Burnham)	PM (Ray D'Hollander)	Project File
Chain-of-Custody Forms	Field Task Leader (Anne L Burnham)	PM (Ray D'Hollander)	Project File
Air Bills	Field Task Leader (Anne L Burnham)	PM (Ray D'Hollander)	Project File
Contractor Daily QC Reports	Field Personnel, Parsons	PM (Ray D'Hollander)	Project File
Deviations	Field Personnel, Parsons	PM (Ray D'Hollander)	Project File
Corrective Action Reports	Field Personnel, Parsons	PM (Ray D'Hollander)	Project File
Correspondence	Various Project Team Members	Various Project Team Members	Project File

Project Assessments			
Record	**Generation**	**Verification**	**Storage location/archival**
Field audit checklists	Field Task Leader (Anne L Burnham)	PM (Ray D'Hollander)	Project File
Data verification checklists	GEL Laboratories, Analyst or Laboratory Supervisor	GEL Laboratories, Laboratory Supervisor or QA staff	Project File
Data validation report	Parsons/Ameriphysics Validator (Maryanne Kosciewicz/Tom Hansen	Parsons/Ameriphysics Validator (Maryanne Kosciewicz/Tom Hansen	Project File
Data usability assessment report	Parsons/Ameriphysics Validator (Maryanne Kosciewicz/Tom Hansen)	Parsons/Ameriphysics Validator (Maryanne Kosciewicz/Tom Hansen	Project File

Laboratory Records			
Record	**Generation**	**Verification**	**Storage location/archival**
Data Summary Report (includes COC, narrative, summary results, and QC results)	GEL Laboratories, Reporting Department	GEL Laboratories, Project Management and Parsons, Data Management	Project File
Instrument Print-Out Report and Raw Data (includes Data Summary Report, instrument raw data, chromatograms, etc.)	GEL Laboratories, Analyst and Section Supervisor	GEL Laboratories, Project Management and Parsons, QA Officer/Data Validator	Project File
Electronic Data Deliverable	GEL Laboratories, Reporting Department	GEL Laboratories, Project Management and Parsons, Data Management	Project File

Worksheet #31, 32 & 33: Assessments and Corrective Action

These tables provide information on the required periodic assessments that will be performed during the course of the project to ensure the planned project activities are implemented in accordance with this QAPP. The type, frequency, and responsible parties of planned assessment activities to be performed for the project are summarized in the table below.

Assessments:

Assessment Type	Responsible Party & Organization	Number/Frequency	Estimated Dates	Assessment Deliverable	Deliverable due date
Non-Conformance Report from field	Parsons	Immediately As Needed	Within 24-48 hours of occurrence	Non-Conformance Report	30 days from occurrence
Field Record Verification	Parsons	Each Day of Sampling	Each day of sampling	After completion of sampling event	Field Record Verification
Corrective Action Report (CAR)	Parsons PM or Laboratory QA Manager	Immediately	Within 48 hours of occurrence	CAR	30 days from occurrence
Approval of the Proposed Corrective Action	Parsons PM or Laboratory QA Manager	Immediately	Within 48 hours of issuing the CAR	CAR with approver's signature	30 days from occurrence
Implementation of Corrective Action	Parsons PM or Laboratory QA Manager	Immediately	Immediately after CAR approval	CAR with approver's signature	30 days from occurrence
Verification of the Corrective Action	Parsons QA Manager or Laboratory QA Manager	Immediately	30 days from CAR approval	Completed CAR	30 days from occurrence
Laboratory Analysis Data Validation	Parsons or Ameriphysics Data Validator	Every Data Package	GEL will submit data package on or before 28 calendar days from sample receipt	Data validation report	Final Deliverable

Assessment Response and Corrective Action:

Assessment Type	Responsibility for responding to assessment findings	Assessment Response Documentation	Timeframe for Response	Responsibility for Implementing Corrective Action	Responsible for monitoring Corrective Action implementation
Non-Conformance Report from field	Parsons PM	Internal Memo	Within 24 hours	Parsons PM	Parsons PM
Field Record Verification	Parsons PM	Internal Memo	Each sampling day	Parsons PM	Parsons PM
Corrective Action Report (CAR)	Parsons PM or Laboratory QA Manager	CARs, updated case narratives, and corrected data submissions	Within 48 hours	Parsons PM or Laboratory Director	Parsons PM and Laboratory Director
Approval of the Proposed Corrective Action	Parsons PM or Laboratory Director	Internal Memo	Within 48 hours of CAR completion	Parsons PM or Laboratory Director	Parsons PM and Laboratory Director
Implementation of Corrective Action	Parsons PM or Laboratory Director	Responses to comments and report revisions	Immediately after CAR approval	Parsons PM or Laboratory Director	Parsons PM and Laboratory Director
Verification of the Corrective Action	Parsons QA Manager or Laboratory QA Manager	Internal Memo	30 days from CAR approval	Parsons PM or Laboratory Director	Parsons PM and Laboratory Director
Laboratory Analysis Data Validation	Parsons or Ameriphysics Data Validator	Internal Memo	GEL will submit data package on or before 28 calendar days from sample receipt	Parsons or Ameriphysics Data Validator	Parsons PM and Data Validator

Worksheet #34: Data Verification and Validation Inputs

This worksheet lists the inputs that will be used during data verification and validation. Inputs include planning documents, field records, and laboratory records. Data verification is a check that all specified activities involved in collecting and analyzing samples have been completed and documented and that the necessary records (objective evidence) are available to proceed to data validation. Data validation is the evaluation of conformance to stated requirements, including those in the contract, methods, SOPs and the QAPP. Data validation includes evaluation of the data against the project specific MPCs in **Worksheet #12**. Data verification and validation procedures and responsibilities are described in **Worksheet #35** and **Worksheet #36**, respectively. Once verification and validation have been completed, a usability assessment is conducted to evaluate whether process execution and resulting data meet DQOs. Usability assessment procedures are described in **Worksheet #37**.

Description	Verification (completeness)	Validation (conformance to specifications)
Approved QAPP	X	
Contract	X	
Field SOPs	X	
Laboratory SOPs	X	
Field logbooks	X	X
Equipment calibration records	X	X
Chain-of-Custody Forms	X	X
Sampling diagrams/surveys	X	X
Drilling logs	X	X
Geophysics reports	X	X
Relevant Correspondence	X	X
Change orders/deviations	X	X
Field audit reports	X	X
Field corrective action reports	X	X
Cover sheet (laboratory identifying information)	X	X
Case narrative	X	X
Internal laboratory chain-of-custody	X	X
Sample receipt records	X	X
Sample chronology (i.e., dates and times of receipt, preparation, & analysis)	X	X
Communication records	X	X

Description	Verification (completeness)	Validation (conformance to specifications)
Project-specific PT sample results	X	X
MDL/RL establishment and verification	X	X
Standards Traceability	X	X
Instrument calibration records	X	X
Definition of laboratory qualifiers	X	X
Results reporting forms	X	X
QC sample results	X	X
Corrective action reports	X	X
Raw data	X	X
Electronic data deliverable	X	X

Worksheet #35: Data Verification Procedures

"Verification" is a completeness check that is performed before the data review process is conducted to determine whether the required information is available for validation. It involves a review of all data inputs to ensure that the required information is present. This step of the data review process determines whether or not the required data inputs are present. The following table summarizes the methods for data verification.

Records Reviewed	Requirement Documents	Process Description	Responsible Person, Organization
Field logbook	QAPP, DIWP, FSP, SOPs	Verify that records are present and complete for each day of field activities. Verify that all planned samples including field QC samples were collected and that sample collection locations are documented. Verify that meteorological data were provided for each day of field activities. Verify that changes/exceptions are documented and were reported in accordance with requirements. Verify that any required field monitoring was performed and results are documented.	Daily – Parsons Field Activities Leader At conclusion of field activities – Parsons PM
Chain-of-custody forms	QAPP, DIWP, FSP, SOPs	Verify the completeness of chain-of-custody records. Examine entries for consistency with the field logbook. Check that appropriate methods and sample preservation have been recorded. Verify that the required volume of sample has been collected and that sufficient sample volume is available for QC samples (e.g., MS/MSD). Verify that all required signatures and dates are present. Check for transcription errors.	Daily – Parsons field staff At conclusion of field activities – Parsons Data Management
Laboratory Deliverable	QAPP, DIWP, DMP, SOPs	Verify that the laboratory deliverable contains all records specified in the QAPP. Check sample receipt records to ensure sample condition upon receipt was noted, and any missing/broken sample containers were noted and reported according to plan. Compare the data package with the chain-of-custody forms to verify that results were provided for all collected samples. Review the narrative to ensure all QC exceptions are described. Check for evidence that any required notifications were provided to project personnel as specified in the QAPP. Verify that necessary signatures and dates are present.	Before release – Laboratory PM Upon receipt – Parsons and Ameriphysics Data Validator
Corrective Action Reports	QAPP, DIWP, SOPs	Examine any field or laboratory corrective action reports. For any deficiencies noted, verify that corrective action was implemented according to plan.	Parsons PM and Parsons QA Manager

No field or laboratory audits are proposed at this time due to the COVID-19 pandemic.

Worksheet #36: Data Validation Procedures

"Validation" is performed to identify and qualify data that do meet the MPCs specified on **Worksheet #12**. Data requiring validation are summarized on **Worksheet #34**. The information in these tables shows what data inputs are required for data validation as well as the processes used to conduct the validation. Project specific elements for data validation on this project are summarized in the tables below.

Data Validator: Parsons and Ameriphysics

Analytical Group/Method:	All Chemical Analyses
Data deliverable requirements:	Full data packages and EDDs
Analytical specifications:	QAPP, laboratory SOPs, analytical method
Measurement performance criteria:	QAPP, laboratory SOPs, analytical method
Percent of data packages to be validated:	100%
Percent of raw data reviewed:	100%
Percent of results to be recalculated:	10%
Validation procedure:	QAPP, USEPA National Functional Guidelines for Organic and Inorganic Superfund Data Review dated January 2017, American Nuclear Society Standard 41.5-2012 (ANSI/ANS 41.5-2012, and analytical method
Validation checklist:	The USEPA National Functional Guidelines for Organic and Inorganic Superfund Data Review dated January 2017 and American Nuclear Society Standard 41.5-2012 (ANSI/ANS 41.5-2012, provide checklists for data validation and qualifying data.
Validation code (*see attached table):	See table below
Electronic validation program/version:	None

Data Validation Codes and Definitions

Data Validation Code	Definition
U	For Organic and Inorganic Data: The analyte was analyzed for but was not detected above the level of the reported sample quantitation limit. For RAD Data: The analyte was less than the critical level (L_C).
J	The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample. Additionally, for RAD data, the uncertainty associated with the results significantly exceeds the reported uncertainty.
UJ	The analyte was analyzed for but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.
J+	The result is an estimated quantity but the result may be biased high. This qualifier is not applicable for RAD data.
J-	The result is an estimated quantity but the result may be biased low. This qualifier is not applicable for RAD data.
NJ	The analyte has been "tentatively identified" or "presumptively" as present and the associated numerical value is the estimated concentration in the sample. This qualifier is not applicable for RAD data.
R	The data are unusable. The sample results are rejected due to serious deficiencies (see note below) in meeting QC criteria. The analyte may or may not be present in the sample.

NOTE: Serious deficiencies include quantitative or qualitative problems that are so severe that the data cannot be used based upon data validation procedures (i.e., acceptance/rejection criteria as defined by the above bodies, and as presented in the QAPP, USEPA National Functional Guidelines for Organic and Inorganic Superfund Data Review dated January 2017, American Nuclear Society Standard 41.5-2012 (ANSI/ANS 41.5-2012, and the analytical method).

In particular for radionuclide analysis, data may be rejected during the validation process depending upon the magnitude or severity of the following:

1. Samples not adhering to method or project specific preservation requirements.
2. Undetected sample results exceeding two times the analytical holding time requirement.
3. Sample specific chemical yield is greater than 110%.
4. Required detection level (RDL) has not been met in the case where the result is less than L_C and the result plus 1.65 times its uncertainty is greater than the Action Level.
5. Misidentified nuclide; energy resolution does not permit proper identification when several radionuclides are present in the sample; if the quench of a sample being counted by liquid scintillation is severe and no corrections have been made for energy correction; and if the energy resolution of the alpha spectral measurement has deteriorated to the point that multiple radionuclide peaks overlap significantly.
6. Negative sample results are more negative than the 2σ combined standard uncertainty (CSU).
7. Improper laboratory sub-sampling or homogenization techniques.
8. Counting efficiency calibrations, energy calibrations, or background determinations fall outside limits causing calculation errors or misidentifications.

Worksheet #37: Data Usability Assessment

A usability assessment considers whether data meet project data quality objectives as they relate to the decision(s) to be made, and evaluates whether data are suitable for making that decision. The usability assessment is the final step of data review and can be performed only on data of known and documented quality (i.e., verified and validated data).

This worksheet documents procedures that will be used to perform the data usability assessment for analytical, laboratory generated data. The data usability assessment is performed at the conclusion of data collection activities, using the outputs from data verification and data validation. It is the data interpretation phase, which involves a qualitative and quantitative evaluation of environmental data to determine if the project data are of the right type, quality, and quantity to support the decisions that need to be made. It involves a retrospective evaluation of the systematic planning process, and, like the systematic planning process, involves participation by key members of the project team. The data usability assessment evaluates whether underlying assumptions used during systematic planning are supported, sources of uncertainty have been accounted for and are acceptable, data are representative of the population of interest, and the results can be used as intended, with the acceptable level of confidence.

Maryanne Kosciewicz (Parsons) and Tom Hansen (Ameriphysics) are responsible for performing the data usability assessments.

Step 1	**Review the project's objectives and sampling design** Review the sampling design and data collection documentation for consistency and completeness with the project objectives observing any potential discrepancies.
Step 2	**Review the data verification and data validation outputs** Data validation will be conducted using the data quality indicators associated with the analytical measurements to be used on the project as specified in **Worksheet #28**. Review deviations from planned activities such as number and locations of samples, holding time exceedances, damaged samples, and SOP deviations and evaluate data using data validation procedures specified in **Worksheet #36**; and evaluate implications on the project data of unacceptable QC sample results to determine data utility and data usability.
Step 3	**Verify the assumptions of the selected statistical method** A suite of statistical tests will be considered to answer PSQ-2. The two-sample *t*-test will be used if the following assumptions are met: 1) Scale of measurement, meaning the data are measured on a continuous or ordinal scale. As the data in this case are continuous, so no further action needed. 2) Random selection, meaning the data is collected from a representative, randomly selected portion of the total population. The FSP describes a random start systematic data collection activity; thus, this assumption is met when samples are obtained at the locations specified in the FSP. 3) Normal distribution, meaning the data, when plotted, results in a normal distribution, bell-shaped distribution curve. A histogram will be used to assess normality.

	4) Sufficient sample size. VSP was used to calculate the number of samples necessary to accomplish the objectives for PSQ-2; thus, no further action is needed when these number of samples are collected. 5) Homogeneity of variance, where homogeneous variance exists when the standard deviations of samples are approximately equal. 6) The soil types are similar in all respects except that background samples do not contain radionuclides as a result of landfilling operations (i.e., the Site and background radionuclide data are independent). The remaining PSQs are estimating questions and are not subject to hypothesis testing
Step 4	Implement the statistical method The testing of populations will include tests of assumptions of normality, homogeneity of variance, and consideration of influence of outliers and censoring (non-detects). In each case an alternate statistical procedure is described to minimize the impact of not meeting the assumptions. Most statistical tests will be performed using USEPA ProUCL 5.1 software. The quantile test will be computed manually or using R software. 1. Identify statistical distribution of background, Lot 2A2, and Buffer Zone data as normal, log-normal, or non-parametric by assessing the histogram and performing goodness-of-fit tests. 2. Test for outliers in background populations using Dixon's test (if n < 26) or Rosner's test (if n>25). 3. Only remove outliers and re-test statistical distribution if further evaluation determines the data are not of acceptable quality. 4. If both populations to be compared are normally distributed, or can be transformed to normal distribution by the same transformation, e.g., logarithmic or other transformation, perform a two-sided *t*-test comparison of transformed populations at 95% confidence. Check result for homogeneity of variance, and use Welch-Satterthwaite *t*-test if normality is met but variances are unequal. Also, if non-detects are present in a population, regardless of whether detection limits are variable or constant, use the Gehan test instead of the *t*-test. 5. If either population to be compared is not normally distributed or cannot be transformed to normal, use the non-parametric Wilcoxon-Mann-Whitney test for comparison of the central tendency of populations. If non-detects are present in a population, and the detection limit is either a constant or variable, and/or above the lowest detected concentration, use the Gehan test instead of the Wilcoxon-Mann-Whitney test. 6. When DUs are not determined to be significantly different from background based on the above tests of the central tendency of the population, perform additional two-sample quantile tests to compare the 75th percentile of populations of Lot 2A2 and Buffer Zone to background populations. 7. Compare box plots of data from Lot 2A2 and Buffer Zone to background levels to see if there are any outlier samples that are significantly elevated above background that may indicate need for further action, based on professional judgement. 8. Given that multiple tests are performed, there will be a multiple lines of evidence evaluation to determine if action is required for a DU.
Step 5	Document data usability and draw conclusions Determine if the data can be used for decision making for PSQ-2 and for estimating for all other PSQs. All data qualifiers will be evaluated and any possible impact to the overall data quality will be discussed in the data usability assessment report. Any data gap due to the field and/or laboratory error will be presented in the report and possible impact to the project will be discussed. The data usability assessment report will describe the rationale for the data used and present any data limitations. The report will include a

	discussion of precision, accuracy, representativeness, completeness, comparability, and sensitivity of the data set and deviations from planned procedures and analysis and the impact on the project objectives. Maps will be generated with validated data and will be presented in project reports. The validated data that are not rejected will be used to determine nature and extent of contamination and to support risk assessment.

ATTACHMENT 1 LABORATORY SOPS AND QA PLAN

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR TOTAL DISSOLVED SOLIDS

(GL-GC-E-001 REVISION 16)

APPLICABLE TO METHODS:
EPA 160.1
Standard Methods 22nd Edition 2540 C-2011

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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL DISSOLVED SOLIDS

2.0 METHOD CODE

2.1 EPA 160.1

2.2 Standard Methods 22nd Edition 2540 C-2011

3.0 METHOD OBJECTIVE / PURPOSE

This procedure is used to measure total dissolved solids (TDS) in waters and wastewaters. TDS are those solids capable of passing through a standard glass fiber filter and dried to a constant weight at 180° C.

4.0 METHOD SUMMARY

4.1 Summary: In this gravimetric procedure, a water sample is filtered through a glass fiber filter into a preweighed porcelain crucible. The filtrate is evaporated to dryness to a constant weight at 180° C. The increase in the dish weight represents the total dissolved solids.

4.2 Synonym: Residue, Total Filterable (Dried at 180° C)

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

Seven days filtration from the time and date of collection unless otherwise specified by contract.

7.0 SAMPLE CONTAINER, PRESERVATION, COLLECTION, AND STORAGE REQUIREMENTS

7.1 Samples may be stored in glass or plastic containers.

7.2 Preservation:

7.2.1 No preservatives are required. Preserved samples should never be analyzed.

7.2.2 Temperature and pH are documented at login. Refer to GL-SR-E-001 for Sample Receipt, Login, and Storage.

7.3 Refrigerate sample at 0° $\leq$ 6° C until analysis to minimize microbiological decomposition of solids.

8.0 INTERFERENCES

8.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and will require prolonged drying, desiccation, and rapid weighing.

8.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180° C to ensure that all the bicarbonate is converted to carbonate.

8.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 10 mg/L to 20,000 mg/L

9.2 Method detection limit (MDL): Refer to current MDL study.

9.3 Method precision: 0-5% RPD.

9.4 Method accuracy: 95-105% recovery.

10.0 DEFINITIONS

10.1 Hygroscopic: Attracting, absorbing, and retaining atmospheric moisture.

10.2 Gravimetric: Pertaining to measurement by weight.

10.3 Desiccant: Material used to absorb moisture present.

10.4 AlphaLIMS: The Laboratory Information Management System used at GEL.

10.5 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

10.6 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

10.7 Laboratory Duplicate (DUP, LCSD, MSD or PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

10.8 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

10.9 Statistical Process Control (SPC) Limits: Statistically derived limits that establish Acceptable Ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

10.10 CRDL: Contract Required Detection Limit

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon the successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data are obtained, they are recorded in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and client sample MSDS forms are maintained in the laboratory.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from the cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION / EQUIPMENT / GLASSWARE

15.1 Sartorius Basic BA210S or comparable analytical balance, capable of weighing to 0.0005g.

NOTE: The balance must be calibrated in accordance with the procedure outlined in the GL-LB-E-002 for Balances.

15.2 VWR 13703M or comparable drying oven for operation at 180° ± 2° C

15.3 VWR 13703M or comparable drying oven for operation at approximately 98° C

15.4 Desiccator with a color-indicating desiccant

15.5 Porcelain crucibles, 100 mL capacity or larger

15.6 Glass fiber filter paper, 4.7 cm

15.7 Filtration flask (Minimum size is 250 mL)

15.8 Magnetic filter funnel

15.9 Tongs

15.10 Vacuum source

15.11 Graduated cylinders (Typical capacity required is 100 mL)

15.12 Thermometers are verified in accordance with GL-QS-E-007 for Thermometer Verification, and capable of recording temperatures up to 182° C.

16.0 REAGENTS

16.1 Sodium chloride, NaCl

16.2 ASTM Type I Deionized (DI) water (Refer to GL-LB-E-016)

17.0 PREPARATION OF SAMPLES

Not Applicable

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards and their preparation is maintained in AlphaLIMS in accordance with to GL-LB-E-007 for Laboratory Standards Documentation.

18.2 Laboratory Control Sample (LCS), 300 mg/L sodium chloride, NaCl: Weigh 0.300 g of NaCl and dilute to 1000 mL with deionized water. The LCS should be discarded after six months.

19.0 INSTRUMENT / EQUIPMENT START-UP PROCEDURES

19.1 Preparation of desiccators:

19.1.1 Ensure that the desiccant is activated by observing the blue color indicator.

NOTE: If < 50% of the indicator desiccant is blue, change the desiccant.

19.1.2 Desiccator must be sealed. Any moisture absorbed by the crucibles can cause erroneous results.

19.1.3 Label desiccators to be used with the date and what they will contain.

19.2 Preparation of crucibles:

19.2.1 Crucibles are cleaned by the glassware technicians, according to GL-LB-E-003 for Glassware Preparation, and stored in a drying oven.

19.2.2 Crucibles are marked by the analyst with a grease pencil and identified with letters and/or numbers.

19.2.3 The analyst is responsible for the preparation of the crucibles as follows:

19.2.3.1 Place cleaned crucibles in the drying oven at 180 ± 2° C.

19.2.3.2 Set the temperature at 180° C.

19.2.3.3 Crucibles should remain at the specified temperature for a minimum of one hour.

NOTE: The oven/furnace temperature should not be allowed to drop below 100° C before the crucibles are removed and placed in desiccators.

19.2.3.4 Using tongs, remove the crucibles from the oven or furnace and place in a desiccator immediately.

19.2.3.5 Allow crucibles to cool in desiccators to room temperature before use. If it is possible, allow crucibles to cool for at least 12 hours.

19.3 Filter Papers (if prewashed, certified filters are being used, no filter preparation is needed):

19.3.1 Place glass fiber filter in filter apparatus.

19.3.2 Rinse with 100 mL of deionized water.

19.3.3 Apply vacuum until water is removed from the filter.

19.3.4 Place the filter in an oven to dry at approximately 100° C and store in a desiccator until needed.

NOTE: If necessary, the filter can be washed just prior to use and can be used without drying in an oven.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC:

20.1.1 A matrix duplicate should be analyzed for every batch of ≤ 10 samples and for each set of ten samples in batches with ≥ 10 samples.

20.1.2 A method blank (MB) and laboratory control sample (LCS) should be analyzed once for every batch containing ≤ 20 samples.

NOTE: LCS duplicates are analyzed if required by contract or requested by client or if matrix QC is not available

20.2 Acceptance limits:

20.2.1 Matrix Relative Percent Difference (RPD): 0-5% RPD.
20.2.2 Method Blank: Less than the CRDL.
20.2.3 LCS: 95%-105% recovery.

20.3 Handling out-of-control situations:

20.3.1 Notify the Group Leader or Team Leader immediately.

20.3.2 If the LCS, LCS RPD, matrix RPD, or blanks fall outside of current acceptance limits, the samples to which the unacceptable QC pertains must be reanalyzed.

20.3.3 The analyst should document, in case narrative for the batch, the specific QC that is out of control and cross-reference data from any subsequent reanalysis.

21.0 SUGGESTED RUN SEQUENCE

21.1 Method blank

21.2 LCS

21.3 Samples 1 through x where x ≤ 10

21.4 Sample x duplicate

21.5 Repeat steps 21.3 through 21.4 for every group of ten samples in the batch.

22.0 PROCEDURE

22.1 Calibration of equipment/instrumentation:

22.1.1 Balance

Ensure that the analytical balance to be used has been calibrated and is within control limits before use. Refer to the balance logbook and GL-LB-E-002 for balances, for limits.

22.1.2 Oven

22.1.2.1 Make sure that the oven to be used is at a temperature that is within acceptance limits.

22.1.2.2 Control limits for the drying oven are documented on the temperature log.

22.1.2.3 The oven temperature log format provides the required documentation to ensure that the oven temperature was in control during the drying process.

22.1.2.4 Refer to GL-LB-E-004 for Temperature Monitoring.

22.2 Analysis:

22.2.1 Remove the prepared crucibles from the desiccator.

NOTE: Crucible should be removed from the desiccator just immediately prior to weighing.

NOTE: NEVER touch the crucibles with your hands. Always use tongs or Kimwipes.

22.2.2 Record the crucible ID, sample number, and the weight of each crucible to be used in AlphaLIMS in the appropriate columns.

22.2.3 Place a prepared glass fiber filter in the filter apparatus.

22.2.4 Thoroughly mix the sample to be analyzed.

22.2.5 Filter the sample through the glass fiber filter into a clean filter flask. Volume of filtrate needed is 70 mL.

22.2.6 Wash filter with three successive 10 mL volumes of DI water, allowing complete drainage between washings, and continue suction for about 3 minutes after filtration is complete.

22.2.7 Transfer total filtrate (with washings) to the designated preweighed crucible.

NOTE: Volume of filtrate used may vary depending upon the matrix of the sample. If more than 10 minutes are required to complete filtration, decrease sample volume.

22.2.8 Place the crucible and filtrate in an oven at approximately 98 ° C until the filtrate evaporates to dryness.

22.2.9 Once sample has evaporated dryness, dry for a minimum of 1 hour in an oven at 180 ± 2° C.

CAUTION: The temperature of the oven must be recorded or results may be considered invalid.

22.2.10 Rinse the used funnel thoroughly before beginning to filter the next sample.

22.2.11 Repeat steps 22.2.3 through 22.2.10 for all samples, blanks, duplicates, and LCS to be analyzed.

22.2.12 Using tongs to remove the crucibles from the oven and cool to room temperature in a desiccator.

22.2.13 Weigh and record the weight of each crucible in AlphaLIMS in the appropriate column.

22.2.14 Put the crucibles back into an oven at 180 ± 2° C for a minimum of one hour.

22.2.15 Repeat 22.2.12 through 22.2.14 until a constant weight is obtained. Constant weight is defined by EPA 160.1 as weight change of ≤ 0.0005 g.

22.3 Calculation/reporting of results:

22.3.1 Calculate TDS as follows:

$$\text{TDS in mg/L} = \frac{(A-B) \times 1{,}000}{C}$$

A = final weight of dried residue + crucible (g)
B = initial weight of crucible (g)
C = volume of filtrate used (L)

22.3.2 Results are reported in mg/L.

22.3.3 LCS recoveries are calculated as follows:

$$\frac{\text{Actual [TDS] mg/L obtained}}{\text{Known [TDS] mg/L}} \times 100$$

22.3.4 RPDs are calculated as follows:

$$\frac{\text{[TDS mg/L] sample - [TDS mg/L] duplicate}}{\text{Average [TDS mg/L] of the sample + duplicate}}$$

23.0 INSTRUMENT AND EQUIPMENT SHUT-DOWN PROCEDURES

Not Applicable

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

Refer to GL-GC-E-092 for General Chemistry Data Review and Packaging.

25.0 DATA TRANSMITTAL

When a batch is given "DONE" status, the data are automatically available to reporting personnel.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT / EQUIPMENT MAINTENANCE

27.1 Ovens and Thermometers

Refer to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators, and other Similar Devices.

27.2 Balances

Refer to GL-LB-E-002 for Balances.

27.3 Procedure for Maintenance of Desiccant

27.3.1 Analysts are responsible for ensuring that the desiccators are maintained by replacing the desiccant whenever 50% of the blue indicator starts to turn pink.

27.3.2 Dry desiccant for reuse as follows:

27.3.2.1 Spread desiccant out in an aluminum pan.

27.3.2.2 Place in drying oven capable of maintaining 105° C for one hour or more.

27.3.2.3 Remove from oven.

NOTE: All desiccants should be blue. If not, discard the dessicant.

27.3.2.4 Place in a desiccator immediately to cool.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper handling and disposal of all types of wastes from this procedure, refer to GL-LB-G-001, the Laboratory Waste Management Plan.

29.0 METHOD VARIATIONS

29.1 Step 19.3.2 differs from the method. The method mentions three 20 mL rinses of the filter paper with deionized water. As written, this SOP asks for the filter papers to be rinsed only once with 100 mL of deionized water.

29.2 Methods SM 2540 C-2011 and EPA 160.1 require that the filtrate be evaporated in a steam bath before being dried at 180° C. This SOP replaces the steam bath with an oven at approximately 98° C.

30.0 METHOD VERIFICATION

MDLs are calculated in accordance with GL-LB-E-001 for Determination of Method Detection Limits.

31.0 REFERENCES

31.1 Federal Register 40 CFR Part 136, “Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act,” April 4, 1995.

31.2 Manual of Methods For Chemical Analysis of Water and Wastes. US EPA Technology Transfer, EPA-625/6-74-003a, 1976.

31.3 Methods for Chemical Analysis of Water and Wastes. EPA 600/4-79-020. March 1979. Method 160.1, "Total Dissolved Solids."

31.4 Standard Methods for the Examination of Water and Wastewater, 22nd Edition Method 2540 C-2011.

31.5 Compilation of ASTM Standard Definitions, sponsored by ASTM Committee on Terminology. 7th Edition, American Society for Testing and Materials 1990.

32.0 HISTORY

Revision 16: Updated acceptance criteria.
Revision 15: TDS calculation revised.
Revision 14: Updated to include model of drying oven and analytical balance being used to comply with SCDHEC audit finding.
Revision 13: Updated Method reference for Standard Methods 2540 C-2011.
Revision 12: Replace Type II with Type I Deionized water.
Revision 11: Changed drying temperature to approximately 98 ° C and added filter washings to procedure.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

pH

(GL-GC-E-008 REVISION 23)

APPLICABLE TO METHODS:
EPA 150.1, SW-846 Method 9040B/9040C,
SW-846 Method 9041A, SW-846 Method 9045C/9045D
Exhibit D Semivolatiles, OLMO4.2, 10.1.4.1 and
Standard Methods 22nd Edition, SM 4500-H^+-00

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1.0 STANDARD OPERATING PROCEDURE FOR pH

2.0 METHOD CODE

2.1 Matrix - Water or multiphase waste where at least 20% of the sample is aqueous

2.1.1 EPA 150.1

2.1.2 Standard Methods 22nd Edition, 4500-H^+-00

2.1.3 SW-846 Method 9040B/9040C

2.2 Matrix – Solids and Sludges

2.2.1 SW-846 Method 9045C/9045D

2.3 Matrix - Liquid samples, where measurement by the methods listed in 2.1 is not possible, and oils

2.3.1 SW-846 Method 9041A (pH paper method) - This procedure is described in Section 22.1 of this SOP.

3.0 METHOD OBJECTIVE/PURPOSE

The purpose of this standard operating procedure (SOP) is to describe the procedures used to determine pH.

4.0 METHOD SUMMARY

4.1 For Methods EPA 150.1, Standard Methods 4500-H^+, SW-846 9040B/9040C, and SW-846 9045C/9045D: The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.

4.2 For SW-846 Method 9041A: The pH is determined with pH paper. Skip directly to Section 22.1 for this procedure.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

5.4 Soil

5.5 Sludge

5.6 Oil

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases the procedure is modified as necessary.

6.0 HOLDING TIME

The Environmental Protection Agency (EPA) ruled on April 4, 1995, that the holding time for pH analysis is 15 minutes or less. Since transport of the samples to the laboratory for analysis exceeds this holding time, analysis occurs upon arrival.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples can be collected in plastic or glass containers with no headspace.

7.2 Samples are unpreserved.

7.3 Samples are refrigerated at 0° ≤ 6° C until the start of analysis in accordance with GL-SR-E-001 for Sample Receipt, Login, and Storage.

8.0 INTERFERENCES/LIMITATIONS

8.1 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a low sodium error electrode.

8.2 Oily material or particulate matter can coat the electrode and impair response. This is removed by gentle wiping and distilled water rinsing or by soaking in 10% hydrochloric acid if needed.

8.3 Temperature affects the pH of different samples in different ways. For this reason both pH and temperature should be recorded at time of analysis.

8.4 The Environmental Protection Agency (EPA) ruled on April 4, 1995, that the holding time for pH analysis is 15 minutes or less. Since transport of the samples to the laboratory for analysis exceeds this holding time, analysis occurs upon arrival. All pH samples will be flagged as being analyzed out of holding.

8.5 The fill hole on the pH probe MUST be in the open position during calibration and analysis for proper performance. It may be closed to prevent evaporation/concentration when not in use.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method range: 0 to 14 pH units (s.u.)

9.2 Calibration range: 4 to 10 pH units (s.u.)

NOTE: Add a pH 2 buffer for acidic or a pH 12 buffer for caustic wastes when a sample is to be analyzed for corrosivity characterization.

9.3 Method precision: Refer to current SPC limits

9.4 Method accuracy: Refer to current SPC limits

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

10.2 Buffer Solution: Solutions with known pH values that are used to perform daily calibrations of the pH meter.

10.3 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

10.4 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample, periodically throughout the run sequence. Its purpose is to determine whether the analytical sequence is in control during sample analysis. It may be prepared from the same source as the calibration standards, and is usually of varied concentration.

10.5 Laboratory Duplicate (DUP, LCSD, MSD, PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

10.6 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and whether the laboratory is capable of making accurate and precise measurements.

10.7 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD, and internal standards.

10.8 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

10.9 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

12.1 Sample preparation data are recorded in AlphaLIMS.

12.2 As analytical data are obtained they are recorded in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the laboratory.

13.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and client sample MSDSs are maintained in the laboratory.

13.3 Personal protective equipment

13.3.1 Approved gloves are required when handling chemicals or samples.

13.3.2 To prevent clothes and skin from being exposed to corrosive materials, wear a lab coat.

13.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.4.1 Wear a dosimeter at all times while working in the lab to monitor radioactive exposure.

13.4.2 Wear a plastic apron over lab coat when working with radioactive samples.

13.4.3 Protect counter tops with counter paper or work from radioactive sample handling trays.

13.4.4 Prohibit admittance to immediate work area.

13.4.5 Post signs indicating radioactive samples are in the area.

13.4.6 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.4.7 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

13.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

13.7 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

13.8 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 Login personnel are responsible for delivering samples for pH analysis to the pH work area in accordance with GL-SR-E-001 for Sample Receipt, Login, and Storage.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Orion Star A111 pH meter or equivalent.

15.2 Orion 8302BNUMD or any other comparable combination pH electrode

15.3 Temperature compensation probe (ATC) Orion 927005 or equivalent.

15.4 Beakers (minimum capacity needed, 25 mL)

15.5 Magnetic stir plate

15.6 Stirrer magnets

15.7 If Method 9045C/9045D is being used:

15.7.1 Centrifuge

15.7.2 Centrifuge tubes (minimum capacity, 50 mL)

15.7.3 Top-loader balance

15.7.4 Spatula

15.7.5 Separatory funnel (optional)

15.8 If Method 9041A is being used:

15.8.1 Wide range pH strips

15.8.2 Narrow range pH strips

16.0 REAGENTS

16.1 pH 4 Calibrating Buffer

16.2 pH 7 Calibrating Buffer (Two sources are required. A second source is needed for a LCS).

NOTE: If the client specifies, a pH 2 buffer will be run as the LCS for a corrosivity batch containing acidic samples. For a corrosivity batch containing caustic samples, a pH 12 buffer will be run.

16.3 pH 10 Calibrating Buffer

16.4 ASTM Type II Deionized (DI) water

16.5 10% Hydrochloric acid (HCL)

16.6 Orion Ag/AgCl Reference Electrode Filling Solution or equivalent.

17.0 PREPARATION OF SAMPLES

Sample preparation for soils, sludges, oils, miscellaneous solids, and liquids where less than 20% of the sample is aqueous:

NOTE: No sample preparation is required when more than 20% of the sample is aqueous. To determine if the sample is > 20% aqueous, look at the sample in the container. If the sample clearly has an aqueous portion that appears to be at least ¼ of the sample volume, proceed with section 22.0. If there is a question concerning the % volume of liquid material in a sample container, request assistance from an experienced analyst or technician.

17.1 Place a beaker or centrifuge tube on the top-loader balance. Tare the balance.

NOTE: The balance must be verified in accordance with GL-LB-E-002 for Balances.

17.2 Transfer 20 g soil/sediment to the container. Add 20 mL of DI water and stir or shake for 5 minutes.

17.3 The mixture is allowed to stand for about one hour to allow most of the suspended material to settle out. Alternatively, the sample may be filtered or centrifuged for at least 5 minutes.

17.4 The aqueous layer is decanted for pH measurement using the calibration pH electrode as described in Section 22.0.

NOTE: If the sample is hygroscopic or another problematic matrix, begin the procedure again using 20 g of sample and 40 mL of DI water.

NOTE: If the sample is classified as a waste material, the mixed suspension is either allowed to stand for 15 minutes or filtered or centrifuged for at least 5 minutes.

NOTE: If the supernatant is multiphasic, decant the oily phase or use a separatory funnel to obtain the aqueous phase to use for the pH determination.

NOTE: If limited sample volume is received, use smaller 1:1 ratio of grams of sample to mL of DI water for the pH determination.

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards is maintained in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

18.2 Laboratory Control Sample(s): Commercially available pH buffer of 7.00 ± 0.01 @ 25°C. This must be from a different source than the calibrating pH 7 buffer.

18.3 Calibration standards:

18.3.1 pH buffers: 4, 7, and 10 pH units.

NOTE: If a sample is being analyzed for corrosivity, the pH meter check must also include buffers of pH 2 and pH 12. These additional buffers are not for calibration, but for checks only.

18.3.2 The buffers for calibration are stored in the Immediates area in the cabinets near the pH meter.

18.3.3 Buffers are discarded when they exceed the manufacturer's expiration date.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURES

The combination pH electrode must be plugged into the pH BNC jack on the rear part of the meter. The temperature compensating electrode is plugged into the ATC jack. A diagram for this is shown on page 7 of the Model 370 Instruction Manual. Make sure the LogR mode is off.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 The pH calibration must be checked by measuring the pH of all buffers used to calibrate the meter. The pH must be within 0.05 pH units of the pH 4, pH 7, and pH 10 buffer solution values and within 0.1 pH units of the pH 2 and pH 12 buffer solution values. The slope value must read 92%-102%. If not, the calibration must be repeated until these criteria are met.

20.2 Frequency of QC:

20.2.1 A matrix duplicate is run for every group of ≤ 10 samples and for each set of ten samples in batches with > 10 samples.

20.2.2 A laboratory control sample is run once per batch unless specified otherwise by the client.

20.2.3 A continuing calibration verification (CCV) is run after every 5 samples and after the last sample in the run.

20.3 Acceptance limits:

20.3.1 Matrix relative percent difference (RPD): Refer to current SPC limits.

20.3.2 LCS: must be ± 0.05 s.u.

20.3.3 CCV must be ± 0.05 s.u.

20.4 Handling out-of-control situations:

All QC data are calculated as soon as the results for the QC samples are known.

20.4.1 If the matrix RPD falls outside of the SPC limits, reanalyze that sample.

20.4.2 If the LCS RPD, or LCS recovery falls outside of the SPC limits, the pH meter is to be recalibrated and all samples bracketed by the LCS and LCS DUP must be reanalyzed.

21.0 RUN SEQUENCE

21.1 Calibration standards: pH 4, 7 and 10 buffer solutions

21.2 pH 7 LCS (2nd Source Standard)

21.3 CCV (Continuing Calibration Verification)

21.4 Samples 1 through x where x ≤ 10

21.5 Sample x duplicate

21.6 Repeat steps 21.3 through 21.5 for every group of 10 samples in the batch. Run an additional CCV after the last analytical sample in the run.

22.0 PROCEDURE

22.1 For sample analysis by SW-846 Method 9041A, "pH Paper Method," for solvents and other samples that could possibly damage the electrodes, paper pH strips may be used to determine pH. Wide range pH strips are listed as 0-14 pH units. Narrow range pH strips come in five different pH unit ranges: 0-2.5, 2.5-4.5, 4.0-7.0, 6.5-10.0, and 11.0-13.0 pH units.

NOTE: This method is not considered to be as accurate for pH measurement as pH meters; for this reason, pH measurements taken by Method 9041A cannot be used to define a waste as alkaline and non-corrosive.

NOTE: If a sample masks color changes on the pH paper, this method is not reliable.

22.1.1 Place a wide range pH strip into a small aliquot of sample.

22.1.2 The color change of the wide range pH strip is compared to the color patterns listed on the pH strip box. Use this value to determine which narrow range pH strips to use. Select the appropriate narrow range strip.

22.1.3 Place the narrow range pH strip into a small aliquot of sample. Compare the color change to the color pattern on the narrow range strip box.

22.1.4 Record the pH in AlphaLIMS.

NOTE: Each batch of pH paper must be calibrated (checked) against certified pH buffers. The paper must read within 0.5 pH units of the certified pH of the buffer. This calibration is recorded in the pH calibration log.

22.1.5 Analyze each sample in duplicate by repeating steps 22.1.1 through 22.1.3.

22.1.6 Using a thermometer verified in accordance with GL-QS-E-007 for Thermometer Verification, measure the temperature of one of the sample

aliquots used during narrow range pH analysis. This is the temperature of the sample at the time the pH was measured.

22.1.7 Record the temperature of the sample in AlphaLIMS.

22.2 Calibration for methods using a pH meter:

22.2.1 Before the meter is calibrated, the combination pH electrode is checked to make sure it is filled with Orion No. 810007 Internal Filling Solution. No filling solutions containing silver are used.

22.2.2 After unit is switched on, confirm LogR mode is off. (If it's on the symbol "LogR" is on the display screen.)

22.2.3 Press the CAL key to initiate calibration sequence. CAL is displayed for 2 seconds. Press scroll (↑,↓) keys until 3 PT is displayed. Press the YES key to accept. The 4 annunciator will be displayed. Using a fresh aliquot of pH 4 buffer, add a small stirring magnet to the beaker and place on top of a magnetic stirrer. Adjust to maintain a slow, steady rate of stirring. Place electrode in pH 4 buffer. Reading will be displayed and updated as calibration continues. When the READY light comes on, press the YES key.

22.2.4 The 7 annunciator will be displayed. Rinse electrode with DI water and place into pH 7 buffer. Add small stirring magnet and stir as indicated above. Reading will be displayed and updated as calibration continues. When the READY light comes on, press the YES key.

22.2.5 The 10 annunciator will be displayed. Proceed as with pH 4 and pH 7 buffers.

22.2.6 SLP will be displayed in the upper field while the calculated slope is displayed. Record this slope reading in LIMS. Meter will automatically proceed to measure mode.

22.3 Sample analysis by methods using a pH meter:

22.3.1 After the meter is calibrated using section 22.2, the unit will proceed to measure mode. The sample pH and temperature is automatically displayed.

22.3.2 Shake each sample prior to analysis. Approximately 40 mL of sample is poured into a beaker.

NOTE: If the sample was prepared as described in 17.1, decanted layer is the sample aliquot.

22.3.3 Place the beaker containing the sample on a magnetic stirring plate and add a clean magnetic stirring bar. Adjust the stir control to maintain a slow, steady rate of stirring.

22.3.4 Lower the pH electrode and the temperature compensating probe into the sample.

22.3.5 When the "Ready" status is displayed, record the pH, temperature, and time for the sample into the appropriate columns of the pH data entry screen in AlphaLIMS.

22.3.6 Repeat steps 22.3.2 through 22.3.5 with successive sample aliquots until the pH values obtained differ by < 0.1 pH units.

22.3.7 Run the samples in the sequence described in section 21.0.

NOTE: If only a few samples are ready to be run at a time, a duplicate sample is run for each set, regardless of whether or not few samples have been run since the last set of QC. The reason for this is to prove electrode repeatability throughout the day.

22.3.8 After all the pH samples present have been analyzed pH electrode is rinsed with DI water and placed back in the pH 7 buffer for storage.

22.4 Calculation/reporting of results:

22.4.1 Each sample result has a corresponding temperature and run time. These are recorded in AlphaLIMS. The final pH reading obtained for a sample after the criteria in 22.3.6 have been met is the one that is reported.

22.4.2 When submitting data for data entry, record the analyst's name, date of analysis, time, temperature, and pH values in AlphaLIMS.

22.4.3 After every duplicate sample value is recorded, the RPD (relative percent difference) of the sample and the duplicate are calculated. This is done by subtracting the lower value from the higher value, dividing by the average of the two and multiplying by 100 as shown in this formula:

$$\frac{\text{High value - Low value}}{\text{Average of the two values}} \times 100 = \text{RPD}$$

22.4.4 If the RPD is within the current control limits for pH, the duplicate is acceptable.

22.4.5 If the RPD is greater than the control limit, the sample and the duplicate are rerun. If the RPD is outside of the acceptance limits after being rerun, the pH meter is recalibrated and all samples analyzed prior to this duplicate and after the last acceptable duplicate are reanalyzed.

22.4.6 LCS RPDs are calculated using the formula described in 22.4.3.

22.4.7 LCS recoveries are calculated using this formula:

$$\frac{\text{actual value obtained}}{\text{theoretical value}} \times 100 = \%\ \text{LCS recovery}$$

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURES

23.1 After all the samples have been run, both the pH electrode and temperature compensating probe are rinsed thoroughly with DI water.

23.2 The electrode and probe are placed in a beaker filled with pH 7 buffer.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-LB-E-005 and GL-GC-E-092 for data review and validation procedures.

25.0 DATA TRANSMITTAL

When a batch is issued "DONE" status, the data become available to reporting personnel.

26.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

27.1 The combination pH electrode is drained and refilled with the appropriate filling solution as needed.

27.2 For problems that occur during operation, refer to the troubleshooting checklists located in the Orion Ross pH Electrode Instruction Manual or the Orion Model EA 940 Expandable Ion Analyzer Instruction Manual.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VARIATION

The pH test paper method SW-846 9041A is used only for miscellaneous samples. For safety reasons, the interference screening procedure described in section 3.1 of SW-846 9041A has not been included in this SOP.

30.0 REFERENCES

30.1 Method for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Method 150.1, “pH, Electrometric”.

30.2 Orion Model 370 PerpHect Ion Selective pH Meter Instruction Manual

30.3 Orion 9272 pH Electrode Instruction Manual

30.4 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1C, SW-846, 3rd Edition, June 1997. USEPA Office of Solid Waste and Emergency Response, Washington, DC. 20460:

30.4.1 Method 9045D, “Soil and Waste pH,” Revision 4, August 2002.

30.4.2 Method 9045C, “Soil and Waste pH,” Revision 3, January 1995.

30.4.3 Method 9040C. “pH Electrometric Measurement,” Revision 3, August 2002.

30.4.4 Method 9040B, “pH Electrometric Measurement,” Revision 2, January 1995.

30.4.5 Method 9041A, “pH Paper Method,” Revision 1, July 1992.

30.5 Standard Methods, 22nd Edition, Method 4500-H^+-00, "pH value."

30.6 Exhibit D, Semivolatiles, Section 10.1.4.1, OLMO4.2

31.0 HISTORY

Revision 19: Changed slope value to 92%-102% in quality control requirements section.

Revision 20: Change LCS requirement to ± 0.05 pH units.

Revision 21: Updated Standard Methods reference

Revision 22: Updated pH meter and flagging requirements.

Revision 23: Added notes requiring fill hole on probe to be in open position during calibration and analysis.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

PAINT FILTER TEST

(GL-GC-E-010 REVISION 10)

APPLICABLE TO METHODS:
EPA SW-846 9095A and 9095B

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1.0 STANDARD OPERATING PROCEDURE FOR PAINT FILTER TEST

2.0 METHOD CODE

EPA SW-846 9095A and 9095B

3.0 METHOD OBJECTIVE / PURPOSE

This method is used to determine the presence of free liquids in a representative sample of waste.

4.0 METHOD SUMMARY

4.1 A sample aliquot is placed on a paint filter. If any of the sample passes through the filter during a five-minute period, the sample is determined to contain free liquids.

4.2 Synonym: Free liquids test

5.0 APPLICABLE MATRICES

5.1 Soil

5.2 Sludge

5.2 Miscellaneous non-soil solids

5.3 Miscellaneous liquids

6.0 HOLDING TIME

No holding time is specified by the method.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 No container, collection, or storage requirements are specified by the method.

7.2 Samples are unpreserved.

8.0 INTERFERENCES/LIMITATIONS

Fine particulates may pass through the filter resulting in a “fail” result even when no free liquids are present.

9.0 PERFORMANCE CHARACTERISTICS

Not Applicable

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

10.2 Pass: When no sample aliquot passes through the paint filter.

10.3 Fail: When a portion of the sample aliquot passes through the paint filter.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze samples without supervision until trained by qualified personnel. Training records are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

12.0 DOCUMENTATION OF DATA

As data are obtained, the results are entered into AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals in the laboratory. A reference file of Material Safety Data Sheets (MSDS) and individual sample MSDS forms provided by the clients are also maintained.

13.3 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.3.1 Wear a plastic apron over lab coat when working with radioactive samples.

13.3.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

13.3.3 Prohibit admittance to immediate work area.

13.3.4 Post signs indicating radioactive samples are in the area.

13.3.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.3.6 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

13.4 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.4.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.4.2 Segregated oil wastes from water-soluble wastes in the satellite area containers.

13.5 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

13.6 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The list is typically in the form of a computer-generated batch sheet and is placed on the clipboard outside of the main cooler. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples on the weekends and after 5:00 p.m.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Paint filter (mesh #60 if available, or comparable fine or medium mesh commercial paint filter)

15.2 Glass funnel

15.3 Ring stand and ring

15.4 Graduated cylinder or beaker (minimum capacity 100 mL)

16.0 REAGENTS

Not Applicable

17.0 PREPARATION OF SAMPLES

Not Applicable

18.0 PREPARATION OF STANDARDS

Not Applicable

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURES

Not Applicable

20.0 QUALITY CONTROL (QC) REQUIREMENTS

A matrix duplicate is run for every batch of $\leq$ 10 samples and for each set of ten samples in batches with > 10 samples.

21.0 RUN SEQUENCE

21.1 Samples 1 through x where x $\leq$ 10

21.2 Sample x duplicate

21.3 Repeat steps 21.1 through 21.2 for every 10 samples.

22.0 PROCEDURE

22.1 Analysis:

22.1.1 Assemble the apparatus.

22.1.2 Obtain a representative sample aliquot.

22.1.2.1 Minimum size required: 100 mL or 100 g

22.1.2.2 If 100 mL or 100 g is not a large enough aliquot to be representative of the entire sample, additional 100 mL or 100 g aliquots can be used. Each portion should be tested individually. If any portion contains free liquids, the entire sample is considered to have free liquids.

22.1.3 Place the sample aliquot on the paint filter.

22.1.3.1 A funnel may be used to provide support for the paint filter. If the sample is of such light bulk density that it overflows the filter, then the sides of the filter can be extended upward by taping filter paper to the inside of the filter and above the mesh. Settling the sample into the paint filter may be facilitated by lightly tapping the side of the filter as it is being filled.

22.1.3.2 In order to assure uniformity and standardization of the test, materials such as sorbent pads or pillows that do not conform to the shape of the paint filter, should be cut into small pieces and poured into the filter. Sample size reduction may be accomplished by cutting the sorbent material with scissors, shears, knife or other such device so as to preserve as much of the original integrity of the sorbent fabric as possible. Sorbents enclosed in fabric should be mixed with the resultant fabric pieces. The particles to be tested should be reduced smaller than 1 cm [i.e., should be capable of passing through a 9.5 mm (0.375 inch) standard sieve]. Grinding sorbent materials should be avoided as this may destroy the integrity of the sorbent and produce many "fine particles" which would not normally be present.

22.1.3.3 For brittle materials larger than 1 cm that do not conform to the filter, light crushing to reduce oversize particles is acceptable if it is not practical to cut the material. Materials such as clay, silica gel, and some polymers may fall into this category.

22.1.4 Allow the sample to drain for a five-minute period.

NOTE: Do not disturb the sample during the five-minute period.

22.1.5 Record the sample and client ID, start and end times, and a sample description (e.g., fine soil) in the appropriate columns of the Paint Filter logbook in AlphaLIMS.

22.1.6 In AlphaLIMS, document whether or not any portion of the sample passed through the filter during the five-minute time period.

NOTE: If a portion of the sample did pass through the filter, include the volume or weight and a description of the filtrate.

22.2 Results are reported as follows:

22.2.1 Pass: If none of the sample aliquot passes through the paint filter, the sample is determined not to contain free liquids and is considered to pass the test.

22.2.2 Fail: If a portion of the aliquot passes through the paint filter, the sample is determined to contain free liquids and is considered to fail the test.

22.2.3 A result of either "pass" or "fail" is entered into the text value of the AlphaLIMS data entry screen. If the filtrate is fine particulate and not free liquids, this is also noted in AlphaLIMS.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURES

Not Applicable

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

24.1 Before submitting results for data entry into AlphaLIMS, check the following items:

24.1.1 The run is dated and initialed.

24.1.2 All crossouts are dated and initialed.

24.1.3 All duplicates are clearly identified.

24.1.4 Each nonconformance has been noted in the comment section.

24.1.5 Any pertinent observations have been noted.

24.2 A data report is generated for the batch. The batch sheet, data report, and case narrative are stapled together.

24.3 The analyst/technician does the initial review.

24.4 A peer analyst does a second review and updates the batch to "DONE" status after all errors are corrected. If acceptance criteria are not met, the nonconformances are dispositioned and samples may be reanalyzed as required.

25.0 DATA TRANSMITTAL

When a batch is issued "DONE" status, the data are automatically available to reporting personnel.

26.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Not Applicable

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

Refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

This is a qualitative analysis; therefore, method detection limits are not required.

30.0 REFERENCES

30.1 "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," Volume 1C, Method 9095A (Revision 1, December 1996).

30.2 "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," Volume 1C, Method 9095B (Revision 2, August 2002).

31.0 HISTORY

Revision 8: Updated SOP to include Method 9095B.

Revision 9: Added the use of a mesh commercial paint filter in equipment section.
Revision 10: Removed gas cylinder reference to safety precautions and hazard warnings.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR TOTAL SUSPENDED SOLIDS

(GL-GC-E-012 REVISION 16)

APPLICABLE TO METHODS:

Standard Methods 22nd Edition 2540 D-2011

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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL SUSPENDED SOLIDS

2.0 METHOD CODE

2.1 Standard Methods 22nd Edition 2540 D-2011

3.0 METHOD OBJECTIVE/PURPOSE

This procedure is used to measure total suspended solids (TSS) in waters and wastewaters. TSS are those solids that are retained by a standard glass fiber filter and dried to a constant weight at 103 to 105 °C.

4.0 METHOD SUMMARY

4.1 Summary: In this gravimetric procedure, a water sample is filtered through a preweighed glass fiber filter. The filter is then dried to a constant weight at 103 to 105 °C. The weight of the residue on the filter represents the total suspended solids.

4.2 Synonym: Residue, total non-filterable

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid samples. In these cases the procedure is modified as necessary.

6.0 HOLDING TIME

Holding time is seven days from the time and date of collection until the start of analysis unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples may be stored in glass or plastic containers.

7.2 No preservatives are required. Preserved samples should not be analyzed.

7.3 Non-homogeneous particles such as leaves, sticks, fish, and lumps of fecal material should be excluded from the sample.

7.4 Refrigerate samples at 0 $\leq$ 6 °C until the start of analysis to minimize microbiological decomposition of solids.

8.0 INTERFERENCES/LIMITATIONS

8.1 Too much residue on the filter will entrap water and may require prolonged drying.

8.2 For samples that are high in dissolved solids, thoroughly wash the filter to ensure the removal of the dissolved material.

8.3 Prolonged filtration times resulting from filter clogging may produce high results due to the excessive capture of solids on the clogged filter.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 4 mg/L to 20,000 mg/L

9.2 Method detection limit (MDL): Refer to current MDL study.

9.3 Method precision: 0-5% RPD.

9.4 Method accuracy: 95-105% recovery.

10.0 DEFINITIONS

10.1 Desiccant: Material used to absorb moisture.

10.2 Gravimetric: Pertaining to measurement by weight.

10.3 Hygroscopic: Attracting, absorbing, and retaining atmospheric moisture.

10.4 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

10.5 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus

10.6 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

10.7 Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

10.8 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

10.9 CRDL: Contract Required Detection Limit

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data are obtained, they are recorded in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNING

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards and limit exposure to

these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and client sample MSDS forms are maintained in the laboratory.

13.3 All personnel performing this procedure are trained in and follow the procedures in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Sartorius Basic BA210S or comparable analytical balance capable of weighing to 0.0001 g

NOTE: The balance must be calibrated in accordance with the procedure outlined in GL-LB-E-002 for Balances.

15.2 VWR 1370FM or comparable drying oven for operation at 103 to 105 °C

NOTE: The oven's temperature is monitored in accordance with GL-LB-E-004.

15.3 Desiccator with a color indicating desiccant

15.4 Glass fiber filter paper, 4.7 cm

NOTE: If filters are not certified to be pre-washed they must be prepared according to step 19.2.

15.5 Filtration flask (minimum size: 1 L)

15.6 Magnetic filter funnel

15.7 Tweezers

15.8 Vacuum source

15.9 Disposable pipets

15.10 Thermometer verified according to GL-QS-E-007 for Thermometer Verification and capable of measuring temperatures of 103 to 105 °C.

15.11 Aluminum weigh boats

15.12 Volumetric flasks and/or beakers, various sizes

15.13 Stirring apparatus and stir bars

15.14 Graduated cylinders of various sizes

16.0 REAGENTS

16.1 ASTM Type I deionized (DI) water. (Refer to GL-LB-E-016)

16.2 Desiccant

16.3 Celite

17.0 PREPARATION OF SAMPLES

NOTE: It is recommended that if less than 250 mL is required, sample is stirred with a magnetic stirrer at a speed to shear larger particles to a more uniform particle size.

18.0 PREPARATION OF STANDARDS

18.1 500 mg/L Celite standard.

NOTE: This standard serves as the LCS.

18.2 Add 0.0500 g of Celite to a 100 mL volumetric flask that is partially filled with DI water.

18.3 Bring to volume with deionized water. Mix well.

18.4 Prepare a separate standard for each LCS and LCS duplicate.

18.5 Document preparation of standards in AlphaLIMS according to GL-LB-E-007 for Laboratory Standards Documentation and GL-GC-E-004 for General Chemistry Standards, Definitions, and Preparation.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

19.1 Preparation of desiccators:

19.1.1 Ensure that the desiccant is activated by observing the blue color indicator.

NOTE: If < 50% of the indicator desiccant is blue, change the desiccant.

19.1.2 Desiccator must be sealed. Any moisture absorbed by the filters can cause erroneous results.

19.2 Filter papers

NOTE: If pre-washed filter papers are being used, proceed to step 22.

19.2.1 Place a glass fiber filter in the filter apparatus.

19.2.2 Rinse with three successive portions of approximately 20 mL of DI water.

19.2.3 Apply vacuum until the water is removed from the filter.

19.2.4 Place the filter on aluminum foil in an oven to dry at 103 to 105 °C for at least one hour.

19.2.5 Remove the filter from the oven and cool it in a desiccator for approximately 30 minutes.

19.2.6 Weigh each filter and record its weight in the appropriately labeled column of AlphaLIMS.

19.2.7 Repeat the cycle of rinsing, drying, desiccating, and weighing until a constant weight is obtained for each filter.

19.2.8 Store the washed and dried filter in a desiccator.

19.2.9 Alternatively, pre-washed filters may be used as purchased.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC:

20.1.1 A matrix duplicate is analyzed for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples.

20.1.2 A MB and LCS are analyzed for every batch containing ≤ 20 samples.

NOTE: An LCS duplicate is analyzed per client request.

20.2 Acceptance limits:

20.2.1 Matrix Relative Percent Difference (RPD): 0-5% RPD.

NOTE: If the difference between the sample concentration and duplicate concentration is less than or equal to the PQL and within a PQL value of each other, the results are acceptable even though the RPD may exceed current SPC limits.

20.2.2 Method blank: CRDL ≤ MB ≤ CRDL or ≤ ½ CRDL for any state of North Carolina samples.

20.2.3 LCS: 95-105% recovery.

20.2.4 LCS RPD: 0-5% RPD.

20.3 Handling out-of-control situations:

20.3.1 Notify the Group Leader immediately.

20.3.2 If the matrix or LCS RPD, MB, and/or LCS recovery fall outside of current acceptance limits, the samples to which the unacceptable quality control (QC) pertains must be reanalyzed.

20.3.3 Document in the case narrative the specific QC that is out of control and cross-reference data from any subsequent reanalysis.

20.3.4 If filtering times are greater than 10 minutes, use less sample aliquot.

21.0 RUN SEQUENCE

21.1 MB

21.2 LCS

21.3 Samples 1 through x where $x \leq 10$

21.4 Sample Duplicate

21.5 Repeat 21.3 through 21.4 for every 10 samples in the batch.

22.0 PROCEDURE

22.1 Calibration of equipment/instrumentation:

22.1.1 Balance

Ensure that the analytical balance to be used has been calibrated and it is within control limits before use. Refer to the balance logbook and GL-LB-E-002 for Balances.

22.1.2 Oven

22.1.2.1 Make sure that the oven to be used is at a temperature that is within acceptance limits.

22.1.2.2 Control limits for the drying oven are documented on the temperature log.

22.1.2.3 The oven temperature log format provides the required documentation to ensure that the oven temperature was in control during the drying process.

22.1.2.4 Refer to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators and Other Similar Devices.

22.2 Analysis:

22.2.1 Label an appropriate number of aluminum weigh boats (one per sample and for each QC sample).

22.2.2 Remove, immediately prior to weighing, the pre-washed glass fiber filter, prepared as described in section 19.0, from the desiccator.

NOTE: NEVER touch the filter with your hands. Always use tweezers or tongs.

22.2.3 Record the weigh boat ID, sample number, and the weight of each filter to be used in the appropriate columns in the data entry screen in AlphaLIMS.

22.2.4 Dry the filters for at least one hour at 103 to 105 °C.

22.2.5 Remove the filters from the oven and cool in a desiccator until they reach room temperature. This takes approximately 30 minutes.

22.2.6 Weigh each filter and record its weight a second time in the appropriately labeled column of AlphaLIMS.

22.2.7 Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained for each filter. Constant weight is defined as a weight loss or gain of ≤ 0.5 mg or 0.0005 g.

22.2.8 Place the filter on the filter apparatus and wet with a small amount of reagent grade water, to seat the filter.

22.2.8.1 If aliquots greater than 250 mL are to be used, shake container and rapidly transfer the sample to the filter by means of a graduated cylinder

NOTE: It is recommended that for volumes less than 250 mL, thoroughly shake the sample to be analyzed. Add a magnetic stir bar and stir at a speed to shear larger particles, to obtain a more uniform particle size.

22.2.8.2 While stirring, pipet a measured volume onto the seated filter, pipeting from the approximated midpoint of the container, but not in the vortex.

22.2.9 Record the volume of sample used in AlphaLIMS.

NOTE: The volume of sample to be used can be increased or decreased depending upon the matrix of the sample. If there is minimal residue (< 1.0 mg) on the filter after filtering 100 mL, additional 100 mL aliquots of the sample must be filtered. In some cases the filter may clog, preventing additional sample from being filtered. The analyst may use less than 1000 mL of sample if the filtration time takes ≥ 10 minutes.

NOTE: 500 mL of DI water must be filtered for the MB.

22.2.10 Apply the vacuum and filter the sample.

22.2.11 Rinse the graduated cylinder three times with DI water and transfer the rinsate to the funnel to ensure that all residue is transferred.

22.2.12 Remove any lingering residue from the funnel by rinsing thoroughly with three successive volumes of DI water (approximately 10 mL each).

22.2.13 Continue to apply the suction after the filtration is complete in order to remove as much water as possible.

22.2.14 Carefully remove the filter from the filter apparatus.

22.2.15 Place the filter back in its aluminum weigh boat.

22.2.16 Repeat steps 22.2.8 through 22.2.15 for each sample or QC sample in the batch.

22.2.17 Dry the filters for at least one hour at 103 to 105 °C.

NOTE: The amount of residue on the filter should fall in the range of 10 to 200 mg.

22.2.18 Remove the weigh boats and filters from drying oven and cool to room temperature in a dessicator.

22.2.19 Weight and record the weight of each filter in AlphaLIMS in the appropriate column and place back in its weigh boat.

22.2.20 Put the weigh boats and filters back in the oven at 103°C to 105°C degree oven for at least an hour.

22.2.21 Repeat steps 22.2.18 through 22.2.20 until constant weight is obtained.

22.3 Calculation/reporting of results:

22.3.1 Calculate TSS as follows:

$$\text{TSS (mg/L)} = \frac{A - B \times 1{,}000}{C}$$

Where:

A = Final weight of the filter plus residue in g

B = Weight of the filter paper in g (This is the last weight of the filter obtained prior to filtration.)

C = Volume of the sample in (L)

22.3.2 Results are reported in mg/L.

22.3.3 RPDs are calculated as follows:

$$\frac{([\text{TSS mg/L}]\ \text{sample} - [\text{TSS mg/L}]\ \text{duplicate})}{\text{Average}\ [\text{TSS mg/L}]\ \text{of sample and duplicate}} \text{X}\ 100$$

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Not Applicable

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for General Chemistry Data Review and Packaging.

25.0 DATA TRANSMITTAL

When a batch is issued a status of DONE, the data are automatically available to reporting personnel.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

27.1 Ovens and Thermometers

Refer to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators, and other Similar Devices.

27.2 Balances

Refer to GL-LB-E-002 for Balances.

27.3 Procedure for the maintenance of desiccant

27.3.1 Analysts are responsible for ensuring that the desiccators are maintained by replacing the desiccant whenever 50% of the blue indicator starts to turn pink.

27.3.2 Dry desiccant for reuse as follows

27.3.2.1 Spread desiccant out in an aluminum pan.

27.3.2.2 Place in drying oven capable of maintaining 105 °C for one hour or more.

27.3.2.3 Remove from the oven.

NOTE: All desiccants should be blue.

27.3.2.4 Place in a desiccator immediately to cool.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VARIATION AND VERIFICATION

29.1 Step 19.2.2 differs from SM 2540 D-2011. Both methods mention three 20 mL

rinses of the filter paper with deionized water during filter preparation. As written, this SOP asks for the filter papers to be rinsed only once with 100 mL of DI water.

29.2 Constant weight is defined in SM 2540 D-2011 as a weight loss or gain of < 4% of the previous weight or 0.0005 g. Constant weight is defined in this SOP as a difference equal to or less than 0.0005 g.

29.3 MDLs are calculated in accordance with GL-LB-E-001 for Determination of Method Detection Limits.

29.4 Step 22.2.8 differs from SM 2540 D-2011, which calls for the pipetting of the sample aliquot to the filter instead of transferring by a graduated cylinder.

30.0 REFERENCES

30.1 Federal Register 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act," April 4, 1995.

30.2 Standard Methods for the Examination of Water and Wastewater, 22nd Edition, Method 2540 D-2011.

30.3 Compilation of ASTM Standard Definitions. Sponsored by ASTM Committee on Terminology, 7th Edition, Philadelphia, American Society for Testing and Materials, 1990.

30.4 Manual of Methods for Chemical Analysis of Water and Wastes. EPA Technology Transfer, EPA-625/6-74-003a, 1976.

31.0 HISTORY

Revision 16: Added process improvements for drying. Updated Acceptance Limits.

Revision 15: TSS calculation revised.

Revision 14: Revised to include model of analytical balance and drying oven being used to comply with SCDHEC audit finding.

Revision 13: Revised quality control requirements for method blank for state of North Carolina samples.

Revision 12: Updated Standard Methods reference for MURII compliance.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

ALKALINITY: TOTAL, BICARBONATE, CARBONATE, HYDROXIDE, AND PHENOLPHTHALEIN

(GL-GC-E-033 REVISION 13)

APPLICABLE TO METHODS:
EPA Method 310.1,
Standard Methods 22nd Edition, SM 2320 B-97

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1.0 STANDARD OPERATING PROCEDURE FOR ALKALINITY: TOTAL, BICARBONATE, CARBONATE, HYDROXIDE, AND PHENOLPHTHALEIN

2.0 METHOD CODE

2.1 EPA Method 310.1

2.2 Standard Methods 22nd Edition, SM 2320 B-97

3.0 METHOD OBJECTIVE AND PURPOSE

This standard operating procedure (SOP) describes the method used to determine the concentration of alkalinity (total, bicarbonate, carbonate, and hydroxide alkalinity) present in water samples.

4.0 METHOD SUMMARY

4.1 Summary: A sample aliquot is titrated with standardized sulfuric acid (H_2SO_4) solution to the phenolphthalein alkalinity (pH of 8.3) endpoint and then to the total alkalinity (pH of 4.5) endpoint. The total alkalinity concentration corresponds directly to the amount of titrant used to reach the pH 4.5 endpoint. Bicarbonate, carbonate, and hydroxide alkalinity can be determined for a sample using an alkalinity relationship table.

4.2 Synonym: Alkalinity as calcium carbonate, $CaCO_3$

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

The holding time is 14 days from the date and time of collection until the start of analysis unless otherwise specified by contract.

7.0 SAMPLE CONTAINER, PRESERVATION, COLLECTION, AND STORAGE REQUIREMENTS

7.1 Samples are collected in glass or plastic containers.

7.2 Samples are unpreserved. Since the alkalinity concentration determination is based on the pH of a sample, preserved samples are not analyzed.

7.3 During collection, samples should not be agitated and/or exposed to the air for a prolonged period. Both conditions could affect the pH of the sample.

7.4 Samples are stored at $0 \leq 6^{\circ}$ C in accordance with GL-SR-E-001 for Sample Receipt, Login, and Storage.

8.0 INTERFERENCES/LIMITATIONS

8.1 Interferences:

8.1.1 Oil and grease can coat the pH electrode and cause a sluggish response.

8.1.2 Salts present in large amounts can cause interference in the pH measurements.

8.1.3 Samples containing high concentrations of mineral acids should be titrated to an electromagnetic endpoint of 3.9. Refer to ASTM Standards, part 3, "WATER," D-1067, Method D (1976).

8.2 Limitations

8.2.1 Avoid titration volumes greater than 50 mL by using one of the following:

8.2.1.1 Use a more concentrated sulfuric acid titrant.

8.2.1.2 Use a smaller sample volume.

8.2.2 The sample cannot be filtered, diluted, or concentrated prior to analysis without compromising the integrity of the results.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method detection limit (MDL): Refer to current MDL limits.

9.2 Method precision: Refer to current SPC limits.

9.3 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

10.2 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

10.3 Laboratory Duplicate (DUP, LCSD, MSD or PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample, and the results are compared to measure precision and accuracy.

10.4 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

10.5 Spike (Matrix Spike or Post Spike): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or PS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or PS corrected for background concentrations.

10.6 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD, and internal standards.

11.0 ANALYST VERIFICATION

Before a technician/analyst is allowed to analyze samples without supervision, he/she will be trained by qualified personnel. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data are obtained, they are recorded in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDS forms are maintained in the laboratory.

13.3 Use care when handling concentrated forms of sulfuric acid.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Beakers: Capacity of 150 mL required

15.2 Graduated cylinders: Minimum capacity of 100 mL is needed

15.3 Magnetic stir plate

15.4 Stir bar

15.5 Magnetic stir bar retriever

15.6 Squeeze bottle for deionized water

15.7 Hot plate

15.8 Burette with 0.05 mL increments: Recommended capacity, 10 mL to 20 mL

15.9 Watch glass

15.10 pH meter and probe

15.11 Oven capable of maintaining 250 ± 50˚ C

NOTE: The temperature of the oven is monitored in accordance with GL-LB-E-004.

15.12 Volumetric flask, 1 L

15.13 Aluminum weigh boat

15.14 Desiccator and desiccant

15.15 Analytical balance: Capable of weighing to 0.0001 g

NOTE: Balances are calibrated in accordance with GL-LB-E-002 for Balances.

16.0 REAGENTS

16.1 Reagents

16.1.1 Sodium carbonate (Na_2CO_3)

16.1.2 Sulfuric acid (H_2SO_4)

16.1.3 ASTM type I deionized (DI) water: See GL-LB-E-016

16.1.4 pH buffers

16.1.4.1 pH = 4

16.1.4.2 pH = 7

16.1.4.3 pH =10

16.1.5 Sodium borate ($Na_2B_4O_7 \bullet 10H_2O$)

16.2 Solutions

16.2.1 0.05 N sodium carbonate solution (Na_2CO_3)

16.2.1.1 Dry 3 to 5 g of sodium carbonate in an oven at 250 ± 50˚ C for 4 hours.

16.2.1.2 Remove the sodium carbonate from the oven, and cool in a desiccator.

16.2.1.3 Weigh 2.5 ± 0.2 g of the dried sodium carbonate and transfer to a 1 L volumetric flask.

NOTE: Record the weight of the sodium carbonate to the nearest mg in the standardization logbook. The weight is needed in the standardization of the sulfuric acid titrant.

16.2.1.4 Bring to volume with deionized water and mix well.

16.2.1.5 Discard after one week.

16.2.2 0.1 N sulfuric acid titrant

16.2.2.1 Transfer 3.0 mL of concentrated sulfuric acid to a 1 L volumetric flask.

16.2.2.2 Bring to volume with deionized water.

16.2.3 Standardization of the 0.1 N sulfuric acid titrant

NOTE: This must be performed monthly

16.2.3.1 Transfer 40.0 mL of 0.05 N sodium carbonate to a 250 mL beaker.

16.2.3.2 Add 60 mL of deionized water.

16.2.3.3 Put a stir bar in the beaker and place on a stir plate.

16.2.3.4 Measure the pH of the solution.

NOTE: Refer to GL-GC-E-008 for pH.

16.2.3.5 Fill a buret with the 0.1 N sulfuric acid solution.

16.2.3.6 Record the initial volume of titrant in the standardization log.

16.2.3.7 Using the sulfuric acid solution as the titrant, titrate the sodium carbonate solution to a pH of approximately 5. Record the volume of titrant used.

16.2.3.8 Remove the beaker from the stir plate.

16.2.3.9 Place a watch glass over the beaker and put the beaker on a hot plate.

16.2.3.10 Boil the solution gently for 3 to 5 minutes.

16.2.3.11 Cool to room temperature.

16.2.3.12 Rinse any moisture or residue on the watch glass into the same beaker of sodium carbonate.

16.2.3.13 Titrate the sodium carbonate solution again with the sulfuric acid titrant until a pH of 4.5 is reached.

16.2.3.14 Record the volume of titrant used in the standardization logbook. Repeat Steps 16.2.3.1 to 16.2.3.13 two more times.

16.2.3.15 Calculate the exact normality of the sulfuric acid solution using this formula:

$$\text{Normality of the } H_2SO_4 \text{ solution} = \frac{A \times B}{53.00 \times C}$$

Where:

A = g of Na_2CO_3 used in preparing Na_2CO_3 solution (refer to 16.2.1.3)

B = volume in mL of the Na_2CO_3 solution transferred to the beaker (refer to 16.2.3.1)

C = total volume of the 0.1 N H_2SO_4 acid titrant used to reach a pH of 4.5.

16.2.4 0.02 N sulfuric acid: Dilute 200 mL of the 0.1 N sulfuric acid to 1L with DI water.

16.2.5 Standardization of the 0.02 N sulfuric acid

16.2.5.1 Standardize the sulfuric acid solution monthly.

16.2.5.2 Transfer 15.0 mL of 0.05 N sodium carbonate solution to a 250 mL beaker.

16.2.5.3 Add 85 mL of deionized water.

16.2.5.4 Put a stir bar in the beaker and place on a stir plate.

16.2.5.5 Measure the pH of the solution.

NOTE: Refer to GL-GC-E-008 for pH.

16.2.5.6 Fill a buret with the 0.02 N sulfuric acid solution.

16.2.5.7 Record the initial volume of titrant in the standardization log.

16.2.5.8 Using the sulfuric acid solution as the titrant, titrate the sodium carbonate solution to a pH of approximately 5. Record the volume of titrant used.

16.2.5.9 Remove the beaker from the stir plate.

16.2.5.10 Place a watch glass over the beaker and put the beaker on a hot plate.

16.2.5.11 Boil the solution gently for 3 to 5 minutes.

16.2.5.12 Cool to room temperature.

16.2.5.13 Rinse any moisture or residue on the watch glass into the same beaker of sodium carbonate.

16.2.5.14 Titrate the sodium carbonate solution again with the sulfuric acid titrant until a pH of 4.5 is reached.

16.2.5.15 Record the volume of titrant used in the standardization logbook.

16.2.5.16 Calculate the exact normality of the sulfuric acid solution using this formula:

$$\text{Normality of the } H_2SO_4 \text{ solution} = \frac{A \times B}{53.00 \times C}$$

Where:

A = grams of Na_2CO_3 used in preparing Na_2CO_3 solution (refer to 16.2.1.3)

B = volume in mL of the Na_2CO_3 solution transferred to the beaker (refer to 16.2.5.2)

C = total volume of the 0.02 N H_2SO_4 acid titrant used to reach a pH of 4.5.

16.2.6 Sodium borate LCS: Weigh 3.814 g of sodium borate decahydrate ($Na_2B_4O_7 \bullet 10H_2O$) into a 1000 mL volumetric flask. Dilute to volume with DI water. Discard after six months.

17.0 PREPARATION OF SAMPLES

Not applicable

18.0 PREPARATION OF STANDARDS

Refer to step 16.2

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

Refer to GL-GC-E-008 for pH.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC:

20.1.1 Matrix duplicate is analyzed for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples.

20.1.2 LCS is analyzed with each alkalinity batch of ≤ 20 samples. Recovery must be 100% ± 10%.

20.1.3 Prepare LCS by diluting 5 mL of sodium borate solution (16.2.6) to 100 mL with DI water. Analyze as if it were a sample.

20.1.4 A matrix spike (MS) is prepared with each alkalinity batch of ≤ 10 samples. Add 5 mL of LCS (sodium borate) solution to 100 mL of sample.

20.2 Acceptance limits:

20.2.1 Matrix relative percent difference (RPD): Refer to current SPC limits.

20.2.2 LCS: 90 – 110%.

20.2.3 MS: Refer to current SPC limits.

21.0 RUN SEQUENCE

21.1 LCS

21.2 Samples 1 through x where x ≤ 10

21.3 Sample x duplicate

21.4 Sample x matrix spike

21.5 Repeat steps 21.3 and 21.5 for the next 10 samples.

22.0 PROCEDURE

22.1 Analysis:

22.1.1 Calibrate the pH meter as described in GL-GC-E-008 for pH.

22.1.2 Record the analyst initials, date, and time of analysis in AlphaLIMS.

22.1.3 Using a graduated cylinder, transfer 10 ml to 100 mL of sample beaker or disposable container.

22.1.4 Record the volume of sample used in AlphaLIMS.

22.1.5 Measure the pH of the sample. (Refer to the GL-GC-E-008 for pH.)

22.1.6 Record this initial pH in AlphaLIMS.

22.1.7 Fill the buret with one of the standardized sulfuric acid titrants, and record the normality of the chosen titrant in AlphaLIMS.

22.1.7.1 Use 0.02 N sulfuric acid if the alkalinity is expected to be < 1000 mg/L of calcium carbonate.

22.1.7.2 Use 0.1 N sulfuric acid if the alkalinity is expected to > 1000 mg/L calcium carbonate.

NOTE: If more than 50 mL of 0.02 N titrant is required, reanalyze the sample using 0.1 N titrant.

22.1.8 Titrate the sample with the sulfuric acid titrant until the appropriate endpoint is obtained.

22.1.8.1 Phenolphthalein alkalinity: Endpoint = pH of 8.3

22.1.8.2 Total alkalinity: Endpoint = pH of 4.5

22.1.8.3 Total alkalinity less than 20 mg/L: Endpoint = pH of 4.5, then titrate to pH 4.2.

22.1.9 Record the total volume of titrant used in AlphaLIMS.

22.1.10 Repeat steps 22.1.3 through 22.1.9 for each sample and quality control sample in the batch.

22.2 Calculation/reporting of results:

22.2.1 Calculate the total alkalinity using this formula:

$$\text{alkalinity in mg/L} = \frac{Vt \times N \times 50000}{Vs} \quad \text{where}$$

Vt = volume in mL of H_2SO_4 used to reach the pH 4.5 endpoint

N = normality of the H_2SO_4 titrant

Vs = volume in mL of sample used

22.2.2 Calculate the total alkalinity for concentrations less than 20 mg/L using this formula:

Alkalinity in mg/L =

$$\frac{((2 \times V_t) - V_{t2}) \times N \times 50000)}{V_s}$$

where

Vt = volume in mL of H_2SO_4 used to reach the pH 4.5 endpoint

V_{t2} = total volume in mL of H_2SO_4 used to reach the pH 4.2 endpoint

N = normality of the H_2SO_4 titrant

Vs = volume in mL of sample used

22.2.3 Calculation of the phenolphthalein alkalinity (P)

Calculate P using this formula

$$\text{P in mg/L} = \frac{Vt \times N \times 50000}{Vs} \quad \text{where}$$

Vt = volume in mL of H_2SO_4 used to reach the pH 8.3 endpoint

N = normality of the H_2SO_4 titrant

Vs = volume in mL of sample used

22.2.4 Calculation of carbonate, bicarbonate, and hydroxide alkalinity.

These forms of alkalinity are calculated using the calculations found in Standard Methods, 18th, 19th, 20th, and 21st Editions, Method 2320B, Table 2320: II.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Refer to the GL-GC-E-008 for pH for shutdown procedures.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for General Chemistry Data Review and Packaging.

25.0 DATA TRANSMITTAL

When a batch is issued "DONE" status, it is automatically transferred via AlphaLIMS to reporting personnel.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to GL-GC-E-008 for pH for instrument maintenance.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

29.1 Method detection limit studies are performed in accordance with GL-LB-E-001 for Method Detection Limits.

29.2 EPA method 310.1 states that analysis should begin as soon as it is practical. This SOP allows 14 days from the date of collection until the start of analysis in accordance with the holding time listed in the Federal Register Volume 49 Number 209 Part 136.3 Table II.

30.0 REFERENCES

30.1 Methods of Chemical Analysis of Water and Wastes. Alkalinity. EPA 600/4 -79-020. Method 310.1 (1979).

30.2 Standard Methods for the Examination of Water and Wastewater 22nd Edition. SM 2320 B-97. "Alkalinity, Titration Method".

30.3 Federal Register 40 CFR Part 136 "Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act," April 4, 1995.

31.0 HISTORY

Revision 9: Updated endpoint and calculations for Total Alkalinity Determinations

Revision 10: Updated Standard Methods reference

Revision 11: Updated run sequence.

Revision 12: Added Titration Steps.

Revision 13: Removed Method Blank requirements.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR BIOCHEMICAL OXYGEN DEMAND (BOD)

(GL-GC-E-045 REVISION 27)

APPLICABLE TO METHODS:
EPA Method 405.1, and
Standard Methods, 22nd Edition, SM 5210 B-01

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APPENDIX 16

1.0 STANDARD OPERATING PROCEDURE FOR BIOCHEMICAL OXYGEN DEMAND (BOD)

2.0 METHOD CODE

2.1 EPA Method 405.1

2.2 Standard Methods 22nd Edition, SM 5210 B-01

3.0 METHOD OBJECTIVE/PURPOSE

This standard operating procedure (SOP) describes the procedure used to determine the biochemical oxygen demand (BOD) of water samples.

4.0 METHOD SUMMARY

The procedure measures the relative oxygen requirements of wastewater effluents, effluents, and polluted water. The biochemical oxygen demand (BOD) analysis is performed by measuring the initial dissolved oxygen content of a seeded sample aliquot, sealing the aliquot, incubating the sample for a five day period, obtaining a final dissolved oxygen (DO) measurement, and then calculating BOD based on the difference in dissolved oxygen content.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

Holding time is 48 hours from the time and date of collection until the time samples are placed in the incubator. Refer to Section 29.0 for the reference document concerning holding times.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples are collected in either glass or plastic containers.

7.2 No preservatives are added to the samples or sample containers.

7.3 Samples are stored at $0° \leq 6°$ C in accordance with GL-SR-E-001 for Sample Receipt, Login, and Storage.

8.0 INTERFERENCES

Samples from industrial wastes containing toxic materials may require special study and treatment.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 1 mg/L through 180,000 mg/L

9.2 Method detection limit (MDL): Refer to current detection limit.

9.3 Method precision: Refer to current control limits.

9.4 Method accuracy: Refer to current control limits.

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

10.2 Calibration Blank (CB): An aliquot of reagent water or other blank matrix. In the case of the CBOD/BOD, it is analyzed after the dissolved oxygen meter has been calibrated and after the last sample has been analyzed.

10.3 Laboratory Control Standard (LCS): A standard, usually of the same matrix as the sample batch being analyzed, taken through the same prep process as the samples, then analyzed with the batch.

10.4 Laboratory Duplicate (DUP): Aliquot of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample, and the results are compared to measure precision and accuracy.

10.5 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MC is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

10.6 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

10.7 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

10.8 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Technician and analysts do not analyze samples without supervision until trained by qualified personnel. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data are obtained, they are recorded in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

SULFURIC ACID IS HIGHLY CORROSIVE. AVOID CONTACT OR SPILLING SOLUTIONS OF THIS CHEMICAL ON YOUR HANDS OR OTHER PARTS OF THE BODY.

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 All chemicals and samples should be treated as potential health hazards, and exposure to these chemicals must be reduced to the lowest level possible. GEL

maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory. A reference file of Material Safety Data Sheets (MSDS) and individual client sample MSDS are also maintained.

13.3 Due to the biological nature of the analysis, gloves must always be worn when handling any sample to prevent health risks to the analyst. No food or drinks allowed in the laboratory.

13.4 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

14.0 SAMPLE RECEIPT FOR ANALYSIS

Login delivers the sample directly to the Biological Lab after samples are logged in. The analyst present in the lab must verify that the sample was not collected 48 hours prior to its receipt to the Biological Lab.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 BOD bottles (300 mL) and stoppers with caps

15.2 Graduated cylinders

15.3 Erlenmeyer flasks

15.4 Volumetric flasks

15.5 Type A pipets, various volumes

15.6 Thermometer: Range 0° to 30° C with 0.1° C increments

NOTE: Thermometers are verified in accordance with GL-QS-E-007 for Thermometer Verification.

15.7 Dissolved oxygen meter and probe

15.7.1 YSI Model #5000 with a range from 0.0 to 60.0 mg/L and a temperature range of -5.0° to +50.0° C.

15.7.2 YSI Oxygen probe #5010.

15.8 Orion PerpHect pH Meter model 370 or equivalent pH meter and probe

15.9 Balance capable of weighing 150 grams with a sensitivity of 1.0 grams and weighing 10.0 grams with a sensitivity of 1.0 milligrams.

NOTE: Balances are calibrated in accordance with GL-LB-E-002 for Balances.

15.10 Incubator capable of maintaining a controlled temperature of 20° ± 1.0° C.

15.11 Aluminum or plastic weigh boats

15.12 Stir plate

15.13 Magnetic stir bars

15.14 Kimwipes

15.15 Parafilm

15.16 Carboy

15.17 Barometer (via the National Weather Service website www.erh.noaa/chs/)

16.0 REAGENTS

16.1 Reagents and solutions:

16.1.1 Deionized (DI) Reagent water (Refer to GL-LB-E-016).

16.1.2 Starch indicator solution

16.1.3 HACH BOD Nutrient Buffer Pillows or equivalent

16.1.3.1 HACH BOD Nutrient Buffer Pillows for preparation of 19 L of dilution water APHA Formulation (Cat# 14863-98) or equivalent.

16.1.3.2 HACH BOD Nutrient Buffer Pillows for preparation of 6 L dilution water APHA Formulation (Cat# 14862-66) or equivalent.

16.1.3.3 HACH BOD Nutrient Buffer Pillows for 300mL sample APHA Formulation (Cat# 14160-66) or equivalent.

16.1.4 Polyseed inoculum solution (gel capsules) or equivalent.

16.1.5 Potassium iodide (KI), 10% (ready to use solution)

16.1.6 Sodium hydroxide (NaOH)

16.1.7 Concentrated sulfuric acid (H_2SO_4)

16.1.8 Sodium sulfite (Na_2SO_3)

16.1.9 HACH Voluette Analytical Standards (Ampules) or equivalent, (GGA) Glucose/Glutamic Acid Standard (ready to use)

16.1.10 Premade purchased pH 4, pH 7, and pH 10 buffers

16.2 Preparation of solutions:

16.2.1 Sodium Hydroxide Solution (0.1 N)

16.2.1.1 In a one liter volumetric flask, dissolve 4.0 g of NaOH in DI water.

16.2.1.2 Bring to volume with DI water and mix well.

NOTE: This solution is good for up to one year after preparation or vendor expiration date, whichever comes first.

16.2.2 Sodium Sulfite Solutions

16.2.2.1 For a 0.025 M solution, in a 250 mL volumetric flask dissolve 0.7876 f of Na_2SO_3 in DI water.

16.2.2.2 For a 0.125 M solution, in a 250 mL volumetric flask, dissolve 3.938g of Na_2SO_3 in DI water.

16.2.2.3 Bring to volume with DI water and mix well.

NOTE: This solution should be prepared daily.

16.2.3 BOD Dilution Water

16.2.3.1 Clean the plastic carboy thoroughly with several rinsing's of DI water.

NOTE: It is recommended that the carboys be cleaned bimonthly with detergent to ensure proper cleanliness.

16.2.3.2 Fill the plastic carboy to either the 19 L or 6 L mark with DI water.

16.2.3.3 Place the cap on the carboy and mix thoroughly by shaking. This will also aerate the solution.

NOTE: An alternate method is to store the deionized water without adding chemicals until ready for use, preferably 24 hours prior. The addition of chemicals to the container before seed preparation is necessary.

16.2.3.4 Make sure that the cap is firmly on the carboy and store at room temperature until needed.

16.2.3.5 Immediately before using the dilution water add HACH Nutrient Buffer Pillows described in section 16.1.3. Ensure that the initial dissolved oxygen (DO) reading of the blank is within the range of 7.0 mg/L to 9.0 mg/L. (DO) values closer to 9.0 will increase sensitivity of the test. An aquarium bubbler will help increase (DO) concentrations.

16.2.4 Seed Inoculum Preparation:

16.2.4.1 Place 500 mL of the prepared dilution water into a 500 mL Erlenmeyer flask with a stir bar.

16.2.4.2 Add one gel capsule of the polyseed inoculum into the dilution water.

16.2.4.3 Briskly stir the solution for a minimum of one hour to thoroughly rehydrate the inoculum.

NOTE: The solution is good for up to six hours after preparation.

16.2.5 1:50 Sulfuric Acid Solution

In a glass container, dilute 1 mL of concentrated sulfuric acid to 50 mL with DI water.

NOTE: This solution is good for one year after preparation or vendor expiration, whichever comes first.

17.0 PREPARATION OF SAMPLES

17.1 Allow each sample to "warm" to room temperature (20 ± 3 °C). The temperature is then checked with a calibrated thermometer.

NOTE: For faster warm-up time, secure the lid to the sample bottle and place in warm water. Monitor the temperature until a reading of 20 ºC is reached

17.2 Check for the presence of residual chlorine

17.2.1 Pour a 50 mL sample aliquot into a clean 250 mL beaker. Repeat for each client sample in the batch.

17.2.2 Add 5 mL of the 1:50 sulfuric acid solution to each sample aliquot using a regular 5 mL pipet (or equivalent) and mix.

17.2.3 Add 5 mL of the 10% potassium iodide solution to each aliquot using a 5 mL pipet (or equivalent) and mix.

17.2.4 Add 1.5 mL of the starch indicator solution to each 250 mL beaker using a 5 mL pipet or an eyedropper and mix.

17.2.5 Observe the color of the treated sample aliquot. A blue color will develop if chlorine is present. If the blue color remains after 10 minutes has elapsed, follow procedure in steps 17.2.5.1 to 17.2.5.3.

17.2.5.1 Using a 1.5 mL transfer pipet, add the 0.025 M sodium sulfite solution or the 0.125 M sodium sulfite solution drop wise while swirling the aliquot. Count each drop as it is added.

17.2.5.2 Continue to add the sodium sulfite solution until the blue color disappears for at least 30 seconds.

17.2.5.3 Record the number of drops required to dechlorinate the 50 mL sample aliquot in the BOD data entry screen in AlphaLIMS.

17.3 Transfer sample aliquots to beakers in volumes as needed for the analysis. These aliquots are referred to as the run portions.

17.4 Add drops of 0.025 M or .125 M sodium sulfite solution to the run portion relative to the number required to dechlorinate the 50 mL sample and swirl the run portion to mix completely.

NOTE: The addition of sodium sulfate must not dilute the sample by more than 0.5%.

Examples: If it took 6 drops to dechlorinate 50 mL, it will take 54 drops to dechlorinate 450 mL of sample. If it took 3 drops to dechlorinate 50 mL, it will take 27 drops to dechlorinate 450 mL of sample.

17.5 Transfer the run portion to a beaker, add a stir bar and place on the stir plate/pH meter. (Refer to section 21.1.1 for the pH meter calibration procedure.)

17.6 Immerse the pH probe into the solution and turn on the stir plate. Record the pH of the sample in AlphaLIMS.

17.7 If the pH is not within 6.0 to 8.0 SU, adjust the pH to 7.0-7.2 using either 0.1 N sodium hydroxide or 1:50 sulfuric acid solution. Record the initial and adjusted pH into the BOD data entry screen in AlphaLIMS.

18.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

18.1 Refer to the YSI Model #5000 Dissolved Oxygen Meter Manual for instructions

on changing the probe membrane.

18.2 Rinse the probe thoroughly with DI water.

18.3 Disassemble the probe cover and lightly blot the membrane with a tissue.

18.4 Reassemble the probe and cover and place in a 300 mL BOD bottle that is filled with 1 inch of DI water.

18.5 Current barometric readings may be obtained from the National Weather Service website www.erh.noaa.gov/chs/.

18.6 Current dissolved oxygen table may be obtained from the USGS DO Tables website (https://water.usgs.gov/software/DOTABLES/)

19.0 QUALITY CONTROL (QC) REQUIREMENTS

19.1 Frequency of QC:

19.1.1 A matrix duplicate is analyzed for every batch of ≤ 10 samples, and for each set of ten samples in batches with > 10 samples.

19.1.2 A method blank and a glucose/glutamic acid (GGA) standard are analyzed for every batch of ≤ 20 samples to monitor the quality of the dilution water, seed effectiveness, and procedure technique. The GGA standard is reported as a laboratory control sample (LCS). If required by contract, LCS duplicates are analyzed with each batch of samples. All three dilutions are averaged together and reported for the GGA LCS.

19.2 Acceptance limits:

19.2.1 Matrix relative percent difference (RPD): Refer to current control limits

19.2.2 Method blank: ≤ 0.20 mg/L

19.2.3 Glucose/Glutamic acid (GGA) standard (LCS): 198 ± 30.5 mg/L

19.2.4 LCS RPD: Refer to current control limits.

19.2.5 A residual oxygen reading of at least 1.0 mg/L

19.2.6 A DO depletion of at least 2.0 mg/L

19.2.7 Calibration Blank: <0.20 mg/L

19.2.8 DO meter calibration when read against USGS DO table: ± 0.20 mg/L of published value at given temperature and barometric pressure.

19.3 Handling out-of-control situations:

19.3.1 After final dissolved oxygen reading, the blanks and seeds are checked for compliance to the acceptance limits. (Refer to section 19.2.) If the DO reading for the blank exceeds the acceptance criteria, the affected clients should be notified by project management and the BOD reported for the samples in the analytical batch should state that blank contamination is indicated.

19.3.2 If the GGA standard recovery does not fall within the acceptance criteria, the data associated with this standard is unacceptable and should not be reported. Notify the project manager immediately.

19.3.3 2:1 Depletion Rule: If the final DO is less than 1 mg/L (meaning the sample was under-diluted) or the oxygen depletion is less than 2 mg/L (meaning the sample was over-diluted), the data is flagged with a "d" as not meeting the 2:1 depletion rule. All values from the sample that meet the 2:1 rule are added together and then averaged to obtain the final concentration of the sample.

NOTE: Samples with low BOD concentrations may not meet this rule as oxygen depletion of at least 2 mg/L may not be obtained. In this case, the neat sample (300 mL) will be reported with a "d" flag.

19.3.4 If blanks change by +/- 0.20 mg/L on the 5-day readback, the DO probe needs to be checked prior to accepting the results. Probe maintenance including a new membrane or a thorough cleaning of the probe end (scrubbing with pencil eraser) usually resolves the readback issues. Ensure the probe is in optimal condition and is accurately calibrated each day before use.

19.3.5 If more than two dilutions are used to obtain a reportable value and the difference between the highest and lowest replicate is greater than 30% difference, flag the average reportable value with an "e". The data is not rejected and is reportable, however it must be flagged. This applies to seed control dilutions and authentic samples.

19.3.6 If the difference between the calibrated DO meter reading at a specific temperature and barometric reading is outside of ± 0.20 mg/L of published DO table value, action must be taken to resolve the problem (i.e. clean or replace probe and/or membrane, check meter for malfunctions, etc.). Only after a successful calibration with acceptable readbacks are obtained can be used for analytical testing.

20.0 RUN SEQUENCE

20.1 Dilution water blank (method blank)

20.2 Dilution water blank duplicate (method blank duplicate)

20.3 Seeded GGA standard - 3 mL of the standard solution

20.4 Seeded GGA standard - 3 mL of the standard solution (duplicate)

20.5 Seeded GGA standard - 3 mL of the standard solution (duplicate)

20.6 Seeded blank: 10 mL of seed

20.7 Seeded blank: 15 mL of seed

20.8 Seeded blank: 20 mL of seed

20.9 Seeded Samples 1 through x where x ≤ 10

20.10 Seeded Sample x duplicate (per 10 samples)

20.11 Repeat steps 20.9 through 20.10 for up to 20 samples

21.0 PROCEDURE

21.1 Calibration of Instrumentation:

21.1.1 pH Meter Calibration, see GL-GC-E-008

21.1.2 Calibration of the Dissolved Oxygen Meter:

21.1.2.1 Remove the DO probe from BOD bottle containing 1 inch of DI waster. Thoroughly rinse the probe, stirrer, and membrane with DI water.

21.1.2.2 COMPLETELY dry the DO membrane by lightly blotting with a Kimwipe and then return probe to BOD bottle containing 1 inch of DI water.

NOTE: Any water droplets left on the DO membrane will cause an error in calibration.

21.1.2.3 Allow the DO probe to stabilize for a minimum of 15 minutes in the BOD bottle before attempting an instrument calibration.

21.1.2.4 From the main mode, press the [CALIBRATE] soft-key to enter the calibration screen.

21.1.2.5 Refer to section 15.17 for determining the barometric pressure. If necessary, calibrate the barometer on the DO meter by pressing the [DO CAL] soft-key. Then press the [NEXT] soft-key until the barometric pressure is flashing. Using the [UP] and [DOWN] soft-keys, enter the actual barometric pressure as indicated on the lab barometer or official NOAA website.

21.1.2.6 Press [ENTER] to confirm new barometric pressure “Pressure Setting Saved” will be displayed.

21.1.2.7 Next press the [AUTO CAL] soft-key. “DO Calibration Saved” will be displayed.

21.1.2.8 Press the [MODE] key to return to the Main Mode/Measurement Screen.

21.2 DO Calibration Verification

21.2.1 To verify the calibration from 21.1.2, compare the saturated air DO reading from the meter to the DO tables listed on the USGS website

outlined in 18.6. If the criteria of ± 0.20 mg/L is met, the verification is complete.

21.2.2 Record the meter DO reading, published DO reading, temperature, and barometric reading in the batch ext data for each being analyzed.

21.3 Analysis:

21.3.1 The standards, samples, and quality control (QC) samples are introduced to the run by adding them to the bottles. A sequence of ID numbers for the bottles is recorded in AlphaLIMS.

21.3.2 The BOD bottles are set up in a sequence according to each sample dilution requirement. A minimum of three dilutions is required on all samples analyzed. Refer to the Appendix for suggested dilutions. If less than 3 mL of sample is used in a dilution, refer to the volumes of 100x diluted sample to use for the testing.

21.3.3 Samples are added to each bottle. The required volume of 3 mL of seed is added only immediately prior to filling the BOD bottle with dilution water. (This is done to minimize the initial dissolved oxygen depletion that can occur between the sample and the seed). When a bottle contains more than 67% of the sample after dilution, add the contents of a HACH Nutrient Buffer Pillow for 300 mL (see 16.1.3.3) use to provide nutrients to the sample.

21.3.4 After filling the bottle, place the DO probe into the sample bottle. Avoid entrapping air bubbles into the sample bottle.

21.3.5 Turn the probe stirrer **ON** and let the O_2 reading stabilize for 2 to 3 minutes. Record the stabilized reading into the appropriate column in the BOD data entry screen in AlphaLIMS. (A minimum initial DO of 7.0 ppm is required before proceeding with the analysis. If the levels are below 7.0 ppm, recap the carboy and shake/aerate the dilution water. Recheck the DO content then proceed if within the 7.0 to 9.0 ppm range.)

NOTE: Samples containing more than 9 mg DO/L at 20° C are supersaturated. Reduce DO to saturation by bringing the sample to 20° C and agitating with vigorous shaking or aerating with clean filtered compressed air.

21.3.6 Turn the probe stirrer off. Carefully remove the probe from the sample bottle and rinse with DI water.

21.3.7 Immediately after each bottle is read. Insert a glass stopper into the bottle, making sure that all of the air is displaced and no air bubbles are present. Then place the plastic cap on top of the BOD bottle.

21.3.8 Repeat steps 21.3.4 through 21.3.7 for each sample and quality control sample in the batch, turning the probe stirrer off before removing the probe from each bottle.

21.3.9 When the dissolved oxygen readings have been completed, rinse the probe thoroughly with DI water, blot dry (lightly) with Kimwipes and place into BOD bottle filled with 1 inch of DI water.

21.3.10 When the initial oxygen readings have been completed and the stoppers and caps have been placed on the top, transfer the bottles to the BOD incubator. Tag the front row of bottles with the appropriate readoff date.

Example: If set up is on Thursday, a readoff date of Tuesday, the following week, will be placed on the bottles as indicated.

21.3.11 Incubate the bottles for five days (± 6 hours) at 20° ± 1° C.

21.3.12 Calibrate the DO meter probe on the fifth day of incubation as in sections 21.1.2 and 21.2.

21.3.13 Remove the bottles from the incubator.

21.3.14 Remove the stopper and cap from a bottle and immediately insert the DO probe into the bottle and turn the probe stirrer on. Allow the reading to stabilize for 1 to 2 minutes. Record the final oxygen reading into the BOD data entry screen in AlphaLIMS.

21.3.15 Repeat step 21.3.14 for each bottle.

21.4 Calculation/Reporting of Results:

21.4.1 The final DO reading is subtracted from the initial DO reading. The difference is called the depletion of the sample. This is used with other numbers calculated from different dilutions, of the same sample, to obtain

$$\text{BOD mg/L} = \frac{[(Is-Fs) - S] \times 300}{V\ \text{sample}}$$

Where:

Is = Initial DO reading in the sample

Fs = Final DO reading in the sample

S = Seed correction factor

300 = Total volume of the BOD bottle

V sample = Total sample volume in mL

21.4.2 The seed correction factor is calculated by the following:

21.4.2.1 The depletion from the 10 mL seeded blank is multiplied by the ratio of the amount of seed added to each sample bottle, and the amount added for it. The ratio for this seeded blank calculates to 0.30 mg/L.

21.4.2.2 The depletion from the 15 mL seeded blank is multiplied by the ratio of the amount of seed added to each sample bottle, and the amount to it. The radio for this seeded blank calculates for 0.20 mg/L.

21.4.2.3 The depletion from the 20 mL seeded blank is multiplied by the ratio of the amount of seed added to each sample bottle, and the amount to it. The ratio for this seeded blank calculates to 0.15 mg/L.

21.4.2.4 All of the values from the seeded blanks that meet the 2:1 rule are added together then averaged to obtain the seed correction factor that is subtracted from each calculated value to obtain a BOD concentration.

21.4.2.5 The optimum seed correction factor listed in the literature is 0.6 to 1.0 mg/L. However, values outside this range can be used as long as the LCS GGA passes.

22.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Refer to the YSI Model 5000 Dissolved Oxygen Meter manual.

23.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for General Chemistry Data Review and Packaging and GL-LB-E-005 for Data Review and Validation.

24.0 DATA TRANSMITTAL

When a batch is given "DONE" status, data are made available to reporting personnel.

25.0 RECORDS MANAGEMENT

All data associated with this analytical procedure, including calibration and maintenance logs, are maintained as quality documents in accordance with GL-QS-E-008 for the Quality Records Management and Disposition.

26.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to the manual for the dissolved oxygen meter.

27.0 LABORATORY WASTE HANDLING AND DISPOSAL

Refer to the Laboratory Waste Management Plan (GL-LB-G-001) for the proper disposal of sample and reagent wastes from this procedure.

28.0 METHOD VERIFICATION

A 48-hour holding time used in this SOP is a variation of the 24-hour holding time as listed in Standard Methods 22nd Edition 5210 B-01. This variation is taken from the EPA Federal Register listed in Section 30.3.

29.0 REFERENCES

29.1 Methods for the Analysis of Water and Waste, EPA 600/4-79-020, Method 405.1, “Biochemical Oxygen Demand.”

29.2 Standard Methods for the Examination of Water and Wastewater, 22nd Edition, Method 5210 B-01, "5 Day BOD Test."

29.3 EPA Federal Register 40 CFR, Part 136, Table II.

29.4 YSI Model 5000 Dissolved Oxygen Meter Manual.

30.0 HISTORY

Revision 27: Updated to clarify analytical start time and updated sodium sulfate concentration.
Revision 26: Added reference website to USGS and amended calibration steps.
Revision 25: Updated Acceptance Criteria.
Revision 24: Added table to Appendix
Revision 23: Orion perpHect pH Meter model 370 and premade purchased buffers added to procedure.

APPENDIX

BOD Measurable with Various Dilutions of Samples

Using Percent Mixtures		By Direct Pipetting into 300 mL Bottle	
% Mixture	Range of BOD	mL	Range of BOD
0.01	20,000-70,000	0.02*	30,000-105,000
0.02	10,000-35,000	0.05*	12,000-42,000
0.05	4,000-14,000	0.10*	6,000-21,000
0.1	2,000-7,000	0.20*	3,000-10,500
0.2	1,000-3,500	0.50*	1,200-4,200
0.5	400-1,400	1.0*	600-2,100
1.0	200-700	2.0*	300-1,050
2.0	100-350	5.0	120-420
5.0	40-140	10.0	60-210
10.0	20-70	20.0	30-105
20.0	10-35	50.0	12-42
50.0	4-14	100	6-21
100	0-7	300	0-7

* Use aliquots below of a 1:100 dilution (3 mL to 300 mL) of sample to dilution water

mL to enter in LIMs	mL of 1:100 sample: dilution water
0.02	2
0.05	5
0.1	10
0.2	20
0.5	50
1.0	100
2.0	200

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE
FOR

CHEMICAL OXYGEN DEMAND (COD) DIGESTION REACTOR METHOD

(GL-GC-E-061 REVISION 21)

APPLICABLE TO METHODS:
HACH Method 8000
EPA 410.4

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR CHEMICAL OXYGEN DEMAND (COD) DIGESTION REACTOR METHOD

2.0 METHOD CODE

2.1 HACH Method 8000

2.2 EPA 410.4 (Method variations are discussed in Section 29.0)

3.0 METHOD OBJECTIVE/PURPOSE

This standard operating procedure (SOP) describes the procedure used to determine the concentration of chemical oxygen demand (COD) in water samples.

4.0 METHOD SUMMARY

Two milliliters of a sample is added to a digestion vial containing potassium dichromate, a strong oxidizing agent. After mixing thoroughly, the vial is placed into a reaction digester block and heated at 150 ˚C for 2 hours. After the reaction time is complete, the vial is removed from the block and allowed to cool to room temperature. The digestion vial is then placed directly into a spectrophotometer. The COD concentration is related to the absorbance of a set of standards.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

Holding time is 28 days from the time and date of collection until the start of analysis unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples must be stored in glass containers. If plastic containers are used, it must be shown that no organic compounds are present in the container material.

7.2 Samples are preserved with sulfuric acid to a pH of $\leq$ 2.

7.3 COD samples must be stored at 0˚ $\leq$ 6˚ C in accordance with GL-SR-E-001 for Sample Receipt, Login, and Storage.

8.0 INTERFERENCES/LIMITATIONS

8.1 Chloride interference:

8.1.1 Chloride is the primary interference when determining COD concentrations.

8.1.2 The COD vial contains enough mercuric sulfate to eliminate chloride interferences up to 1000 mg/L.

8.1.3 Samples with an estimated chloride concentration > 1000 mg/L must be diluted to reduce the chloride concentration. If samples are presumed to contain > 1000 mg/L chloride and the dilution method causes the COD concentration level to be below detection levels, refer to the HACH Company "Water Analysis Handbook" to correct the problem.

8.2 Limitations:

The highest standard in the calibration curve is a 1000 mg/L standard; therefore, if the sample concentration exceeds the absorbance of the 1000 mg/L standard, the sample must be diluted and redigested so the sample concentration falls within the calibration range.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Calibration range: 20 to 1000 mg/L.

9.2 Method detection limit (MDL): Refer to current MDL study.

9.3 Method precision: Refer to current SPC limits.

9.4 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

10.2 Continuing Calibration Blank (CCB): An aliquot of reagent water or other blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

10.3 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample, periodically throughout the run sequence. Its purpose is to determine whether the analytical sequence is in control during sample analysis. It may be prepared from the same source as the calibration standards and is usually of varied concentration.

10.4 Independent Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination after injection of the mid-level ICV.

10.5 Independent Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of blank or sample matrix. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

10.6 Instrument Performance Check Solution (IPC): A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

10.7 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

10.8 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

10.9 Lab-wide used definitions can be found in GL-QS-B-001 the Quality Assurance plan.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data are obtained, they are entered into AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

COD DIGESTION VIALS CONTAIN MERCURIC SULFATE, POTASSIUM DICHROMATE, SILVER SULFATE, SULFAMIC ACID, AND SULFURIC ACID. ORAL INGESTION MAY BE FATAL! POISONING CAN OCCUR BY INHALATION OR SKIN ADSORPTION. THE SOLUTIONS CAUSE SEVERE BURNS. HANDLE THE VIALS CAUTIOUSLY AND WEAR GLOVES. AVOID CONTACT WITH EYES, SKIN, AND CLOTHING. AVOID BREATHING SOLUTION SPRAY. WHEN HEATED, MERCURIC SULFATE SOLUTION CAN DECOMPOSE AND RELEASE MERCURY VAPOR.

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDS forms are maintained in the laboratory.

13.3 Gloves are required when handling chemicals or samples.

13.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

13.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, complete an accident report form and turn it in to the safety committee.

13.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

13.8 Refer to SOP GL-LB-N-001 Safety, Health and Chemical Hygiene for additional general safety and health information pertaining to the laboratory.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Spectrophotometer for use at 620 nm with a light path of 1.25 cm.

15.2 Cell holder - 1.25 cm

15.3 Stray-light filter - 420 -890 nm

15.4 Glass volumetric flasks (Capacity needed - 100 mL)

15.5 Class A volumetric pipets (Capacity needed - 2 mL, 25 mL)

15.6 Air displacement pipet - range required 1 -5 mL

15.7 Micropipet with tips; range required 0.1 - 1 mL

NOTE: The pipets used in step 15.6 and 15.7 must be calibrated in accordance with GL-LB-E-010 for the Maintenance and Use of Air Displacement Pipets.

15.8 Locked Excel Spreadsheet

15.9 COD Reactor Digestion Block--25 vial capacity with timer shut-off capability

15.10 Wire test tube rack

15.11 Thermometer capable of measuring to 150 ± 2° C

NOTE: Thermometers are verified in accordance with GL-QS-E-007 for Thermometer Verification.

16.0 REAGENTS

16.1 ASTM TYPE I deionized (DI) water

16.2 COD digestion reagent vials are purchased from a certified vendor and are rated as follows:

16.2.1 High range [0 mg/L - 1500 mg/L COD]

16.3 Potassium acid phthalate standards prepared from 10,000 mg/L potassium acid phthalate stock. Stocks can be purchased from certified standard vendors.

16.3.1 Potassium acid phthalate is to be dried overnight at 120 °C to allow for constant weight of the standard.

17.0 PREPARATION OF SAMPLES

Samples are prepped according to section 22.0.

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards and their preparation is maintained in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

18.2 Calibration standards:

18.2.1 Weigh 8.5 g of potassium acid phthalate and dilute to 1 L of DI water to make the 10,000 mg/L potassium acid phthalate (KHP) stock. This stock is assigned a one year expiration date from the date of preparation or the parent chemical expiration date, whichever comes sooner. Stocks can be purchased from certified standard vendors.

18.2.2 Calibration standards are prepared from the 10,000 mg/L potassium acid phthalate (KHP) stock solution.

18.2.3 Calibration standard preparation

18.2.3.1 Calibration standards are prepared directly from the 10,000 mg/L KHP standard and are used to establish a calibration curve.

18.2.3.2 The calibration standards can be kept for up to 30 days if stored in the dark or otherwise protected from light.

18.2.3.3 Follow these steps when preparing calibration standards:

18.2.3.3.1 Partially fill a 100 mL volumetric flask with DI water.

18.2.3.3.2 Pipette a specific volume of the 10,000 mg/L KHP stock standard in the flask. (The volume pipeted is dependent upon the concentration of the standard being prepared.) (Refer to Section 18.2.3.4 for required volumes.)

18.2.3.3.3 Bring to volume with DI water and mix thoroughly.

18.2.3.4 Calibration standard preparation table:

Calibration Standard mg/L	Volume of 10,000 mg/L KHP needed (mL)
20	0.2
75	0.75
100	1.0
150	1.5
500	5.0
1000	10.0

18.2.4 LCS, high range (500 mg/L): A volume of 5 mL of the 10,000 mg/L potassium acid solution is brought up to a final volume of 100 mL with DI water.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

19.1 HACH COD Reactor Digestion Block:

19.1.1 Set the **Power** switch to the **On** position and the **Temperature** switch to 150˚ C.

19.1.2 Verify that the timer is set to infinity.

19.1.3 Allow the digestion block to heat to 150˚ C.

NOTE: Approximate warm-up time: 30 minutes

19.1.4 When the heating indicator light begins to cycle on and off, the block temperature is stable. Record the temperature of the digestion block on the COD logbook page in AlphaLIMS.

19.1.5 The digestion block is now ready for vial digestion.

19.1.6 Set the timer switch to the timer position and set the Elapsed Time Indicator to a 2-hour digestion.

19.2 Spectrophotometer:

19.2.1 Begin the start-up after samples have been digested and are cooling.

19.2.2 Put the 1.25 cm cuvette holder in place as needed.

19.2.3 Insert the 420 to 890 nm stray light filter into position.

NOTE: The stray light filter must be wiped with a Kimwipe prior to use.

19.2.4 Changing a stray light filter:

19.2.4.1 Removing a filter:

19.2.4.1.1 Push back the handle of the filter slightly to disengage the lock.

19.2.4.1.2 Lift the filter straight up.

19.2.4.2 Inserting a filter:

19.2.4.2.1 Carefully insert the proper filter into position.

19.2.4.2.2 The filter will automatically lock into place.

19.2.4.2.3 Do not touch the surface of the filter with your fingers. If you do, clean the filter prior to insertion.

19.2.5 Adjust the wavelength to 620 nm.

19.2.6 Carefully wipe the calibration blank COD vial with a Kimwipe and place the vial into the cuvette holder.

19.2.7 Close the lid of the cuvette holder.

19.2.8 Set the **Mode** switch to *ABS*.

19.2.9 Adjust the **100% T/OA Coarse** knob to approximately 0.000.

19.2.10 Adjust the **100% T/OA Fine** knob to exactly 0.000.

19.2.11 Record the 0.00 absorbency reading in the calibration section of the COD data entry screen in AlphaLIMS.

19.2.12 Remove the COD vial. The spectrophotometer is ready to be used.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Correlation coefficient: 0.995 or greater for the calibration curve.

20.2 Frequency of QC:

20.2.1 A matrix spike, and matrix duplicate are analyzed for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples.

20.2.2 LCS and method blank (MB): An LCS and MB are analyzed with every batch of ≤ 20 samples.

20.2.3 An LCS Duplicate is analyzed if requested by a client.

20.2.4 MDL and/or MDL verifications are performed every 6 months. These values are submitted for quality review.

20.2.5 Linear Calibration Range (LCR) checks are performed on a 6 month basis. The high standard of the curve is read back against the calibration and must recover ±10%. If this procedure fails, the problem must be investigated and rectified. Alternatively, the recovery of the high standard concentration analyzed with each batch can be used to verify the LCR.

20.3 Acceptance limits:

20.3.1 Matrix Duplicate relative percent difference (RPD): 0-5% RPD.

20.3.2 Matrix spike recovery: 90-110%.

20.3.3 Method blank, CCB, and ICB < lowest calibration standard

20.3.4 LCS: 90-110%

20.3.5 LCS RPD: Refer to current SPC limits

20.3.6 ICV and CCV: ± 10% of known value

20.3.7 Matrix Spike Duplicate relative percent difference (RPD): Refer to current SPC limits.

20.4 Out-of-control situations

Digested vials with absorbances greater than the absorbance of the highest calibration standard: Another sample aliquot must be diluted then digested to bring the absorbance to a level between the absorbance of the lowest and highest calibration standard.

21.0 TYPICAL RUN SEQUENCE

21.1 Calibration blank

21.2 Typical Calibration standards:

21.2.1 High range: 20 mg/L, 75mg/L, 150 mg/L, 500 mg/L, and 1000 mg/L

21.3 ICV and ICB

21.4 MB an LCS

21.5 Samples 1 through x where x ≤ 10

21.6 Sample x duplicate

21.7 Sample x spike

21.8 CCV and CCB

21.9 Repeat steps 21.5 through 21.8 for every set of 10 samples in the batch.

22.0 PROCEDURE

22.1 Analysis:

22.1.1 Record the identification numbers of the quality control samples, calibration and method blanks, standards, and samples in the appropriate column in the COD data entry screen in AlphaLIMS.

22.1.2 Label each vial appropriately.

22.1.3 Remove the cap from the COD digestion reagent vial.

22.1.4 The calibration blank is prepared by holding the vial at an angle and pipetting 2.0 mL of DI water into the vial. (use 2.0 mL total volume for preparing standards or samples)

22.1.5 Replace the vial cap and tighten.

22.1.6 Hold the vial by the cap; invert gently several times to mix the contents.

22.1.7 Place the vial in the preheated COD digestion block.

22.1.8 Record the volume added to the digestion vial in the appropriate column of the COD data entry screen in AlphaLIMS.

22.1.9 Repeat steps 22.1.2 through 22.1.8 for each of the calibration standards required as found in 21.0. (Refer to 18.2.3.4 for standard preparation.)

22.1.10 Repeat steps 22.1.2 through 22.1.8 for each sample, method blank, laboratory control sample, matrix duplicate, and matrix spikes in the batch.

22.1.10.1 Matrix spike nominal concentration = 500 mg/L.

A volume of 0.1 mL of the 10,000 mg/L COD solution is added to 2 mL of the sample to create the matrix spike.

22.1.10.2 LCS nominal concentration = 500 mg/L

A volume of 2.0 mL of the LCS solution from 18.2.4 is added to the vial.

NOTE: If the solution in the vial turns green upon addition of the sample, a dilution of the sample needs to be made in order to bring the sample concentration into range. Document any dilutions in the appropriate column in the COD data entry screen of AlphaLIMS.

22.1.11 When all the vials have been loaded into the COD digestion block, set the **Timer** switch to the Timer position and set the **Elapsed Time Indicator** to 120 minute.

22.1.12 After two hours have past, the COD digestion block will automatically turn the heater block off and will start to cool down.

22.1.13 Wait approximately 20 minutes for the vials to cool to 120˚ C or less.

22.1.14 Remove the vials from the COD digestion block, invert each several times, then place into the wire rack and allow them to cool to the touch.

22.1.15 While the vials are cooling, follow the instructions in section 19.2 to start-up the spectrophotometer.

22.1.16 Measure the absorbency of all standards, blanks, samples and quality control samples. Record the absorbances in the COD data entry screen in AlphaLIMS.

22.2 Calculation/reporting of results:

22.2.1 The COD concentration is calculated using the following formula:

$$COD = C \times D_F$$

Where:

COD = Chemical Oxygen Demand, mg/L

C = Concentration of sample read from the calibration curve in mg/L

D_F = Dilution factor

22.2.2 The relative percent difference between matrix duplicates is calculated as:

$$\frac{[COD]_{original\ sample} - [COD]_{duplicate}}{[COD]_{average}} \times 100$$

22.2.3 The percent spike recovery is calculated using the formula below:

$$\frac{[\text{COD}]\text{spiked sample} - [\text{COD}]\text{sample}}{\text{Nominal Concentration}} \times 100$$

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURES

23.1 COD Digestion Block:

Turn the **Power** switch on the back of the reactor to the **Off** position.

23.2 Spectrophotometer:

23.2.1 Remove the vial from the cuvette holder. Close the lid of the cuvette holder.

23.2.2 Turn the **Mode** switch to the **Off** position.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

Refer to GL-GC-E-092 for General Chemistry Data Review and Packaging.

25.0 DATA TRANSMITTAL

When a batch is given "DONE" status, the data are automatically available to reporting personnel.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

27.1 HACH COD digestion block:

Any routine instrument/equipment maintenance performed on the COD reactor should be done by a qualified repair technician. Reference the HACH COD reactor digestion block manual for trouble-shooting or contact the in-house repair technician.

27.2 Spectrophotometer:

27.2.1 A wavelength calibration check is performed on the Thermospectronic quarterly using a didymium filter. If the instrument fails to meet the acceptance criteria as defined in the filter's instructions, notify the instrument service technician.

27.2.2 Refer to the Operator's Manual Spectronic® 20+ Series Spectrophotometer for Thermospectronic.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

28.1 All wastes from the COD digestion reagent vials contain high levels of mercuric sulfate.

28.2 All liquid wastes are collected in original vials by waste management.

28.3 All vials are rinsed thoroughly with deionized water and the rinsate collected into the waste jug. The vials are then disposed of properly.

28.4 For the proper handling and disposal of all types of wastes from this procedure, refer to GL-LB-G-001, the Laboratory Waste Management Plan.

29.0 METHOD VERIFICATION AND VARIATION

29.1 Method detection limit studies are performed in accordance with the GL-LB-E-001 for The Determination of Method Detection Limits.

29.2 The method deviates from EPA 410.4 by not making the final determinations of COD concentration using semi-automated colorimetry.

29.3 This procedure deviates from EPA 410.4 by using the manufacturer's suggested high level wavelength of 620 nm instead of the published 600 nm.

30.0 REFERENCES

30.1 HACH Company, Water Analysis Handbook, 2nd Edition, pp. 494-495, 502-503.

30.2 EPA Method 410.4, The Determination of Chemical Oxygen Demand by Semi-Automated Colorimetry, August 1993.

30.3 Operator's Manual Spectronic® 20+ series, Spectrophotometer.

31.0 HISTORY

Revision 17: Referenced matrix spike recovery 90-110%.

Revision 18: Updated to remove LCS low range detection limits.

Revision 19: Updated reagents sections to include potassium acid phthalate. Updated standards sections with correct name. Updated section 22.1.10 with correct nominal concentration for MS and LCS.

Revision 20: Update RPD limits for sample duplicate and add matrix spike duplicate RPD statement.

Revision 21: Removed reference to the use of Method 5220D 2011

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

CYANIDE SAMPLE DISTILLATION

(GL-GC-E-067 REVISION 23)

APPLICABLE TO METHODS:
EPA Method 335.4
SW-846 Methods 9010B and 9010C
SW-846 Methods 9012B
Standard Methods 22nd Edition, 4500 CN^- C-2011

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1.0 STANDARD OPERATING PROCEDURE FOR CYANIDE SAMPLE DISTILLATION

2.0 METHOD CODE

2.1 EPA Method 335.4

2.2 SW-846 Methods 9010B, 9010C, and 9012B

2.3 Standard Methods 22nd Edition, 4500-CN^- C-2011

3.0 METHOD OBJECTIVE/PURPOSE

This standard operating procedure provides the necessary instructions for distilling samples of various matrices prior to analysis to determine the concentration of cyanide (compounds containing the cyano group, CN) present.

Refer to GL-GC-E-095 for the analytical SOP.

4.0 METHOD SUMMARY

In this procedure, cyanide is released from cyanide complexes by acidification and heating. The cyanide in the form of hydrocyanic acid (HCN) is carried into a hydroxide scrubber solution. The cyanide in this solution is then determined by automated colorimetric means as detailed in GL-GC-E-095.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

5.4 Soil

5.5 Sludge

5.6 Oil

NOTE: Clients may request that this analysis be performed on miscellaneous liquid, solid, air, or stack samples. In these cases the procedure is modified as necessary.

NOTE: DHEC requires SW-846 Methods 9012B to be run for any matrices other than drinking and wastewater when data are to be used for regulatory purposes.

6.0 HOLDING TIME

Holding time for non-South Carolina samples is 14 days from the time and date of collection until the start of analysis, unless otherwise specified by the contract. Samples reported for compliance in South Carolina must be analyzed within 24 hours of sample preparation.

NOTE: US EPA CLP requirements specify a holding time of 12 days following sample receipt by the contractor.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples should be stored in a 500 mL or larger plastic bottle.

7.2 Any liquid sample should be preserved with approximately 2 mL of 10 N sodium hydroxide per liter of sample.

7.3 The sample is stored at $0° \leq 6°$ C.

8.0 INTERFERENCES/LIMITATIONS

8.1 Possible sulfide interference is eliminated by the addition of bismuth nitrate as stated in SW-846 Methods 9010B, 9010C, and 9012B.

8.2 Oxidizing agents that decompose cyanides may be removed by the addition of ascorbic acid or sodium arsenite. SW-846 Methods 9010B and 9010C recommend sodium arsenite, while 9012B recommends ascorbic acid. Sodium arsenite appears to yield more consistent results.

8.3 Thiocyanates produce a positive interference when they are decomposed to cyanide by ultraviolet digestion. This interference can be reduced by manual distillation.

8.4 Interferences from nitrates and nitrites are eliminated by using sulfamic acid.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 5 to 500 µg/L

9.2 Calibration range: 5 to 200 µg/L

9.3 Method detection limit (MDL): Updated biannually (Refer to current study).

9.4 Method precision: Refer to current SPC (Statistical Process Control) limits.

9.5 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

10.2 Initial Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination after injection of the mid-level ICV.

10.3 Initial Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of Blank or sample matrix. The ICV is obtained from a source external to the laboratory and with a different lot number than the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

10.4 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD, and internal standards.

10.5 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

10.6 Total Cyanide: Refers to all inorganic cyanides present, including those as soluble salts or metal complexes.

10.7 Laboratory Duplicate (DUP, LCSD, MSD or PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory

conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

10.8 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

10.9 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until they have been fully trained and have demonstrated the ability to generate acceptable data. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

Sample preparation data is recorded in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

SULFURIC ACID, ACETIC ACID, AND SODIUM HYDROXIDE ARE HIGHLY CORROSIVE

POTASSIUM CYANIDE IS A CORROSIVE AND A CHEMICAL ASPHYXIANT.

POTASSIUM CYANIDE EMITS TOXIC FUMES WHEN HEATED OR MIXED WITH AN ACID.

USE CAUTION WHEN HANDLING. SODIUM ARSENITE IS A CARCINOGEN. AVOID INHALATION OR INGESTION.

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

13.1 Wear eye protection with side shields while in the laboratory.

13.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). Individual sample MSDS forms provided by the clients are also maintained.

13.3 Personal Protective Equipment

13.3.1 Gloves are required when handling the chemicals in this procedure. The gloves recommended for this procedure are:

13.3.1.1 Nitrile gloves for concentrated acids and bases, potassium cyanide, and sodium arsenite in neat form.

13.3.1.2 General purpose latex or vinyl gloves for sulfamic acid, bismuth nitrate, and magnesium chloride.

13.3.2 Work under a hood when using concentrated acids and bases.

13.4 Prior to handling radioactive samples, analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.4.1 Wear a plastic apron over lab coat when working with radioactive samples.

13.4.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

13.4.3 Prohibit admittance to immediate work area.

13.4.4 Post signs indicating radioactive samples are in the area.

13.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.4.6 Segregate radioactive wastes in the waste containers obtained from Waste Management.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

13.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

13.7 Refer to GL-LB-N-001 the Safety, Health and Chemical Hygiene Plan for additional general safety and health information pertaining to the laboratory.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives a list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from the cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Equipment

15.1.1 Simple Cyanide Distillation System with all related glassware

15.1.2 Vacuum source

15.1.3 Well ventilated hood

15.1.4 Analytical balance capable of weighing to 2 decimal places

NOTE: Balance must be calibrated in accordance with GL-LB-E-002 for Balances.

15.1.5 10 to 100 µL adjustable air displacement pipet

15.1.6 100 to 1000 µL adjustable air displacement pipet

15.1.7 1 to 5 mL adjustable pipet

15.1.8 Potassium iodide (KI) starch paper strips

15.1.9 Analytical balance capable of weighing to 4 decimal places

15.1.10 50 mL graduated cylinders

15.1.11 1 to 10 mL repeater pipet

15.1.12 TCLP Tumbler

15.1.13 10 mL Luer-lock syringe

15.1.14 Acrodisk, 0.45 µm pore syringe filters

15.1.15 1000 mL bottles

15.1.16 1 oz portion cups

NOTE: All pipets must be calibrated in accordance with GL-LB-E-010.

15.2 Glassware

15.2.1 Various sizes of volumetric flasks for reagent preparation

15.2.2 20 mL vials

16.0 REAGENTS

16.1 Raw materials:

16.1.1 ASTM Type I deionized (DI) water

16.1.2 Potassium cyanide, KCN (FW 56.11), certified standard (1 mL = 1000 µg CN^-)

16.1.3 Sodium hydroxide, NaOH (FW 40.00)

16.1.4 Sulfamic acid, H_3NO_3S (FW 97.10)

16.1.5 Bismuth nitrate pentahydrate, $Bi(NO_3)_3 \bullet 5H_2O$ (FW 485.07)

16.1.6 Magnesium chloride hexahydrate, $MgCl_2 \bullet 6H_2O$

16.1.7 Glacial acetic acid, CH_3COOH

16.1.8 Antifoam

16.1.9 Sodium arsenite, $NaAsO_2$

16.1.10 Sulfuric acid, H_2SO_4

16.1.11 Glass beads and /or boiling chips

16.1.12 Solid Reference Material (SRM), cyanide in soil

16.2 Preparation of reagents:

16.2.1 Sodium hydroxide absorbing solution, 0.25 N

16.2.1.1 Weigh out 10 g NaOH pellets and place in a 1 L volumetric flask.

16.2.1.2 Dissolve and dilute to volume with DI water.

NOTE: This reagent may be prepared in larger quantities if the same proportions are used.

16.2.2 Bismuth nitrate solution, (0.124 M)

16.2.2.1 Dissolve 60 g bismuth nitrate pentahydrate $Bi(NO_3)_3 \bullet 5H_2O$ in 100 mL DI water.

16.2.2.2 While stirring, add 250 mL glacial acetic acid.

16.2.2.3 Pour solution into a 1000 mL volumetric flask and dilute to the mark with DI water.

16.2.3 Sulfamic acid solution, H_3NO_3S, (0.8 N).

16.2.3.1 In a 1000 mL volumetric flask dissolve 80 g sulfamic acid.

16.2.3.2 Mix well and dilute to the mark with DI water.

16.2.4 Magnesium chloride solution

16.2.4.1 Weigh out 510 g $MgCl_2 \cdot 6H_2O$

16.2.4.2 Add to a 1 L volumetric flask, dissolve, and dilute to volume with DI water.

16.2.5 Sodium arsenite solution (0.4 M $NaAsO_2$)

CAUTION: Avoid skin contact. Wear gloves when preparing this solution.

16.2.5.1 In a 1000 mL volumetric flask dissolve 51.2 g sodium arsenite using DI water.

16.2.5.2 Bring up to volume with DI water and store in a Nalgene or glass container.

16.2.6 1:1 Sulfuric acid solution H_2SO_4

16.2.6.1 Pour 500 mL DI water into a 1000 mL glass graduated cylinder or glass volumetric flask.

16.2.6.2 Under a hood, **carefully** add 500 mL concentrated sulfuric acid to the cylinder.

CAUTION: Solution will be very hot!

16.2.6.3 Wait at least 20 minutes for the solution to cool, then store in a 1 L Nalgene or glass container.

WARNING: The preparation of this solution generates a tremendous amount of heat.

16.2.7 Potassium cyanide (KCN) solution, (1 mL = 1000 µg CN^-)

16.2.7.1 Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of DI water.

16.2.7.2 Standardize with 0.0192 N silver nitrate, $AgNO_3$.

16.2.7.3 Dilute to 1 L to achieve 1 mL = 1000 µg of CN^-.

16.2.7.4 Alternatively a certified standard may be purchased.

NOTE: Working standards as detailed in Appendix 1 are prepared from 100 µg/L stock solution.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater," 22nd Edition, Method 4500-CN^- D-2011

NOTE: All reagents are good for 6 months unless otherwise noted.

16.2.8 50% Sodium hydroxide solution (50% NaOH)

16.2.8.1 In a 500 mL volumetric flask, dissolve 250 g of NaOH in 250 mL of DI water.

16.2.8.2 Cool and dilute to the mark with DI water.

CAUTION: This reaction will produce heat.

17.0 PREPARATION OF SAMPLES

17.1 Distillation of aqueous or homogenous solid samples using a Simple Cyanide distillation unit.

17.1.1 The unit should be assembled as described in the Simple Cyanide Instruction Manual. Turn hot block on and set to 110° C.

17.1.2 Using potassium iodide strips, test for presence of chlorine. If the paper turns blue after being placed in the sample, chlorine is present. Remove any chlorine by adding sodium arsenite solution dropwise until the potassium iodide starch paper shows no color change.

17.1.3 Check pH of each sample and record in AlphaLIMS.

17.1.4 Fill reflux tube with 25 mL liquid sample or a recorded weight of solid sample to which 25 mL of 0.25 N sodium hydroxide solution is added.

NOTE: A sample weight of 0.5 g is normally used for solid samples.

17.1.5 For method blanks, use 25 mL of 0.25 N sodium hydroxide solution.

17.1.6 For matrix spikes, pipet 25 µL of 100 mg/L stock standard solution into 25 mL of sample.

17.1.7 For the liquid LCS, pipet 12.5 µL of the second source 100 mg/L stock standard solution into 25 mL of 0.25 N sodium hydroxide solution. This is the low, 50 µg/L standard. For homogenous solid samples, weigh out 0.25 g to use as the LCS.

17.1.8 For ICVs, pipet 37.5 µL of the second source 100 mg/L stock standard solution into 25 mL of 0.25 N sodium hydroxide solution. This is the high, 150 µg/L standard. Both solid and liquid batches have the same ICV.

17.1.9 Add 20 mL of 0.25 N sodium hydroxide solution to the 25 mL collection traps and add several glass boiling beads to each reflux tube.

17.1.10 Assemble all components of the Simple Cyanide unit and make sure all connections are tight.

17.1.11 Turn on vacuum source.

17.1.12 Adjust each vacuum valve to rate of at least three bubbles per second is observed in each reflux tube.

17.1.13 Add 1.25 mL of bismuth nitrate through each air inlet to every sample to remove any sulfites that may be present in the samples.

17.1.14 Pipet 1.25 mL of sulfamic acid through each air inlet to eliminate interfaces from nitrates.

17.1.15 Slowly pipet 2.5 mL of 1:1 sulfuric acid through the air inlet of each Reflux impinger.

17.1.16 Pipet 1 mL of magnesium chloride solution though the air inlet.

17.1.17 If the sample foams, add anti-foaming agent drop wise until the foaming stops and add to the MB and LCS. Note on the prep logbook in AlphaLIMS.

17.1.18 Turn the heating block off after 30 minutes.

17.1.19 Disconnect a collection trap from the two port cap insert then disconnect the vacuum line. Allow the vacuum to continue to bubble in the remaining traps.

17.1.20 Using a wash bottle filled with 0.25 N sodium hydroxide, bring the volume to the 25 mL fill line in the collection trap. Swirl to mix and transfer to a labeled 20 mL scintillation vial.

NOTE: A 20 mL scintillation vial contains adequate headspace to accommodate a 25 mL volume for this step.

17.1.21 Once all collection traps are removed and transferred, turn off vacuum source.

17.2 The analyst performing the distillations records the date, time, analyst initials, batch number, client, lab number, volume or weight of sample, and any necessary comments about the distillation into AlphaLIMS and prints a Prep Logbook.

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards is handled as described in GL-LB-E-007 for Laboratory Standards Documentation.

18.2 All calibration curve standards are prepared according to the recipes found in Appendix 1.

18.3 Each batch of samples must include the following pretreated and distilled QC items: Method Blank (MB), Laboratory Control Standard (LCS), Matrix Spike (MS), Sample Duplicate (DUP) and Matrix Spike Duplicate (MSD) if requested by client.

18.4 An ICV is prepped each day a cyanide sample is prepped. The 150 µg/L ICV is prepped with the 0.25 N sodium hydroxide solution.

18.5 A MB is run for every batch of samples. For both solids and liquid preps appropriate amounts of 0.25N sodium hydroxide solution is used.

18.6 A LCS is run at least once for every batch of 20 samples or less. A LCS DUP is run only upon client request.

18.6.1 For liquid samples, the LCS is normally a 50 (low) µg/L standard taken through the same process as the samples.

18.6.2 For solid batches, the LCS is a solid standard from a standards supplier that is taken through the same process as the samples.

18.7 A MS and sample duplicate are run for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples.

18.8 An initial calibration verification (ICV) is run immediately after the calibration curve. This standard must be made from a different source than the calibration standards and is normally prepared and distilled at 150 (high) µg/L. Both solid and liquid batches have the same ICV.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

Refer to Section 17 of this method for details on startup of distillation apparatus.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Batch QC

20.1.1 A MS and sample duplicate are run for every batch of < 10 samples and for each set of ten samples in batches with > 10 samples.

20.1.2 An ICV standard is prepared each day. This is a 150 µg/L standard made up from the second source stock standard. Both liquid and solid batches have the same ICV.

20.1.3 A MB, LCS and (LCS duplicate if requested by the client) are run at least once for every batch of 20 samples or less.

20.1.4 The LCS is normally a 50 µg/L standard taken through the same process as the liquid samples.

20.1.5 For solid batches, the LCS is usually a solid standard from a standards supplier that is taken through the same process as the samples.

20.1.6 SM4500CN-C requires a MSD for every batch of < 10 samples and for each set of ten samples in batches with > 10 samples.

NOTE: For solid batches, a dilution of the LCS may be required prior to instrument analysis.

20.2 Actions Required if the Quality Control Requirements Are Not Met

If any of the QC criteria from 20.1.1 through 20.1.5 cannot be satisfied, the analyst should inform the Group Leader or Team leader and initiate a Data Exception Report as outlined in GL-QS-E-004.

21.0 RUN SEQUENCE

Refer to GL-GC-E-095 for Cyanide Analysis by Lachat QuikChem 8000 FIA for the analytical run sequence.

22.0 PROCEDURE

This SOP is a prep method. For analytical methodology, refer to GL-GC-E-095 for Cyanide Analysis by Lachat QuikChem 8000 FIA.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Refer to Section 17 for details of shutting the distillation apparatus down.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

After distillation is complete, the prep batch data are entered into AlphaLIMS and the batch is assigned DONE status. The analytical results are generated using GL-GC-E-095. Refer to GL-LB-E-005 and GL-GC-E-092 for data review and validation procedures.

25.0 DATA TRANSMITTAL

When a batch is assigned "DONE" status, the data become available to reporting personnel.

26.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

28.0 METHOD VARIATIONS

28.1 The three different methods sometimes call for different reagents to remove interferences. For consistency, most of the reagents used in this SOP come from Methods 9010B, 9010C, and 9012B. Refer to Section 8 for more detailed explanations.

28.2 The concentrations of the bismuth nitrate and sulfamic acid solutions are doubled from the concentrations listed in Methods 9010B, 9010C, and 9012B. This allows half the volume being added to the samples, avoiding dilution problems.

28.3 For solid samples with an aqueous phase, a representative 10 g aliquot is used and treated as a solid.

28.4 GEL Laboratories, LLC developed the processes described in Section 17 from the referenced methods. Reduced volumes/masses of samples and reagents are used for the simple distillation unit. Validation of the process included initial demonstrations of capability, detection limit studies, and acceptable performance testing (PT) samples.

29.0 REFERENCES

29.1 EPA Method 335.4, “Determination of Total Cyanide by Semi-Automated Colorimetry," Revision 1.0, August 1993.

29.2 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume IC. SW-846, Third Edition, November 1986. Method 9012, “Total and Amenable Cyanide (Colorimetric, Automated UV),” Revision 0, September 1986. USEPA Office of Solid Waste and Emergency Response, Washington, D.C.

29.3 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume IC. SW-846, Third Edition, November 1986. Method 9010A, “Total and Amenable Cyanide (Colorimetric, Manual),” Revision 1, July 1992. USEPA Office of Solid Waste and Emergency Response, Washington, D.C.

29.4 Standard Methods 22nd Edition, 4500-CN^- C-2011.

29.5 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume IC. SW-846, Third Edition, June 1997. USEPA Office of Solid Waste and Emergency Response, Washington, D.C. 20460.

29.5.1 Method 9010B, “Total and Amenable Cyanide (Distillation),” Revision 2, December 1996.

29.5.2 Method 9012B, “Total and Amenable Cyanide (Colorimetric, Automated UV),” Revision 2, August 2002.

29.5.3 Method 9010C, “Total and Amenable Cyanide (Distillation),” Revision 3, August 2002.

29.5.4 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.0 DOE QSAS Version 3.0, July 2013.

29.5.5 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.1, DOE QSAS Version 3.1 January 2017.

29.6 Methods for Chemical Analysis of Water and Wastes. March 1983, EPA-600/4-79-020, Cyanides, Amenable to Chlorination, Method 335.1 (Titrimetric; Spectrophotometric) Storet No. 00722, Environmental Monitoring Systems Laboratory, Environmental Protection Agency, Cincinnati, OH 45268.

30.0 HISTORY

Revision 23: Remove reference to Methods 335.3 and CLP Method 335.2 M.
Revision 22: Updated ICV in Definitions Section. Updated Sections 17.1.7. Removed reference to method 9012A.
Revision 21: Updated the time for turning off hot block
Revision 20: Updated QC requirements 20.1.6. SM4500CN-C requires a MSD for every batch of < 10 samples and for each set of ten samples in batches with > 10 samples.
Revision 19: The 150 µg/L ICV is distilled (18.8). Deleted obsolete note on EPA 335.4.

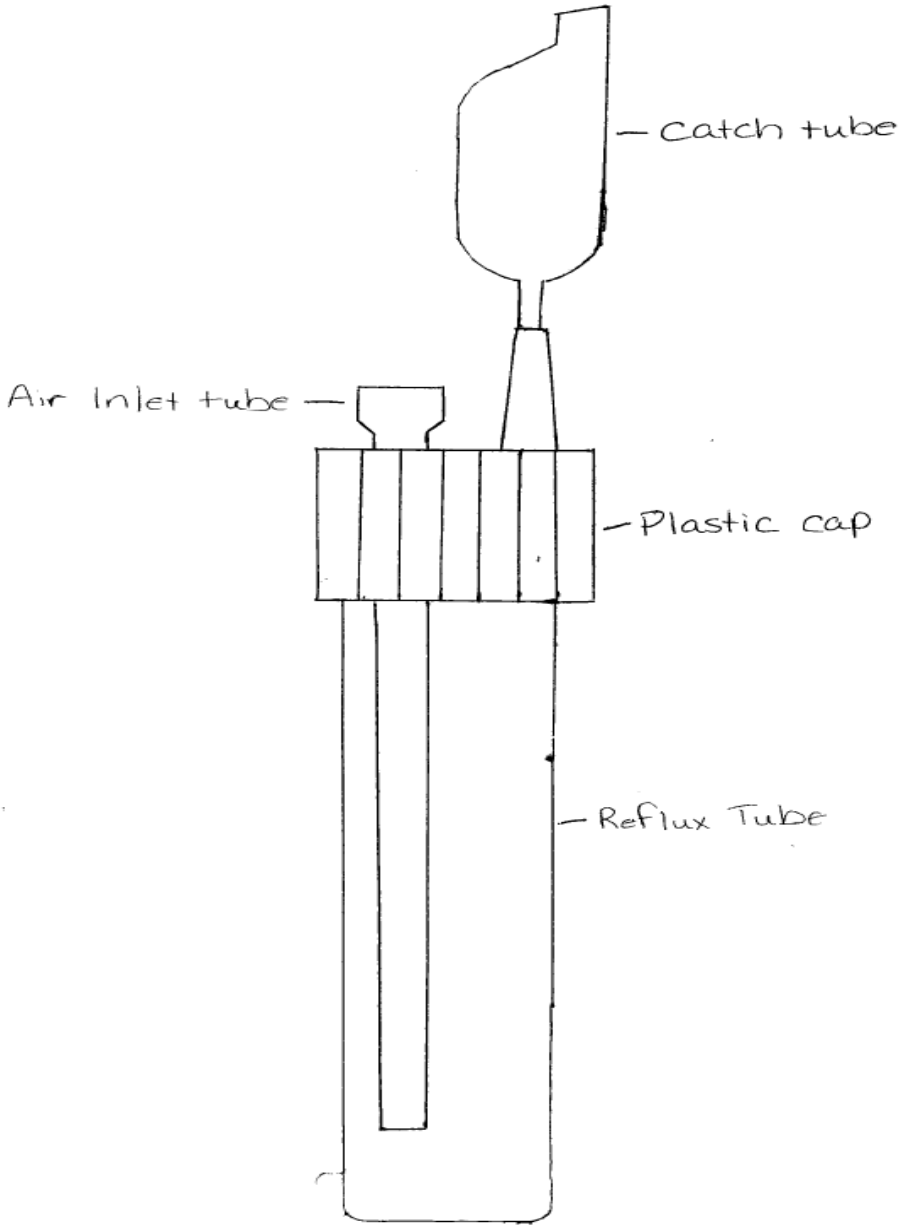
APPENDIX 1

Conc of Std	Init Vol of Stock	Final Vol of Std
200 ppb	200 µl of 100 ppm std	100 mL 0.25 N NaOH
150 ppb	150 µl of 100 ppm std	100 mL 0.25 N NaOH
100 ppb	100 µl of 100 ppm std	100 mL 0.25 N NaOH
50 ppb	50 µl of 100 ppm std	100 mL 0.25 N NaOH
10 ppb	10 µl of 100 ppm std	100 mL 0.25 N NaOH
5 ppb	5 µl of 100 ppm std	100 mL 0.25 N NaOH

WAD, Amenable, Total, Reactive, Free

APPENDIX 2

SIMPLE CYANIDE GLASSWARE



VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR ACID-SOLUBLE SULFIDES

(GL-GC-E-082 REVISION 13)

APPLICABLE TO METHODS:
EPA SW-846 Methods 9030B and 9034

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1.0 STANDARD OPERATING PROCEDURE FOR ACID-SOLUBLE SULFIDES

2.0 METHOD CODE

EPA SW-846 Methods 9030B and 9034

3.0 METHOD OBJECTIVE/PURPOSE

Determination of acid-soluble sulfides in aqueous and solid waste materials or effluents.

4.0 METHOD SUMMARY

4.1 Separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70 °C and the hydrogen sulfide (H_2S) that is formed is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate gas scrubbing bottles where it is precipitated as zinc sulfide.

4.2 The sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known excess amount of iodine. Then the excess iodine is determined by titration with a standard solution of sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantitation is based on the volume of sodium thiosulfate.

5.0 APPLICABLE MATRICES

5.1 Ground water

5.2 Domestic and industrial wastewater

5.3 Sludge

5.4 Soil

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or miscellaneous solid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

6.1 The holding time for aqueous samples is seven days from the time and date of collection until the start of analysis unless otherwise specified by contract.

6.2 A holding time is not specified by the method for solid matrices.

7.0 SAMPLE CONTAINER, PRESERVATION, COLLECTION, AND STORAGE REQUIREMENTS

7.1 Samples may be collected in glass or plastic containers.

7.2 Sample preservation is matrix dependent and is performed as described below:

7.2.1 All aqueous samples and effluents must be preserved with zinc acetate and sodium hydroxide.

Use four drops of 2 N zinc acetate solution per 100 mL of sample.

Adjust the pH to greater than 9 with 6 N sodium hydroxide solution.

Fill the sample bottle completely and stopper with a minimum of aeration.

7.2.2 For solid samples, fill the surface of the solid with 2 N zinc acetate until moistened.

7.3 Samples are to be stored headspace-free at 0° ≤ 6° C prior to analysis.

8.0 INTERFERENCES/LIMITATIONS

8.1 Aqueous samples must be taken with a minimum of aeration to avoid volatilization of sulfide or reaction with oxygen, which oxidizes sulfide to sulfur compounds that are not detected.

8.2 Reduced sulfur compounds, such as sulfite and hydrosulfite, decompose in acid, and may form sulfur dioxide. This gas may be carried over to the zinc acetate gas scrubbing bottles and may subsequently react with the iodine solution yielding false high values. The addition of formaldehyde into the zinc acetate gas scrubbing bottles removes this interference. Any sulfur dioxide entering the scrubber will form an addition compound with the formaldehyde that is unreactive towards the iodine in the acidified mixture. This method shows no sensitivity to sulfite or hydrosulfite at concentrations up to 10 mg/kg of the interferant.

8.3 Sodium sulfite and sodium thiosulfate are known to interfere in the procedure for soluble sulfides. Sulfur also interferes because it may be reduced to sulfide by tin (II) chloride in this procedure.

8.4 The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 0.2 to 50 mg/kg (or mg/L)

9.2 Method detection limit (MDL): Refer to current MDL study.

9.3 Method precision: Refer to current SPC limits.

9.4 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

10.2 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

10.3 Laboratory Duplicate (DUP, LCSD, MSD or PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample, and the results are compared to measure precision and accuracy.

10.4 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The

MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

10.5 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

10.6 Spike (Matrix Spike or Post Spike): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or PS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or PS corrected for background concentrations.

10.7 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD, and internal standards.

10.8 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

10.9 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

12.1 Sample preparation data are recorded in AlphaLIMS.

12.2 As data is obtained, the results are recorded in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

ZINC ACETATE DIHYDRATE IS HARMFUL IF SWALLOWED OR INHALED. MAY CAUSE IRRITATION.

SODIUM HYDROXIDE PELLETS ARE CORROSIVE, WILL CAUSE BURNS. HARMFUL IF INHALED. AVOID CONTACT WITH EYES AND SKIN.

FORMALDEHYDE (37%) MAY BE FATAL IF INHALED, INGESTED, OR ABSORBED THROUGH SKIN. CAUSES SEVERE EYE IRRITATION. MAY BE IRRITATING TO MUCOUS MEMBRANES AND UPPER RESPIRATORY TRACT.

CONCENTRATED HYDROCHLORIC ACID IS HIGHLY TOXIC AND CORROSIVE TO SKIN AND EYES.

CONCENTRATED SULFURIC ACID IS HIGHLY TOXIC AND CORROSIVE TO RESPIRATORY TRACT IF INHALED. HIGHLY CORROSIVE TO SKIN AND EYES. VIOLENT EXOTHERMIC REACTION WITH WATER.

NITROGEN GAS MAY PRODUCE SUFFOCATION BY DILUTING THE CONCENTRATION OF OXYGEN IN AIR BELOW LEVELS NECESSARY TO SUPPORT LIFE.

POTASSIUM IODIDE CAUSES IRRITATION TO EYES AND SKIN. HARMFUL IF SWALLOWED.

IODINE MAY BE FATAL IF SWALLOWED OR INHALED. CAUSES SEVERE BURNS. STRONG OXIDIZER. CONTACT WITH OTHER MATERIAL MAY CAUSE FIRE.

WARNING

SODIUM THIOSULFATE MAY CAUSE IRRITATION TO SKIN AND EYES. MAY CAUSE RESPIRATORY IRRITATION.

SODIUM SULFIDE NONAHYDRATE DUSTS MAY CAUSE SEVERE IRRITATION OF THE MUCOUS MEMBRANES. CONTACT WITH MOISTURE MAY RELEASE HYDROGEN SULFIDE GAS. IF SUFFICIENT QUANTITIES ARE INHALED, PULMONARY EDEMA MAY DEVELOP. DIRECT CONTACT WITH SKIN MAY CAUSE SEVERE IRRITATION.

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and client sample MSDS forms are maintained in the laboratory.

13.3 Gloves are required when handling chemicals or samples.

13.4 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.4.1 Wear a plastic apron over lab coat when working with radioactive samples.

13.4.2 Protect counter tops with counter paper, or work from radioactive sample handling trays.

13.4.3 Prohibit admittance to immediate work area.

13.4.4 Post signs indicating radioactive samples are in the area.

13.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.4.6 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

13.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

13.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION, EQUIPMENT, AND GLASSWARE

15.1 Equipment

15.1.1 Hot plate with stirring capability

15.1.2 Stand to hold stirring apparatus and glassware in place

15.1.3 Nitrogen gas (in-house supplied)

15.1.4 Analytical balance capable of measuring to 0.1 g

NOTE: Balance is calibrated in accordance with GL-LB-E-002 for Balances.

15.1.5 Flow meters

15.1.6 Water bath

15.1.7 Fume hood

15.1.8 pH strips

15.1.9 Teflon sealing tape

15.1.10 Teflon tubing

15.1.11 Thermometer capable of reading to 70° C ± 10° C

NOTE: Thermometers are monitored in accordance with GL-LB-E-004.

15.2 Glassware

15.2.1 500 mL three-neck round-bottom flask with ground glass joints

15.2.2 Gas scrubbing bottles, 250 mL capacity, with glass frits

15.2.3 Dropping funnels

15.2.4 Glass stirring rods with Teflon propellers attached

16.0 REAGENTS

16.1 Reagent grade chemicals shall be used in all tests.

16.2 ASTM Type I deionized (DI) water

16.3 Zinc acetate solution for sample preservation, 2 N $Zn(CH_3COO)_2 \bullet 2H_2O$: Dissolve 220 g of zinc acetate dihydrate in 500 mL of reagent water.

16.4 Sodium hydroxide, 1 N NaOH: Dissolve 40 g of NaOH in reagent water and dilute to 1 L.

16.5 Formaldehyde (37% solution), CH_2O. This solution is commercially available.

16.6 Zinc acetate solution (approximately 0.5 M):

16.6.1 Dissolve about 110 g zinc acetate dihydrate in 200 mL of reagent water.

16.6.2 Add 1 mL hydrochloric acid (concentrated HCl), to prevent precipitation of zinc hydroxide. Dilute to 1 L.

16.7 Concentrated Sulfuric acid, H_2SO_4

16.8 Starch solution: Use either an aqueous solution or soluble starch powder mixtures. Prepare an aqueous solution as follows. Dissolve 2 g soluble starch and 2 g salicylic acid, $C_7H_6O_3$, as a preservative, in 100 mL hot reagent water. (This solution is commercially available).

16.9 Nitrogen gas

16.10 Iodine solution (approximately 0.025 N)

16.10.1 Preparation

Dissolve 25 g potassium iodide, KI, in 700 mL of reagent water in a one-liter volumetric flask. Add 3.2 g iodine, I_2. Allow to dissolve. Add 2.0 mL of 6 N hydrochloric acid, HCl. Dilute to 1 L and standardize.

NOTE: If using a commercially available iodine solution that does not contain HCl, the HCl must be added prior to use.

16.10.2 Standardization

Dissolve approximately 2 g potassium iodide in 150 mL of reagent water in an Erlenmeyer flask. Add exactly 20 mL of the iodine solution and dilute to 300 mL with reagent water.

Titrate with 0.025 N sodium thiosulfate until the amber color fades to yellow. Add starch indicator solution. Continue titration drop by drop until the blue color disappears.

Run in replicate. Repeat steps 16.10.2.1 and 16.10.2.2 two more times.

Calculate the normality:

$$\text{Normality } (I_2) = \frac{\text{mL of titrant x normality of titrant}}{\text{sample volume in mL}}$$

The iodine solution must be standardized prior to each use.

16.11 16.11 Sodium hydroxide (6 N NaOH): Dissolve 240 g of sodium hydroxide in 1 L of reagent water.

16.12 16.12 Hydrochloric acid (6 N HCl): Place 51 mL of reagent water in a 100 mL Class A volumetric flask. Slowly add concentrated hydrochloric acid to bring the total volume to 100 mL.

17.0 PREPARATION OF SAMPLE

NOTE: It is assumed that material within the sample container is considered the "sample." Removal of any extraneous material (leaves, twigs, large rocks, etc.) must be documented in the case narrative and in bench logbooks.

17.1 For an efficient distillation, the mixture in the distillation flask must be of such a consistency that the motion of the stirring bar is sufficient to keep the solids from settling. The mixture must be free of solid objects that could disrupt the stirring bar. Prepare the sample using one of the procedures in this Section then proceed with the distillation.

17.2 If the sample is aqueous:

17.2.1 Shake the sample container and quickly decant the appropriate volume (up to 200 mL) of the sample to a graduated cylinder.

17.2.2 Transfer to the sample aliquot to the distillation flask.

17.3 If the sample contains solids that absorb water and swell, limit the sample size to 20 g dry weight in order to prevent the solids from restricting the fluid motion and lowering the recovery.

17.4 If the sample contains objects that cannot be reduced in size by tumbling, the solids must be broken manually.

Clay-like solids should be cut with a spatula or scalpel in a crystallizing dish. If the solids can be reduced to a size that can be suspended by the stirring bar, the solid and liquid can be proportionately weighed.

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards and their preparation is kept in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

18.2 Standard sodium thiosulfate solution (0.025 N), $Na_2S_2O_3 \cdot 5H_2O$: Dissolve 6.205 g ± 0.005 g $Na_2S_2O_3 \cdot 5H_2O$ in 500 mL reagent water. Add 9 mL 1 N NaOH and dilute to 1 L.

18.3 Sodium sulfide nonahydrate stock solution, 100 mg/L S: Dissolve 0.7500 g $Na_2S \cdot 9H_2O$ in 1 L of reagent water. This solution should be prepared daily.

18.4 LCS: Add 180 mL of DI water to distillation flask, then pipet 20 mL of stock solution being careful to hold the pipet tip below the surface of the liquid.

18.5 Matrix Spike: Add 200 mL of sample to distillation flask, then pipet 20 mL of stock solution being careful to hold the pipet tip below the surface of the liquid.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURES

Refer to Section 22.0.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC:

20.1.1 A matrix spike and matrix duplicate are run once for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples. A method blank is run for every batch of samples.

20.1.2 An LCS is run at least once for every batch of 20 samples or less. An LCS duplicate is run only upon client request.

20.2 Acceptance limits:

20.2.1 Matrix relative percent difference (RPD): Refer to current SPC limits.

20.2.2 Matrix spike recovery: Refer to current SPC limits.

20.2.3 Method blank: Less than PQL

20.2.4 LCS: Refer to current SPC limits.

20.2.5 LCS RPD: Refer to current SPC limits.

20.3 Handling out-of-control situations:

If the LCS recoveries or LCS RPD fall outside of current acceptance limits, the batch must be reanalyzed and the Group Leader notified.

21.0 TYPICAL RUN SEQUENCE

21.1 Method blank

21.2 LCS

21.3 Sample 1

21.4 Sample 1 duplicate

21.5 Sample 1 spike

21.6 Samples 2 through 11

21.7 Sample 11 Duplicate

21.8 Sample 11 Spike

21.9 Repeat Duplicate and Spike combination after every 10 samples

22.0 PROCEDURE

22.1 Soils

22.1.1 Place a known amount of sample or sample slurry in a beaker.

22.1.2 Add reagent water until the total volume is 200 mL.

22.1.3 Proceed to Section 22.2.2.

22.2 Liquids

22.2.1 Choose a sample size that will contain between 0.2 and 50 mg/L sulfide.

22.2.2 Put the measured amount of sample in a beaker and bring the total volume to 200 mL using DI water.

22.2.3 Stir the mixture and determine the pH.

22.2.4 Slowly add sulfuric acid until the pH is less than or equal to 1.

22.2.5 Record the amount of sulfuric acid required to change pH to < 1.

22.2.6 Discard this preliminary sample.

22.2.7 Use the amounts determined in steps 22.2.1 through 22.2.5 to determine how much acid is required to acidify the sample to be placed in the distillation flask during the distillation portion of the procedure.

22.3 Prepare the gas evolution apparatus as shown in Appendix 1 in a fume hood.

22.3.1 Place a thermometer in the water bath and monitor the temperature to maintain the bath at 70° C.

22.3.2 Assemble the three-neck 500 mL flask, fritted gas inlet tube, and exhaust tube.

22.3.3 Into each gas scrubbing bottle, place 10 ± 0.5 mL of the 0.5 M zinc acetate solution, 5 ± 0.1 mL of 37% formaldehyde and 100 ± 5 mL reagent water.

22.3.4 Connect the gas evolution flask and gas scrubbing bottles as shown in Appendix 1. Secure all fittings and joints.

22.4 Place sample aliquot in flask

22.5 Place the dropping funnel onto the flask making sure its stopcock is closed. Add the volume of sulfuric acid calculated in section 22.2.7 plus an additional 50 mL into the dropping funnel. The bottom stopcock must be closed.

22.6 Attach the nitrogen inlet to the top of the dropping funnel gas shut-off valve. Turn on the nitrogen purge gas and adjust the flow through the sample flask to 25 mL/min. The nitrogen in the gas washing bottles should bubble at about five bubbles per second. Nitrogen pressure should be limited to approximately 10 psi to prevent excess stress on the glass system and fittings.

22.7 Verify that there are no leaks in the system.

22.8 Purge the system for 15 minutes with nitrogen to remove oxygen.

22.9 Heat sample to 70° C. Open dropping funnel to a position that will allow a flow of sulfuric acid of approximately 5 mL/min. Monitor the system until most of the sulfuric acid within the dropping funnel has entered the sample flask.

22.10 Purge, stir, and maintain a temperature of 70° C for a total of 90 minutes from start to finish.

22.11 Shut off nitrogen supply. Turn off heat.

22.12 Titration of Distillate

22.13 **NOTE**: For reactive sulfide analysis, volumes are cut in half if reactive cyanide protocol is being performed on the samples.

22.13.1 Pipet a known amount of standardized 0.025 N iodine solution in a 500 mL flask, adding an amount in excess of that needed to oxidize the sulfide.

22.13.2 Add enough reagent water to bring the volume to 100 mL.

22.13.3 For acid-soluble sulfide analysis, add 2 mL of 6 N hydrochloric acid to the flask. For reactive sulfide analysis, pH the trapping solution to a pH of 2 using the 6 N hydrochloric acid solution.

22.13.4 Pipet both of the gas washing bottle solutions to the flask, keeping the end of the pipet below the surface of the iodine solution.

NOTE: If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025 N iodine must be added. This additional amount must be added to the amount from Section 22.12.1. Record the total volume of standardized 0.025 N iodine solution used.

22.13.5 Rinse any remaining traces of sample from the gas washing bottles with reagent water, and transfer the rinsate to the flask as stated in 22.12.4.

22.13.6 Titrate the solution in the flask with standard 0.025 N sodium thiosulfate solution until the amber color fades to yellow.

22.13.7 Add enough starch indicator for the solution to turn dark blue and titrate until blue disappears. Record the volume of titrant used.

Calculate the concentration of sulfide using the following equation:

$$\frac{(\text{mL } I_2 \times \text{N } I_2) - (\text{mL titrant} \times \text{N titrant}) \times (32.06 \text{ g/2 eq})}{\text{sample weight (kg) or sample volume (L)}} = \text{sulfide (mg/kg) or (mg/L)}$$

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

23.1 Refer to Section 22.11.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for General Chemistry Data Packaging and Validation.

25.0 DATA TRANSMITTAL

When a batch is issued a status of "DONE," it is automatically transferred via AlphaLIMS to Data Management department for generation of the appropriate report.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Not applicable

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

Method detection limit studies are conducted in accordance with GL-LB-E-001 for The Determination of Method Detection Limits.

30.0 REFERENCES

30.1 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1C, EPA SW-846, 3rd Edition, 1990. Method 9030B, "Acid-Soluble and Acid-Insoluble Sulfides: Distillation," Revision 2, December 1996.

30.2 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1C, EPA SW-846, 3rd Edition, 1990. Method 9034, "Titrimetric Procedure for Acid-Soluble and Acid-Insoluble Sulfides," Revision 0, December 1996.

31.0 HISTORY

Revision 13: Updated the documentation of data.

Revision 12: Updated section 16.10.2.3 to repeat steps in procedure as required.

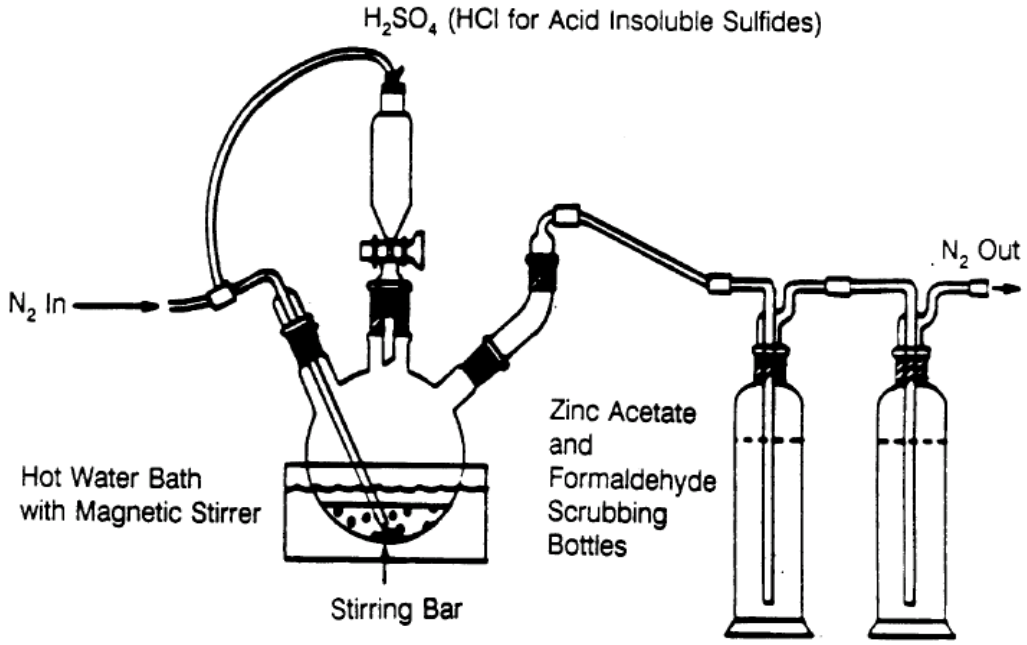
Revision 11: Updated to include pH adjustment for reactive sulfide analysis.

Revision 10: Replace type II with type I DI water

Revision 9: Added sentence pertaining to the commercial availability of starch solution.

APPENDIX 1: GAS EVOLUTION APPARATUS

FIGURE 1.
GAS EVOLUTION APPARATUS



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VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR ION CHROMATOGRAPHY (IC)

(GL-GC-E-086 REVISION 27)

APPLICABLE TO METHODS:
EPA Method 300.0
SW-846 Method 9056A

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR ION CHROMATOGRAPHY (IC)

2.0 METHOD CODES

2.1 EPA Method 300.0

2.2 SW-846 Method 9056A

3.0 METHOD OBJECTIVE/PURPOSE

3.1 This standard operating procedure (SOP) provides necessary instructions for the determination of the following inorganic anions by ion chromatography: bromide, chloride, fluoride, nitrate-N, nitrite-N, sulfate, orthophosphate-P, and iodide.

NOTE: For EPA Method 314.0 (Perchlorates by IC) refer to GL-GC-E-096.

3.2 The applicable matrixes to this method are as follows:

3.2.1 Drinking water

3.2.2 Surface water

3.2.3 Groundwater

3.2.4 Wastewater

3.2.5 Reagent waters

3.2.6 Aqueous extracts of solids

3.2.7 Leachates (when no acetic acid is used)

3.2.8 Collected solutions from bomb combustion of solid waste (Method 5050)

3.3 A small volume of sample is introduced into the ion chromatograph (IC). The anions of interest are separated and measured after traveling through a series of columns and a suppressor device. The sample passes through a conductivity detector (CD).

3.4 An extraction procedure must be performed to use this method for solids.

3.5 Approximately 4.9 mL of sample is flushed through the sample loop prior to injecting the sample. The large amount of sample flushing prevents sample cross-contamination.

4.0 METHOD APPLICABILITY

4.1 Method Detection Limit: The MDL is updated and verified every six months. For DoD QSM, LOD is verified quarterly.

NOTE: Because iodide reference Method 300.0 when analyzed, these MDLs are determined semiannually.

4.2 Method Precision: The limits are static at 100 ±10%.

4.3 Method Accuracy: Refer to the current SPC limits for these methods.

4.4 Technicians and analysts do not analyze client samples without supervision until they have been fully trained and have demonstrated the ability to generate acceptable data. Training records are maintained as quality records.

5.0 DEFINITIONS

5.1 Calibration Blank: A volume of reagent water without the analytes, internal standards or surrogates used within the calibration curve.

5.2 Calibration Standard (CAL): A solution prepared from the primary stock solution. The CAL solutions are used to calibrate the instrument.

5.3 Continuing Calibration Verification (CCV): A solution of the method analytes used to evaluate the performance of the instrument with respect to a defined set of criteria. The CCV concentration is varied throughout the calibration range.

5.4 Instrument Calibration Verification (ICV): A solution of the method analytes used to evaluate the performance of the instrument with respect to a defined set of criteria. The ICV concentration is at or near the calibration midpoint and is prepared from a different source than the calibration standards. A synonym for ICVs is an Instrument Performance Check (IPC).

5.5 Laboratory Control Sample (LCS): An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether methodology is in control. A synonym for LCS is a Lab Fortified Blank (LFB).

5.6 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

5.7 Matrix Spike (MS): An aliquot of a known sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed like a sample and its purpose is to determine whether the sample matrix contributes to the analytical results. distribute

5.8 Method Blank (MB): An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents and reagents which are used with other samples. The Method Blank is used to determine if method analytes or other interferences are present in the laboratory environment.

5.9 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

5.10 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

6.0 METHOD VARIATIONS

6.1 Iodide is analyzed using a different instrument setup than that used for normal anions in accordance with SW846 9056A and EPA 300.0. These differences are described in section 14.3.

6.2 Retention Time study is done over a 3 day period instead of a 24-hour period.

7.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

HYDROCHLORIC ACID IS A CORROSIVE AND A POISON.

SODIUM HYDROXIDE IS A CORROSIVE AND A POISON.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

7.1 Wear eye protection with side shields while in the laboratory.

7.2 All chemicals and samples should be treated as potential health hazards, and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). Individual sample MSDS forms provided by the clients are also maintained.

7.3 Personal protective equipment

7.3.1 Gloves are required when handling the chemicals in this procedure. The gloves approved for this procedure are:

7.3.1.1 Nitrile gloves for concentrated acids and bases.

7.3.1.2 Non-sterile ambidextrous gloves for sample prep and standard handling.

7.3.2 Work under a hood when using concentrated acids and bases, and acetonitrile.

7.4 Prior to handling radioactive samples, analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

7.4.1 Protect counter tops with counter paper or work from radioactive sample handling trays.

7.4.2 Prohibit admittance to immediate work area.

7.4.3 Post signs indicating radioactive samples are in the area.

7.4.4 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

7.4.5 Segregate radioactive wastes in radioactive waste containers are obtained from Waste Management.

7.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

7.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

7.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

7.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

7.7 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

7.8 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

8.0 INTERFERENCES/LIMITATIONS

8.1 Interferences may be caused by substances with similar retention times which overlap those of the anions of interest. High concentrations of one analyte may interfere with the detection of another analyte. Usually a sample dilution and/or a gradient elution will overcome interferences evidenced by retention time problems.

8.2 Limitations may occur if particulates remain in a sample after filtration, or if the client insists that the sample is analyzed without filtration.

8.3 Many interferences are caused by contaminants in the reagent water, reagents, glassware, etc., which lead to elevated baselines or artifacts on the chromatograms.

8.4 Any anion that is not retained by the column or just slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant.

8.5 Because nitrite, orthophosphate, and bromide elute very closely together, they are potential interferants. When any of these anions are to be quantified in the presence of others, dilutions may be necessary to completely resolve the analytes.

9.0 APPARATUS, MATERIALS, REAGENTS, EQUIPMENT AND INSTRUMENTATION

9.1 Apparatus and Equipment for Dionex IC:

9.1.1 Dionex 5 mL sample vials and filter caps or equivalent

9.1.2 Dionex 5 mL automated sampler cassettes or equivalent

9.1.3 4 L reservoirs

9.1.4 Helium tanks (minimum purity, 99.995%) or equivalent

9.1.5 1-5 mL Oxford, 10-100 µL, and 100-1000 µL Eppendorf pipets or equivalent

9.1.6 0.20 µm Acrodisc syringe filters or equivalent

9.1.7 10 cc disposable syringes or equivalent

9.1.8 10, 50, 100, 250 and 500 mL volumetric flasks

9.1.9 25, 50 and 100 mL graduated cylinders

9.2 Analyte Reagents: All reagents must be American Chemical Society certified or equivalent.

9.2.1 Sodium chloride (NaCl)

9.2.2 Sodium hydroxide (NaOH)

9.2.3 Acetonitrile

9.2.4 Hydrochloric acid (HCl), concentrated

9.2.5 Sodium carbonate

9.2.6 Sodium bicarbonate

9.2.7 Stock standards for anions of interest at concentration of 1000 ppm or greater. These are usually purchased as certified solutions either in individual standards or in mixes of anions.

9.2.8 Teflon chip, glass beads or sand.

9.3 Eluent for IC methods 9056A/300.0 performed on the Dionex ICs

9.3.1 Eluent stock: 225 mM sodium carbonate/40 mM sodium bicarbonate.

9.3.1.1 Add 47.7 g of sodium carbonate and 6.72 g of sodium bicarbonate to a 2000 mL volumetric flask and fill to volume with DI water.

9.3.1.2 Working eluent: Dilute 80 mL stock (from 9.3.1.1) per four liters of DI water to make 4.5 nM sodium carbonate/0.8 sodium bicarbonate.

9.3.1.3 Sparge with helium to degas, if required.

9.3.2 Eluent for Iodide: 50 mM sodium hydroxide

9.3.2.1 Add 16.0 g of sodium hydroxide 50/50% solution to a 4L flask and bring to volume with DI water.

9.3.2.2 Sparge with helium to degas, if required.

9.4 Column Cleaning Solution: Combine 800 mL acetonitrile with 20 mL of concentrated hydrochloric acid and 180 mL DI water for the Dionex ICs.

9.5 Instrumentation:

9.5.1 Dionex ICS 1600 Ion Chromatography instrument consisting of the following components:

9.5.1.1 SP Isocratic pump

9.5.1.2 Autosampler Models AS40 or better

9.5.1.3 CD Conductivity Detector

9.5.1.4 DC separation Center with Rheodyne valve and suppressor

9.5.1.5 Computer Pentium IV, 1.0 G RAM, or comparable Windows 2000 (SP4), Windows 7

9.5.1.6 Instrument Operation Software: Chromeleon 7.2

9.5.1.7 50 µL sample loop (used for anion method)

9.5.2 Dionex ICS 5000 Ion Chromatography instrument consisting of the following components:

9.5.2.1 SP Isocratic pump

9.5.2.2 Autosampler Models AS40 or better

9.5.2.3 CD Conductivity Detector

9.5.2.4 DC separation Center with Rheodyne valve and suppressor

9.5.2.5 Computer Pentium IV, 1.0 G RAM, or comparable Windows 2000 (SP4), Windows 7

9.5.2.6 Instrument Operation Software: Chromeleon 6.80 SP2

9.5.2.7 50 µL sample loop (used for anion method)

9.5.3 Dionex ICS 3000 Ion Chromatography instrument consisting of the following components:

9.5.3.1 SP Isocratic pump

9.5.3.2 Autosampler Models AS40 or better

9.5.3.3 CD Conductivity Detector

9.5.3.4 DC separation Center with Rheodyne valve and suppressor

9.5.3.5 Computer Pentium IV, 1.0 G RAM, or comparable Windows 2000 (SP4), Windows 7

9.5.3.6 Instrument Operation Software: Chromeleon 6.80 SP2

9.5.3.7 50 µL sample loop (used for anion method)

9.5.4 Dionex Aquion I Ion Chromatography instrument consisting of the following components:

9.5.4.1 IC separation Center with Rheodyne valve and suppressor and CD.

9.5.4.2 Autosampler Model AS-DV

9.5.4.3 Computer Microsoft Windows 8.1 or Windows 7 or better.

9.5.4.4 Instrument Operation Software: Chromeleon 7.2 SR4.

9.5.4.5 50 µL sample loop (used for iodide method)

9.5.5 Dionex columns for anions by 9056A/300.0

9.5.5.1 Analytical Column; AS23

9.5.5.2 Guard Column; AG23

9.5.6 Dionex columns for iodide by 9056/300.0

9.5.6.1 Analytical Column; Dionex AS16

9.5.6.2 Guard Column; Dionex AG16

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Sample containers can be either glass or plastic. Samples should have no chemical additives for preservation purposes. All samples should be stored at an approximate temperature range of $0° \leq 6°C$ from the time of collection until the time of analysis.

10.2 All anions and iodide have 28-day holding times except nitrate (NO_3), nitrite (NO_2) and o-phosphate (PO_4), which have 48 hours. Holding times are calculated from the time and date of collection until the start of analysis, unless otherwise specified by the contract.

NOTE: The 48-hour hold time for solid samples (nitrate, nitrite, and o-phosphate) are calculated from the time of extraction.

10.3 If sample analysis is not performed before the holding time expires, the Project Manager will be notified. The Project Manager will determine if analysis should continue. If for any reason the Project Manager is unavailable, analysis will be performed and appropriate people notified as soon as possible.

10.4 Sample retrieval

10.4.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from the cooler and scans them in AlphaLIMS to the appropriate code for the area delivers. The analyst takes custody of the samples and scans them in AlphaLIMS to the Batch number and area where the samples are to be prepared and analyzed.

10.4.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

11.0 PREPARATION OF SAMPLES

11.1 All IC samples are marked in login as "UNPRESERVED." Only unpreserved samples should be run on the IC. Any sample preparation is done only with the consent of the analyst. Most sample preparations are in the form of filtrations and can be performed by using 0.2 µm acrodisc filters and a syringe.

NOTE: It is assumed that material within the sample container is considered the sample. Removal of any extraneous material (leaves, twigs, large rocks, etc.) must be documented in the case narrative.

11.2 Extractions: Most extractions are performed on soil samples where a known weight of approximately 4.0 g of sample is diluted with DI water to a volume of 40 mL. Mix thoroughly for a minimum 5-10 minutes. The sample is then allowed to settle for a minimum of 1 hour. After 1 hour, if necessary, a centrifuge may be used. The extract is then filtered prior to injecting on the instrument. All prep data are recorded in AlphaLIMS prep logbooks.

11.3 Bomb Prep: Bomb preps are performed on sample matrices such as coal or oil. Here a known weight of approximately 0.5 g of sample is used and after being

bombed, the residuals are filtered into a 100 mL volumetric flask and brought to volume with DI water. For instructions on performing a bomb prep, refer to GL-GC-E-079 for Bomb Preparation Method for Solid Waste. This prep procedure will not involve the various reagents from ASTM D 808-91 since the final analysis will be done by ion chromatography rather than gravimetrically. All prep data are recorded in the AlphaLIMS Prep logbook.

12.0 PREPARATION OF STANDARDS SOLUTIONS AND QUALITY CONTROL STANDARDS

12.1 Vendor-prepared stock standards are used to prepare calibration and check standard solutions for this analysis. Both individual analyte solutions and mixes of analytes may be purchased for use as standards. All stock standards are stable for at least one month when stored at $0° \leq 6°C$. Unopened stock solutions may be stored at ambient temperatures and their expiration is 1 year from receipt or the manufacturer's expiration date, whichever is sooner. There must be at least two independent sources of standards materials for calibration and calibration verification standard preparation.

12.2 Calibration standards are prepared from stock standards at a minimum of five concentration levels per analyte. The working standards for anions that include nitrate, nitrite and orthophosphate are prepared fresh daily and expire 48 hours after preparation. The working standards for iodide are prepared weekly (7 days). Refer to Appendix 2 for standard concentration.

12.3 Standard preparations are recorded in the AlphaLIMS system for documentation and recording of standards and reagents. Refer to GC-LB-E-007 for details on assigning unique standard IDs and establishing traceability.

12.4 Laboratory control sample(s) (LCS) may be prepared from the calibration standard source.

12.5 ICVs are separate sources from the standards used in the calibration curve.

12.6 CCVs are varied in concentration and may be from the same source as the calibration standards.

12.7 Spiking compounds are added from commercially prepared standards solutions.

13.0 INSTRUMENT CALIBRATION AND PERFORMANCE

13.1 Establish ion chromatographic operating conditions for the determination of target ions. An external calibration is then performed.

13.1.1 For each analyte of interest, prepare a minimum of five calibration standards and a blank by adding accurately measured volumes of source standards to a known volume of reagent water. One of the calibration standards shall be at the PQL/LOQ.

13.1.2 The standards are placed on the instrument for analysis from highest to lowest. To automatically update the calibration curve enter AUTOCAL in the sample ID, followed by the level number.

13.1.3 Tabulate each concentration against area count. Include the blank in the linear calibration curve. Do not force the points through zero. The results determine a calibration curve.

13.1.4 The final calibration curve must have a correlation coefficient of 0.995 or better. If one standard is inconsistent with the rest of the standards it is acceptable to rerun the outlying standard and replace it in the curve.

13.1.5 If a sample analyte concentration is greater than the highest standard in the calibration range, the sample will be diluted with reagent water to approximately mid-range and reanalyzed.

13.1.6 The analyte's retention time is updated from the last standard run. A typical retention window size is 5-10%. This can be modified based on the analyst's experience.

13.1.7 Retention time must be updated after method set-up and after major maintenance. The acceptance criteria for RT width is ± 3 times standard deviation for each analyte over a 24-hour period. The RT window width position must be established once per multipoint calibration and position shall be at midpoint of initial calibration curve.

13.2 Calibration is verified daily or with every batch of samples. If the concentration or retention time window shifts by more than 10% from the expected value, a new calibration must be performed prior to the analysis of any samples.

13.3 Linear Calibration Range (LCR): The LCR is determined initially by acceptance criteria of the curve (0.995 correlation coefficient or better for each analyte). It is verified by using a blank and at least 3 standards. The ICV which is run daily may be used as a LCR verification, and the alternating concentrations of CCVs may also be considered for the same purpose. Acceptance criteria are 90-110% for all of these standards.

14.0 ANALYSIS AND INSTRUMENT OPERATION

14.1 Typical Run Sequence

14.1.1 ICV/IPC

14.1.2 ICB

14.1.3 MB

14.1.4 LCS (and LCS Duplicate if required)/LFB

14.1.5 Sample 1 through 8

14.1.6 CCV

14.1.7 CCB

NOTE: One LCS (and LCS duplicate, if applicable) per batch of 20 samples, and one matrix duplicate, matrix spike, and matrix spike duplicate (if applicable) for every 10 samples in a batch.

NOTE: A CCV and CCB are to be run after every 10 samples and at the end of the analysis sequence.

14.2 Analysis by Dionex ICS 3000

14.2.1 Fill the eluent reservoir as necessary with the proper eluent for the method that will be analyzed. This will be performed at the start of the working day. This will allow the daily checks to verify the calibration curve due to changing eluent.

14.2.2 All components should be turned on and the AS-DV autosampler should be in local position.

14.2.3 On the computer go to Chromeleon icon. ICS 3000 Panel will come up. Click on startup button. Make sure all switches turn green except the prime off button it should remain red.

14.2.4 Go to window tab on toolbar and go to Browser window. This will pull the method and sequence.

14.2.5 Sequence: It is good practice to create a new sequence daily. Rename previous sequence the new date and edit accordingly.

14.2.6 Go to batch tab on toolbar, on dropdown go to edit and a window will open go to Batch list tab and add the days sequence. Click on Ready check button. If everything is good click ok. Go to AS40 autosampler and hit load button. When plunger is all the way down hit start button in window.

14.2.7 Shutdown: The shutdown method is the loaded from the sequence.

14.3 Analysis by Dionex Aquion for Iodide Only

14.3.1 Fill the eluent reservoir as necessary with the proper eluent for the method that will be analyzed. This will be performed at the start of the working day. This will allow the daily checks to verify the calibration curve due to the changing eluent.

14.3.2 To connect the computer to components open icon Chromeleon 7. Click on Instruments (to turn to blue) go to Home tab. On the instrument images (Pump_ECD+AS-DV) click the top left buttons to turn green. Go to Pump_ECD tab to turn on Pump and Suppressor. Make sure all switches are greens.

14.3.3 Click on DATA (to turn blue). Edit schedule accordingly. You may also access the instrument method and process method if needed.

14.3.4 After editing daily schedule go to Instruments (turn to blue) and go to Queue tab click on add button to instrument and data, go to IC10folder and double click on the sequence to be loaded.

NOTE: For the CD, the temperature compensation defaults to 1.7, and the output range is set to 10.0 µS. With the Sodium Hydroxide eluent, the pump will flow at 1.2 ml/min for, and the pump pressure should normally be between 1600 and 2000 psi when using Dionex columns.

14.3.6 Prepare the initial rack of samples according to the run sequence:

14.3.7 Place 5 mL of the samples to be analyzed in the sample vials and place in the Autosampler AS-DV and push button on autosample to reset to #1 spot.

14.3.8 To start your daily sequence you can either click start button in queue or click on the start or resume button on the sequence page.

14.3.9 Go to the computer terminal and pull up the main menu "Run" screen.

14.3.10 On the run screen, under "load" choose "schedule."

NOTE: A method should have been loaded in the start-up procedure. Sample, method, and datafile names are located in each schedule. Creating a schedule allows the analyst to designate which method to use for each sample in the run, as well as where and with what file name the analyst wishes to store the data. Remember, this run information should be entered in the main menu "Schedule" screen and saved with the appropriate naming convention.

14.3.11 At the load schedule screen, give the name of the schedule for the run. On the next screen, designate the injection number if other than 1 to start the run.

14.3.12 At this point (still under main menu run) make sure the auto sampler is in the run position and choose the "run" command.

14.3.13 Under run, select "start" and confirm at the OK prompt. The run will begin.

NOTE: Instrument shutdown is performed manually.

14.4 Manual Shutdown:

14.4.1 Go to instruments, then Pump_ECD tab turn off Pump and Suppressor.

14.4.2 Turn off pressure valve on eluent tank and the pressure valve on water bottle.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Routine maintenance for the IC most often includes the changing of eluent or of the helium tank, as well as, priming the pump and clearing the flow lines of any trapped air bubbles. It may also include any column work, such as cleaning, or it may call for regenerating the suppressor or changing of filters. The column cleaning solution is made as detailed in section 8.4.

16.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

16.1 The raw data are processed by the IC software system. The software creates a data file including the method, which is stored on the network drive. The software then provides a printout with the following information: sample name, method used to process data, date and time run, (if report time differs from collection time both will be listed), analytes found with concentration, analytes not found and the sample chromatography.

16.2 An external program is used to generate a runlog, which is placed in the runlog binder. The runlog contains the following information in summary format: sample name, date and time run, batch number, dilution, QC type and description.

16.3 The following calculations are used in processing the data.

CSTD % Recovery = Reported Value/Expected Value x100

RPD = Sample 1 - Sample 2/(Sample 1+ Sample 2)/2 x100

% Rec = Spike - Sample/Nominal Concentration x100

Bomb Prep = Sample x Final Volume/Sample Weight

Extraction = Sample x Final Volume/Sample Weight

16.4 For Bomb Calculation:

16.4.1 Calculate the concentrations of each element detected in the sample according to the following equation:

$$C_o = \frac{C_{com} \times V_{com} \times DF \times \%moisture \times 100}{W_o}$$

Where:

C_o = Concentration of element in the sample, mg/kg

C_{com} = Concentration of element in the combustate, mg/L

V_{com} = Total volume of combustate, mL

DF = Dilution Factor

W_o = Weight of sample combusted, g

16.4.2 Percentage by weight of sulfur in sulfate (SO_4):

Where:

S = 32.06 amu,

O= 15.9994 amu x 4 = 63.9976 amu

SO_4= 96.0576 total amu

32.06 amu (S)/96.0586 amu (SO_4) = 0.333758 or 33.37% S in SO_4

16.4.3 MDLs and PQLs are 10X for all bombs.

16.5 Each compound of interest must be within the acceptable range to be reported as a positive detection. If the instrument is re calibrated during the day, the retention windows will be reset after the multipoint is complete.

17.0 QUALITY CONTROL (QC) REQUIREMENTS

17.1 According to EPA Method 300.0, a formal Quality Control Program for this method must be maintained by each laboratory. The GEL QC Program for method 300.0 consists of 2 main components.

17.1.1 MDL Study: a new MDL study covering IC analytes under EPA 300.0 Part A is performed every 6 months, using the guidelines set forth in GL-LB-E-001. For DoD samples LOD is verified quarterly on each instrument used for DoD sample analyses.

17.1.2 Quality Control Sample (QCS) study: A commercially available standard (traceable to NIST standards when possible) is run each time a client, state, or federal performance evaluation study is done. The results of this known must be within the vendor guidelines for the PE sample result to be considered acceptable. If the result is not acceptable the analyst must troubleshoot the problem immediately and reanalyze both the vendor known and the PE sample.

18.0 INSTRUMENT AND BATCH QC REQUIREMENTS

18.1 Instrument QC

18.1.1 A calibration curve is run any time the values or retention times of the check standards shift by more than 10%.

18.1.2 An initial calibration verification (ICV) is run as the first sample in each day's run.

18.1.3 An initial calibration blank (ICB) is run following the ICV.

18.1.4 A continuing calibration verification (CCV) of varying concentration is run after every 10 analytical samples and after the last analytical samples in the run.

18.1.5 A continuing calibration blank (CCB) is run after every CCV.

18.1.6 The ICV, ICB, CCVs of varying concentrations, and CCBs are used throughout the analysis to constantly check the linear range of the instrument. The ICB and CCB must not exceed the concentration of the low standard in the calibration curve. The ICV and CCVs of the varying concentrations must recover within 10% of the true value of the standard.

18.2 Batch QC

18.2.1 A sample spike and sample duplicate are run for every batch of <10 samples and for each set of ten samples in batches with >10 samples.

18.2.2 A Method Blank (MB) and Laboratory Control Sample (LCS) are run at least once for every batch of 20 samples or less. For solid batches, 4g of Teflon chips or sand is used.

18.2.3 For solid batches where the sample is prepped using DI water extraction, the LCS is made by spiking the aliquot of the Source standard onto 4 g of Teflon chips or sand to dilute to 40 mL with DI water.

18.2.4 For nonaqueous liquids or solids not easily DI extracted, the LCS and method blank are bomb prepped in the same manner as the samples.

NOTE: Some clients have statements of work that call for additional QC such as LCS Duplicates or Matrix Spike Duplicates.

18.3 Acceptance limits:

18.3.1 Correlation coefficient must be 0.995 or greater.

18.3.2 ICV recovery must be 90-110% for all batches.

18.3.3 CCV recovery must be 90-110% recovery for all batches.

18.3.4 Matrix relative percent difference (RPD): Determined yearly by the Statistical Process Control (SPC) system of AlphaLIMS. The limits are given in spreadsheet form to each analyst.

NOTE: DoD requires RPD limits of 0 < 10% for sample DUPs and 0 ≤ 15% for MS/MSD.

18.3.5 Matrix spike recovery: The Limits are static at 90-110% recovery for samples analyzed by EPA 300.0. Matrix spike limits for samples analyzed by SW-846 9056 are determined yearly by the Statistical Process Control (SPC) system of AlphaLIMS.

18.3.6 Method Blank: Must be less than the CRDL or Practical Quantitation Limits (PQL). DoD QSM requires the method blank to be < ½ RL.

18.3.7 LCS: Determined yearly by the Statistical Process Control (SPC) system of AlphaLIMS. The limits are given in spreadsheet form to each analyst. If the % Recovery falls outside these limits, the batch must be reanalyzed. For Method 300.0 the LCS acceptance limits are set at 90-110% for all liquid matrix batches.

18.3.8 LCS RPD: Determined yearly by the Statistical Process Control (SPC) system of AlphaLIMS. If the RPD falls outside these limits, the batch must be reanalyzed.

19.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

19.1 Before submitting results for data entry into AlphaLIMS, check the following items:

19.1.1 The run is dated and initialed.

19.1.2 All cross-outs are dated and initialed.

19.1.3 Standard preparation is documented in the AlphaLIMS standards logbook and standard identification numbers are recorded with the run in AlphaLIMS.

19.1.4 All dilution factors are clearly marked.

19.1.5 Sample prep logbook in AlphaLIMS has been filled out completely (if applicable).

19.1.6 Correlation coefficient is recorded accurately and is $\geq$ 0.995.

19.1.7 All quality control samples such as blanks, duplicates, and spikes are clearly identified and fall within current acceptance limits.

19.1.8 The correct units are recorded for the results.

19.1.9 Each nonconformance has been noted in the Case Narrative.

19.1.10 All manual reprocessing of chromatograms must have a reason for the reprocess. The changes must be signed by the person doing the reprocessing and a qualified peer.

19.2 After ensuring that the above items are properly documented, print the batch report. (Data are automatically transferred to AlphaLIMS.)

19.3 Review data report to ensure that all data are in, then status the batch to “Review.” This will trigger the qualifiers.

19.4 The batch sheet, data report, and case narrative are stapled together. This is the package that enters the main data review process.

19.5 The data review is done by the analyst who performed the analysis. The analyst completes the review, noting and correcting any discrepancies. When the analyst has a correct report of the data, the package is passed on for peer review.

19.6 When the data package associated with a given batch satisfactorily passes review, the batch status is updated to "DONE" in AlphaLIMS.

20.0 RECORDS MANAGEMENT

All data associated with the activity described in this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

21.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

22.0 REFERENCES

22.1 EPA Method 300.0, “The Determination of Inorganic Anions in Water by Ion Chromatography.”

22.2 SW-846, Method 9056A, Rev.1, “Determination of Inorganic Anions by Ion Chromatography,” February 2007.

22.3 Dionex Chromeleon software

22.4 Dionex ICS 3000 Ion Chromatography Instruction Manual

22.5 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) Version 5.3, July 2019.

23.0 HISTORY

Revision 27: Update to include the use of Teflon chips or sand for solid batches and removed bomb prep standards (which are found in GL-GC-E-079).
Revision 26: Updated for new instrument. Update the reference section for current DoD QSM. Version 5.2, December 2018.
Revision 25: Updated for current concentration of standards and dilutions used. Corrected typos
Revision 24: Added clarification to section 6.0 and 13.1.7.
Revision 23: Updated to include iodide.

APPENDIX 1: ACCEPTANCE LIMITS

Acceptance Criteria	GEL Standard	DoD QSM
CCV/ICV	90% - 110%	90% - 110%
CCB/ICB	± RL	± RL
Method Blank	<CRDL	± ½ RL, reprep failures, B flag for continued failures
LCS - liquid LCS - soil	90% - 110%	90% - 110% Glass beads/Teflon chips/Sand for solids, flag failures with Q if reprep not possible.
Matrix Spikes/ Matrix Spike Duplicates	90% - 110%	90% - 110%, when applicable. Flag failures with J.
Sample Duplicates	0% <= 20% when greater than 5X RL, +/-RL when less than 5X RL	0% <= 10% Flag failures with J.
MS/MSD RPD	RPD 0% <= 20% between MS/MSD	RPD 0% <= 15% between MS/MSD, J flag failures.
Qualifiers	COA = U/J/B for samples or MB. * for LCS, MS, MSD, DUP.	U for non detects, J for values estimated between LOD and LOQ
MDL/MDLV	MDL and MDLV are performed bi-annually per the methods	LODV performed quarterly on all instruments used for DoD analysis.

APPENDIX 2: CALIBRATION STANDARDS FOR IC

(For Illustrative Purposes Only)

Autocal 6
20 mg/L SO_4
10 mg/L Cl
5 mg/L Fl, NO_2, NO_3, I
3 mg/L Br, PO_4

Autocal 5
4 mg/L SO_4
2 mg/L Cl
1 mg/L Fl, NO_2, NO_3
2.5 mg/L Br, PO_4, I

Autocal 4
2 mg/L SO_4, I
1 mg/L Cl, Br, PO_4
0.5 mg/L Fl, NO_2, NO_3

Autocal 3
1 mg/L SO_4, I
0.5 mg/L Cl, Br, PO_4
0.25 mg/L Fl, NO_2, NO_3

Autocal 2
0.5 mg/L I
0.4 mg/L SO_4
0.2 mg/L Cl, Br, PO_4
0.1 mg/L Fl, NO_2, NO_3

Autocal 1
DI water

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR TOTAL, TOTAL INORGANIC, AND TOTAL ORGANIC CARBON (TOC)

(GL-GC-E-093 REVISION 16)

APPLICABLE TO METHODS:
EPA Method 415.1
EPA SW-846 Methods 9060/9060A
Standard Methods 22nd Edition, SM 5310 B-2011

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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL, TOTAL INORGANIC, AND TOTAL ORGANIC CARBON (TOC)

2.0 METHOD CODE

2.1 EPA Method 415.1

2.2 EPA SW-846 Method 9060/9060A

2.3 Standard Methods 22nd Edition, SM 5310 B-2011

3.0 METHOD OBJECTIVE/PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to describe the procedure used to run samples for total, total inorganic, and total organic carbon using the OI Analytical Model 1030W Aurora TOC analyzer.

4.0 METHOD SUMMARY

4.1 Total organic carbon is converted to carbon dioxide by chemical oxidation of the organic carbon in the sample. The carbon dioxide is measured using a non-dispersive infrared detector.

4.2 Synonym: Non-purgeable organic carbon

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. If the sample is very viscous or heavily particulated, the sample is treated as a solid and SOP GL-GC-E-062 is used.

NOTE: SC DHEC requires analysis by SW-846 9060/9060A if samples are not drinking water or wastewater and the data are to be used for regulatory purposes.

6.0 HOLDING TIME

Holding time is 28 days from the time and date of collection until the start of analysis unless otherwise specified.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Storage of samples in amber glass bottles is preferred. Polyethylene bottles may be used if blanks are collected to show that the containers do not contaminate the samples.

7.2 Unless samples are to be analyzed within 15 minutes of collection, they should be acidified to a pH of less than 2 with sulfuric acid, phosphoric acid or hydrochloric acid.

7.3 Samples should be stored at $0° \leq 6°$ C.

7.4 If the concentration of dissolved organic carbon is to be determined, samples should be filtered through a 0.45 µm filter at the time of collection.

8.0 INTERFERENCES

Carbonates and bicarbonates must be removed before analysis for TOC. The sparging of liquid samples removes carbonate and bicarbonate interferants.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 0.00 to 20 mg/L with the sample loop set at 5 mL loop size.

9.2 Calibration range: 1 to 20 mg/L.

9.3 Method detection limit (MDL): Refer to current MDL study.

9.4 Method precision: < or equal to 20% RPD.

9.5 Method accuracy: 85%-115%.

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL.

10.2 Laboratory Control Sample (LCS): A standard, usually of the same matrix as the sample batch being organized, taken through the same prep process as the samples then analyzed with the batch.

10.3 Total Organic Carbon: All carbon in a sample besides carbonates and bicarbonates.

10.4 Non-purgeable Organic Carbon: All organic carbon that is not removed by sparging.

10.5 Total Carbon: Total amount of carbon in a sample.

10.6 Total Inorganic Carbon: All inorganic carbon in a sample that is separated from organic carbon by acidification.

10.7 Dissolved Organic Carbon: All organic carbon in a sample that has been filtered through a 0.45 micron filter.

10.8 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data are obtained, computer printouts of the data are generated. These dated hard copies of the data are stored in the TOC 1030W binder. Results are uploaded into AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDS forms are maintained in the laboratory.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 IO Analytical Model 1030W Aurora TOC Analyzer including:

15.1.1 Reaction module

15.1.2 Detector/electronics module

15.1.3 Printer module

15.1.4 Autosampler module

15.2 Compressed nitrogen (zero grade) and two stage regulator

15.3 Flow meter

15.4 Personal computer (for entering data)

16.0 REAGENTS

16.1 Raw materials: (Chemicals should be at least ACS grade or equivalent)

16.1.1 Potassium acid phthalate, $KHC_8H_4O_4$

16.1.2 Concentrated phosphoric acid, H_3PO_4 (85%)

16.1.3 5% (by volume) Phosphoric acid reagent: Carefully add 59 mL concentrated phosphoric acid to 500 mL DI water, and dilute to 1 L.

16.1.4 ASTM Type I deionized water (see GL-LB-E-016)

16.1.5 Sodium bicarbonate, $NaHCO_3$

16.2 Persulfate reagent:

16.2.1 Dissolve 100 g sodium persulfate in a 1 liter volumetric flask using deionized (DI) water.

16.2.2 Bring to volume with DI water.

17.0 PREPARATION OF SAMPLES

Not applicable.

18.0 PREPARATION OF STANDARDS

Potassium Phthalate (also known as potassium hydrogen phthalate) is used for the preparation of standards. The standard is valid for one year from opened date or manufacturer's expiration date, whichever is shortest.

18.1 TIC Standard Solution (2000mg/L)

18.1.1 Weigh 14 g of Sodium Bicarbonate and dilute to 500 mL of DI water in a volumetric flask. This yields a 2000 mg/L solution which expires in 6

months. This solution should be purchased from a certified vendor, if available.

18.2 Primary TOC Standard Solution (2000 mg/L)

18.2.1 Weigh 0.850 g of potassium acid phthalate and dilute to 200 mL volume with DI water in a 200 mL volumetric flask. This yields a 2000 mg/L solution. Standard expires six months from preparation date. This solution should be purchased from a certified vendor, if available.

18.3 TIC/TOC Working Standard (20 mg/L)

18.3.1 Transfer 2.5 mL of the primary TIC/TOC stock standard solution to the 250 mL volumetric flask and dilute to 250 mL with DI water.

18.4 TIC/TOC Working Standard (10 mg/L)

18.4.1 Transfer 2.5 mL of the primary TIC/TOC stock standard solution using 500 mL volumetric flask and dilute to 500 mL with DI water.

18.5 TIC/TOC Working Standard (1 mg/L)

18.5.1 Transfer 0.125 mL of the primary TIC/TOC standard solution to the 250 mL volumetric flask and dilute to 250 mL with DI water.

18.6 TOC Working Standard (5 mg/L)

18.6.1 Transfer 0.625 mL of the TIC/TOC to the partially filled flask. Dilute to 250 mL with DI water.

NOTE: Working standards expire 1 week after preparation.

18.7 Secondary TIC/TIC Stock Standard

18.7.1 Using a different lot number of Sodium Bicarbonate, weigh 14 g of Sodium Bicarbonate a dilute to 500 mL with DI water in a volumetric flask. This yields a 2000 mg/L solution which expire after 6 months. This solution should be purchased from a certified vendor, if available.

18.8 Secondary TOC Stock Standard

18.8.1 Using a different lot of potassium phthalate, weigh 0.850 g of potassium acid phthalate and dilute to 200 mL volume with DI water in a 200 mL volumetric flask. This yields a 2000 mg/L solution. Standard expires six months from preparation date. This solution should be purchased from a certified vendor, if available.

18.9 10 mg/L Working LCS/ICV/CCV

18.9.1 Transfer 2.5 mL of the secondary TIC/TOC stock standard to the 500 mL volumetric flask and dilute to 500 mL with DI water. This solution expires one week from preparation.

19.0 PREPARATION OF STANDARDS AND QUALITY CONTROL SAMPLES

19.1 Documentation of standards and their preparation are maintained in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

19.2 Laboratory Control Sample (LCS): (See 18.9)

19.3 Calibration standards: The concentrations used are listed below:

19.3.1 0.0 mg/L

19.3.2 1 mg/L

19.3.3 5 mg/L

19.3.4 10 mg/L

19.3.5 20 mg/L

19.3.6 Calibration standards are made up using primary source stock standard.

19.4 Initial Calibration Verification (ICV): The ICV is a 10.0 mg/L standard made from the second source stock standard. The ICV must be analyzed immediately after the calibration standards and analyzed at the start of each analytical week. The ICV standards are made up on a weekly basis. (See 18.9)

19.5 Continuing Calibration Verification (CCV): The CCV is a 10.0 mg/L standard made from the second source stock standard. A CCV must be run after every 10 samples and after the last sample in the run. The CCV standards are made up on a weekly basis. (See 18.9)

20.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

20.1 Refer to Chapter 4: Operation of the OI Model 1030W Aurora TOC Analyzer Operator's Manual.

20.2 Before a run is started, make sure there is an adequate amount of sodium persulfate reagent to complete the analysis. Also make sure the 5% phosphoric acid solution and DI H_2O containers are full.

20.3 Prior to the start of analysis, ensure that the nitrogen flow is between 40 and 60 psi.

21.0 QUALITY CONTROL (QC) REQUIREMENTS

21.1 Instrument QC

21.1.1 An initial calibration verification (ICV) is analyzed immediately after the calibration standards and at the start of each analytical week. This standard must be made from a different source than the calibration standards.

21.1.2 An initial calibration blank (ICB) is analyzed following the ICV.

21.1.3 A continuing calibration verification (CCV) is analyzed after every 10 analytical samples and after the last analytical sample in the run.

21.1.4 A continuing calibration blank (CCB) is analyzed after every CCV.

21.2 Batch QC

21.2.1 A matrix spike and a matrix duplicate are analyzed for every batch of $\leq$ 10 samples and for each set of ten samples in batches with > 10 samples (unless otherwise required by client contract).

21.2.2 A method blank and laboratory control sample (LCS) are analyzed at least once for every batch of 20 samples or less.

21.2.3 For liquid samples, the LCS is normally a 10 mg/L standard taken through the same process as the samples.

21.2.4 LCS duplicates are analyzed if required by client contract.

21.3 Acceptance limits:

21.3.1 Correlation coefficient must be 0.995 or greater.

21.3.2 ICV recovery must be 90-110% for all batches (unless otherwise specified by client contract). If not, the ICV should be remade and reanalyzed. If the ICV continues to be out of range, a re-calibration is then required.

21.3.3 CCV recovery must be 90-110% for all batches (unless otherwise specified by client contract). Any samples bracketed by a failing CCV must be reanalyzed with passing bracketing CCVs. If the CCV continues to be out of range, the instrument must be recalibrated.

21.3.4 Matrix relative percent difference (RPD): < or equal to 20% of RPD.

21.3.5 Matrix spike recovery: 85% -115%.

21.3.6 Method blank: Must be less than the CRDL.

21.3.7 LCS: refer to current SPC limits which are static for Drinking Water samples.

21.3.8 LCS RPD: refer to current SPC limits which are static for Drinking Water samples.

21.3.9 If analysis by EPA Method 415.1 is requested, the samples are analyzed in duplicate. The relative percent difference (RPD) between the two values must be ≤ 20% when the values are greater than 5 mg/L.

21.3.10 If analysis by SW-846 9060/9060A is requested, samples are analyzed in quadruplicate. The relative percent difference (RPD) between the values must be ≤ 20% when the values are greater than 5 mg/L.

21.4 Handling out-of-control situations:

21.4.1 If a sample result exceeds the concentration of the highest calibration standard, the sample must be diluted appropriately with DI water and reanalyzed.

21.4.2 The correlation coefficient must be at least 0.995. If it is less than 0.995 the calibration standards must be reanalyzed. Analysis of samples cannot begin until a correlation coefficient of 0.995 is obtained.

22.0 RUN SEQUENCE

22.1 Calibration standards, including DI water blank

22.2 ICV

22.3 ICB

22.4 Up to 10 analytical samples including LCS, method blank, and sample QC (refer to Section 20)

22.5 CCV (Continuing Calibration Verification)

22.6 CCB

22.7 Repeat steps 21.5 through 21.7 for remaining samples in the run ending with CCV and CCB.

23.0 PROCEDURE

23.1 Analysis: Refer to Chapter 4 (pages. 62 through 71), Operation of the Model 1030W Aurora Analyzer Operator's Manual.

23.2 Calculation/reporting of results:

23.2.1 As the data are obtained, they are uploaded into AlphaLIMS.

23.2.2 If a sample is analyzed by EPA 415.1, the average of the two replicates is reported for the TOC or Total Carbon Concentration.

23.2.3 For samples analyzed by SW 846-9060/9060A, all four replicates plus the average are reported for the TOC concentration.

24.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURES

Refer to OI Analytical Model 1030W Aurora TOC analyzer.

25.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for General Chemistry Data Review and Packaging.

26.0 DATA TRANSMITTAL

When a batch is issued "DONE" status, it is made available to reporting personnel.

27.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

28.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to Chapter 4, page 74, Operation of the Model 1010 Wet Oxidation Total Organic Carbon Analyzer Operator's Manual.

29.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

30.0 METHOD VERIFICATION

30.1 To ensure accuracy, % error is calculated for the duplicate values of all concentrations greater than 1 mg/L.

30.2 The % error must be 10% or less for samples logged according to Method 415.1. If not, the samples must be reanalyzed.

31.0 REFERENCES

31.1 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, “Organic Carbon, Total,” Method 415.1 (Combustion or Oxidation), March 1979.

31.2 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1C, SW-846, Third Edition, November 1986. Method 9060, “Total Organic Carbon,” Revision 0, September 1996. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

31.3 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1C, SW-846, Third Edition, November 1986. Method 9060A,

"Total Organic Carbon," Revision 1, August 2002. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

31.4 OI Analytical Model 1030W Aurora Analyzer Operator's Manual.

31.5 Standard Methods 22nd Edition, SM 5310 B-2011. High-Temperature Combustion Method.

31.6 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.3, July, 2019.

32.0 HISTORY

Revision 12: Preparation of Standards section added.

Revision 13: Updated procedure to include new instrument information and remove reference to old instrument. Updated the process of working standards.

Revision 14: Further method and procedure clarifications and updated to new instrument.

Revision 15: Updated the method concentration range from 0.2 to 0.00. Added reference to QAP in definitions. Added current DOD/DOE QSM version 5.1 and version 3.1, January 2017.

Revision 16: Updated sample preservation. Updated DoD QSM reference to Version 5.3, July 2019. Clarify acceptance limits for Drinking Water.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

N-HEXANE EXTRACTABLE MATERIAL (HEM; OIL AND GREASE) AND SILICA GEL TREATED N-HEXANE EXTRACTABLE MATERIAL (SGT-HEM, NON-POLAR MATERIAL) IN AQUEOUS MATRICES

(GL-GC-E-094 REVISION 18)

APPLICABLE TO METHODS:
EPA 1664A
EPA 1664B

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR N-HEXANE EXTRACTABLE MATERIAL (HEM; OIL AND GREASE) AND SILICA GEL TREATED N-HEXANE EXTRACTABLE MATERIAL (SGT-HEM, NON-POLAR MATERIAL) IN AQUEOUS MATRICES

2.0 METHOD CODE

EPA 1664A

EPA 1664B

3.0 METHOD OBJECTIVE/PURPOSE

This standard operating procedure (SOP) describes the procedure used to determine the concentration of n-hexane extractable material (HEM) and HEM that is not adsorbed by silica gel (SGT-HEM). HEM may include non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related materials.

4.0 METHOD SUMMARY

The concentration of HEM in aqueous samples is determined using solid phase hexane extraction. The hexane is evaporated and the HEM is determined gravimetrically.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

Holding time is 28 days from the time and date of collection until the start of extraction, unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples should be collected in glass, one-liter containers with a PTFE-lined screw cap. At least two and preferably three aliquots should be collected per sample to allow for potential quality control failures and to provide sufficient aliquots to meet the methods quality control criteria.

NOTE: If SGT-HEM is to be determined and the concentration of HEM > 100 mg/aliquot, then if possible, four sample aliquots should be collected.

7.2 Samples are preserved to a pH < 2 with hydrochloric acid or sulfuric acid at the time of collection.

7.3 Samples are stored at 0 ≤ 6° C in accordance with GL-SR-E-001 for Sample Receipt, Login and Storage.

7.4 Samples must be collected as grab samples. Composite sampling is not allowed since extractable materials may stick to the sampling equipment.

8.0 INTERFERENCES AND LIMITATIONS

8.1 This procedure is not applicable to materials that volatilize below 85° C. Such materials may be partially lost when the solvent is evaporated.

8.2 Recoveries of some crude oils and heavy fuel oils may be low if they contain significant percentages of material that is not extractable in n-hexane.

8.3 Samples containing a significant total suspended solid concentration may cause the speed disk to become clogged requiring more than one disk to be used per sample. Glass wool can be utilized to remove interferences. If glass wool is utilized, the MB, LCS, MSD and LCSD must also use glass wool.

8.4 Low recoveries may be obtained if the surfaces that come into contact with stearic acid are not rinsed thoroughly. This includes sample container, solid phase extraction device, sodium sulfate used in drying the extract, and surfaces of the evaporating dish.

8.5 If a sample contains a significant concentration of sulfur, elevated results may be obtained when the sulfur is converted to thiosulfate upon acidification. This compound is extractable in n-hexane. In such cases, it is recommended that the sample not be acidified.

8.6 Both polar and non-polar substances such as glycerides, detergents, and fats will be extracted in n-hexane. The amount of polar materials such as petroleum hydrocarbons can be calculated by subtracting the amount of SGT-HEM from the concentration of total HEM.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 5 mg/L to 1000 mg/L. This range may be extended by the analysis of a smaller sample volume collected separately.

9.2 Method detection limit (MDL): Refer to current MDL study. The maximum allowed MDL for EPA 1664A and EPA 1664B is 1.4 mg/L.

9.3 Method precision: Precision is determined by the relative percent difference (RPD) between the laboratory control sample (LCS) and LCS duplicate (LCSD), when required, or the matrix spike (MS) and MS duplicate (MSD).

9.4 Method accuracy: Accuracy is determined by the percent recovery on LCSs and MSs.

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

10.2 Hexane-extractable material (HEM): Any substance present in a sample that can be extracted with n-hexane. This includes both polar and non-polar substances.

10.3 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to

determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

10.4 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

10.5 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

10.6 Silica gel treated HEM (SGT-HEM): Any substance present in a sample that can be extracted with n-hexane and not be adsorbed by silica gel. SGT-HEM consists of non-polar compounds.

10.7 Spike (Matrix Spike or Post Spike): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or PS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or PS corrected for background concentrations.

10.8 Statistical Process Control (SPC) Limits: Statistically derived limits which establish Acceptable Ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

10.9 Laboratory Duplicate (DUP, LCSD, MSD, or PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

10.10 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST AND METHOD VERIFICATION

11.1 Technicians and analysts do not analyze samples without supervision until trained by qualified personnel. Training records are maintained as quality records.

11.2 To establish the ability to generate acceptable precision and accuracy, the laboratory must perform the following operations:

11.2.1 Determine the concentration of four HEM and SGT-HEM in four samples of Precision and Recovery (PAR) standards according to the procedures listed in section 22.0.

11.2.1.1 Using the results from the set of four analyses, compute the average percent recovery (X) and the standard deviation of

the percent recovery (s) for the HEM and for the SGT-HEM. When determining SGT-HEM, the true concentration (T) must be divided by 2 to reflect the concentration of hexadecane that remains after removal of stearic acid. Use the following equation for calculation of the standard deviation of the percent recovery:

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

Where:

n = Number of samples

x = % Recovery in each sample

11.2.1.2 Compare s and x with the corresponding limits for initial precision and accuracy recovery in Table 1 of the method. If s and x meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or x falls outside of the acceptance range, system performance is unacceptable. Correct the problem and repeat the test.

12.0 DOCUMENTATION OF DATA

As data are obtained, they are recorded in AlphaLIMS. Upon completion of analysis, the results are entered into AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

N-HEXANE HAS BEEN SHOWN TO HAVE INCREASED NEUROTOXIC EFFECTS OVER OTHER HEXANES AND SOME OTHER SOLVENTS. PERFORM ALL OPERATIONS WITH N-HEXANE IN A WELL VENTILATED AREA IN ORDER TO MINIMZE INHALATION OF THIS SOLVENT.

SULFURIC ACID AND HYDROCHLORIC ACID ARE HIGHLY CORROSIVE. AVOID CONTACT OR SPILLING SOLUTIONS OF THIS CHEMICAL ON YOUR HANDS OR OTHER PARTS OF THE BODY.

13.1 Treat all chemicals and samples as potential health hazards and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDS forms are maintained in the laboratory.

13.2 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related standard operating procedures.

13.3 Prior to handling radioactive samples, analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.3.1 Wear eye protection with side shields while performing procedures in the lab.

13.3.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

13.3.3 Post signs indicating radioactive samples are in the area.

13.3.4 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.3.5 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

13.3.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

13.3.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician can supply the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Instrumentation and Equipment

15.1.1 Analytical balance capable of weighing to 0.0001g.

NOTE: This balance should be calibrated in accordance with GL-LB-E-002 for Balances.

15.1.2 Speedisk™ Extraction Manifold

15.1.3 Vacuum source with a minimum 20 mm Hg

15.1.4 Flexible tubing to connect vacuum to the manifold and manifold to a glass waste container with spout.

15.1.5 JT Baker Speedisk™ or equivalent

NOTE: The thermometer must be verified in accordance with GL-QS-E-007 for Thermometer Verification.

15.1.6 Aluminum weighing pans with a minimum capacity of 70 mL

15.1.7 1PS silicone treated 125mm filter paper

15.1.8 SPEED-VAPTM II 9000 Solvent Evaporation System capable of maintaining a temperature of 40° C.

15.1.9 Extraction port adapter

15.1.10 Oven capable of drying the sodium sulfate and silica gel.

15.1.11 Desiccator and desiccant

15.2 Speedisk

NOTE: Parts for the speedisks are provided by Environmental Express.

15.2.1 Parts

15.2.1.1 Speedisk shells

15.2.1.2 Funnels

15.2.1.3 Screens

15.2.1.4 Filters

15.2.1.5 Glass wool (needed)

15.2.2 Speedisk Assembly

15.2.2.1 Place one screen inside the speedisk shell.

15.2.2.2 Place one filter on top of the screen inside the speedisk shell.

15.2.2.3 Next put one additional screen on top of the filter.

15.2.2.4 Place the funnel in the speedisk shell on top of the screen, filter, and screen stack.

15.2.2.5 Secure the funnel in the speedisk shell by pressing firmly using a speedisk assembly tool. Place one hand on the speedisk shell and the other on the speedisk assembly tool.

15.2.2.6 Check for any gaps along the outside of the speedisk shell. If any are detected continue to use the speedisk assembly tool to close the gaps.

15.2.2.7 Check for any wrinkles in the top screens. If any part of the top screen is not under the funnel then disassemble the funnel and replace the screen.

NOTE: The top and bottom screens are necessary in order for the filter to remain intact throughout the procedure. All parts of the speedisk are given to the dishwasher after the analysis and reused. Inspection of all parts is mandatory prior to each assembly to ensure that no contamination has occurred. All radioactive

samples analyzed must have their designated speedisk parts rinsed with DI water three times and collected in the nonflammable radioactive waste water container prior to them being washed by the dishwasher.

15.3 Glassware

15.3.1 Glass collection chambers (~50 mm diameter)

15.3.2 40 mL glass collection vials with Teflon coated septum.

15.3.3 Glass funnels

15.3.4 Volumetric flask (250 mL, 500 mL, etc.)

15.3.5 Glass stirring rods

15.3.6 Plastic disposable transfer pipets (minimum capacity 3 mL)

15.3.7 Tilting DispHead 10mL

15.3.8 Plastic squirt reagent bottles

16.0 EQUIPMENT MAINTENANCE

16.1 Monthly maintenance

16.1.1 Pump Maintenance

NOTE: Only use Duo Seal pump oil manufactured especially for use in Welch belt-drive vacuum pump.

16.1.1.1 Pump oil should be changed every 3-4 weeks depending on usage.

16.1.1.2 The oil level must be monitored throughout every batch analyzed.

16.1.1.3 Observe any oil or water that may enter the pump oil level reservoir during analysis.

16.1.1.4 Drain these water levels off when the analysis permits.

16.1.1.5 Do not allow the oil level to drop less than a quarter of the way full inside the oil level reservoir.

16.1.1.6 Do not allow the oil or water level to exceed three-quarters of the way full inside the oil level reservoir.

16.1.2 Pump Oil Change

16.1.2.1 Remove tubing from the hood that covers the exhaust recirculating filter.

16.1.2.2 Unscrew and remove exhaust recirculating filter from the oil filled reservoir.

16.1.2.3 Connect the end of a hose to the oil drain on the pump, and place the other end of the hose inside a used oil collecting bottle.

16.1.2.4 Open drain valve completely and allow all of the old oil to exit the pump.

16.1.2.5 Leave the drain valve open and pour approximately 200 mL of new oil into the oil fill reservoir using a small funnel. This will help remove dirt from inside the pump.

16.1.2.6 Close the drain valve and fill the pump with new oil up to the quarter fill mark on the oil level reservoir.

16.1.2.7 Reattach the exhaust recirculating filter and hood hose. Make sure the switch for the exhaust recirculating filter is in the up position to ensure its proper function.

17.0 REAGENTS AND SOLUTIONS

17.1 ASTM Type I Deionized (DI) Water

17.2 Sodium Sulfate (Na_2SO_4), ACS-grade, anhydrous crystal

NOTE: Prior to being used, the sodium sulfate should be dried in an oven at 200 to 250° C for a minimum of 24 hours and stored in a tightly sealed container.

17.3 N-Hexane (85% minimum purity, 99% minimum saturated C6 isomers)

17.4 Hydrochloric acid, concentrated (HCl)

17.5 Methanol (ACS/HPLC/GC Grade)

17.6 Silica gel, anhydrous for the determination of SGT-HEM

17.6.1 75 –150 micrometers, Davisil Grade 923 (Supelco 21447-7A or equivalent)

17.6.2 Silica gel must be dried at 200 to 250°C for a minimum of 24 hours and stored in a tightly sealed container or desiccator prior to use.

17.6.3 Silica gel must be screened as indicated below prior to its use:

17.6.3.1 Extract 30 g of silica gel in n-hexane.

17.6.3.2 Evaporate the n-hexane to dryness in a pre-weighed aluminum weigh boat.

17.6.3.3 Determine the amount of residue gravimetrically.

17.6.3.4 The silica gel must contain less than 5 mg HEM per 30 g silica gel.

17.6.3.5 Document the screening results and silica gel lot number in the appropriate logbook.

18.0 PREPARATION OF SAMPLES

Not applicable

19.0 PREPARATION OF STANDARDS

19.1 Method Blank (MB): Fill a 1250 mL amber glass bottle with 1000 mL DI water. Preserve by acidifying to a pH < 2 with approximately 1 mL of hydrochloric acid. Cover and shake well.

19.2 Laboratory Control Standard (LCS): Fill a 1250 mL amber glass bottle with 1000 mL DI water. Preserve by acidifying with approximately 1 mL of hydrochloric

acid. Add the standard (1:1 ratio of stearic acid and hexadecane at a concentration of 40 mg/L) to the DI water and shake until the solution is homogeneous. Cover and shake well.

19.3 Matrix Spike (MS): The MS will consist of a duplicate sample provided by the client, spiked with a spiking solution. The spiking solution used in the LCS can be used to spike the MS. No preservation is necessary as the sample provided by the client should be at pH < 2.

20.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

20.1 Connect the vacuum source to the manifold and the manifold to the waste container using Nalgene tubing.

20.2 Attach one end of flexible tubing to the spout of the appropriate waste container and insert the other end into plastic waste drum.

21.0 ANALYSIS OF NONRADIOACTIVE AND RADIOACTIVE SAMPLES

21.1 Segregation of wastewater using filters requiring methanol activation

21.1.1 Wastewater is divided into four separate channels:

21.1.1.1 Channel 1: Non-radioactive/Non-Flammable wastewater

21.1.1.2 Channel 2: Hexane

21.1.1.3 Channel 3: Radioactive/Non-Flammable wastewater

NOTE: Channels are controlled by switches on the left outside wall of the hood.

21.2 Start procedure with Channel 2 open (in the 12 o'clock position) and all other channels closed (in the 9 o'clock position).

21.3 Continue to steps 24.4.

21.4 Segregation of wastewater using pre-activated filters

21.4.1 For nonradioactive samples: After step 24.4.7 is completed, open channel 1 and close channel 2. Pour samples into their designated speedisk as the suction valve is open to its maximum for each speedisk.

21.4.2 For radioactive samples: After step 24.4.7 is completed, open channel 3 and close channel 2. Pour samples into their designated speedisk as the suction valve is opened to its mazimum for each speedisk.

NOTE: Radioactive samples must be analyzed at different times than nonradioactive samples.

NOTE: If a sample contains hazardous waste, it must be analyzed separately. Observe whether the sample is radioactive or nonradioactive in order to segregate the waste properly. Contact Waste Management for proper segregation and disposal of hazardous waste.

NOTE: 1250 mL amber glass containers used for MBs and LCSs can be reused. After using one as an LCS, allow it to dry in the hood for no less than 8 hours without a lid.

Use the same bottle as a MB to confirm that no contamination has entered the bottle. This process can be used with 40 mL glass vials as well.

22.0 QUALITY CONTROL (QC) REQUIREMENTS

22.1 Frequency of QC:

22.1.1 A MB must be analyzed with each analytical batch. The MB is a 1000 mL aliquot of DI water acidified to pH < 2 with hydrochloric acid. The blank must be subjected to the same procedural steps as the samples. All samples must be associated with an uncontaminated MB before results can be reported.

22.1.2 A LCS and/or laboratory control sample duplicate (LCS DUP) is analyzed with every batch. The LCS is also referred as the Ongoing Precision and Recovery (OPR) standard. This standard is a 1:1 mixture of stearic acid and hexadecane at a concentration of 40 mg/L. It is bought commercially from an approved vendor such as o2si.

22.1.3 A MS is required for each batch to demonstrate recovery and to monitor matrix interference. A matrix spike duplicate (MSD) is analyzed if required by contract and if enough sample aliquots are provided. The spiking solution used in the LCS can be used to spike the MS and its MSD. The laboratory must spike a minimum of 5 percent of all samples from a given sampling site or a given discharge/waste stream

22.2 Acceptance limits:

22.2.1 Matrix duplicate relative percent difference (RPD): Refer to SPC limits

22.2.2 Method blank: < Contract Required Detection Limit (CRDL)

22.2.3 The LCS must recover within the method specified limits of 78% to 114% for HEM and 64% to 132% for SGT-HEM.

22.2.4 The LCS RPD is not specified by the method. Therefore, the MS/MSD RPD will be used. The RPD value must be less than 18% for HEM and 34% for SGT-HEM.

22.2.5 The MS must recover within the method specified limits of 78% to 114% for HEM and 64% to 132% for SGT-HEM.

22.2.6 The MS/MSD RPD value must be less than 18% for HEM and 34% for SGT-HEM.

22.3 The analytical balance must be verified twice daily, before and after each analytical batch. The balance must be calibrated using a 2 mg and a 1000 mg weight. Calibration shall be within ± 10% (i.e. ± 0.2 mg) at 2 mg and ± 0.5% (i.e. ± 5 mg) at 1000mg. If values are not within these limits, recalibrate the balance.

22.4 Handling out-of-control situations:

22.4.1 If the MS recovery does not fall within the acceptance criteria and the recovery of the LCS and LCSD RPD is acceptable, then the result for

that sample may not be reported or used for regulatory purposes. The laboratory should try to identify the source of the interferences.

22.4.1.1 If the source of interference is thought to originate from the manner of sampling, the client should be advised that the sample should be recollected. The analysis is then repeated on the newly collected sample and an MS of that sample.

22.4.1.2 If the MS recovery is not acceptable due to matrix interferences, the sample and spike should be reanalyzed.

NOTE: Most matrix interferences are due to emulsions. If all steps possible are taken to reduce the formation or increase the dispersion of emulsions this source of interference should be significantly reduced.

22.4.2 If both an MS and an MSD are analyzed and the RPD does not fall within the acceptance criteria, the analytical batch should be reanalyzed and the Group Leader notified.

22.4.3 If the concentration of HEM or SGT-HEM in the MB exceeds the CRDL, the data cannot be reported for regulatory compliance purposes. The associated samples should be reanalyzed and the Group Leader should be notified immediately.

22.4.4 If the LCS recovery or RPD do not meet the acceptance criteria, notify the Group Leader. The analytical batch must be reanalyzed.

22.4.5 If a sample is not preserved correctly, the Project Manager should be notified, the sample acidified if it is not to be recollected, and a nonconformance written. The results for a sample preserved incorrectly must be flagged, as these results can not be used for compliance purposes.

22.4.6 If the balance calibration is not verified as described in 22.3, all measurements must be taken again following the specified protocol.

23.0 RUN SEQUENCE

23.1 MB

23.2 LCS

23.3 Sample 1

23.4 MS of sample 1 (followed by MSD if required.)

23.5 Samples 2 – x where x < 20

23.6 LCS DUP (Use only if there isn't enough sample provided by the client to perform a matrix QC)

24.0 PROCEDURE

NOTE: Allow samples to come to room temperature while performing steps 24.1 through 24.4.

NOTE: If the concentration of SGT-HEM is being determined, both the concentration of HEM and that of SGT-HEM must be determined for each sample unless it is known to contain < 100 mg/aliquot HEM.

24.1 Rinse the collection vials (one per sample) with n-hexane. Repeat twice.

24.2 Rinse the extraction port adapters with n-hexane. Repeat twice.

24.3 Mark each sample bottle at volume level with a marker (ex. Sharpie). The sample volume will be determined in step 24.38.

24.4 Condition the Speedisk™

24.4.1 Mount a Speedisk™ onto each manifold port.

NOTE: Ensure that the vacuum is on (start with channel 2 open) prior to mounting the Speedisk™ and the vacuum valve to each port is closed.

24.4.2 Wash disk with 10 mL of n-hexane.

24.4.3 Open vacuum valves to pull a small amount of solvent through the disk.

24.4.4 Close the vacuum valves and allow the disks to soak for one minute in the remaining solvent.

24.4.5 Pull the remaining solvent through the disks by reopening the vacuum valves.

24.4.6 Allow the disks to dry.

24.4.7 Repeat steps 24.4.2 through 24.4.6.

NOTE: When using no methanol required filters, skip steps 24.4.8-24.4.10 and continue to step 24.5. Finish procedure as indicated. Ignore the waste segregation procedure in section 21.0. Instead refer to section 21.2.

24.4.8 Add 10 mL of methanol.

24.4.9 Repeat steps 24.4.3 through 24.4.5 with the following exception: At step 22.4.4, allow the disk to soak for three (3) minutes with the remaining solvent.

24.4.10 Repeat the 3-minute methanol soak. Pull most of the methanol through, leaving 3 to 5 mm of methanol above the surface of the disk.

WARNING: Do not allow disks to dry after addition of methanol.

24.5 Invert each sample several times.

24.6 Verify that the pH of each sample is < 2 by touching glass rod or similar tool to the sample and allowing the liquid to drip onto the pH strip . If the pH exceeds 2 and the sample is not scheduled for recollection, then acidify the sample to an acceptable pH with concentrated hydrochloric acid. Document the preservation in the batch narrative. Rinse the glass rod or similar tool with hexane.

24.7 Following the run sequence provided in section 21, pour a portion of each sample through its designated disk.

24.8 Open the vacuum valve to maximum suction and continue to add additional sample aliquots to each disk in a manner so the disks are NEVER allowed to dry and the entire sample volumes are transferred.

24.9 Air dry the disks for 15 to 20 minutes at full vacuum.

24.10 Close the vacuum valves.

24.11 Remove the disks from the manifold ports and insert n-hexane-rinsed collection vials into the collection chamber.

24.12 Mount the disks on the collection setup.

24.13 Rinse the empty sample bottles with 10 mL of n-hexane.

24.14 Transfer to the rinsates to the appropriate disk in such a manner so that the entire disk is rinsed.

24.15 Open the vacuum valves pulling approximately 5 mL of the n-hexane into the collection chamber.

24.16 Close the valves and allow the disks to soak in the remaining n-hexane for 2 minutes.

24.17 Open the valves and pull remaining n-hexane into the collection chamber.

24.18 Repeat steps 24.13 through 24.17 two more times.

24.19 Close the valves and remove the collection chambers from the manifold.

24.20 Remove the collection vials from the chambers using the plastic peg on the manifold.

24.21 Close vials using Teflon-lined caps.

24.22 Using a Sharpie, label aluminum pans with sample numbers.

24.23 Rinse aluminum pans with n-hexane. Allow them to dry thoroughly.

24.24 Weigh each pan to the nearest 0.0001 g and record the weights in AlphaLIMs.

24.25 Rinse glass funnels with n-hexane. Repeat twice.

24.26 Fold 1PS filter paper and place in the glass funnel.

24.27 Add approximately 10 g of Na_2SO4 to the 1PS filter paper.

24.28 Rinse the filter paper and Na_2SO_4 with n-hexane. Repeat twice.

24.29 Filter the extracts through a designated funnel into the appropriate weigh pan. Rinse the vial and filter with n-hexane several times to ensure complete transfer.

24.30 Turn on the SPEED-VAP II 9000 and adjust the temperature control so that the temperature stays less than 40° C. Document the temperature in the data entry screen in AlphaLIMS.

24.31 Place the weigh pans on the SPEED-VAP™ II 9000.

24.32 Allow the n-hexane to evaporate to dryness. The samples are to evaporate within a two-hour maximum time period to prevent the loss of hexadecane.

24.33 Remove the weigh pans from the heat source and place in a desiccator for a minimum of 30 minutes. Record the time in AlphaLIMS.

24.34 When the temperature of the pans has reached room temperature, remove the pans from the desiccator, record the date and time in AlphaLIMS, and obtain the weight of the pan plus residue.

24.35 Repeat the cycle of desiccating and weighing until the weight loss is less than 4% of the previous weight or less than 0.5 mg, whichever is less.

NOTE: If crystals are observed, re-dissolve the extract in n-hexane and quantitatively transfer through a filter to another pre-weighed boat.

24.36 If the sample was from the HEM procedure, determine the HEM (W_h) by subtracting the tared weight of the pan (section 24.23) from the total weight of the pan.

24.37 Calculating the results:

24.37.1 HEM and SGT-HEM:

$$[\text{HEM or SGT - HEM in mg/L}] = \frac{A - B}{C}$$

Where:

A = Final weight of the aluminum pan + dried residue in mg

B = Initial weight of the aluminum pan in mg

C = Sample volume in L

24.38 To determine the volume of sample used, fill the sample bottle up to the mark made in step 24.3. Transfer this aliquot to a graduated cylinder and record the volume in AlphaLIMS.

25.0 SGT-HEM DETERMINATION

25.1 Silica gel capacity

To ensure that the capacity of the silica gel will not be exceeded, the amount of HEM must be less than 100 mg, or if greater than 100 mg, must be known.

25.1.1 If the HEM is less than 100 mg, the laboratory may proceed with the determination of SGT-HEM per section 25.2.

25.1.2 If, however, the amount of HEM is unknown, HEM must first be determined as described in section 24.0.

25.2 Extractable materials in silica gel

Because the capacity of the silica gel is not known for all substances, it is presumed that 3 g will normally absorb 100 mg of all absorbable materials. Therefore, for samples containing 1000 mg of HEM, 30 g of silica gel will be needed. The silica gel amount has been limited to 30 g because of concerns about

possible impurities in the silica gel. If the amount of HEM exceeds 1000 mg, split the extract per the following procedures:

25.2.1 Add 50 mL of n-hexane to the pan. If necessary, warm the solution to completely redissolve the HEM.

25.2.2 Quantitatively transfer the extract to a 250 mL beaker. Dilute to 100 mL with n-hexane.

25.2.3 Calculate the extract volume that contains 1000 mg of extractable material according to the following equation:

$$V_a = \frac{(1000)(V_t)}{W_h}$$

Where:

V_a = Volume of aliquot to be withdrawn (mL)

V_t = Total volume of solvent used in section 25.2.2

W_h = Weight of extractable material HEM measurement (mg)

25.2.4 Using a calibrated pipet, remove the volume to be withdrawn (V_a) and place it in a boiling flask. Dilute to approximately 100 mL with n-hexane.

25.3 Adsorption with silica gel

25.3.1 Add 3.0 + 0.3 g of anhydrous silica gel (17.6) to the flask or beaker for every 100 mg of HEM or fraction thereof, to a maximum of 30 g of silica gel. For example, if the weight of HEM is 735 mg, add 3 x 8 = 24 g of silica gel.

25.3.2 Swirl and stir sample for a minimum of 5 minutes.

25.3.3 Filter the solution through an n-hexane pre-moistened filter paper into a tared pan. Rinse the silica gel and filter paper with several small amounts of n-hexane to complete the transfer.

25.3.4 Evaporate and determine the weight of SGT-HEM as per sections 24.31 through 24.35.

NOTE: If silica gel is observed in the pan after this final step, the results could be biased high. Re-dissolve the residue by adding 50 mL of n-hexane to the pan. If necessary, warm the solution to completely re-dissolve the HEM. Quantitatively transfer the extract to a 250 mL beaker. Make sure all the silica gel is rinsed into the beaker. Repeat steps 25.3.3 and 25.3.4.

26.0 DATA ANALYSIS AND CALCULATION

26.1 N-Hexane extractable material

Calculate the concentration of HEM (oil and grease) in the sample per the following equation:

$$HEM\,(mg\,/\,L) = \frac{W_h\,(mg)}{V_s\,(L)}$$

Where:

W_h = Weight of extractable material from section 24.36 (mg)

V_s = Sample volume from 24.38 (L)

26.2 Silica gel treated n-hexane extractable material

Calculate the concentration of SGT-HEM (non-polar material) in the sample per the equation above, substituting W_s (from section 25.3.4) for W_h. If the extract was split to decrease the total amount of material to 1,000 mg, determine the corrected total weight of SGT-HEM in the un-split extract (W_c) using the following equation:

$$W_c\,(mg) = \frac{V_t}{V_a} W_d\,(mg)$$

Where:

W_d = Weight in the portion of the extract split for adsorption (Sections 24.38 and 25.2.4)

V_t and V_a= are defined in Section 25.2.3

Use the corrected total weight of SGT-HEM in the un-split extract (W_c) to determine the total SGT-HEM in the sample by substituting W_c for W_h in Section 26.1.

26.3 Matrix spike recovery

$$\text{MS recovery} = \frac{(A - B) \times 100}{C}$$

Where:

A= [HEM or SGT-HEM in mg/L] in spiked sample

B = [HEM or SGT-HEM in mg/L] in sample

C = Nominal concentration of spike in mg/L

26.4 Relative percent difference for LCSD or MSD:

$$RPD = \frac{(High - Low) \times 100}{Average}$$

Where:

High = Highest concentration in mg/L determined for either the MS/MSD or LCS/LCSD combination

Low = Lowest concentration in mg/L determined for either the MS/MSD or LCS/LCSD combination

Average = Average concentration in mg/L of MS and MSD or LCS and LCSD

26.5 LCS recovery:

$$\text{LCS recovery} = \frac{A \times 100}{B}$$

Where:

A= [HEM or SGT-HEM in mg/L] in LCS

B = Nominal concentration of the LCS in mg/L

27.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

27.1 Turn off the vacuum.

27.2 Remove the stopper from the waste container to relieve the vacuum pressure.

27.3 Open the spout from the waste container in order to drain the waste into the plastic waste drum.

27.4 Hexane waste is poured into the flammable waste container.

28.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-LB-E-005 for Data Review and Validation and GL-GC-E-092 for General Chemistry Data Review and Packaging.

29.0 DATA TRANSMITTAL

When a batch is given General Chemistry departmental "DONE" status, data are automatically available to reporting personnel.

30.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

31.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to manufacturer's instructions.

32.0 LABORATORY WASTE HANDLING AND DISPOSAL

Refer to the Laboratory Waste Management Plan, GL-LB-G-001.

33.0 METHOD VERIFICATION

33.1 Method detection limits are determined in accordance with GL-LB-E-001 for the Determination of Method Detection Limits.

33.2 Constant weight is defined in EPA 1664A and 1664B as a weight difference not exceeding 4% of the previous weight, or 5 mg, whichever is less. This SOP defines constant weight as a difference not exceeding 5 mg.

34.0 REFERENCES

34.1 EPA Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry. EPA 821-R-98-002. PB99-121949. February 1999.

34.2 EPA Analytical Method Guidance for EPA Method 1664A Implementation and Use (40 CFR Part 136.) EPA/821-R-00-003. February 2000.

34.3 EPA Method 1664, Revision B: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry. EPA 821-R-10-001. PB99-121949. February 2010.

35.0 HISTORY

Revision 13: Removed RPD criteria of falling within the range of 78 to 114% for HEM and 64 to 132% for SGT-HEM and method accuracy recoveries falling within the method specified acceptance range of 78 to 114% for HEM and 64 to 132% for SGT-HEM.

Revision 14: Added Detail to pH Testing procedures in 24.6.

Revision 15: Procedure updated to current practices.

Revision 16: Added NOTE to section 25.3.4 to address the occurrence of residual silica gel in pan.

Revision 17: Update the section for determining acceptance criteria for this procedure.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

CYANIDE ANALYSIS BY LACHAT QUICKCHEM 8000 FIA
(GL-GC-E-095 REVISION 22)

APPLICABLE TO METHODS:
EPA Method 335.4,
SW-846 Methods 9010B, 9010C, 9012A, and 9012B,
Standard Methods 22nd Edition, 4500 CN^- C-2011 and 4500 CN^- E-2011

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1.0 STANDARD OPERATING PROCEDURE CYANIDE ANALYSIS BY LACHAT QUICKCHEM 8000 FIA

2.0 METHOD CODE

2.1 EPA Methods 335.4

2.2 SW-846 Methods 9010B, 9010C, 9012A, and 9012B

2.3 Standard Methods 22nd Edition, 4500 CN-C-2011 (Distillation) and 4500 CN-E-2011 (Colorimetric Determination)

3.0 METHOD OBJECTIVE/PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to determine total cyanide in various sample matrices using the Lachat Quickchem 8000 Flow Injection Analyzer after the samples have been distilled by GL-GC-E-067, GL-GC-E-069, and/or GL-GC-E-077, and if necessary, pretreated for amenability to chlorination as in GL-GC-E-040.

4.0 METHOD SUMMARY

Cyanide is released from cyanide complexes by digestion and distillation. The liberated hydrogen cyanide is converted to cyanogen chloride by reaction with chloramine-T reagent at a pH of less than eight. The cyanogen chloride then reacts with the pyridine-barbituric acid reagent to form a red colored complex. This complex is measured colorimetrically at 570nm.

5.0 APPLICABLE MATRICES

5.1 Groundwater
5.2 Drinking water
5.3 Domestic and industrial wastewater
5.4 Soil
5.5 Sludge
5.6 Oil

NOTE: Clients may request that this analysis be performed on miscellaneous liquid, solid, air, or stack samples. In these cases the procedure is modified as necessary.

NOTE: SC DHEC requires SW-846 Methods 9012A and 9012B to be run form any matrices other than drinking water and wastewater when data are to be used for regulatory purposes.

6.0 HOLDING TIME

Holding time for non-South Carolina samples is 14 days from the time and date of collection until sample preparation, unless otherwise specified by the contract. Samples reported from compliance in South Carolina must be analyzed within 24 hours of sample preparation.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples should be stored in 500mL or larger plastic or glass bottles.

7.2 Liquid samples are preserved with approximately 2 mL of 10 N sodium hydroxide per liter of sample to obtain a pH of 12 or higher.

7.3 The sample is refrigerated at 0° ≤ 6° C.

8.0 INTERFERERNCES/LIMITATIONS

8.1 Possible sulfide interference is eliminated by the addition of bismuth nitrate as stated in SW-846 Methods 9010B, 9010C, 9012A, and 9012B. This is added during distillation as detailed in GL-GC-E-067.

8.2 Oxidizing agents that decompose cyanides may be removed by the addition of ascorbic acid or sodium arsenite. SW-846 Methods 9010B, 9010C, 9012A, and 9012B recommend sodium arsenite. Sodium arsenite has produced consistent results and is added during distillation as detailed in GL-GC-E-067.

8.3 Thiocyanates produce a positive interference when they are decomposed to cyanide by ultraviolet digestion. This interference can be reduced by manual distillation.

8.4 Interference from nitrates and nitrites is eliminated by using sulfamic acid. It is added during distillation as detailed in GL-GC-E-067.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 5 to 500µg/L

9.2 Calibration range: 5 to 200µg/L.

9.3 Method detection limit (MDL): MDL and verification limit studies are performed in accordance with GL-LB-E-001 for the determination of method detection limits and method quantitation limits.

9.4 Method precision: Refer to current Statistical Process Control (SPC) limits for relative percent difference (RPD).

9.5 Method Accuracy: Refer to current SPC limits from % Spike Recovery.

10.0 DEFINITIONS

10.1 CRDL: Contract required detection limits.

10.2 Total Cyanide: Refers to all inorganic cyanides present including those as soluble salts or metal complexes.

10.3 Initial Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination after injection of the mid-level ICV.

10.4 Initial Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of Blank of sample matrix. The ICV is obtained from a source external to the laboratory and with a different lot number from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

10.5 Continuing Calibration Blank (CCB): An aliquot of reagent water or blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

10.6 Continuing Calibration Verification (CCV) Standard: Aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample, periodically throughout the run sequence. Is purpose is to determine whether the analytical sequence is in control during sample analysis. It may be prepared from the same source as the calibration standards, and is usually of varied concentration.

10.7 Limit of Detection (LOD): An analyte, method and matrix specific estimate of the minimum amount of a substance that can be reliably detected. GEL has established LOD = 2 x MDL.

10.8 Limit of Quantitation (LOQ): An analyte, method and matrix specific estimate of the minimum amount of a substance that can be reported with a specific level of confidence. The LOQ is set at or above the concentration of the lowest initial calibration standard. The laboratory must empirically demonstrate precision and bias at the LOQ. The LOQ and associated precision and bias must meet client requirements and must be reported. GEL uses the following guidance (LOD < LOQ):

When LOD < PQL, PQL = LOQ

When LOD > PQL, LOQ is raised to next lowest calibration standard

10.9 Practical Quantitation Limit (PQL): The PQL is typically at or above the lowest point on an acceptable initial calibration curve. It may also be determined by multiplying the MDL by approximately 2 to 10. Concentrations of a target analyte determined to be greater than its PQL are defined as quantitative results. This limit is not used in DoD ELAP reporting.

10.10 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Technicians and analysts are not allowed to analyze samples without supervision until trained by qualified personnel. Qualified personnel will document initial demonstration of capability with a verification signature. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

When cyanide analysis is complete, the results are uploaded into AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

SODIUM HYDROXIDE IS HIGHLY CORROSIVE.
HYDROCHLORIC ACID IS A CORROSIVE AND A POISON.
POTASSIUM CYANIDE IS A CORROSIVE AND A CHEMICAL ASPHYXIANT.
PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.
WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

WARNING

POTASSIUM CYANIDE EMITS TOXIC FUMES WHEN HEATED OR MIXED WITH AN ACID. USE CAUTION WHEN HANDLING AND WEAR GLOVES.

WARNING

PYRIDINE IS FLAMMABLE AND A TOXIC UPON INHALATION. PREVENT INHALATION BY USING PYRIDINE UNDER A HOOD.

13.1 Wear safety glasses while in the laboratory.

13.2 Treat all chemicals and samples as potential health hazards and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and client sample MSDS forms are maintained in the laboratory.

13.3 Personal protective equipment

13.3.1 Gloves are required when handling the chemicals in this procedure. The gloves approved for this procedure are:

13.3.1.1 Nitrile gloves for concentrated acids and bases, and potassium cyanide in neat form.

13.3.1.2 Butyl gloves for pyridine.

13.3.2 Work under a hood when using concentrated acids and bases, pyridine.

13.4 Prior to handling radioactive samples, analysts must have radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines to follow:

13.4.1 Wear a plastic apron over lab coat when working with radioactive samples.

13.4.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

13.4.3 Prohibit admittance to immediate work area.

13.4.4 Post signs indicating radioactive samples are in the area.

13.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.4.6 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

13.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

13.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

13.8 Refer to GL-LB-N-001 the Safety, Health and Chemical Hygiene Plan for additional general safety and health information to the laboratory.

14.0 SAMPLE RECEIPT FOR ANALYSIS

Sample distillates are retrieved from the sample refrigerator in the General Chemistry main lab. The analyst takes custody of the daughter samples in AlphaLIMS.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Instrumentation

15.1.1 Lachat QuikChem 8000 Flow Injection Analyzer including:

15.1.1.1 Model ASX-500 XYZ autosampler

15.1.1.2 Model RP-100 Multichannel peristaltic cartridge pump

15.1.1.3 Reaction unit or manifold

15.1.1.4 Colorimetric detector

15.1.1.5 Data System

15.1.1.6 DRD Autodilutor Module

15.1.2 Equipment

15.1.2.1 25 µL syringe

15.1.2.2 10 to 100 µL adjustable micropipette

15.1.2.3 100 to 1000 µL adjustable micropipette

15.1.2.4 10 mL disposable sample cups

15.1.2.5 pH strips

15.1.2.6 250 µL syringe

16.0 REAGENTS

16.1 Raw materials: (Chemicals used for standards should be of ACS grade or equivalent.)

16.1.1 Barbituric acid, $C_4H_4NO_3$ (FW 128.09)

16.1.2 Chloramine-T, $CH_3C_6H_4SO_2NNaCl \cdot 3H_2O$ (FW 281.70)

16.1.3 ASTM Type I deionized (DI) water (See GL-LB-E-016)

16.1.4 Hydrochloric acid, concentrated HCl (FW 36.46)

16.1.5 Potassium phosphate monobasic, KH_2PO_4 (FW 136.09)

16.1.6 Pyridine, C_5H_5N (FW 79.10)

16.1.7 Sodium hydroxide, NaOH (FW 40.00)

16.1.8 Potassium cyanide, KCN (FW 56.11), certified standard (1 mL = 1000 µg CN-)

16.1.9 Silver nitrate, 0.0192 N AgNO3

16.1.10 Potassium hydroxide (KOH)

16.1.11 Solid Reference Material (SRM), cyanide in soil

16.2 Preparation of reagents:

16.2.1 Carrier, 0.25 N Sodium hydroxide

16.2.1.1 In a 1 L plastic container dissolve 10.0 g NaOH in 1 L DI water.

16.2.2 Phosphate buffer, 0.71 M

16.2.2.1 In a 1 L volumetric flask dissolve 97g potassium phosphate, monobasic, anhydrous, (KH_2PO_4) in approximately 800 mL DI water.

16.2.2.2 Dilute to just below the mark with DI water and invert to mix. Stir for 30 minutes to dissolve completely. Prepare fresh monthly.

16.2.3 Chloramine-T

16.2.3.1 In a 500 mL volumetric flask dissolve 2.0 chloramine-T in approximately 200 mL DI water.

16.2.3.2 Dilute to mark with DI water and mix well.

16.2.3.3 This reagent must be prepared daily.

16.2.4 Pyridine-Barbituric Acid Reagent

16.2.4.1 Working under a hood, place 15.0 g barbituric acid into a 1 L beaker. Use approximately 100 mL DI water to rinse the sides of the beaker.

16.2.4.2 Place the beaker on a stirring plate and insert a magnetic stirring bar.

16.2.4.3 While the solution is stirring, add 75.0 mL pyridine and 15.0 mL hydrochloric acid.

16.2.4.4 Add 600 mL more DI water, cover the beaker, and continue stirring until the barbituric acid is completely dissolved.

16.2.4.5 Transfer the solution to a 1000 mL volumetric flask, dilute to the mark with DI water and mix well.

16.2.4.6 This reagent is usable for 6 months from preparation date if kept refrigerated.

16.2.5 Potassium Cyanide (KCN) solution, (1 mL = 1000 µg CN-).

16.2.5.1 Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of DI water.

16.2.5.2 Standardize with 0.0192 N silver nitrate, AgNO3.

16.2.5.3 Dilute to 1 L to achieve 1 mL = 1000 µg of CN-.

16.2.5.4 Alternatively a certified standard may be purchased.

NOTE: Working standards as detailed in Appendix 1 are prepared from 100µg/L stock solution.

NOTE: Detailed procedure for silver nitrate standardization is described in "Standard Methods for the Examination of Water and Wastewater," 22nd Edition, 2011, Method 4500 CN-D-2011.

NOTE: All reagents may be used from 6 months unless otherwise noted.

17.0 PREPARATION OF SAMPLES

Refer to Cyanide Sample Distillation, GL-GC-E-067

NOTE: It is assumed that material within the sample container is considered "the sample. Removal of any extraneous material (twigs, leavers, large rock, etc.) must be documented in the case narrative and bench logbooks.

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards is handled as described in GL-LB-E-007 for laboratory Standards Documentation.

18.2 All standards are prepared from traceable solutions according to the protocol found in Appendix 1.

18.3 All cyanide standards, blanks, and samples are prepared using 0.25 N sodium hydroxide as diluent.

18.4 All cyanide calibration standards are prepared fresh daily.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

19.1 System start-up procedure:

NOTE: Before applying power to the system, check all electrical and hydraulic connections.

19.1.1 Press the power switch "ON" to apply power to the system.

19.1.2 Set up manifold as shown in Appendix 2.

19.1.3 Connect all reagent tubes and the sample line to containers of freshly prepared DI water. Turn on pump and allow DI water to pump through the system as the instrument warms up to temperature.

19.1.4 Set the temperature to 60 °C and allow 15 minutes to warm up.

19.1.5 Once the heater reaches 60 °C move the reagent tubes from the DI water and place them in the appropriate reagents. Allow the flow of reagents to stabilize for 2 minutes. The flow should be smooth and consistent.

19.1.6 Place samples and/or standards in the autosampler. Input the information required by the data system, such as concentrations, replicates and QC scheme.

19.1.7 Place autodiluter diluent line in 0.25 N sodium hydroxide diluent.

19.1.8 Calibrate the instrument by injecting the standards and begin analysis.

19.2 Software startup:

19.2.1 Power up the computer, monitor, and printer.

19.2.2 Click on 'Omnion FIA' icon.

19.2.3 Refer to Lachat Software User Manual.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Instrument QC

20.1.1 Press the power switch "ON" to apply power to the system.

20.1.2 Set up manifold as shown in Appendix 2.

20.1.3 Connect all reagent tubes and the sample line to containers of freshly prepared DI water. Turn on pump and allow DI water to pump through the system as the instrument warms up to temperature.

20.1.4 Set the temperature to 60 °C and allow 15 minutes to warm up.

20.1.5 Once the heater reaches 60 °C move the reagent tubes from the DI water and place them in the appropriate reagents. Allow the flow of reagents to stabilize for 2 minutes. The flow should be smooth and consistent.

20.1.6 Place samples and/or standards in the autosampler. Input the information required by the data system, such as concentrations, replicates and QC scheme.

20.1.7 Place autodiluter diluent line in 0.25 N sodium hydroxide diluent.

20.1.8 Calibrate the instrument by injecting the standards and begin analysis.

20.1.9 Linear Calibration Range (LCR) checks are performed on a 6 month basis. The high standard of the curve is read back against the calibration and must recover ± 10%. If this procedure fails, the problem must be investigated and rectified.

20.1.10 Calculated curve readbacks are: 50%-150% for the first point (low-end) and 90%-110% for all the other points. The calculated zero points must be ± ½ RL. Any failure will require re-calibration of the instrument.

20.2 Batch QC

20.2.1 A matrix spike, and matrix duplicate are run for every batch of < 10 samples and for each set of ten samples in batches with > 10 samples. A method blank is run for every batch of samples.

20.2.2 An ICV standard is prepped with each batch. This is a 150 µg/L (high) standard made up from the second source stock standard.

20.2.3 An LCS is run at least once for every batch of 20 samples or less. An LCS duplicate is run upon client request or if high RAD ALARA concerns exist.

20.2.4 For liquid samples, the LCS is normally a 50 µg/L (low) standard taken through the same process as the samples.

20.2.5 For solid batches, the LCS is a solid standard from a standards supplier that is taken through the same process as the samples. The recovery limits for the SRM are the supplier's limits. This LCS is diluted prior to being analyzed due to high concentration.

NOTE: For solids batches, a 150 µg/L liquid standard ICV is also prepped.

20.3 Acceptance limits:

20.3.1 The correlation coefficient (r) must be 0.995 or greater. If the calibration fails, the calibration curve must be reanalyzed. If it still fails, all calibration standards must be re-made and a new calibration conducted.

NOTE: Refer to GL-QS-E-014 for the Quality Assurance Measurement Calculations and Processes. The intercept should be evaluated as stated in Section 9.2. The absolute value of the intercept should be less than 3 times the MDL.

20.3.2 ICV recovery must be 90-110% for most EPA methods. DoD QSM recovery must be 85-115%. If the ICV fails, the calibration curve must be reanalyzed. If the ICV fails again, new standards must be re-made and a new calibration conducted.

20.3.3 CRDL recovery must be 50-150%. If the CRDL fails, the calibration curve must be reanalyzed. If the CRDL fails again, standards must be re-made and a new calibration conducted.

20.3.4 CCV recovery must be 90-110%. If the CCV fails, all samples bracketed by the out of control CCV must be re-analyzed.

20.3.5 The liquid LCS recovery must be 90-110% for most EPA methods. DoD QSM recovery must be 80-120%. If the LCS fails, the analyst may choose to reanalyze the LCS with entire batch again or reprep the batch.

20.3.6 Matrix relative percent difference (RPD): Refer to current acceptance limits in AlphaLIMS. If the RPD falls outside these limits, the analyst must enter a text value comment into AlphaLIMS.

20.3.7 Matrix spike recovery: Refer to current acceptance limits in AlphaLIMS. If the %Spike Recovery falls outside these limits, the analyst must enter a text value comment into AlphaLIMS.

NOTE: The matrix spike recovery for CLP batches must fall between 75-125%. If not, the affected samples and QC are reprepped and reanalyzed. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more.

20.3.8 Prep blank and/or calibration blanks: Must be < PQL for most clients depending on client contract. DoD QSM requires <1/2 PQL where PQL = LOQ. If the method blank values are > PQL, sample results may be used if they are >10 times the method blank contamination. If the method blank fails, the analyst may choose to reanalyze the method blank with the entire batch again or reprep the batch.

20.3.9 LCS RPD: Refer to current acceptance limits in AlphaLIMS. If the RPD falls outside these limits, the batch must be reanalyzed.

20.3.10 Due to the scope of the test and method, peaks are verified visually. These peaks should have a steady rise and fall. Any peak that is sharp in nature with jagged edges must be reanalyzed for verification.

20.4 Actions Required if the Quality Control Requirements Are Not Met
If any of the QC criteria in Section 20 cannot be satisfied, the analyst should notify the Group Leader and initiate a Nonconformance Report as outlined in GL-QS-E-004.

21.0 RUN SEQUENCE

21.1 Calibration Standards: 200, 150, 100, 50, 10, 5, and 0 µg/L
21.2 ICV
21.3 ICB
21.4 5 µg/L standard (CRDL)
21.5 Up to 10 analytical samples including LCS, method blank, and sample QC (refer to Section 20)
21.6 CCV
21.7 CCB
21.8 Repeat steps 21.4 through 21.7 for remaining samples in the run. End with CCV and CCB.

22.0 PROCEDURE

22.1 Create Sample Table:

22.1.1 Click on 'Open' and choose file to open.

22.1.2 Fill in the Sample table according to the Run Sequence 21.0 and change dates on calibration standards sample names.

22.1.3 Enter the sample ID and dilution factor

22.1.4 Check to ensure the cup location is incremented correctly.

22.1.5 Load samples onto the autosample as listed as listed on the printed sample table.

22.2 Check to make sure all reagents and lines are pumping correctly.

22.3 Click on 'Start'

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

23.1 Place the reagent lines in DI water and allow DI water to pump through the system for 5 minutes.

23.2 Remove the reagent tubes from the DI water and allow air pump through the system for 5 minutes, or until water no longer appears in the lines.

23.3 Turn off power, and release platen tension.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

24.1 Refer to GL-LB-E-005 and GL-GC-E-092 for data review and validation procedures.

24.2 Data Reduction

24.2.1 Linear regression is used for calibration. The analyst must not force the calibration line through the origin.

24.2.2 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response

a = slope of line (also called the "coefficient of x")

x = concentration of the calibration standard

b = the intercept

24.2.2.1 The analyst should not force the line through the origin, but have the intercept calculated from the standard data points.

24.2.2.2 The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be ≥ 0.995. The calculated intercept value needs to be evaluated before reporting sample results.

24.2.2.3 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y - b)}{a}$$

24.2.2.4 The curve must meet all criteria set forth in Section 20.0.

24.3 Calculation

24.3.1 Record the values for the Total CN concentration and the Chlorinated CN concentration in AlphaLIMS.

24.3.2 Subtract the Chlorinated value from the Total value to get the CN Amenable to Chlorination concentration (which is calculated in AlphaLIMS).

24.3.3 If the final value is less than "0," the Amenable to Chlorination concentration is reported as "0" with a text value comment to explain the result which is calculated in AlphaLIMS.

24.3.4 If the Total CN value is less than the PQL (5 µg/L), the Amenable to Chlorination result is reported as "0."

24.4 Data Upload

24.4.1 The data are exported as a CSV file automatically when the analysis has completed.

24.4.2 Click on "Upload to AlphaLIMS" from desktop screen.

25.0 DATA TRANSMITTAL

Refer to GL-LB-E-005 and GL-GC-E-092 for data review and validation procedures.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to the Lachat QuikChem 8000 Operation Manual.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

29.1 The three different methods sometimes call for different reagents to remove interferences. For consistency, most of the reagents used in this SOP come from Method 9010B and 9010C. Refer to Section 8 for more detailed explanations.

29.2 The pyridine/barbituric acid concentration comes from the Lachat method. This is one-fourth the concentration listed in Method 9012A and 9012B.

29.3 The standard curve concentrations listed in Section 7.4.1 of Methods 9012A and 9012B are not representative of the needs of the environmental testing industry. The industry standard is to have a PQL of either 5 µg/L or 10 µg/L. Therefore, the curve shows lower concentration values. PQL = LOQ for this analysis.

29.4 For solid samples with an aqueous phase, a representative 10 g aliquot is used and treated as a solid.

29.5 SM 4500CN-C2011 requires a 1 mg/L distilled standard to be analyzed with a recovery yielding 96%-104%. GEL uses a 150 µg/L distilled standard, as it's within the calibration range, with a recovery yielding 90%-110%. SM 4500CN-C2011 suggests potassium ferricyanide and GEL uses potassium cyanide.

30.0 REFERENCES

30.1 EPA Method for 335.4, "Determination of Total cyanide by Semi-Automated Colorimetry, "Revision 1.0, August 1993.

30.2 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume IC. SW-846, Third Edition, June 1997. USEPA Office of Solid Waste and Emergency Response, Washington, D.C. 20460.

30.2.1 Method 9012A, "Total and Amenable Cyanide (Colormetric, Automated UV)," Revision 1, December 1996.

30.2.2 Method 9010B, Total and Amenable Cyanide (Distillation)," Revision 2, December 1996.

30.2.3 Method 9012B, "Total and Amenable Cyanide (Colorimetric, Automated UV)," Revision 2, August 2002.

30.2.4 Method 9010C, "Total and Amenable Cyanide (Distillation)," Revision 3, August 2002.

30.3 Lachat QuikChem 8000 Operation Manual, August, 2000, Lachat Instruments, Milwaukee, WI 53218.

30.4 QuikChem Method 10-204-00-1-A, "Determination of Cyanide in Waters," Revision 08/28/00.

30.5 Standard Methods 22nd Edition, 4500 CN^- C-2011, Total Cyanide After Distillation

30.6 Standard Methods 22nd Edition, 4500 CN^- E-2011, Colorimetric Method.

30.7 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 4.2, October 2010, Version 5.0, July 2013 and Version 5.1, January 2017.

31.0 HISTORY

Revision 18: Made clarification to ICV in Definitions Section.

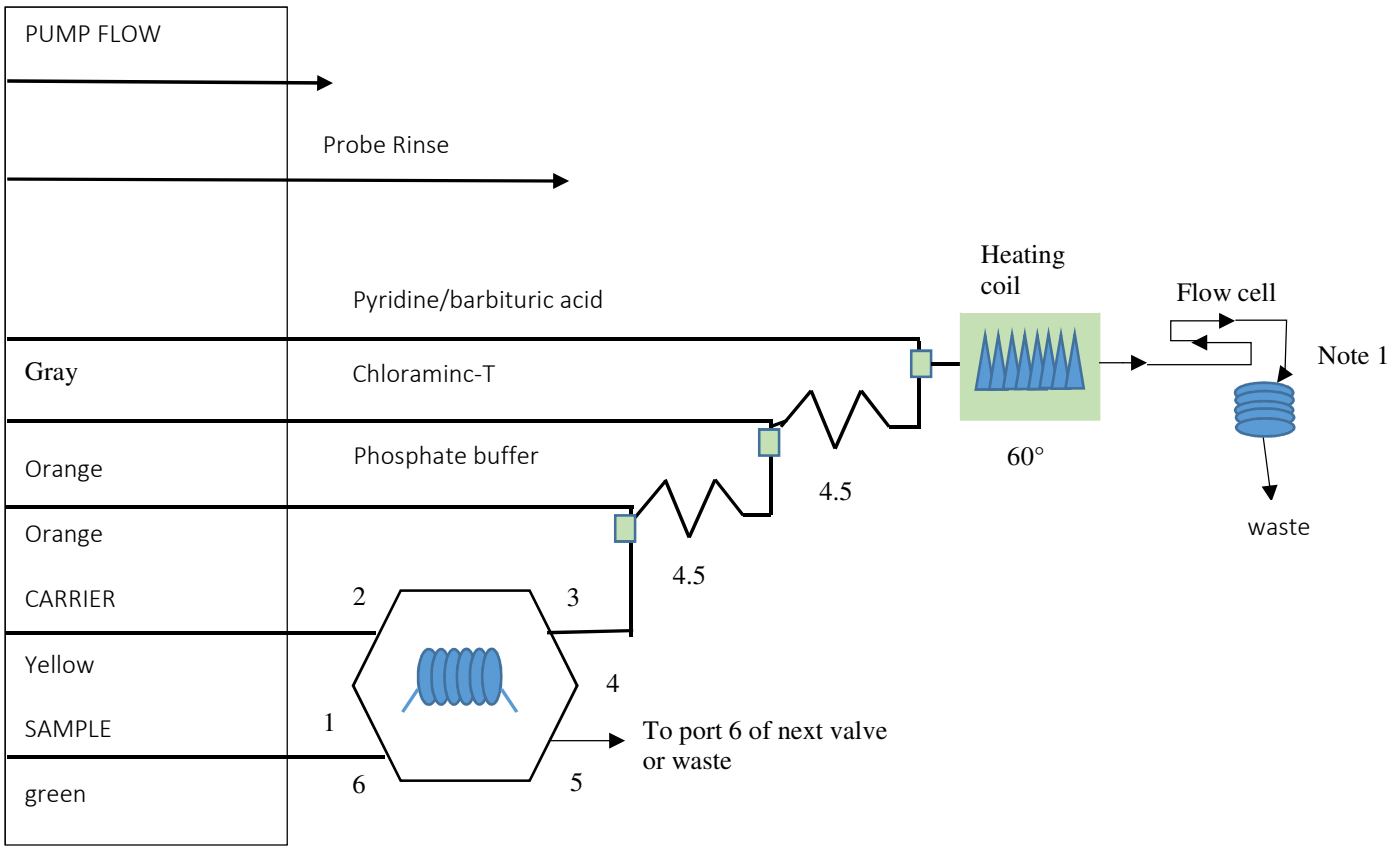
Revision 19: Removed reference to 335.3 and CLP method 335.2-M.
Revision 20: Added clarification for process when CRDL recovery fails.
Revision 21: Updated the frequency at which the reagent is prepared and preserved. Added readback requirements to calibration curve.
Revision 22: Added Appendix 1:Typical Standards Calibration.

APPENDIX 1: TYPICAL CALIBRATION STANDARDS (TOTAL CYANIDE)

Concentration of Standard	Volume of Stock	Final Volume of Standard
200 ppb	200 µL of 100 ppm std	100 mL 0.25 N NaOH
150 ppb	150 µL of 100 ppm std	100 mL 0.25 N NaOH
100 ppb	100 µL of 100 ppm std	100 mL 0.25 N NaOH
50 ppb	50 µL of 100 ppm std	100 mL 0.25 N NaOH
10 ppb	10 µL of 100 ppm std	100 mL 0.25 N NaOH
5 ppb	5 µL of 100 ppm std	100 mL 0.25 N NaOH

APPENDIX 2: TOTAL CYANIDE

(CYANIDE MANIFOLD DIAGRAM)



Carrier: 0.25 M sodium hydroxide solution (Reagent 1)
Manifold: 0.8 mm (0.032 in) i.d. This is 5.2 µL/cm
AE Sample Loop: 150 cm x 0.8 mm i.d.
QC8000Sample Loop: 150 cm x 0.8 mm i.d.
Interference Filter: 570 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and colormetric detector module is required. The Heating Coil shows 650 cm of tubing wrapped around the heater block at the specified temperature.
4.5: 70 cm of tubing on a 4.5 cm coil support

Note 1: 200 cm backpressure loop, 0.52 mm i.d.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

TOTAL HARDNESS BY TITRATION

(GL-GC-E-100 REVISION 8)

APPLICABLE TO METHODS:
Standard Methods, 22nd Edition, Method 2340C-97

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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL HARDNESS BY TITRATION

2.0 METHOD CODE

Standard Methods, 22nd Edition, Method 2340C-97

3.0 METHOD OBJECTIVE / PURPOSE

This procedure is used to measure the Total Hardness of samples in mg/L of $CaCO_3$.

4.0 METHOD SUMMARY

4.1 Summary: Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point to the reaction is detected by means of an indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

5.4 Saline water

5.5 Surface waters

6.0 HOLDING TIME

Samples must be analyzed within 180 days of collection.

7.0 SAMPLE CONTAINER, PRESERVATION, COLLECTION, STORAGE REQUIREMENTS

7.1 Samples may be stored in glass or plastic containers.

7.2 Preservation:

7.2.1 Samples are preserved with HNO_3 to a pH of < 2.

7.2.2 Documentation of temperature and pH are documented at Login. Refer to GL-SR-E-001 for Sample Receipt, Login, and Storage.

7.3 Refrigerate sample at $0 \leq 6°$ C until analysis.

8.0 INTERFERENCES

8.1 Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method range: The method is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, it is recommended that a sample aliquot containing no more than 25 mg $CaCO_3$ be used.

9.2 Method detection limit (MDL): Refer to current MDL study

9.3 Method precision

9.3.1 Sample Duplicate: Refer to current SPC limits.

9.3.2 Matrix Spike: Refer to current SPC limits.

9.4 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 AlphaLIMS - The data system used at GEL Laboratories, LLC.

10.2 Independent Calibration Verification (ICV) - A solution of method analytes of known concentrations that is used to fortify an aliquot of Blank or sample matrix. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

10.3 Laboratory Control Standard (LCS) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

10.4 Method Blank (MB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

10.5 Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

10.6 Spike (Matrix Spike or Post Spike) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or PS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or PS corrected for background concentrations.

10.7 Statistical Process Control (SPC) Limits - Statistically derived limits which establish Acceptable Ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

10.8 Stock Standard Solution - A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

10.9 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data is obtained, it is entered directly into AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 All chemicals and samples should be treated as a potential health hazard and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents are maintained in the laboratory. Individual sample MSDS forms provided by the clients are kept in login.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Beakers: Capacity of 100 mL minimum required

15.2 Graduated cylinders: Minimum capacity of 100 mL is needed

15.3 Magnetic stir plate

15.4 Stir bar

15.5 Magnetic stir bar retriever

15.6 Squeeze bottle for deionized water

15.7 Hot plate

15.8 Buret with 0.05 mL increments: Recommended capacity, 10 mL to 20 mL

15.9 Watch glass

15.10 pH meter and probe

15.11 Oven capable of maintaining 250 ± 50°C

NOTE: The temperature of the oven is monitored in accordance with GL-LB-E-004.

15.12 Volumetric flask, 1 L

15.13 Aluminum weigh boat

15.14 Desiccator and desiccant

15.15 Analytical balance: capable of weighing to 0.0001g

16.0 REAGENTS

16.1 Buffer Solution

16.1.1 A commercially available "odorless buffer" is purchased (example: HACH Buffer Solution Hardness 1). The buffer solution expires 1 year from the date opened.

16.2 Indicator Solution

16.2.1 A commercially available indicator such as Calmagite indicator is used.

16.3 Standard EDTA titrant, 0.02 N.

16.3.1 Place 3.723g of analytical reagent grade disodium ethylenediamine tetraacetate dihydrate, $Na_2C_{10}H_{14}O_8N_2*2H_2O$, in a 1 L volumetric flask and dilute to the mark with DI water. Store in polyethylene. Standardize daily (18.1.1)

16.4 Hydrochloric acid solution, 1 + 1.

17.0 STANDARDS

17.1 1000 mg/L $CaCO_3$ spiking standard.

17.1.1 Place 1.000g of anhydrous calcium carbonate in approximately 500 mLs of DI water.

17.1.2 Add, a little at a time, 1 + 1 HCl until all of the $CaCO_3$ has dissolved.

17.1.3 Add 200 mLs of DI Water.

17.1.4 Boil for a few minutes to expel CO_2.

17.1.5 Cool.

17.1.6 Bring to a 1L volume in a volumetric flask with DI Water.

17.1.7 The standard expires 1 year from preparation date.

17.2 2500 mg/L $CaCO_3$ LCS standard.

17.2.1 Place 2.500g of anhydrous calcium carbonate in approximately 500 mLs of DI water.

17.2.2 Add, a little at a time, 1 + 1 HCl until all of the $CaCO_3$ has dissolved.

17.2.3 Add 200 mLs of DI Water.

17.2.4 Boil for a few minutes to expel CO_2.

17.2.5 Cool.

17.2.6 Bring to a 1L volume in a volumetric flask with DI Water.

17.2.7 The standard expires 1 year from preparation date.

18.0 STANDARDIZATION OF REAGENTS

18.1 EDTA titrant, 0.02 N.

18.1.1 Pipette 10 mLs of the 1000 mg/L spiking standard into a beaker containing 40 mLs of DI water.

18.1.2 Add 1 mL of buffer solution.

18.1.3 Add 1-2 drops of indicator.

18.1.4 Titrate slowly with continuous stirring until the last reddish tinge disappears. The end point color is blue.

18.1.5 Repeat step 18.1.4 two more times.

18.1.6 Calculate the Normality of the EDTA titrant using the average of the three titrations. The following formula is used to calculate normality:

$$N \text{ of EDTA} = 0.2 / \text{mLs of EDTA}$$

18.1.7 Standardization must be performed at least monthly.

19.0 QUALITY CONTROL (QC) REQUIREMENTS

19.1 Frequency of QC:

19.1.1 A method blank (MB) and a laboratory control sample (LCS) are analyzed every 20 samples.

19.1.2 A sample duplicate and matrix spike are analyzed for every 10 samples.

19.2 Acceptance limits:

19.2.1 Matrix relative percent differences (RPD): limits 0-10%.

19.2.2 Matrix spike recoveries (% recovery: limits 90%-110%.

19.2.3 LCS recoveries (% recovery): limits 90% - 110%.

19.2.4 MB criteria: less than the RL.

19.3 Handling out-of-control situations:

19.3.1 Notify the group leader, team task leader, or PM immediately.

19.3.2 If the MB should fall outside of the control limits, the entire batch must be reanalyzed.

19.3.3 If the LCS recovery should fall outside of the SPC limits, the entire batch must be reananlyzed.

19.3.4 Samples may exhibit matrix interferences, which cause matrix QC to fall outside of the SPC limits. When this occurs, the analyst should determine that this is the case and narrate the interferences in the case narrative system in AlphaLIMS.

19.3.5 The analyst should document in the case narrative the specific QC that is out-of-control and cross-reference data from any subsequent reanalysis.

20.0 RUN SEQUENCE

20.1 Method Blank (MB)

20.2 Laboratory Control Sample (LCS)

20.3 Samples 1 through x where x < 10

20.4 Sample x duplicate

20.5 Sample x spike

20.6 Repeat steps 20.3 - 20.5 for every group of ten samples in the batch.

21.0 PROCEDURE

21.1 The sample should require < 15 mLs of EDTA titrant and the titration should be completed within 5 minutes of buffer addition. If the sample requires >/= 15 mLs of EDTA titrant, a smaller sample volume shall be used.

21.2 Place 25 mLs of sample in a titration vessel and dilute to approximately 50 mLs with DI water.

21.3 Add 1 to 2 mLs of buffer solution.

21.4 Add 1 to 2 drops of indicator solution.

21.5 Titrate slowly with continuous stirring with standard EDTA titrant until the last reddish tint disappears. The solution is normally blue at the end point.

21.6 To create the LCS, dilute 5 mLs of the 2500 mg/L LCS standard to 25 mLs total volume with DI Water. This creates a 500 mg/L LCS working standard.

21.7 To spike samples, add 5 mLs of the 1000 mg/L spiking standard to 25 mLs of sample. This creates a 200 mg/L spike.

22.0 CALCULATIONS

22.1 The following formula is used to calculate Total Hardness (mg/L as $CaCO_3$):

Hardness = (A x N x 50,000) / mLs of sample

Where: A = mLs of EDTA titrant
N = normality of EDTA titrant

23.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

23.1 Data review is performed In accordance with GL-GC-E-092 for Data Packaging and Validation.

24.0 DATA TRANSMITTAL

24.1 When a batch is given General Chemistry departmental "DONE" status, it is made available to reporting personnel.

25.0 RECORDS MANAGEMENT

Data is maintained in AlphaLIMS.

26.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

26.1 Refer to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators, and other Similar Devices.

27.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to GL-LB-G-001, Laboratory Waste Management Plan.

28.0 METHOD VERIFICATION

28.1 Method detection limit studies are performed in accordance with the GL-LB-E-001 for the determination of Method detection limits.

29.0 REFERENCES

29.1 Standard Methods, 22nd Edition, Method 2340C-97, 2012.

30.0 HISTORY

Revision 8: Updated SPC limits and MB Blank Criteria
Revision 7: Updated standard method reference.
Revision 6: Removed Ammonium Hydroxide, 1N from reagents section and updated steps for creating the LCS.
Revision 5: Changed volume requirements and deleted EPA 130.2 references.
Revision 4: Added equipment list and standardization frequency.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR TOTAL RECOVERABLE PHENOL BY THE LACHAT QUIKCHEM FIA+ 8000 SERIES

(GL-GC-E-102 REVISION 10)

APPLICABLE TO METHODS:
EPA 420.4
SW-846 9066

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL RECOVERABLE PHENOL BY THE LACHAT QUIKCHEM FIA+ 8000 SERIES

2.0 METHOD CODES

2.1 EPA Method 420.4, Determination of Total Recoverable Phenolics by Semi-Automated Colorimetry [Phenolics (Colorimetric, Automated 4-AAP with Distillation)] (liquids)

2.2 SW-846 9066 Third Edition. [Phenolics (Colorimetric, Automated 4-AAP with Distillation)] (solids)

3.0 METHOD OBJECTIVE/PURPOSE

The purpose of this method is to describe the determination of phenols in drinking, surface, and saline waters, and domestic and industrial wastes. Technicians and analysts do not analyze client samples without supervision until they have been fully trained and have demonstrated the ability to generate acceptable data. Training records are maintained as quality records.

4.0 METHOD SUMMARY

This method is based on the distillation of phenol and the subsequent reaction of the distillate with alkaline ferricyanide [$K_3Fe(CN)_6$] and 4-aminoantipyrine (4-AAP) to form a red complex, which is measured at 500 nm.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases the procedure is modified as necessary.

6.0 HOLDING TIME

Holding time for non-South Carolina samples is 28 days from the time and date of collection until the start of analysis unless otherwise specified by contract. Samples reported for compliance in South Carolina must be analyzed within 24 hours of sample preparation.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples are collected in amber glass containers and preserved at time of collection with sulfuric acid to a pH less than 2.

7.2 Samples are stored at $0° \leq 6° \geq$ C until analyzed.

8.0 INTERFERENCES/LIMITATIONS

8.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of < 4.0 with sulfuric acid and aerating. Copper sulfate may also be added to eliminate sulfur compounds.

8.2 If oxidizing agents such as chlorine are thought to be present, they should be removed immediately after sampling by the addition of ferrous ammonium sulfate. If the chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

8.3 Glass calibration vials must be used.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Calibration range: 5.0 to 200 µg/L

9.2 Method precision: Refer to current SPC limits.

9.3 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

10.2 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

10.3 Continuing Calibration Blank (CCB): An aliquot of reagent water or other blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

10.4 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample, periodically throughout the run sequence. Its purpose is to determine whether the analytical sequence is in control during sample analysis. It may be prepared from the same source as the calibration standards, and is usually of varied concentration.

10.5 CRDL: Contract required detection limits.

10.6 Initial Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination after injection of the mid-level ICV.

10.7 Initial Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of blank or sample matrix. The ICV is obtained from a source external to the laboratory and with a different lot number than the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

10.8 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to

determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

10.9 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

10.10 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

10.11 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. For this method, MDLs are determined every 6 months.

10.12 Spike (Matrix Spike or Post Spike): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or PS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or PS corrected for background concentrations.

10.13 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD, and internal standards.

10.14 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

10.15 Laboratory Duplicate (DUP, LCSD, MSD or PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

10.16 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 DOCUMENTATION OF DATA

11.1 Sample preparation data is recorded in AlphaLIMS.

11.2 As data are acquired, computer printouts of the data are generated. These dated hard copies of the data are kept in the Phenol binder in the Lachat lab. Results are entered into AlphaLIMS.

12.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

12.1 Wear safety glasses while in the laboratory.

12.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). Individual sample MSDS forms provided by the clients are also maintained.

12.3 In order to prevent instrument damage, ensure that the correct pump lines are placed in the proper reagents.

13.0 SAMPLE RECEIPT FOR ANALYSIS

13.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from the cooler either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

13.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

13.3 Previously distilled samples are stored in the General Chemistry refrigerator until they are retrieved by the analyst just prior to analysis.

14.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

14.1 Instrumentation: Lachat QuikChem FIA+ 8000 Series analyzer.

14.1.1 Sampler

14.1.2 Multichannel proportioning pump

14.1.3 Reaction unit or manifold

14.1.4 Colorimetric detector

14.1.5 Data system

14.1.6 Amber glass calibration vials

14.2 Equipment

14.2.1 Air Displacement Pipets

Various volumes required for spikes standards and dilutions. Pipets are calibrated in accordance with GL-LB-E-010.

14.2.2 25 µL syringe

14.2.3 Analytical balance capable of weighing to the nearest 0.0001 g. Balances are calibrated in accordance to GL-LB-E-002.

14.2.4 Carboy for disposal of sample reagents and residue

14.2.5 Glassware should be cleaned using the standard glassware cleaning procedure. It should be rinsed thoroughly using deionized (DI) water before use.

14.2.6 pH strips

14.2.7 Micro Block Distillation Unit

15.0 REAGENTS

15.1 Raw Reagents

NOTE: Unless otherwise specified, all chemicals should be of ACS grade or equivalent.

15.1.1 ASTM Type II deionized (DI) water

15.1.2 Sodium hydroxide (NaOH)

15.1.3 Sulfuric acid, concentrated (H_2SO_4)

15.1.4 Ferrous ammonium sulfate, hexahydrate [$Fe(NH_4)_2(SO_4)_2 \bullet 6H_2O$]

15.1.5 4-Aminoantipyrine (4-AAP)

15.1.6 Potassium ferricyanide [$K_3Fe(CN)_6$]

15.1.7 Boric acid (H_3BO_3)

15.1.8 Potassium chloride (KCl)

15.1.9 Copper sulfate pentahydrate ($CuSO_4 \bullet 5H_2O$)

15.1.10 100 mg/L Phenol standard (2 independent sources are required): These certified standards are ordered from a vendor.

15.1.11 Brij-35

15.2 Reagent Preparation

15.2.1 Ferrous ammonium sulfate (used to remove oxidizing agents in samples): In a 500 mL volumetric flask, dissolve 0.55 g of ferrous ammonium sulfate in 250 mL of DI water containing 0.5 mL of sulfuric acid and dilute to the mark with freshly boiled and cooled DI water. Store at room temperature and prepare every 6 months.

15.2.2 Aminoantipyrine color reagent: In a 250 mL volumetric flask dissolve 0.16 g of 4-aminoantipyrine in 250 mL of DI water. Store in amber glass and prepare fresh daily.

15.2.3 Buffered potassium ferricyanide, pH 10.3: In a 1 L volumetric flask dissolve 2.0 g of potassium ferricyanide [$K_3Fe(CN)_6$], 3.1 g of boric acid (H_3BO_3), and 3.75 g of potassium chloride (KCl) in about 800 mL of DI water. Add 1 N sodium hydroxide to bring solution to a pH of 10.3; typically GEL uses 47 mL. Add 0.5 mL Brij-35 and dilute to the mark. Stir to mix. Store in amber glass and prepare fresh weekly.

15.2.4 50% Sodium hydroxide solution: In a 500 mL volumetric flask, dissolve 250 g of NaOH in 250 mL of DI water. Cool and dilute to the mark with DI water. Store at room temperature and prepare every 6 months.

15.2.5 1 N Sodium hydroxide solution: In a 500 mL volumetric flask, dissolve 20 g of NaOH in 250 mL of DI water. Cool and dilute to the mark with DI water. Store at room temperature and prepare every 6 months.

15.2.6 Distillation reagent (0.1 N sodium hydroxide solution): In a 100 mL volumetric flask, dilute 10 mL of 1 N sodium hydroxide to the mark with DI water. Invert to mix. Store at room temperature and prepare every 6 months.

15.2.7 Distillation reagent (0.04 N sulfuric acid): Dilute 22.4 mL of concentrated sulfuric acid (H_2SO_4) to 20 L of DI water. Shake to mix. Store at room temperature and prepare every 6 months.

15.2.8 0.1 N Sulfuric acid (H_2SO_4): Slowly add 10 mL concentrated sulfuric acid to 70 mL DI water. Cool and dilute to 100 mL with DI water. Store at room temperature and prepare every 6 months.

15.2.9 50% Sulfuric acid solution: Add 250 mL of DI water to a 500 mL volumetric flask. SLOWLY add 250 mL concentrated sulfuric acid. Cool and dilute to the mark with DI water. CAUTION: This solution gets very hot!

16.0 PREPARATION OF SAMPLES

16.1 Preserved samples are adjusted to a pH of 4.0 using sodium hydroxide solution and/or sulfuric acid solution before being distilled. If the samples are thought to contain sulfur compounds, copper sulfate should be added (1 g/L).

16.1.1 For QC, a sample duplicate, matrix spike, method blank, and LCS are distilled by the same process. Additional QC may be required by client contract.

16.1.2 The method blank sample consists of 50 mL of 0.04 N sulfuric acid.

16.1.3 The LCS consists of 50 mL of 0.04 N sulfuric acid spiked with 25 µL of 100 mg/L standard.

16.2 Micro Block Distillation Procedure

16.2.1 Pipette 50 mL of sample into the reaction tube (for soils, weigh approximately 1 g of sample and add 50 mL of 0.04 N sulfuric acid). Adjust the pH to 4.0 with sodium hydroxide solution and/or sulfuric acid solution.

16.2.2 Add a pinch of boiling chips.

16.2.3 Repeat steps 16.2.1 through 16.2.2 for all samples.

16.2.4 Spike the matrix spike and LCS with 25 µL of 100 mg/L standard.

16.2.5 Add 5 mL of DI reagent water to each reaction tube.

16.2.6 Assemble the distillation glassware setup and position in the heating block.

16.2.7 Turn on the tap water to cool the Cold Fingers after ensuring all tubing connections are tight. Check for leaks.

16.2.8 Turn power “ON” and set heater block temperature to 190° C.

16.2.9 When 50 mL of sample is collected in the receiver tube, remove the receiver tube from the assembly. Pour off the distillate into amber glass containers.

NOTE: The heater block is still hot so the distillation process will continue. Place a collection tray or beaker under the outlet tube to catch any further distillate.

16.2.10 When all samples have distilled, turn the power OFF.

16.2.11 When the heater temperature falls below 100° C, the assembly is ready for prep again.

17.0 PREPARATION OF STANDARDS

17.1 Documentation of standards and their preparation is found in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

17.2 All standards are prepared using Type II DI water.

17.3 All phenol calibration standards are prepared fresh daily.

17.4 All standards are prepared from traceable solutions according to the recipes found in Appendix 1.

18.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

18.1 Refer to QuikChem Method 10-210-00-1-A: Determination of Total Recoverable Phenolics by Flow Injection Analysis Colorimetry for instrument and equipment start-up procedures.

18.2 Refer to the QuikChem FIA+ 8000 Series User Manual for instrument and equipment start-up procedures.

19.0 QUALITY CONTROL (QC) REQUIREMENTS

19.1 Instrument QC: Refer to GL-QS-E-014.

19.1.1 An initial calibration verification (ICV) is run immediately after the calibration curve. This standard must be made from a different source than the calibration standards.

19.1.2 An initial calibration blank (ICB) is run following the ICV.

19.1.3 A CRDL is analyzed after the ICB.

19.1.4 To continually check the validity of the instrument calibration, a continuing calibration verification (CCV) is run after every 10 analytical samples and after the last analytical sample in the run.

19.1.5 A continuing calibration blank (CCB) is run after every CCV.

19.1.6 MDL and/or MDL verifications are performed every 6 months. These values are submitted for Quality review.

19.1.7 Linear Calibration Range (LCR) checks are performed initially, on a 6-month basis, or when significant changes in the instrument occur. The

calibration standards and blank are compared to the curve for verification purposes. The recoveries must within 10% of the true values. If this procedure fails, the problem must be identified and rectified. Records of the verification are kept on file, available upon request.

19.2 Batch QC

NOTE: Additional/alternate QC is analyzed if required by client contract.

19.2.1 A matrix spike and matrix spike duplicate are analyzed for every batch of ≤ 10 samples and for each set of ten samples in batches with ≥ 10 samples.

19.2.2 A MB and LCS are analyzed at least once for every batch of 20 samples or less.

19.2.3 MDL and/or MDL verifications are performed every 6 months. These values are submitted for Quality review.

19.3 Acceptance limits:

19.3.1 The correlational coefficient for the calibration curve must be 0.995 or greater and cannot be forced through the 0,0 point.

19.3.2 ICV recovery must be 90-110% for all batches unless otherwise specified by client contract requirements. If the ICV fails, the calibration curve must be reanalyzed. If the ICV fails again, new standards must be made and a new calibration conducted.

19.3.3 CCV recovery must be 90-110% for all batches unless otherwise specified by client contract requirements. If the CCV fails, all samples bracketed by the out-of-control CCV must be reanalyzed.

19.3.4 Matrix relative percent difference (RPD): Refer to current SPC limits.

19.3.5 Matrix spike recovery: 90-110% for EPA 420.4 and current SPC limits for SW-846 9066.

19.3.6 Method blank: Must be less than the practical quantitation limit (PQL).

19.3.7 LCS: If the %Recovery falls outside 90-110% limits or other limits directed by project specifications, the batch must be reanalyzed when liquids are analyzed by Method 420.4. SPC studies, maintained in AlphaLIMS, are consulted for solids samples analyzed by the SW-846 9066.

19.3.8 LCS RPD: Refer to current SPC limits.

19.4 Handling out-of-control situations:

19.4.1 If a sample result exceeds the highest calibration standard, the sample must be diluted and reanalyzed.

19.4.2 The correlational coefficient must be a value of at least 0.995. If it is less than 0.995, reanalyze the calibration standards. If this does not bring the correlation coefficient to a value greater than 0.995, then the calibrants must be made up fresh and the run reanalyzed.

NOTE: Refer to GL-QS-E-014 for Quality Assurance Measurement Calculations and Processes. The intercept should be evaluated as stated in Section 9.2. The absolute value of the intercept should be less than 3 times the MDL.

19.4.3 If the duplicates or matrix spikes of a batch do not meet the acceptance limits and the analyst feels the out-of-range recovery is due to a problem in the analysis or prep process, the batch should be reprepped and/or reanalyzed.

19.4.4 If the LCS and/or LCS duplicates fail to meet the above acceptance limits, the batch is reprepped and reanalyzed.

19.4.5 Due to the scope of the test and method, peaks are verified visually. They should have a steady rise and fall. Any peak that is sharp in nature with jagged edges must be reanalyzed for verification.

19.4.6 Client samples that are less than the negative PQL are analyzed for verification. If the reanalysis is still more negative, a dilution is performed until the matrix suppression is less than the absolute value of the PQL.

20.0 TYPICAL RUN SEQUENCE

20.1 Calibration curve from high standard to calibration blank
20.2 ICV (Initial Calibration Verification standard)
20.3 ICB (Initial Calibration Blank)
20.4 CRDL 5 µg/L standard
20.5 Method Blank
20.6 LCS
20.7 Sample
20.8 Matrix spike
20.9 Matrix spike duplicate
20.10 Up to 7 more samples
20.11 CCV
20.12 CCB
20.13 Up to 8 samples
20.14 Matrix spike
20.15 Matrix spike duplicate
20.16 CCV

20.17 CCB

20.18 Remaining samples (no more than 20 samples may be in a batch)

20.19 CCV

20.20 CCB

21.0 PROCEDURE

21.1 Create Sample Table:

21.1.1 Click on 'Open' and choose file to open.

21.1.2 Fill in the Sample table according to the Run Sequence 20.0 and change dates on calibration standards sample names.

21.1.3 Enter the sample ID and dilution factor.

21.1.4 Check to ensure the cup location is incremented correctly.

21.1.5 Load samples onto the autosampler as listed on the printed sample table.

21.2 Check to make sure all reagents and lines are pumping correctly

21.3 Click on 'Start'.

21.4 Refer to QuikChem Method 10-210-00-1-A: Determination of Total Recoverable Phenolics by Flow Injection Analysis Colorimetry for instrument and equipment procedures.

21.5 Refer to the QuikChem FIA+ 8000 Series User Manual for instrument and equipment procedures.

22.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

22.1 Place the reagent lines in deionized water and allow DI water to pump through the system for 5 minutes.

22.2 Remove the reagent tubes from the DI water and allow air to pump through the system for 5 minutes, or until water no longer appears in the lines.

22.3 Turn off power, and release platen tension.

22.4 Refer to the QuikChem FIA+ 8000 Series User Manual for instrument shutdown procedures.

22.5 Refer to the Instruction Manual Enviro Midi-Dist Distillation System manual for Micro Block Distiller shutdown procedures.

23.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

23.1 Refer to GL-LB-E-005 and GL-GC-E-092 for data review and validation procedures.

23.2 Data Reduction

23.2.1 Linear regression is used for calibration. The analyst must not force the calibration line through the origin.

23.2.1.1 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response

a = slope of the line (also called the "coefficient of x)

x = concentration of the calibration standard

b = the intercept

23.2.1.2 The analyst should not force the line through the origin, but have the intercept calculated form the standard data points.

23.2.1.3 The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be ≥ 0.995. The calculated intercept value needs to be evaluated before reporting sample results.

23.2.1.4 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y-b)}{a}$$

23.2.1.5 The curve must meet all criteria set forth in Section 19.0 and in GL-QS-E-014.

24.0 DATA TRANSMITTAL

Once data are obtained, they are entered into AlphaLIMS. All raw data are submitted with batch data for validation/verification.

25.0 RECORDS MANAGEMENT

25.1 Phenol hard copy binder is maintained in the Lachat lab.

25.2 Lachat standards are maintained in AlphaLIMS.

25.3 The Lachat Maintenance Logbook is kept in the Lachat lab.

25.4 The Micro Block distiller Maintenance Logbook is kept in the Lachat lab.

26.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

26.1 Refer to the QuikChem FIA+ 8000 Series User Manual.

26.2 Refer to the Instruction Manual Enviro Midi-Dist Distillation System manual for Micro Block Distiller maintenance.

27.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

28.0 METHOD VERIFICATION

28.1 Method detection limit studies are performed in accordance with GL-LB-E-001 for Method Detection Limits. For this method, they are performed every 6 months.

28.2 Reagents are prepared in accordance with QuickChem Method 10-210-00-1-A: Determination of Total Recoverable Phenolics by Flow Injection Analysis Colorimetry

29.0 METHOD VARIATION

29.1 EPA Method 420.4 states that the addition of reagent water occurs near the end of the distillation process. To ease in distillation using the Midi-Dist system, the addition of reagent water is added at the beginning of the distillation process.

29.2 pH adjustment is measured using pH test strips, rather than a pH meter (Section 16.1).

30.0 REFERENCES

30.1 EPA Method 420.4, Determination of Total Recoverable Phenolics by Semi-Automated Colorimetry, August 1993.

30.2 SW-846 9066 Third Edition. [Phenolics (Colorimetric, Automated 4-AAP with Distillation)]

30.3 QuikChem Method 10-210-00-1-A: Determination of Total Recoverable Phenolics by Flow Injection Analysis Colorimetry. Revision Date 2/12/01. Lachat Instruments 6645 West Mill Road Milwaukee, WI 53218-1239.

30.4 QuikChem FIA+ 8000 Series User Manual. Latest revision April 25, 2002. Lachat Instruments 6645 West Mill Road Milwaukee, WI 53218-1239.

30.5 Instruction Manual Enviro Midi-Dist Distillation System manual for Micro Block Distiller. Glastron Inc. 510 N.W. Boulevard P.O. Box 687 Vineland, NJ 08360.

31.0 HISTORY

Revision 7: Revised holding time to reflect South Carolina requirement.
Revision 8: Referenced matrix spike recovery 90-110% for EPA 420.4 and current SPC limits for SW-846 9066. Changed correlation coefficient from r^2 to r.

Revision 9: Made clarification to ICV in Definitions Section.

Revision 10: Revised Linear calibration range checks.

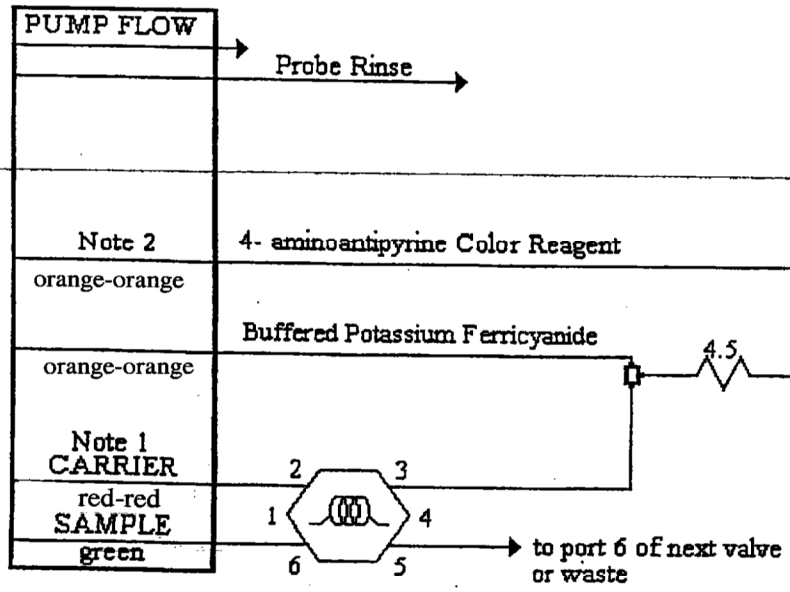
APPENDIX 1: TYPICAL CALIBRATION STANDARDS

Conc. of std	Volume of Stock	Final Volume of Std
200 ppb	200 µL of 100 ppm std	100 mL Type II DI water
100 ppb	100 µL of 100 ppm std	100 mL Type II DI water
50 ppb	50 µL of 100 ppm std	100 mL Type II DI water
10 ppb	10 µL of 100 ppm std	100 mL Type II DI water
5 ppb	5 µL of 100 ppm std	100 mL Type II DI water

Total Phenols

APPENDIX 2

PHENOL MANIFOLD DIAGRAM



Carrier: **Helium degassed DI water**
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm.**
AE Sample Loop: 150 cm
QC8000 Sample Loop: 150 cm
Interference Filter: 500 nm

Apparatus: An injection valve, a 10 mm path length flow cell , and a colorimetric detector module is required.

4.5: **70** cm of tubing on a 4.5 cm coil support
12: **255** cm of tubing on a 12 cm coil support

Note 1: **Carrier Line** for the AE: use a green/green pump tube.
Note 2: Transmission tubing should be replaced with 100 cm of Teflon manifold tubing (0.8mm i.d.) as transmission tubing may contain leachable phenolics. Use Teflon tube connectors (Lachat Part No. 50008) with PTA as line weights with pin removed.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR TOTAL PHOSPHORUS BY THE LACHAT QUIKCHEM FIA + 8000 SERIES INSTRUMENT

(GL-GC-E-103 REVISION 11)

APPLICABLE TO METHOD:
EPA 365.4
Standard Methods 22nd Edition, 4500 P H-2011

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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL PHOSPHORUS BY THE LACHAT QUIKCHEM FIA+ 8000 SERIES INSTRUMENT

2.0 METHOD CODE

EPA Method 365.4 (Colorimetric, Automated, Block Digester AAII) and Standard Methods 22nd Edition 4500 P H-2011

3.0 METHOD OBJECTIVE/PURPOSE

This Standard Operating Procedure (SOP) provides the necessary instructions to determine the concentration of total phosphorus (PO_4-Total) by flow injection analysis colorimetry using the Lachat QuikChem FIA+ 8000 Series instrument.

4.0 METHOD SUMMARY

4.1 Total phosphorus is first converted to orthophosphorus by hydrolysis with sulfuric acid, mercuric oxide, and potassium sulfate. The determination of orthophosphorus is then based on the colorimetric method in which a blue color is formed by the reaction of orthophosphate, ammonium molybdate, and antimony potassium tartrate followed by reduction with ascorbic acid at an acidic pH. This complex is then read at 880 nm.

4.2 Samples are digested prior to analysis using a block digestor.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

Holding time for non-South Carolina samples is 28 days from the time and date of collection until the start of analysis unless otherwise specified by contract. Samples reported for compliance in South Carolina must be analyzed within 24 hours of sample preparation.

7.0 SAMPLE CONTAINER/COLLECTION/PRESERVATION/STORAGE REQUIREMENTS

7.1 Samples may be collected in plastic or glass containers.

7.2 Samples are preserved at time of collection with sulfuric acid to a pH less than 2.

7.3 Samples are stored at $0 \leq 6$ °C until analyzed.

8.0 INTERFERENCES

8.1 High concentrations of iron may cause the phosphorus in samples to precipitate out.

8.2 If samples contain arsenate in concentrations higher than phosphorus, the arsenate could serve as a positive interference.

8.3 Silica forms a pale blue complex that also absorbs at 880 nm.

8.4 Sample color that absorbs in the wavelength range used for analysis will interfere.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 0.01 to 20 mg/L

9.2 Calibration range: 0.05 to 3.0 mg/L

9.3 Method detection limit (MDL): Refer to current MDL studies.

9.4 Method precision: Refer to current Statistical Process Control (SPC) limits.

9.5 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

10.2 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

10.3 Continuing Calibration Blank (CCB): An aliquot of reagent water or other blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

10.4 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample, periodically throughout the run sequence. Its purpose is to determine whether the analytical sequence is in control during sample analysis. It may be prepared from the same source as the calibration standards, and is usually of varied concentration.

10.5 Independent Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination after injection of the mid-level ICV.

10.6 Independent Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of blank or sample matrix. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

10.7 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

10.8 Laboratory Duplicate (DUP, LCSD, MSD or PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

10.9 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

10.10 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

10.11 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

10.12 Spike (Matrix Spike or Post Spike): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or PS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or PS corrected for background concentrations.

10.13 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

10.14 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

10.15 Total Phosphorus: Refers to the concentration of all phosphorus present in the sample, regardless of form. This includes phosphorus in orthophosphate, $[(PO_4)^{3-}]$, polyphosphate $[(P_2O_7)^{4-}]$, and organic phosphorus forms.

10.16 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Before a technician/analyst is allowed to analyze samples without supervision, he/she is trained by qualified personnel and will be required to successfully analyze a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

12.1 As data are acquired, computer printouts of the data are generated. These dated hard copies of the data are kept in the PO_4-Total binder in the Lachat lab. When the analysis is complete, the results are submitted for data entry into AlphaLIMS.

12.2 Documentation of standards preparation is maintained in AlphaLIMS.

12.3 Prep data are entered in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

SULFURIC ACID IS AN EXTREME CORROSIVE.

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

WARNING

ANTIMONY POTASSSIUM TARTRATE IS TOXIC IF INGESTED AND HARMFUL IF INHALED.

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT.

WORK UNDER A HOOD TO AVOID INHALATION.

13.1 Wear safety glasses while in the laboratory.

13.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). Individual sample MSDS forms provided by the clients are also maintained.

13.3 Personal protective equipment

13.3.1 Gloves are required when making reagents in this procedure. The gloves approved for this procedure are nitrile gloves for sulfuric acid and antimony potassium tartrate.

13.3.2 Work under a hood when using the concentrated acids in this procedure.

13.3.3 A protective apron over a lab coat is required when working with sulfuric acid.

13.4 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.4.1 Protect counter tops with counter paper or work from radioactive sample handling trays.

13.4.2 Post signs indicating radioactive samples are in the area.

13.4.3 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.4.4 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

13.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from the cooler and either delivers them to the analyst/technician or places them on the pickup shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

14.3 Previously digested samples are stored in the General Chemistry refrigerator until they are retrieved by the analyst, just prior to analysis.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Instrumentation: Lachat QuikChem FIA+ 8000 Series analyzer.

15.1.1 Autosampler

15.1.2 Multichannel proportioning pump

15.1.3 Reaction unit or manifold

15.1.4 Colorimetric detector

15.1.5 Data system

15.2 Equipment

15.2.1 Air Displacement Pipets

15.2.1.1 10-100 µL with tips

15.2.1.2 100-1000 µL with tips

15.2.1.3 1.00-5.00 mL with tips

NOTE: Pipets are calibrated in accordance with GL-LB-E-012.

15.2.2 Carboy for disposal of sample reagents and residue.

15.2.3 Helium degassing tube

16.0 REAGENTS

NOTE: Unless otherwise specified, all chemicals should be of ACS grade or equivalent.

16.1 Helium gas

16.2 Red Mercuric Oxide (HgO)

16.3 Potassium Sulfate (K_2SO_4)

16.4 Ammonium Molybdate Tetrahydrate [$(NH_4)_6Mo_7O_{24}\bullet 4H_2O$]

16.5 Antimony Potassium Tartrate (potassium antimonyl tartrate trihydrate $C_8H_4O_{12}K_2Sb_2\bullet 3H_2O$)

16.6 Ascorbic Acid ($C_6H_8O_6$)

16.7 Sulfuric Acid, concentrated (H_2SO_4)

16.8 Sodium Dodecyl Sulfate (SDS), [$CH_3(CH_2)_{11}OSO_3Na$]

16.9 Sodium Chloride (NaCl)

16.10 Sodium Hydroxide (NaOH)

16.11 Type I water: Deionized (DI) water (See GL-LB-E-016)

16.12 1000 mg/L Total Phosphorus standard (2 separate independent sources)

16.13 Reagent Preparation

16.13.1 Stock Mercuric Sulfate Solution

To a 50 mL volumetric flask, add 20 mL of DI Water, 5 mL of concentrated sulfuric acid, and 4 g of red mercuric oxide. Stir with a magnetic stirrer at low heat until dissolved, dilute to the mark, and invert to mix. Use solution immediately after preparation.

16.13.2 Digestion Solution

In a 1 L flask, add approximately 700 mL of DI Water, then add 200 mL of concentrated sulfuric acid. Add 133 g of potassium sulfate. Add 25 mL of stock mercuric sulfate solution and dilute to the mark. Mix with a magnetic stirrer and allow the solution to cool. Dilute to the mark after the solution has cooled. This reagent can be stored at room temperature for one month.

16.13.3 Diluent / Carrier

In a 1 L volumetric flask containing approximately 600 mL of DI water, add 200 mL of the digestion solution, dilute to the mark and invert to mix. This reagent can be stored at room temperature and must be prepared fresh weekly.

16.13.4 Stock Ammonium Molybdate Solution

In a 1 L volumetric flask, dissolve 40.0 g of ammonium molybdate tetrahydrate in approximately 800 mL of DI water. Dilute to the mark with DI water and mix with a magnetic stirrer for at least four hours. This reagent must be refrigerated in a plastic container and is good for six months.

16.13.5 Stock Antimony Potassium Tartrate Solution

In a 1 L volumetric flask, dissolve 3.22 g of antimony potassium tartrate in approximately 800 mL of DI water. Dilute to the mark with DI water and mix with a magnetic stirrer until dissolved. This reagent can be stored for up to two months in a dark bottle and refrigerated.

16.13.6 Molybdate Color Reagent

To a 1 L volumetric flask, add about 500 mL of DI water and then add 213 mL of ammonium molybdate solution and 72 mL of antimony potassium tartrate solution. Dilute to the mark with DI water and invert to mix. Degas this reagent with helium. This reagent may be stored at room temperature for up to six months.

16.13.7 Ascorbic Acid Reducing Solution

In a 1 L volumetric flask, dissolve 60.0 g of ascorbic acid in about 700 mL of DI water. Add 1.0 g of sodium dodecyl sulfate. Dilute to the mark with DI water and mix with a magnetic stirrer. Degas this reagent with helium. This reagent may be stored at room temperature and must be prepared fresh every two days.

16.13.8 Sodium Chloride/Sodium Hydroxide Solution

In a 1 L volumetric flask, dissolve 160 g of sodium chloride and 20 g of sodium hydroxide in about 600 mL of DI water. Dilute to the mark with DI water and mix with a magnetic stirrer. Degas this reagent with helium. This reagent may be stored at room temperature and must be prepared fresh weekly.

17.0 PREPARATION OF SAMPLES

Refer to GL-GC-E-071 for Total Phosphorus and Total Kjeldahl Nitrogen Sample Preparation.

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards and their preparation is maintained in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

18.2 All standards are prepared from traceable solutions according to the protocol found in Appendix I.

18.3 All total phosphorous standards and blanks are prepared exactly as samples and are digested.

18.4 All total phosphorous standards are prepared fresh daily.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

19.1 Set up the Phosphorus Manifold as shown in Appendix I.

19.2 Refer to the Lachat QuikChem Method 10-115-01-1-C: Determination of Total Phosphorus by Flow Injection Analysis Colorimetry for instrument start-up procedures.

19.3 Refer to the Lachat QuikChem FIA+ 8000 Series User Manual for instrument start-up procedures.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Instrument QC

20.1.1 An Initial Calibration Verification (ICV) is run immediately after the calibration curve. This standard must be made from a different source than the calibration standards.

20.1.2 An Initial Calibration Blank (ICB) is run following the ICV.

20.1.3 A Continuing Calibration Verification (CCV) is run after every 10 analytical samples and after the last analytical sample is run.

20.1.4 A Continuing Calibration Blank (CCB) is run after every CCV.

20.1.5 MDL and/or MDL verifications are performed in accordance with GL-LB-E-001 for the determination of method detection limits and method quantitation limits.

20.1.6 Linear calibration range (LCR) checks are performed on a 6-month basis. The high standard of the curve is read back against the calibration and must recover ± 10%. If this procedure fails, the problem must be identified and rectified.

20.1.7 Calculated curve readbacks are: 50%-150% for the first point (low-end) and 90%-110% for all the other points. The calculated zero point must be ± ½ RL. Any failure will require re-calibration of the instrument.

20.2 Batch QC

20.2.1 A matrix spike and matrix duplicate are run for every 10 samples in a batch.

20.2.2 A MB and an LCS are run at least once for every batch of 20 or less samples.

20.2.3 For liquid samples, the LCS is normally a 1 mg/L standard taken through the same process as the samples.

20.3 Acceptance limits

20.3.1 Correlation coefficient (r) must be 0.995 or greater

20.3.2 ICV recovery must be 90-110% for all batches. If the ICV fails, the calibration curve must be reanalyzed. If the ICV fails again, new standards must be made and a new calibration conducted.

20.3.3 CCV recovery must be 90-110% for all batches. If the CCV fails, all samples bracketed by the out-of-control CCV must be reanalyzed.

20.3.4 Matrix Relevant Percent Difference (RPD): Refer to current SPC limits.

20.3.5 Matrix spike recovery: Refer to current SPC limits.

20.3.6 Method Blank: - PQL < MB < PQL

NOTE: Some clients may require MB ≤ ½ PQL.

20.3.7 LCS: Refer to current SPC limits. If the percent recovery falls outside these limits, the batch must be reanalyzed.

20.3.8 LCS RPD: Refer to current SPC limits.

20.3.9 Due to the scope of the test and method, peaks are verified visually. These peaks should have a steady rise and fall. Any peak that is sharp with jagged edges must be re-analyzed for verification.

20.4 Handling out-of-control situations:

20.4.1 If a sample result exceeds the highest calibration standard, the sample must be diluted and reanalyzed.

20.4.2 The correlation coefficient must be a value of at least 0.995. If it is less than 0.995, reanalyze the calibration standards. If this does not bring the correlation coefficient to a value greater than 0.995, all calibration standards must be re-made and a new calibration conducted.

NOTE: Refer to GL-QS-E-014 for Quality Assurance Measurement Calculations and Processes. The intercept should be evaluated as stated in Section 9.2. The absolute value of the intercept should be less than 3 times the MDL.

NOTE: If the batch must be redigested, notify the Group Leader.

21.0 TYPICAL RUN SEQUENCE

21.1 Calibration Curve (analyzed from high standard to blank)
21.2 ICV (Initial Calibration Verification standard)
21.3 ICB (Initial Calibration Blank)
21.4 Method Blank
21.5 LCS
21.6 Sample
21.7 Sample duplicate (if required)
21.8 Matrix spike of the sample (if required)
21.9 Up to 5 more samples
21.10 CCV (Continuing Calibration Verification standard)
21.11 CCB (Continuing Calibration Blank)
21.12 Sample
21.13 Sample duplicate (if required)
21.14 Matrix spike of the sample (if required)
21.15 Up to 7 more samples
21.16 CCV

21.17 CCB

21.18 Remaining samples (a maximum of 20 samples is allowed per batch)

21.19 CCV

21.20 CCB

22.0 PROCEDURE

22.1 Create Sample Table:

22.1.1 Click on 'Open' and choose file to open.

22.1.2 Fill in the Sample table according to the Run Sequence 21.0 and change dates on calibration standards sample names.

22.1.3 Enter the sample ID and dilution factor.

22.1.4 Check to ensure the cup location is incremented correctly.

22.1.5 Load samples onto the autosampler as listed on the printed sample table.

22.2 Check to make sure all reagents and lines are pumping correctly.

22.3 Click on 'Start'.

22.4 Refer to the Lachat QuikChem Method 10-115-01-1-C: Determination of Total Phosphorous by Flow Injection Analysis Colorimetry.

22.5 Refer to the Lachat QuikChem FIA + 8000 Series User Manual.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

23.1 Place the reagent lines in DI water and allow DI water to pump through the system for 5 minutes.

23.2 Remove the reagent tubes from the DI water and allow air to pump through the system for 5 minutes, or until water no longer appears in the lines.

23.3 Turn off power, and release platen tension.

23.4 Refer to the Lachat QuikChem FIA + 8000 Series User Manual for instrument shutdown procedure(s).

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

24.1 Refer to GL-GC-E-092 for General Chemistry Data Review Packaging and GL-LB-E-005 for Data Review and Validation.

24.2 Data Reduction

24.2.1 Linear regression is used for calibration. The analyst must not force the calibration line through the origin.

24.2.1.1 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response

a = slope of line (also called the "coefficient of x")

x = concentration of the calibration standard

b = the intercept

24.2.1.2 The analyst should not force the line through the origin, but have the intercept calculated from the standard data points.

24.2.1.3 The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be ≥ 0.995. The calculated intercept value needs to be evaluated before reporting sample results.

24.2.1.4 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y - b)}{a}$$

24.2.1.5 The curve must meet all criteria set forth in section 20.0.

25.0 DATA TRANSMITTAL

Data are entered in AlphaLIMS as they are obtained.

26.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

27.1 Refer to the Lachat QuikChem FIA+ 8000 Series User Manual for routine instrument maintenance.

27.2 The Lachat QuikChem FIA+ 8000 Series instrument maintenance logbook is maintained in the Lachat lab.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

Method detection limit studies are performed in accordance with GL-LB-E-001.

30.0 REFERENCES

30.1 "Phosphorous, Total," EPA Method 365.4 (Colorimetric, Automated, Block Digester AA II) Storet No. 00665. Issued 1996.

30.2 Lachat QuikChem Method 10-115-01-1-C: Determination of Total Phosphorus by Flow Injection Analysis Colorimetry. Lachat Instruments 6645 West Mill Rd. Milwaukee, WI 53218.

30.3 Lachat QuikChem FIA+ 8000 Series User Manual. Lachat Instruments 6645 West Mill Rd. Milwaukee, WI 53218.

30.4 Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 4500 P H-2011, Manual Digestion and Flow Injection Analysis for Total Phosphorus.

31.0 HISTORY

Revision 8: Updates made to Appendix I.
Revision 9: Updated DI water type in accordance with GL-LB-E-016, updated Standard Methods reference per MUR II.
Revision 10: Revised reference for Std Methods reference method.
Revision 11: Added readback requirements for calibration curve.

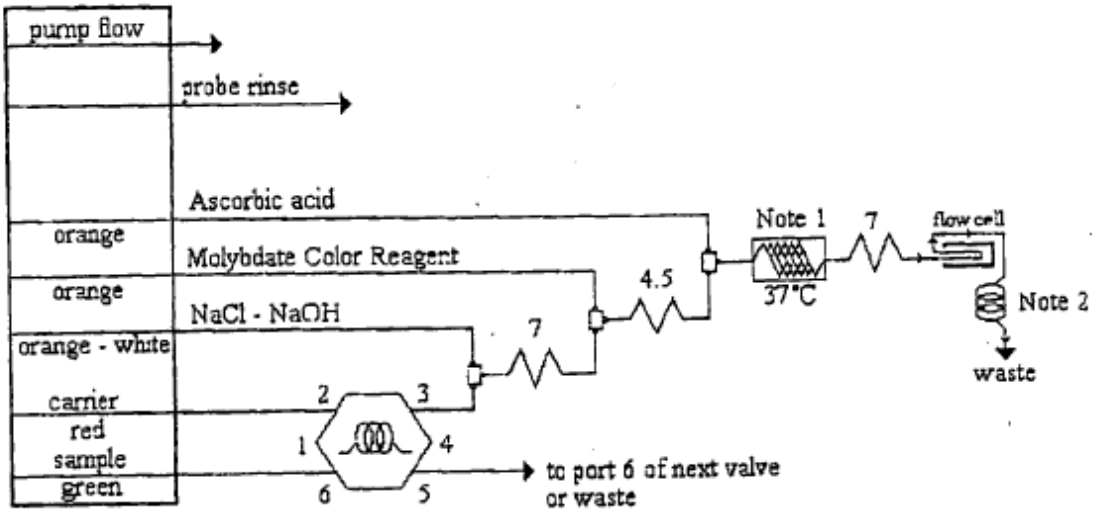
APPENDIX I

Conc of STD	Vol of Stock	Final Vol of Std
3 ppm	0.6 mL of 100 ppm std	20 mL 0.04 N H_2SO_4
1 ppm	0.2 mL of 100 ppm std	20 mL 0.04 N H_2SO_4
0.5 ppm	0.1 mL of 100 ppm std	20 mL 0.04 N H_2SO_4
0.1 ppm	0.02 mL of 100 ppm std	20 mL 0.04 N H_2SO_4
0.05 ppm	0.01 mL of 100 ppm std	20 mL 0.04 N H_2SO_4

Total phosphorous

APPENDIX II

PHOSPHORUS MANIFOLD DIAGRAM



Carrier: TKN/PO_4 Diluent/Carrier
Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2 µL/cm.
AE Sample Loop: 25 cm
QC8000 Sample Loop: 30.5 cm
Interference Filter: 880 nm

Apparatus: An injection valve, a 10 mm path length flow cell , and a colorimetric detector module is required.

4.5: 70 cm of tubing on a 4.5 cm coil support
7: 135 cm of tubing on a 7 cm coil support

Note 1: 175 cm of tubing on the heater.
Note 2: 200 cm restrictor coil, 0.52 mm (0.022 in.) i.d.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

AMMONIA DETERMINATION BY THE LACHAT QUIKCHEM FIA + 8000 SERIES

(GL-GC-E-106 REVISION 10)

APPLICABLE TO METHODS:
EPA 350.1 Revision 2
Standard Methods, 22nd Edition, Method 4500-NH_3 H-2011

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1.0 STANDARD OPERATING PROCEDURE FOR AMMONIA DETERMINATION BY THE LACHAT QUIKCHEM FIA+ 8000 SERIES

2.0 METHOD CODE

2.1 EPA Method 350.1 Revision 2, Determination of Ammonia Nitrogen by Semi-Automated Colorimetry

2.2 Standard Methods, 22nd Edition, Method 4500-NH_3 H-2011.

3.0 METHOD OBJECTIVE/PURPOSE

The purpose of this method is to describe the determination of ammonia in drinking, surface, and saline waters, and in domestic and industrial wastes.

4.0 METHOD SUMMARY

In this method, ammonia in the sample is reacted with alkaline phenol and sodium hypochlorite to form indophenol blue. This color is intensified using sodium nitroprusside. This blue color is then measured at 630 nm.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

Holding time for non-South Carolina samples is 28 days from the time and date of collection until the start of analysis unless otherwise specified by contract. Samples reported for compliance in South Carolina must be analyzed within 24 hrs of sample preparation.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples are collected in plastic or glass containers and preserved at time of collection with sulfuric acid to a pH less than 2.

7.2 Samples are stored at $0 \leq 6$ °C until analyzed.

8.0 INTERFERENCES/LIMITATIONS

8.1 Sufficient concentration of calcium and magnesium ions may cause precipitation problems during analysis. EDTA is added to the sample in-line in order to prevent this problem.

8.2 Sample color and turbidity may also interfere with the colorimetric analysis. This may be removed from most samples by filtration or distillation.

8.3 Eliminate any marked variation in pH among samples because intensity of measured color is pH-dependent. Likewise, ensure that the pH of ammonia standard solutions approximates that of the samples.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Calibration range: 0.05 to 2.0 mg/L

9.2 Method precision: Refer to current control limits.

9.3 Method accuracy: Refer to current control limits.

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

10.2 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analystes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

10.3 Continuing Calibration Blank (CCB): An aliquot of reagent water or other blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

10.4 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample, periodically throughout the run sequence. Its purpose is to determine whether the analytical sequence is in control during sample analysis. It may be prepared from the same source as the calibration standards, and is usually of varied concentration.

10.5 EDTA: Disodium ethylenediamine tetraacetate

10.6 Independent Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination after injection of the mid-level ICV.

10.7 Independent Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of MB or sample matrix. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

10.8 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

10.9 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

10.10 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other

samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

10.11 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

10.12 Spike (Matrix Spike or Post Spike): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or PS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or PS corrected for background concentrations.

10.13 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD, and internal standards.

10.14 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

10.15 Laboratory Duplicate (DUP, LCSD, MSD, or PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

10.16 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide use definitions.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until they have been fully trained and have demonstrated the ability to generate acceptable data. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

12.1 Sample preparation data are recorded in AlphaLIMS.

12.2 As data are acquired, computer printouts of the data are generated. These dated hard copies of the data are kept in the NH_3 binder in the Lachat lab. Results are entered into AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear safety glasses while in the laboratory.

13.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the

laboratory as well as a reference file of Material Safety Data Sheets (MSDS). Individual sample MSDS forms provided by the clients are also maintained.

13.3 In order to prevent instrument damage, ensure that the correct pump lines are placed in the proper reagents

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from the cooler and either delivers them to the analyst/technician or places them on the pickup shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

14.3 Previously distilled samples are stored in the General Chemistry refrigerator until retrieved by an analyst.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Instrumentation: Lachat QuikChem FIA+ 8000 Series analyzer.

15.1.1 Sampler

15.1.2 Multichannel proportioning pump

15.1.3 Reaction unit or manifold

15.1.4 Colorimetric detector

15.1.5 Data system

15.1.6 Heating unit

15.1.7 PVC pump tubes

15.1.8 Helium tank and helium degassing tube

15.2 Equipment

15.2.1 Air Displacement Pipets

15.2.1.1 100 µL with tips

15.2.1.2 100-1000 µL with tips

15.2.1.3 1.00-5.00 mL with tips

NOTE: Pipets are calibrated in accordance with GL-LB-E-010.

15.2.2 Autosampler vials

15.2.3 Analytical balance capable of weighing to the nearest 0.0001 g.

NOTE: Balance must be calibrated in accordance with GL-LB-E-002.

15.2.4 Carboy for disposal of sample reagents and residue

15.3 Glassware should be cleaned using the standard glassware cleaning procedure. It should be rinsed thoroughly using deionized (DI) water before use.

16.0 REAGENTS

Unless otherwise specified, all chemicals should be of ACS grade or equivalent.

16.1 Ammonium chloride, NH_4Cl, or purchased ammonia standard (2 separate independent sources are required)

16.2 Disodium ethylenediamine tetraacetate dihydrate, EDTA, $Na_2C_{10}H_{14}O_8N_2 \bullet 2H_2O$

16.3 88% Liquified phenol or crystalline phenol (C_6H_5OH)

16.4 Sodium hydroxide, NaOH

16.5 Sodium hypochlorite, 5.25% solution, NaOCl

16.6 Sodium nitroprusside, $Na_2Fe(CN)_5NO \bullet 2H_2O$

16.7 Sulfuric Acid, concentrated (H_2SO_4)

16.8 Helium

16.9 Reagent preparation

NOTE: If needed, to prevent bubble formation, degas all solutions except the standards with helium (unless otherwise noted). Bubble helium through the solution for approximately one minute.

16.9.1 Sodium phenolate (Prepare every 6 months)

CAUTION: Wear gloves. Phenol causes severe burns and is rapidly absorbed into the body through the skin.

In a 1 L volumetric flask, dissolve 88 mL of 88% liquefied phenol or 83 g of crystalline phenol (C_6H_5OH) in approximately 600 mL of DI water. While stirring, slowly add 32 g of sodium hydroxide (NaOH). Cool and invert to mix thoroughly. Store at room temperature. DO NOT DEGAS THIS REAGENT!

16.9.2 Sodium hypochlorite (PREPARE FRESH MONTHLY)

In a 500 mL volumetric flask, dilute 250 mL of 5.25% sodium hypochlorite (NaOCl) to the mark with DI water. Invert to mix. Store at room temperature.

16.9.3 Buffer (Prepare every 6 months)

In a 1 L volumetric flask, dissolve 50.0 g of disodium ethylenediamine tetraacetate dihydrate ($Na_2EDTA \bullet 2H_2O$) and 9.0 g of sodium hydroxide (NaOH) in approximately 900 mL of DI water. Dilute to the mark and mix with a magnetic stirrer until dissolved. Store at room temperature.

16.9.4 Sodium nitroprusside (Prepare every 6 months)

To a 1 L volumetric flask, dissolve 3.50 g of sodium nitroprusside [sodium nitroferricyanide [$Na_2Fe(CN)_5NO \bullet 2H_2O$]. Dilute to the mark with DI water and invert to mix. Store at room temperature.

16.9.5 Carrier and diluent (0.04 N sulfuric acid) (Prepare every 6 months)

To a 1 L volumetric flask, add approximately 900 mL of DI water. Then slowly add 1.12 mL of concentrated sulfuric acid (H_2SO_4). Dilute to the mark with DI water and invert to mix. Store at room temperature.

16.9.6 In a 1 L volumetric flask, dilute 834 mL of 6% sodium hypochlorite to the mark with DI water. Invert to mix. This reagent may be stored at room temperature and must be prepared fresh every six months.

17.0 PREPARATION OF SAMPLES

All samples are prepared in accordance with GL-GC-E-072 for Ammonia-Nitrogen Sample Preparation.

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards and their preparation is found in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

18.2 All standards are prepared from traceable solutions according to the recipes found in Appendix 1.

18.3 All ammonia standards, blanks, and carriers are prepared using 0.04 N sulfuric acid as diluent.

18.4 All ammonia calibration standards are prepared fresh daily.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURES

19.1 Refer to QuikChem Method 10-107-06-1-B: Determination of Ammonia (Phenolate) by Flow Injection Analysis (Colorimetry) for instrument and equipment start-up procedures.

19.2 Refer to the QuikChem FIA+ 8000 Series User Manual for instrument and equipment start-up procedures.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Instrument QC

20.1.1 An ICV is run immediately after the calibration curve. This standard must be made from a different source than the calibration standards.

20.1.2 An ICB is run following the ICV.

20.1.3 A CCV is run after every 10 analytical samples and after the last analytical sample in the run.

20.1.4 A CCB is run after every CCV.

20.1.5 MDL and/or MDL verifications are performed in accordance with GL-LB-E-001 the Determination of Method Detection Limits and Method Quantitation Limits.

20.1.6 Linear Calibration Range (LCR) checks are performed on a 6 month basis. The high standard of the curve is read back against the calibration and must recover ± 10%. If this procedure fails, the problem must be investigated and rectified.

20.1.7 Calculated curve readbacks are: 50%-150% for the first point (low-end) and 90%-110% for all the other points. The calculated zero point must be ± ½ RL. Any failure will require re-calibration of the instrument.

20.2 Batch QC

NOTE: Additional/alternate QC is analyzed if required by client contract.

20.2.1 A DUP, MSD, and MS are analyzed for every batch of < 10 samples and for each set of ten samples in batches with > 10 samples.

20.2.2 A MB and LCS are analyzed at least once for every batch of 20 samples or less.

20.3 Acceptance limits:

20.3.1 The correlation coefficient for the calibration curve must be 0.995 or greater.

NOTE: Refer to GL-QS-E-014 for the Quality Assurance Measurement Calculations and Processes. The intercept should be evaluated as stated in Section 9.2. The absolute value of the intercept should be less than 3 times the MDL.

20.3.2 ICV recovery must be 90 to 110% for all batches unless otherwise specified by client contract requirements. If the ICV fails, the calibration curve must be reanalyzed. If the ICV fails again, new standards must be made and a new calibration conducted.

20.3.3 CCV recovery must be 90 to 110% for all batches unless otherwise specified by client contract requirements. If the CCV fails, all samples bracketed by the out-of-control CCV must be reanalyzed.

20.3.4 Matrix RPD: Refer to current SPC limits.

20.3.5 Matrix Spike recovery: 90 to 110% unless otherwise specified by client contract.

20.3.6 MB: - PQL < MB < PQL

20.3.7 LCS: Refer to current SPC limits. If the % recovery falls outside these limits or other limits directed by project specifications, the batch must be reanalyzed.

20.3.8 LCS RPD: Refer to current SPC limits.

20.3.9 Due to the scope of the test and method, peaks are verified visually. These peaks should have a steady rise and fall. Any peak that is sharp with jagged edges must be reanalyzed for verification.

20.4 Handling out-of-control situations

20.4.1 If a sample result exceeds the highest calibration standard, the sample must be diluted with 0.04 N sulfuric acid solution and reanalyzed.

20.4.2 The correlation coefficient must be a value of at least 0.995. If it is less than 0.995, reanalyze the calibration standards. If this does not bring the correlation coefficient to a value greater than 0.995, then fresh reagents must be made and the run reanalyzed.

20.4.3 If the duplicates or MSs of a batch do not meet the acceptance limits and the analyst feels the out-of-range recovery is due to a problem in the analysis or prep process, the batch should be reprepped and/or reanalyzed.

20.4.4 If the LCS and/or LCS duplicates fail to meet the above acceptance limits, the batch is reprepped and reanalyzed.

20.4.5 Client samples that are less than the negative PQL are analyzed for verification. If the reanalysis is still more negative and the sample was distilled, a dilution is performed until the matrix suppression is less than the absolute value of the PQL. If the sample was not distilled, then it should be taken through the distillation process and reanalyzed.

21.0 TYPICAL RUN SEQUENCE

21.1 Calibration curve (analyzed from high standard to blank)

21.2 ICV (Initial Calibration Verification standard)

21.3 ICB (Initial Calibration Blank)

21.4 MB

21.5 LCS

21.6 Sample

21.7 Sample duplicate (if required)

21.8 MS (if required)

21.9 Up to 5 more samples

21.10 CCV

21.11 CCB

21.12 Up to 8 samples

21.13 Sample duplicate (if required)

21.14 MS (if required)

21.15 CCV

21.16 CCB

21.17 Remaining samples (no more than 20 samples may be in a batch)

21.18 CCV

21.19 CCB

22.0 PROCEDURE

22.1 Create Sample Table:

22.1.1 Click on 'Open' and choose file to open.

22.1.2 Fill in the Sample table according to the Run Sequence 21.0, and change dates on calibration standards sample names.

22.1.3 Enter the sample ID and dilution factor.

22.1.4 Check to ensure the cup location is incremented correctly.

22.1.5 Load samples onto the autosampler as listed on the printed sample table.

22.2 Check to make sure all reagents and lines are pumping correctly

22.3 Click on 'Start.'

22.4 Refer to QuikChem Method 10-107-06-1-B: Determination of Ammonia (Phenolate) by Flow Injection Analysis (Colorimetry) for instrument and equipment procedures.

22.5 Refer to the QuikChem FIA+ 8000 Series User Manual for instrument and equipment procedures.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURES

23.1 Place the reagent lines in DI water and allow DI water to pump through the system for 5 minutes.

23.2 Remove the reagent tubes from the DI water and allow air to pump through the system for 5 minutes or until water no longer appears in the lines.

23.3 Turn off power, and release platen tension.

23.4 Refer to the QuikChem FIA+ 8000 Series User Manual for instrument shut-down procedures.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE(S)

24.1 Refer to GL-LB-E-005 and GL-GC-E-092 for data review and validation procedures.

24.2 Data Reduction

Linear regression is used for calibration. The analyst must not force the calibration line through the origin.

24.2.1 Make certain that the instrument response is treated as the dependant variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response

a = slope of the line (also called the "coefficient of x")

x = concentration of the calibration standard

b = the intercept

24.2.2 The analyst should not force the line through the origin, but have the intercept calculated form the standard data points.

24.2.3 The regression calculation will generate a correlation coefficient (R^2) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, R^2 must be ≥ 0.995. The calculated intercept value needs to be evaluated before reporting sample results.

24.2.4 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y - b)}{a}$$

24.2.5 The curve must meet all criteria set forth in section 20.0.

25.0 DATA TRANSMITTAL

Once data are obtained, they are entered into AlphaLIMS.

26.0 RECORDS MANAGEMENT

26.1 Ammonia hard copy binder is maintained in the Lachat lab.

26.2 Lachat standards are maintained in AlphaLIMS.

26.3 The Lachat Maintenance Logbook is kept in the Lachat lab.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to the QuikChem FIA+ 8000 Series User Manual.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001 for Laboratory Wastes.

29.0 METHOD VERIFICATION

29.1 Method detection limit studies are performed in accordance with GL-LB-E-001 for The Determination of Method Detection Limits.

29.2 Reagents are prepared in accordance with QuikChem Method 10-107-06-1-B: Determination of Ammonia (Phenolate) by Flow Injection Analysis (Colorimetry).

30.0 REFERENCES

30.1 EPA Method 350.1 (Revision 2.0 – August 1993). "Determination of Ammonia Nitrogen by Semi-Automated Colorimetry."

30.2 Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012. Method 4500-NH_3 B-2011. Preliminary Distillation Step.

30.3 Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012. Method 4500-NH_3 H-2011 Flow Injection Analysis.

30.4 QuikChem Method 10-107-06-1-B: Determination of Ammonia (Phenolate) by Flow Injection Analysis (Colorimetry). Revision Date 9/13/00. Lachat Instruments, 6645 West Mill Road Milwaukee, WI 53218-1239.

30.5 QuikChem FIA+ 8000 Series User Manual. Latest revision 25Apr02. Lachat Instruments, 6645 West Mill Road Milwaukee, WI 53218-1239.

31.0 HISTORY

Revision 7: Changed holding time for compliance with South Carolina requirement.

Revision 8: Updated Standard Method Reference for preparatory method.

Revision 9: Updated Standard Method Reference for determinative method.

Revision 10: Added readback requirements for calibration curve standard.

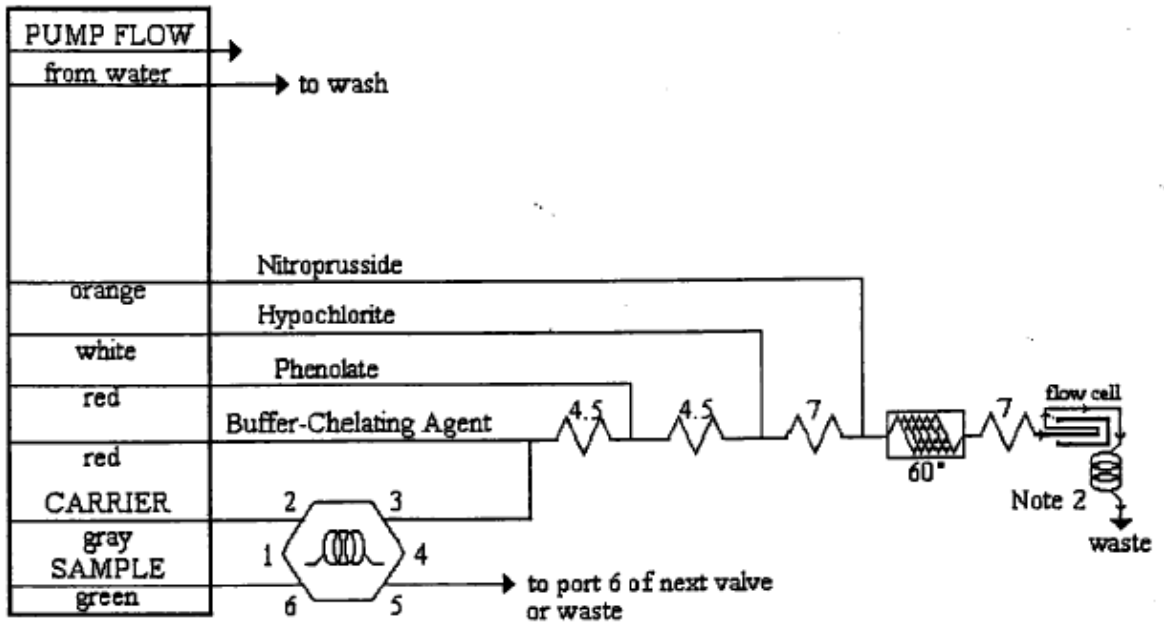
APPENDIX 1

Concentration of Standard	Volume of Stock	Final Volume of Standard
2 ppm	2 mL of 100 ppm std	100 mL 0.04 N H_2SO_4
1 ppm	1 mL of 100 ppm std	100 mL 0.04 N H_2SO_4
0.5 ppm	0.5 mL of 100 ppm std	100 mL 0.04 N H_2SO_4
0.1 ppm	0.1 mL of 100 ppm std	100 mL 0.04 N H_2SO_4
0.05 ppm	0.05 mL of 100 ppm std	100 mL 0.04 N H_2SO_4

Ammonia, Nitrogen

APPENDIX 2

AMMONIA MANIFOLD DIAGRAM



Carrier: 0.04 N H_2SO_4
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm**.
AE Sample Loop: 75 cm
QC8000 Sample Loop: 75cm
Interference Filter: 630 nm

Apparatus: An injection valve, a 10 mm path length flow cell , and a colorimetric detector module is required. The shows 650 cm of tubing wrapped around the heater block at the specified temperature.

4.5: **70** cm of tubing on a 4.5 cm coil support
7: **135** cm of tubing on a 7 cm coil support

Note 1: PVC PUMP TUBES MUST BE USED FOR THIS METHOD
Note 2: 200 cm x 0.022" i.d. backpressure loop.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

NITRATE/NITRITE (NO_3+NO_2) ANALYSIS USING THE LACHAT QUIKCHEM FIA+ 8000 SERIES INSTRUMENT

(GL-GC-E-128 REVISION 10)

APPLICABLE TO METHODS:

EPA 353.2
Standard Methods 22nd, 4500 NO_3 F-2011

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1.0 STANDARD OPERATING PROCEDURE FOR NITRATE/NITRITE (NO_3+NO_2) ANALYSIS USING THE LACHAT QUIKCHEM FIA+ 8000 SERIES INSTRUMENT

2.0 METHOD CODE

2.1 EPA Method 353.2 (Determination of Nitrate+Nitrite Nitrogen by Semi-Automated Colorimetry)

2.2 Standard Methods 22nd Edition, 4500 NO_3^- F-2011

3.0 METHOD OBJECTIVE/PURPOSE

The purpose of this SOP is to provide the necessary instructions to determine the concentration of total nitrate+nitrite nitrogen in samples using the Lachat QuikChem FIA+ 8000 Series Instrument.

4.0 METHOD SUMMARY

Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Nitrite alone also can be determined by removing or circumventing the cadmium column if holding time of 48 hours is observed.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on soils, sludge, miscellaneous liquid or solid samples. In these cases, the procedure is modified as necessary. Modification is not permitted for samples being reported to SC DHEC for regulatory monitoring or NPDES.

6.0 HOLDING TIME

Holding time is 28 days from the time and date of collection until the start of analysis unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples may be collected in plastic or glass containers.

7.2 Samples are preserved at time of collection with sulfuric acid to a pH less than 2.

7.3 Samples are stored at $0° \leq 6°$ C until analyzed.

8.0 INTERFERENCES/LIMITATIONS

8.1 Residual chlorine can interfere by oxidizing the cadmium column.

8.2 Low results would be obtained for samples that contain high concentrations of iron, copper, or other metals. In this method, EDTA is added to the buffer to reduce this interference.

8.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

8.4 Sample turbidity may interfere. Turbidity can be removed by filtration through a 0.45 µm pore diameter membrane filter prior to analysis.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 0.01 to 2.00 mg/L

9.2 Calibration range: 0.02 to 1.50 mg/L

9.3 Method detection limit (MDL): Refer to current MDL study.

9.4 Method precision: Refer to current SPC limits.

9.5 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

10.2 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

10.3 Continuing Calibration Blank (CCB): An aliquot of reagent water or other blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

10.4 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample, periodically throughout the run sequence. Its purpose is to determine whether the analytical sequence is in control during sample analysis. It may be prepared from the same source as the calibration standards, and is usually of varied concentration.

10.5 Independent Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination after injection of the mid-level ICV.

10.6 Independent Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of Blank or sample matrix. The ICV is obtained from a source external to the

laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

10.7 Instrument Performance Check Solution (IPC): A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

10.8 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

10.9 Laboratory Duplicate (DUP, LCSD, MSD or PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

10.10 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

10.11 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

10.12 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

10.13 Spike (Matrix Spike or Post Spike): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or PS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or PS corrected for background concentrations.

10.14 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

10.15 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

10.16 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Technicians and analysts are not allowed to analyze samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

12.1 As data are acquired, computer printouts of the data are generated. These dated hardcopies of the data are kept in the NO_3+NO_2 binder in the Lachat lab. Results are uploaded into AlphaLIMS as data are obtained.

12.2 Documentation of standards preparation is maintained in AlphaLIMS.

12.3 Prep data are entered in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNINGS

HYDROCHLORIC ACID, PHOSPHORIC ACID, AND SODIUM HYDROXIDE ARE HIGHLY CORROSIVE.

POTASSIUM NITRITE IS TOXIC AND A POSSIBLE MUTAGEN.

N-(1-NAPHTHYL) ETHYLENEDIAMINE DIHYDROCHLORIDE IS IRRITATING TO MUCOUS MEMBRANES AND UPPER RESPIRATORY TRACT.

COPPER SULFATE MAY BE TOXIC UPON INGESTION. DEATH COULD OCCUR FROM SHOCK OR RENAL FAILURE.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

PREVENT INHALATION AND SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT.

13.1 Wear eye protection with side shields while in the laboratory.

13.2 Treat all chemicals and samples as potential health hazards and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and individual sample MSDS forms are maintained in the laboratory and on AlphaLIMS.

13.3 Personal protective equipment: Gloves are required when handling the chemicals in this procedure.

13.4 Prior to handling radioactive samples, analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.4.1 Wear a plastic apron over lab coat when working with radioactive samples.

13.4.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

13.4.3 Prohibit admittance to immediate work area.

13.4.4 Post signs indicating radioactive samples are in the area.

13.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.4.6 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from the cooler and either delivers them to the analyst/technician or places them on the pickup shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENT/EQUIPMENT/GLASSWARE

15.1 Instrumentation: Lachat QuikChem FIA+ 8000 Series

15.1.1 Autosampler

15.1.2 Multichannel proportioning pump

15.1.3 Reaction Unit or Manifold

15.1.4 Colorimetric detector

15.1.5 Data System

15.2 Equipment

15.2.1 Air Displacement Pipets

15.2.1.1 10-100 µL with tips

15.2.1.2 100-1000 µL with tips

15.2.1.3 1.00-5.00 mL with tips

NOTE: Pipets must be calibrated in accordance with GL-LB-E-010.

15.2.2 Carboy for disposal of sample reagents and residue

15.2.3 Analytical balance capable of accurately weighing to the nearest

0.0001 g.

NOTE: The balance must be calibrated in accordance with the procedure outline in GL-LB-E-002 for Balances.

15.2.4 PVC pump tubes

15.2.5 Nitrite test strips

15.2.6 10 mL Luer-lock syringe

15.2.7 Acrodisk, 0.45 µm pore syringe filters

15.2.8 40 mL centrifuge tubes with lids

16.0 REAGENTS

NOTE: Unless otherwise specified, all chemicals should be of ACS grade or equivalent.

16.1 ASTM Type I deionized (DI) water (see GL-LB-E-016)

16.2 0.04 N Sulfuric Acid (0.04 N H_2SO_4): Carefully add 22.4 mL of concentrated sulfuric acid to 20 L of DI water.

16.3 Dilute Hydrochloric Acid (HCl): Carefully add 500 mL concentrated HCl to 500 mL DI water.

16.4 Sodium Hydroxide (NaOH)

16.5 Ammonium Chloride (NH_4Cl)

16.6 Disodium Ethylenediamine Tetraacetic acid dihydrate ($Na_2EDTA•2H_2O$)

16.7 85% Phosphoric Acid (H_3PO_4)

16.8 Sulfanilamide ($C_6H_8N_2O_2S$)

16.9 N-(1-naphthyl) ethylenediamine dihydrochloride (NED)

16.10 Copper Sulfate ($CuSO_4•5H_2O$)

NOTE: All reagents are good for six months unless otherwise noted.

16.11 15 N Sodium Hydroxide

CAUTION! This solution will get very hot!

Add 150 g of NaOH very slowly to 250 mL of DI water. Swirl until dissolved. Cool and store in a plastic bottle.

16.12 Ammonium Chloride buffer, pH 8.5

In a 1 L volumetric flask, dissolve 85.0 g of NH_4Cl and 1.0 g of $Na_2EDTA•2H_2O$ in about 800 mL of DI water. Adjust the pH to 8.5 with 15 N NaOH solution. Dilute to the mark and mix.

16.13 Sulfanilamide color reagent

To a 1 L volumetric flask, add about 600 mL of DI water. Then add 100 mL of 85% phosphoric acid, 40.0 g of sulfanilamide, and 1.0 g of NED. Shake to wet and stir for 30 minutes to dissolve. Bring to volume. Store in a dark bottle. This solution is stable for one month.

16.14 Granulated cadmium: 40-60 mesh (CASRN 7440-43-9). Other mesh sizes may be used.

16.15 2% Copper Sulfate Solution

Dissolve 20.0 g of $CuSO_4$•$5H_2O$ in 500 mL of DI water and dilute to 1 L.

16.16 Copper-cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner (also known as re-generating the cadmium column):

16.16.1 Wash the cadmium with dilute hydrochloric acid and rinse with distilled water. The color of the treated cadmium should be silver.

16.16.2 Swirl 10 g cadmium in 100 mL portions of 2% solution of copper sulfate for five minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

16.16.3 Wash the copper-cadmium with reagent water (at least 10 times) to remove all the precipitated copper. The color of the treated cadmium should be black.

NOTE: Typically, the cadmium columns are purchased new and are not regenerated.

16.17 100 mg/L Stock Standard (NO_3+NO_2), certified standard purchased from vendor (2 independent sources are required.)

16.18 100 mg/L Nitrate Standard (Nitrate as N), certified standard purchased from vendor. May require refrigerated storage, per the manufacturer.

16.19 100 mg/L Nitrite Standard (Nitrite as N), certified standard purchased from vendor. This standard material must be stored under refrigeration.

17.0 PREPARATION OF SAMPLES

17.1 All samples are tested for approximate nitrate concentration with test strips.

17.2 DI water extraction for solid samples:

17.2.1 Weigh out 4.0 g or other recorded weight of sample into a 40 mL centrifuge tube. Be careful to get a portion homogeneous to the entire sample.

17.2.2 Fill centrifuge tube to 40 mL with 0.04 N sulfuric acid.

17.2.3 Spike MS/MSD with 0.4 mL stock standard.

17.2.4 Cap the tube and shake several times every few minutes for approximately 30 minutes.

17.2.5 Let sample sit and allow all solid matter to settle out.

17.2.6 Decant the liquid off the top for analysis. The liquid may need to be filtered through an Acrodisk or similar disposable filter to remove all solid particles.

17.2.7 The initial sample weight and the volume of 0.04 N sulfuric acid used to extract is recorded in AlphaLIMS.

17.3 No preparation is required for water matrix samples.

18.0 PREPARATION OF STANDARDS

Documentation of standards and their preparation is maintained in AlphaLIMS in accordance with GL-GC-E-007 for Laboratory Standards Documentation. Each standard is prepared fresh daily.

18.1 100 mg/L primary stock NO_3+NO_2 standard purchased commercially

18.2 100 mg/L secondary stock NO_3+NO_2 standard purchased commercially

Dilute 1.0 mL of the 100 mg/L secondary stock NO_3+NO_2 standard in DI water to a volume of 100 mL using a 100 mL volumetric flask.

18.3 100 mg/L NO_3 stock standard purchased commercially

18.4 100 mg/L NO_2 stock standard purchased commercially

18.5 1.0 mg/L NO_3 standard

Dilute 1.0 mL of the 100 mg/L NO_3 stock standard in DI water to a volume of 100 mL using a 100 mL volumetric flask.

18.6 1.0 mg/L NO_2 standard

Dilute 1.0 mL of the 100 mg/L NO_2 stock standard in DI water to a volume of 100 mL using a 100 mL volumetric flask

18.7 Calibration curve standards

18.7.1 1.5 mg/L working standard by diluting 1.5 mL of the 100 mg/L primary stock NO_3+NO_2 standard in DI water to a volume of 100 mL using a 100 mL volumetric flask.

18.7.2 1.0 mg/L working standard by diluting 1.0 mL of the 100 mg/L primary stock NO_3+NO_2 standard in DI water to a volume of 100 mL using a 100 mL volumetric flask. This standard also serves as the CCV.

18.7.3 0.5 mg/L working standard by diluting 0.5 mL of the 100 mg/L primary stock NO_3+NO_2 standard in DI water to a volume of 100 mL using a 100 mL volumetric flask.

18.7.4 0.1 mg/L working standard by diluting 0.1 mL of the 100 mg/L primary stock NO_3+NO_2 standard in DI water to a volume of 100 mL using a 100 mL volumetric flask.

18.7.5 0.05 mg/L working standard by diluting 0.05 mL of the 100 mg/L primary stock NO_3+NO_2 standard in DI water to a volume of 100 mL using a 100 mL volumetric flask.

18.7.6 0.02 mg/L working standard by diluting 0.02 mL of the 100 mg/L primary stock NO_3+NO_2 standard in DI water to a volume of 100 mL using a 100 mL volumetric flask. This standard is used only

for SC samples.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

19.1 Set up the Manifold as shown in Appendix 1.

19.2 DI water should never be run through the cadmium column. Turn switch to off to rinse lines.

19.3 Refer to the Lachat QuikChem Method 10-107-04-1-C: Determination of Nitrate/Nitrite in Surface and Wastewaters by Flow Injection Analysis for instrument start-up procedures.

19.4 Refer to the Lachat QuikChem FIA+ 8000 Series User Manual for instrument start-up procedures.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Instrument QC

20.1.1 An initial calibration verification (ICV) is run immediately after the calibration curve. This standard must be made from a different source than the calibration standards. The concentration is 1.0 mg/L. If the ICV fails, the calibration curve must be reanalyzed See section 20.3.2. If the ICV fails again, new standards must be made and a new calibration conducted.

20.1.2 An initial calibration blank (ICB) is run following the ICV.

20.1.3 A 1.0 mg/L nitrate (NO_3) check standard is analyzed after the ICB to verify the reduction of nitrate by the cadmium column.

20.1.4 A 1.0 mg/L nitrite (NO_2) check standard is analyzed after the 1.0 mg/L nitrate (NO_3) standard.

20.1.5 A continuing calibration verification (CCV 1.0 mg/L) is run after every 10 analytical samples and after the last analytical sample in the run. If the CCV fails, all samples bracketed by the out of control CCV must be reanalyzed. See section 20.3.3.

20.1.6 A continuing calibration blank (CCB) is run after every CCV as prepared in 18.7.2.

20.1.7 MDL and/or MDL verifications are performed every 6 months. These values are submitted for Quality review.

20.1.8 Linear Calibration Range (LCR) checks are performed every 6 months. The high standard of the curve is read back against the calibration and must recover ± 10%. If this procedure fails, the problem must be identified and rectified.

20.1.9 Calculated curve readbacks are: 50%-150% for the first point (low-end) and 90%-110% for all the other points. The calculated zero point must be ± ½ RL. Any failure will require re-calibration of the instrument.

20.2 Batch QC

20.2.1 For liquid batches, a matrix duplicate (DUP) and post spike (PS) are run for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples.

20.2.2 A LCS and method blank (MB) are run at least once for every batch of 20 samples or less.

20.2.3 For liquid samples, the LCS is normally a 1 mg/L standard taken through the same process as the samples. For solid samples, 1.0 g of sand is weighed out and spiked with an appropriate amount of secondary stock standard.

20.2.4 The post spike is normally prepared by adding 0.05 mL of 100 mg/L stock standard solution to 5 mL of sample.

20.2.5 Linear Calibration Range (LCR) checks are performed on a 6 month basis. The high standard of the curve is read back against the calibration and must recover ± 10 %. If this procedure fails, the problem must be investigated and rectified.

20.2.6 For solid batches a DUP, MS, and MSD are run for every batch of ≤ 10 samples and for each set of 10 samples in batches with > 10 samples.

20.3 Acceptance limits

20.3.1 Coefficient of determination (r^2) must be 0.995 or greater.

20.3.2 ICV recovery must be 90-110% for all batches unless otherwise directed by project specifications.

20.3.3 CCV recovery must be 90-110% for all batches unless otherwise directed by project specifications.

20.3.4 Matrix relative percent difference (RPD): Refer to current SPC limits.

20.3.5 Matrix spike recovery: Refer to current SPC limits.

20.3.6 Method Blank: MB<PQL for most clients depending on client contract. If the MB fails, the analyst must reanalyze the MB with the entire batch.

20.3.7 LCS: Refer to current SPC limits. If the %Recovery falls outside these limits or other limits directed by project specifications, the batch must be reanalyzed.

20.3.8 LCS RPD: Refer to current SPC limits. If the RPD falls outside these limits or other limits directed by project specifications, the batch must be reanalyzed.

20.3.9 The 1.0 mg/L NO_3 standard and the 1.0 mg/L NO_2 standard must be within ± 10% of each other and of their true value.

20.4 Handling out-of-control situations:

20.4.1 If a sample result exceeds the highest calibration standard, the

sample must be diluted with the diluents reagent and reanalyzed.

NOTE: QC sets must be manually diluted.

20.4.2 The coefficient of determination must be a value of at least 0.995. If it is less than 0.995, reanalyze the calibration standards. If this does not bring the correlation coefficient to a value $\geq$ 0.995, then the reagents must be made up fresh and the calibrants reanalyzed. If these steps do not correct the problem, the calibration standards must be remade.

NOTE: Refer to GL-QS-E-014 for the Quality Assurance Measurement Calculations and Processes. The absolute value of the intercept should be less than 3 times the MDL.

20.4.3 If the 1.0 mg/L NO_3 standard does not recover within 10% of its true value or within 10% of the NO_2 standard, the cadmium column must be replaced with a new column.

20.4.4 Due to the scope of the test and method, peaks are verified visually. They should have a steady rise and fall. Any peak that is sharp in nature with jagged edges must be reanalyzed for verification.

20.4.5 Client samples that are less than the negative PQL are analyzed for verification. If the reanalysis is still more negative, a dilution is performed until the matrix suppression is less than the absolute value of the PQL.

21.0 RUN SEQUENCE

21.1 Calibration Standards (analyzed from high standard to blank)

21.2 ICV (Initial Calibration Verification standard)

21.3 ICB (Initial Calibration Blank)

21.4 1.0 mg/L NO_3 standard

21.5 1.0 mg/L NO_2 standard

21.6 Method blank

21.7 LCS

21.8 Sample

21.9 Sample duplicate (if required)

21.10 Post spike (if required)

21.11 Up to 7 samples

21.12 CCV

21.13 CCB

21.14 Up to 8 samples

21.15 Sample duplicate (if required)

21.16 Post spike (if required)

21.17 CCV

21.18 CCB

21.19 Remaining samples in batch (a batch may have no more than 20 samples)

21.20 CCV

21.21 CCB

22.0 PROCEDURE

22.1 Create Sample Table:

22.1.1 Click on "Open" and choose file to open.

22.1.2 Fill in the Sample table according to the Run Sequence 21.0 and change dates on calibration standards sample names.

22.1.3 Enter the sample ID and dilution factor.

22.1.4 Check to ensure the cup location is incremented correctly.

22.1.5 Load samples onto the autosampler as listed on the printed sample table.

22.2 Check to make sure all reagents and lines are pumping correctly.

NOTE: Allow reagents to pump through reagent lines for approximately two minutes before turning cadmium column to "in-line."

22.3 Click on "Start."

22.4 Refer to the Method 10-107-04-1-C: Determination of Nitrate/Nitrite in Surface and Wastewaters by Flow Injection Analysis for the analytical procedures.

22.5 Refer to the Lachat QuikChem FIA+ 8000 Series User Manual for analytical procedures.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

23.1 Turn the cadmium column to "off-line."

23.2 Place the reagent lines in DI water and allow for DI water to pump through the system for 5 minutes.

23.3 Remove the reagent tubes from the DI water and allow air to pump through the system for 5 minutes, or until water no longer appears in the lines.

23.4 Turn off power, and release platen tension.

23.5 Refer to the Lachat QuikChem FIA+ 8000 Series User Manual for instrument/equipment shut-down procedures.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

24.1 Refer to GL-GC-E-092 for General Chemistry Data Review and Packaging and GL-LB-E-005 for Data Review and Validation.

24.2 Data Reduction

24.2.1 Linear regression is used for calibration. The analyst must not

force the calibration line through the origin.

24.2.1.1 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response

a = slope of line (also called the "coeffiecient of x")

x = concentration of the calibration standard

b = the intercept

24.2.1.2 The analyst should not force the line through the origin, but have the intercept calculated from the standard data points.

24.2.1.3 The regression calculation will generate a correlation coefficient (r^2) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r^2 must be $\geq$ 0.995. The calculated intercept value needs to be evaluated before reporting sample results.

24.2.1.4 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y - b)}{a}$$

24.2.1.5 The curve must meet all criteria set forth in Section 20.0 and GL-QS-E-014 for Quality Assurance Measurement Calculations and Processes.

25.0 DATA TRANSMITTAL

Data are uploaded in AlphaLIMS as they are obtained.

26.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

27.1 Refer to the Lachat QuikChem FIA+ 8000 Series User Manual for routine instrument maintenance.

27.2 The Lachat QuikChem FIA+ 8000 Series instrument maintenance logbook is maintained in the Lachat lab.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

Method detection limit studies are performed every six months in accordance with GL-LB-E-001 for The Determination of Method Detection Limits.

30.0 REFERENCES

30.1 EPA Method 353.2, Revision 2.0, August 1993. Determination of Nitrate+Nitrite Nitrogen by Semi-Automated Colorimetry.

30.2 EPA Method 353.2, Revision 1.0, 1978. Determination of Nitrate+Nitrite Nitrogen by Semi-Automated Colorimetry.

30.3 EPA Method 353.2, Revision 0, 1974. Determination of Nitrate+Nitrite Nitrogen by Semi-Automated Colorimetry.

30.4 Method 10-107-04-1-C: Determination of Nitrate/Nitrite in Surface and Wastewaters by Flow Injection Analysis. Lachat Instruments 6645 West Mill Rd., Milwaukee, WI 53218.

30.5 Lachat QuickChem FIA+ 8000 Series User Manual. Lachat Instruments 6645 West Mill Rd., Milwaukee, WI 53218.

30.6 Standard Methods, 22nd Edition, 4500 NO_3^- F-2011

31.0 HISTORY

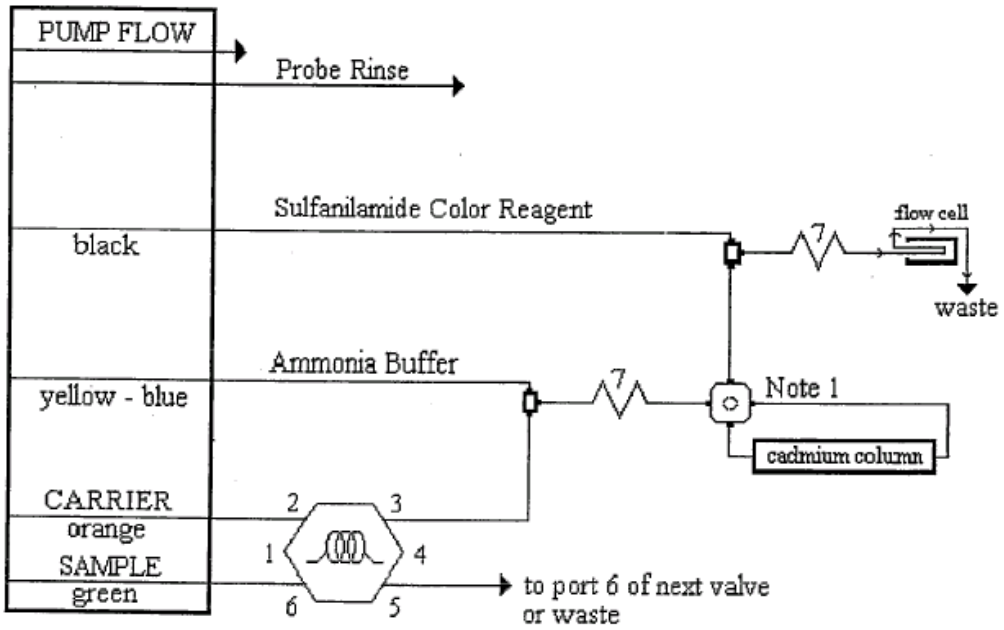
Revision 7: Deleted "The intercept should be evaluated as stated in section 7.2.2.5.3." from section 20.4.2.

Revision 8: Updated Standard Methods reference to 22nd Edition in accordance with MUR II, updated DI Water in accordance with GL-LB-E-016.

Revision 9: Added refrigeration requirements for single component standards.

Revision 10: Added readback requirements for calibration curve standards.

APPENDIX 1: NITRATE/NITRITE MANIFOLD DIAGRAM

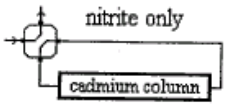


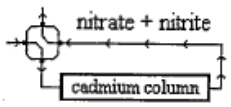
Carrier: Helium Degassed DI water
Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2 µL/cm.
AE Sample Loop: 17 cm x 0.8 mm i.d.
QC8000 Sample Loop: 22.5 cm x 0.8 mm i.d.
Interference Filter: 520 nm

Apparatus: An injection valve, a 10 mm path length flow cell , and a colorimetric detector module is required.

7: **135** cm of tubing on a 7 cm coil support

Note 1: This a 2 state switching valve used to place the cadmium column in-line with the manifold





APPENDIX 2

Conc of STD	Vol of Stock	Final Vol of Std
1.5 ppm	1.5 mL of 100 ppm std	100 mL DI H_2O
1.0 ppm	1.0 mL of 100 ppm std	100 mL DI H_2O
0.5 ppm	0.5 mL of 100 ppm std	100 mL DI H_2O
0.1 ppm	0.1 mL of 100 ppm std	100 mL DI H_2O
0.05 ppm	0.05 mL of 100 ppm std	100 mL DI H_2O
0.02 ppm	0.02 mL of 100 ppm std	100 mL DI H_2O

NO_x (Nitrate/Nitrite)

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

TOXICITY CHARACTERISTIC

LEACHING PROCEDURE PREPARATION

(GL-LB-E-006 REVISION 22)

APPLICABLE METHOD:
SW-846 1311

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1.0 STANDARD OPERATING PROCEDURE FOR TOXICITY CHARACTERISTIC LEACHING PROCEDURE PREPARATION

2.0 PURPOSE

This Standard Operating Procedure (SOP) provides the necessary instructions to prepare Toxicity Characteristic Leaching Procedure (TCLP) samples for extraction to determine the mobility of inorganic and organic contaminants present in liquid, solid, and multiphase wastes, in accordance with SW-846 Method 1311. See appropriate individual analytical standard operating procedure for the necessary instructions for subsequent analysis of prepared TCLP extracts.

3.0 DISCUSSION

3.1 TCLP is used to determine whether or not a waste passes or fails the toxicity characteristic by simulating leaching that would occur in a landfill. The TCLP leachate may be analyzed for the parameters listed in Appendix 1.

3.2 For liquid wastes (those containing less than 0.5% solid material), the wastes after filtration through a 0.6 to 0.8 µm glass fiber filter are defined as the TCLP extract.

3.3 TCLP extracts are analyzed for any combination of semivolatiles, volatiles, and/or metals. Once extracted, the metals fraction is spiked in the TCLP laboratory. This spike addition occurs before preservation with nitric acid to a pH<2.

3.4 For wastes containing greater than or equal to 0.5% solids, the liquid is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. Zero-Head Space Extraction Vessel (ZHE) is used when testing for the volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

3.5 If compatible, the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquid is analyzed separately and the results are mathematically combined.

3.6 Analysts must be familiar with the reference method and understand how to refer to it.

3.7 Preservatives shall not be added to samples before extraction.

3.8 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample including precipitate should be extracted.

3.9 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH <2, unless precipitation

occurs. If a precipitation occurs then a non-preserved portion of the extract shall be analyzed as soon as possible after filtration.

4.0 DEFINITIONS

4.1 Solid: yields no liquid upon filtration through a 0.6 to 0.8 µm glass fiber filter at a maximum pressure of 50 psi.

4.2 Liquid: yields <0.5% solid when filtered through a 0.6 to 0.8 µm glass fiber filter at a maximum pressure of 50 psi.

4.3 Matrix Spike and Matrix Spike Duplicate (MS and MSD): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations.

4.4 Semi-solid: Yields 0.5% or greater of solid when filtered through a 0.6 to 0.8 µm glass fiber filter at a maximum pressure of 50 psi.

4.5 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

5.0 EQUIPMENT

5.1 Agitation Apparatus: capable of39 rotating extraction vessels in an end-over-end fashion at 30 ± 2 rpm.

5.2 2 L High density polyethylene (HDPE), polypropylene (PP) or polyvinyl chloride (PVC) may be used to tumble sample for analysis of metals. Glass, polytetrafluoroethylene (PTFE) or stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components.

5.3 ZHE: used when waste is being tested for the mobility of volatile analytes. Should have an internal volume of 500 - 600 mL and be equipped to accommodate a 90 - 110 mm filter.

5.4 Positive Pressure Filtration Device and Glass Fiber Filter: used to filter semivolatile and metals samples. It should be capable of reaching 50 psi and supporting a glass fiber filter.

5.5 pH paper and pH meter. The pH meter should be accurate to ± 0.05 units at 25°C.

5.6 40 mL volatile vials are used to collect volatile extracts upon filtration.

5.7 Laboratory Balance: Minimum accuracy 0.01 g.

5.8 Glass beaker (150 mL) used to do pH test.

5.9 Watch glass: covers beaker during pH test.

5.10 Magnetic stirrer: stirs sample during pH test.

5.11 Deionized Water (DI).

5.12 Sieve: 9.5 mm mesh for use in particle size reduction for extraction.
5.13 Sieve: 1 mm mesh for use in particle size reduction for pH test.
5.14 Hotplate: Heats sample during pH test.
5.15 Linear pump: used to transfer extraction fluid into the ZHE
5.16 Nalgene tubing
5.17 Gas tight syringe
5.18 hypodermic needle
5.19 syringe
5.20 Crimpable glass 2.5mL vials
5.21 syringe filters (0.7µm)

6.0 REAGENTS, CHEMICALS, AND STANDARDS

NOTE: All reagents are purchased from an approved vendor. The reagents are screened before use to verify the integrity of the reagent. Logbooks are kept on all reagents.

6.1 1N Hydrochloric Acid (HC1) made from American Chemical Society (ACS) reagent grade HC1. Add 41.7 mL of concentrated HCl acid to approximately 400 mL of DI water. Stir. Cool to room temperature and dilute to total volume of 500 mL.

6.2 1N HNO_3 made from ACS reagent grade HNO_3. Add 31.3 mL of concentrated HNO_3 to 400 mL of DI water. Stir. Cool to room temperature and dilute to total volume of 500 mL.

6.3 1N NaOH made from ACS reagent grade NaOH. Add 40 g NaOH to a 1L glass Erlenmeyer flask. Bring up to 1L with DI water. Stir.

6.4 TCLP Extraction Fluid #1 (this may be ordered ready for use):

6.4.1 Add 30L of DI water into a carboy. Add 285 mL of Glacial Acetic Acid, ACS reagent grade.

6.4.2 Weigh 128.7 g NaOH in 1L plastic beaker. Add 500 mL DI water. Stir and pour the NaOH solution into the carboy. Repeat adding DI water, stirring and pouring until all NaOH pellets are dissolved.

6.4.3 Add DI water to 50L. Shake the carboy well.

6.4.4 Check the pH of this fluid. When accurately prepared, the pH will be 4.93 ± 0.05. Record all information in AlphaLIMS.

6.5 TCLP Extraction Fluid #2 (this may be ordered ready for use):

6.5.1 Add 30L of DI water into a carboy. Add 285 mL of Glacial Acetic Acid.

6.5.2 Add DI water to 50L. Shake the carboy well.

6.5.3 Check the pH of this fluid. When accurately prepared, the pH will be 2.88 ± 0.05. Record all information in AlphaLIMS.

6.6 Metals Spike

6.6.1 The TCLP spiking solutions for metals are ordered from approved vendors. The solutions typically contain multiple analytes in varied concentrations. Analytes in the TCLP spike mixes are at concentrations appropriate for RCRA level analysis.

6.6.2 All reagents, chemicals and standard spike solutions are recorded in electronic logbooks, according to related laboratory standard operating procedures.

7.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon the successful analysis of a proficiency sample. Training records are maintained as quality records. See SOP GL-QS-E-011 for initial demonstration of proficiency protocols.

8.0 PRELIMINARY EVALUATIONS

NOTE: Preliminary TCLP evaluations are performed on a minimum of 100 grams of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (section 9.0); (2) determination of whether the waste contains insignificant solids and is therefore, its own extract after filtration (section 9.13); (3) determination of whether the solid portion of the waste requires particle size reduction (section 9.14); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 9.15).

9.0 DETERMINATION OF THE PERCENT SOLIDS

9.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to section 9.14. Record this observation on the TCLP preliminary evaluation queue sheet.

9.2 If the sample is liquid or multi-phasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves using the filtration device.

9.3 Insert filter into filtration device. Thoroughly wet filter by adding >20 mL of DI water. Securely close device. Evacuate water by injecting 20 psi of compressed nitrogen for 10 seconds. Disassemble unit and weigh moist filter. Record as pre-filter weight on the TCLP preliminary evaluation queue sheet.

9.4 Reassemble filtration device with moist filter. Pre-weigh container to catch filtrate (i.e. 1 L polypropylene, etc.). Record weight on preliminary queue sheet. Place the pre-weighed container under the filtration device to catch the filtrate. Try to get the bottle as close to the bottom of the device as possible to avoid lost volume through splattering.

9.5 Tare balance. Place beaker/container on the balance. If a) limited sample is available and no VOAs are needed, quantitatively transfer entire contents to the beaker/container; b) limited sample is available and VOAs are needed, quantitatively transfer two-thirds of entire contents to the beaker/container; c) sample volumes are adequate and solids are minimal, quantitatively transfer contents to the beaker/container; d) sample volumes are adequate and solids are relatively high, quantitatively transfer enough sample to give ample solids to work with, but never too much to clog filter or give over 100 g of solid material. For examples c) and d), be sure to set aside enough volume for VOAs, preferably up to 500 g (~ 0.5 L).

9.6 Record the weight to the nearest 0.1 g unit on the TCLP preliminary evaluation queue sheet under the "Beaker with aliquot weight" column.

9.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). When possible, spread the waste sample evenly over the surface of the filter. If filtration of the waste at 0 to </= 6° C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering. Gradually apply a vacuum or gentle pressure of 1-10 psi until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi, stop the filtration.

NOTE: If the filter is clogged, testing will need to be repeated at a lesser volume.

9.8 Weigh beaker/container containing sample residue on tared balance. Enter this information on the queue sheet under the "Beaker with residue weight" column. The sample sub-aliquot is defined as "Beaker with aliquot weight" minus "Beaker with residue weight." This value is recorded in the data entry column "Sub-sample aliquot" in LIMS.

9.9 The material in the filter holder is defined as the solid phase of the waste and filtrate is defined as the liquid phase.

NOTE: Some wastes such as oily wastes and some paints will obviously contain some material that appears to be a liquid. If after applying pressure filtration, as described in 9.7 and the material does not filter, then the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. If after applying pressure, as described in 9.7 and the material does filter, then the waste liquid will be treated as its own extract. Due to the saturated nature of the filter when filtering these matrices, percent solids are nearly impossible to determine. If

no visible solids are noted, the filter will be discarded. If solids are noted, the filter will be kept for tumbling. The weight used for tumbling will be calculated using:

$$(\text{Post-filter oily weight})^{9.11} - (\text{Pre-filter weight})^{9.3}$$

This value is used as the wet solid weight in section 10.4.3. For all oily waste extractions that do not require tumbling of the filter, document in the batch narrative.

9.10 Weigh the container used to collect the filtrate on a tared balance. Record this value in the "post-container weight" column. The difference between the pre- and post-container weights is the filtrate weight, entered as "Filtrate weight."

9.11 Weigh the moist filter with solids on a tared balance. Enter this weight as "Post-filter weight." The difference between the post-filter and pre-filter weights is recorded as the "wet solid weight." If <0.5 % TCLP solids, discard filter and proceed to step 10.5. The filtrate is its own extract.

9.12 Calculate the % TCLP solids as follows:

$$\frac{(\text{Post-filter weight})^{9.11} - (\text{Pre-filter weight})^{9.3}}{(\text{Sub-sample aliquot})^{9.8}} \times 100 = \%\ \text{TCLP solids}$$

9.13 Determination of insignificant solids

9.13.1 If the percent TCLP solids determined in Section 9.12 is equal to or greater than 0.5 %, proceed to Section 9.14. Retain the liquid fraction to combine with the solid portion in step 10.4.6.2. Store the liquid fraction at 0 to </= 6 °C until ready to combine.

9.13.2 If the percent TCLP solids determined in Section 9.12 is less than 0.5%, then the liquid phase is its own extract. Proceed to step 10.5 for preservation of TCLP extracts.

9.14 Determination of the necessity of particle size reduction

9.14.1 Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. Special precautions, as outlined in Method 1311 section 15.3, must be followed when performing particle size reduction for volatile constituents.

NOTE: To meet method requirements, the object must fit through the sieve with its narrowest dimension, i.e. a pencil would fit yet a dime would not.

9.15 Determination of appropriate extraction fluid:

NOTE: If the solid content of the waste is greater than or equal to 0.5% and the waste will be extracted for volatile constituents, use extraction fluid #1 and proceed to section 11.0 for extraction of volatile constituents. If the solid content of the waste is greater than or equal to 0.5% and the waste will be extracted for nonvolatile (metals and organics) constituents, determine the appropriate extraction fluid by the following steps.

9.15.1 Weigh out a suitable glass beaker. If conditions 9.5 a) or 9.5 b) exist, there will not be enough solid sample to do the pH determination. In this case, extraction fluid #2 will be utilized for the tumble. If conditions 9.5 c) or 9.5 d) exists, reassemble filtration device with a fresh filter and filter enough sample to obtain 5.0 grams of solid material. Dispose of the liquid phase from this filtration.

9.15.2 For conditions 9.5 c) or 9.5 d), add 96.5 mL of DI water to the beaker and cover with a watch glass. Stir vigorously for 5 minutes using magnetic stirrer. Turn magnetic stirrer to low, so that it remains spinning slowly. Measure and record the initial pH on TCLP prep queue sheet. If the pH$\leq$ 5.0 use extraction fluid #1. Proceed to section 10.0 for extraction of non-volatile organics.

9.15.3 If the pH from section 9.15.2 is >5.0 add 3.5 mL 1N HCl. Slurry briefly. Cover with a watch glass, heat to 50°C and hold for 10 minutes.

9.15.4 Let the solution cool to room temperature. The final pH is recorded on TCLP prep queue sheet. If the final pH is ≤5.0, use extraction fluid #1. If the final pH is >5.0, use extraction fluid #2. Proceed to section 10.0 for extraction of non-volatile constituents.

NOTE: Due to ALARA (As Low As Reasonably Achievable), reduced sample volumes or difficult sample matrices the more aggressive fluid #2 may be used. For these conditions, the client must be contacted via the Project Manager, and approval must be received prior to proceeding. The deviation from the method will be documented via the batch narrative.

10.0 NON-VOLATILES PROCEDURE

10.1 A minimum sample size of 100 grams (solid and liquid phases) is recommended. If 100 grams is not available the client must be contacted via the project manager, and approval must be received prior to proceeding. If the analysis is continued with less than 100 grams the comment is added to the batch narrative. In some cases a larger sample size may be necessary. This is especially true when the % solids is near 0.5%.

NOTE: For ALARA (As Low As Reasonably Achievable) purposes, RAD 2 and RAD 3 samples may use a reduced volume. This also applies to difficult sample matrices (metal, construction debris, etc). The volume of extraction fluid will be proportioned at 20:1 with the weight of the sample. For these conditions, the client must be contacted via the Project Manager, and approval must be received prior to proceeding. The deviation from the method will be documented via the batch narrative.

10.2 If the aliquot of the waste used for the preliminary evaluation was determined to be 100% solid at step 9.1, that aliquot may be used for extraction in this section. At least 100 grams should remain for non-volatile extractions. Proceed to step 10.4.1 for determinations on the amount of the extraction fluid to use.

10.3 If the aliquot of the waste required liquid/solid separation as determined by the preliminary evaluations proceed to step 10.4 with the solid fraction from step 9.8. Enough solids should be generated by filtration to support the analyses required of the TCLP extract. Use percent solids information to determine the optimum sample size for filtration.

10.4 Solid TCLP extraction for non-volatile constituents.

10.4.1 If not already performed prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Step 9.14.

10.4.2 Transfer the solid material into an extractor bottle. Record the net weight of the solid sample on the TCLP preparation queue sheet. For samples <100% solid, the filter used to separate the liquid and solid phases will also be included in the extractor bottle. (Do not include the weight of the filter in the aliquot weight).

10.4.3 Determine the amount of extraction fluid to add to the extractor vessel by multiplying (20 X wet solid weight).

Example Calculations:

Where waste is a dry solid and
Aliquot size = 100.0 g
Extraction fluid is calculated as 20 X aliquot size
(20 X 100.0 = 2000 mL)

10.4.4 Slowly add the calculated amount of extraction fluid to the extractor vessel. Close the extractor bottle tightly and secure in the rotary agitation device (TCLP Tumbler). Prepare required tumble blanks at this time and tumble with the samples being analyzed.

Rotate at 30 +/- 2 rpm for 18 +/- 2 hours. The ambient temperature shall be maintained at 23 +/- 2°C during the extraction period.

NOTE: As tumbling occurs, pressure may build up with in the extractor bottle for some types of wastes. To relieve excess pressure, the extractor bottle may be periodically opened and vented into a hood.

10.4.5 Following the 18 +/- 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter. For final filtration the filter may be changed to facilitate filtration. Discard the solid portion and retain the liquid portion. The liquid portion is the extract.

10.4.6 Prepare the TCLP extract as follows:

10.4.6.1 If the initial waste was 100% solid, the filtered extraction liquid from step 10.4.5 is the only extraction liquid. This liquid fraction is defined as the TCLP extract. Proceed to sample preservation with the liquid fraction to step 10.5.

10.4.6.2 If the initial waste was greater than 0.5% solid but less than 100% solid, determine if the filtered extraction fluid from step 10.4.5 and the initial separated liquid fraction from step (9.7) are miscible. If the two extracts are not miscible, contact the project manager. The extract liquid from the solid fraction and the initial liquid fraction will be prepared and analyzed separately and their results will be mathematically combined. Together, each separate extract is defined as the TCLP extract. Proceed to sample preservation with each fraction to step 10.5.

10.4.6.3 If the two extracts are miscible, combine the two extracts into a single suitable container. This combined liquid is defined as the TCLP extract. Proceed to sample preservation with the liquid fraction to step 10.5.

10.5 Preservation of TCLP extracts.

10.5.1 Measure the pH of each liquid fraction and record the value on the TCLP data entry screen.

10.5.2 The TCLP extracts for organic analyses are not to be preserved with nitric acid and are chilled at 0 to </=6ºC until analyzed or prepped by the Organics laboratory.

10.5.3 The TCLP extracts for metals analysis shall have a fraction set aside for matrix spike and spike duplicate if necessary. After the spike solution is added to the spike sample, each sample and spike sample shall be preserved to a pH of < 2.0 with nitric acid. If precipitation is observed after adding nitric acid to a small aliquot of the filtrate then the remaining filtrate will not be preserved, a comment will be added to the batch narrative, and the extract will be analyzed as soon as possible.

NOTE: If the sample matrix is oil that passes through the glass fiber filter then spiking and preservation will occur in the inorganic prep lab.

10.6 Once the extracts are labeled and entered into LIMS they are delivered to the laboratory for further fractional prep.

11.0 VOLATILES PROCEDURE

11.1 The ZHE device is used for volatiles extraction. Volatiles samples should not be exposed to the air for more time than is absolutely necessary. Any manipulation of volatiles samples should be performed at 0 to </= 6ºC to minimize loss of volatiles. Perform all necessary particle size reduction following step 9.14 at this time.

11.2 Assemble the ZHE device.

11.2.1 Place the ZHE piston within the body of ZHE. Make sure gas inlet/outlet valve is closed.

11.2.2 Place a glass fiber filter between two support screens.

11.3 If the sample is 100% solid, weigh out a 25 g subsample of the waste in to the ZHE body. Record weight on the TCLP Prep Queue Sheet.

11.3.1 Secure filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions.

11.3.2 Tighten all ZHE fittings and place the device in a vertical position with liquid inlet/outlet valve on top. Open SLOWLY. Apply pressure of 1 - 10 psi or more when needed up to 50 psi to force out any headspace.

11.3.3 Vent the compressed air side of the ZHE. Add 500 mL of extraction fluid #1 with a gas tight syringe or linear pump. Proceed to section 11.12.

NOTE: Prepare an empty ZHE for preparation blank. 500 mL of extraction fluid #1 is used as the preparation blank unless the sample is < 0.5 solids in which case Deionized water is used.

11.4 If the sample contains < 0.5% solids, the liquid portion of the sample after filtration, is defined as the TCLP extract. Tumbling is not required for samples classified as liquids.

11.4.1 Weigh at least 50 mL of liquid sample into the ZHE body. Record the weight in the data entry screen.

11.4.2 Proceed to 11.10 immediately.

11.5 If the sample contains ≥0.5% solids, but ≤5%, weigh out 500 g of sample into ZHE body. Proceed to Section 11.8.

11.6 If the sample contains ≥5% solids, but less than 100% solids, use the percent wet solids information recorded in 9.12 to determine the amount of sample needed in ZHE. Recommended sample size:

$$\text{Wt. of waste needed} = \frac{25}{\%solids} \times 100 \text{ (volume should never exceed 500 g)}$$

Example: % solids = 10%; Wt. needed = (25/10) x 100 = 250 g

11.6.1 Weigh out sample (liquid and solid phases) into ZHE body and record the weight on the TCLP data entry screen.

11.7 Secure filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions.

11.7.1 Tighten all ZHE fittings and place the device in a vertical position with liquid inlet/outlet valve on top. Open SLOWLY. Apply pressure of 1 - 10 psi or more when needed up to 50 psi to force out any headspace. When adding pressure, check the ZHE vessel and piston O-rings for leakage.

11.7.2 At the first appearance of liquid, quickly close the valve.

11.8 Attach male fitting to inlet/outlet valve on top of ZHE. Attach precut Nalgene tubing to male fitting, and place labeled volatiles vial or other glass container at end of tubing to collect extract. Make sure whatever container used is large enough to handle the volume anticipated with the filtering process.

11.8.1 Attach gas line to gas inlet/outlet valve on bottom.

11.8.2 Apply gas pressure of 1-10 psi and open liquid inlet/outlet valve on top so liquid will flow through Nalgene tubing and into volatiles vial or glass container.

11.8.3 Increase pressure at 10 psi increments until no more liquid is expelled or you reach a maximum of 50 psi.

11.8.4 Close liquid inlet/outlet valve.

11.8.5 Turn off gas pressure and release pressure at gas inlet/outlet valve on the bottom of the ZHE.

11.8.6 Store the liquid filtered off at 0 to </= 6ºC until the solid portion is extracted.

11.9 If the sample is <0.5% solids, this filtrate is considered the TCLP extract. Make sure the 40 ml volatile vial is labeled properly. Proceed to step 11.16.

11.10 Using a gas tight syringe or linear pump, add an amount of extraction fluid #1 equal to 20 times the weight of the solid phase remaining in the ZHE unit. Extraction fluid #1 is used in all cases. Record the volume of extraction fluid on the data entry screen.

Volume of extraction fluid #1 = [(Wt. of waste used x % solids)/100] x 20

Example: % solid = 10%, Wt. used = 250 g; Volume of Extraction fluid #1 = [(250 x 10)/100] x 20 = 500 ml

NOTE: Prepare an empty ZHE for preparation blank. 500 mL of extraction fluid #1 is used as the preparation blank unless the sample is < 0.5% solids in which case Deionized water is used.

11.11 Place the ZHE in the rotary agitation apparatus and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature shall be maintained at 23 ± 2° C during agitation.

11.12 After the sample has completed the tumbling process, attach male fitting to inlet/outlet valve on top of ZHE. Attach precut Nalgene tubing to male fitting, and place labeled volatiles vial (if samples was 100% solid) or other glass container (if less than 100% solid samples was used) at end of tubing to collect extract. Make sure the glass container used for the samples that were less than 100% solid is large enough to handle the volume anticipated with the filtering process.

11.12.1 Attach gas line to gas inlet/outlet valve on bottom.

11.12.2 Apply gas pressure of 1-10 psi and open liquid inlet/outlet valve on top so liquid will flow through Nalgene tubing and into volatiles vial or glass container.

11.12.3 Increase pressure at 10 psi increments until no more liquid is expelled or you reach a maximum of 50 psi.

11.12.4 Close liquid inlet/outlet valve.

11.13 Turn off gas pressure and release pressure at gas inlet/outlet valve on the bottom of the ZHE.

11.14 For samples that were less than 100%, combine the entire tumbled extracted sample liquid with the liquid collected from Section 11.9. After mixing thoroughly, but not so vigorous as to liberate volatile compounds, filled a labeled 40 ml volatile vial. For samples that were 100% solid, the tumbled extracted sample liquid is considered the TCLP extract liquid and a 40 ml labeled vial is filled.

NOTE: If the initial liquid filtrate and the TCLP extract do not combine, then these two layers must be prepared and analyzed as two separate samples. Project Management will be notified and the final results mathematically combined according to the ratio of the two original layers.

11.15 Place each labeled volatile vial in a vial rack and transfer custody to the VOAs area.

11.16 For ALARA (As Low As Reasonably Achievable) purposes RAD category 2 and 3 samples will use a reduced volume procedure for TCLP volatiles. Difficult organic and potential highly contaminating matrices (i.e. greases, oils, paints, solvents, etc.) will also use a reduced volume procedure for TCLP volatiles. Place 2.25 grams of sample in a 45 mL glass vial. Fill the vial with 45 mL of TCLP fluid #1, making sure to eliminate the presence of air bubbles from the vial. Seal the samples and place them on the tumbler for 18 ± 2 hours.

11.17 Remove samples from the tumbler after allotted time. Place a hypodermic needle on a 10 mL Luer-lock syringe. Insert needle into septum of 45 mL glass vial and withdraw 10 mL extract. Replace needle with filter cartridge, and divide extract taken in 3 glass vials 2.5 mL each. Cap and crimp vials placing them in centrifuge tubes with sample ID. After extraction the plastic bags or centrifuge tubes containing sample extracts should be stored in the areas of required tests.

12.0 HOLDING TIMES

12.1 Samples must undergo TCLP extraction with the following holding times:

Sample Maximum Holding Times (Days)				
	From:	From:	From:	
	Field Coll.	TCLPP Extract.	Prep Extract	
	To:	To:	To:	Total Elapsed
	TCLP Extract	Prep Extract.	Analysis	Time (Days):
Volatiles	14	N/A	14	28
Semivolatiles	14	7	40	61
Mercury	28	N/A	28	56
Metals (exc. Hg)	180	N/A	180	360

N/A = Not applicable

If the sample holding times are exceeded, the values obtained will be considered minimum concentrations. Exceeding holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time does not invalidate characterization if the waste exceeds the regulatory level.

13.0 QUALITY ASSURANCE

13.1 A minimum of one blank must be analyzed for every 20 samples that have been extracted. Use the same extraction fluid that is used for samples. If both types are used make a separate blank for fluid #1 and fluid # 2.

13.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate that the waste property exceeds the regulatory level.

13.3 Matrix spike solutions for metals are added after filtration of the TCLP extract and before acid preservation. Organic TCLP extracts are spiked according to the prep and analytical method requirements and spiking is performed by the organic laboratory responsible for preparation or analysis of the TCLP extract.

NOTE: Some organic analytes have shown degradation when spiking materials are added to the TCLP matrix and a delay occurs between spiking and completing the preparation of the samples. Spiking solutions for organics analyses should be added during the extraction/sample prep procedure, as with prep of non-TCLP sample extracts.

13.4 Tumbler rotation shall be checked on a weekly basis and documented in LIMS.

13.5 The temperature in the tumbler room is monitored constantly and is recorded in LIMS.

13.6 Prior to accepting extraction fluid #1 for use it is screened in the organics labs. If methanol or volatile compounds are detected at levels > PQL, the extraction fluid is not logged for use in TCLP. Records of the screens are maintained with the COA for the extraction fluid.

14.0 EQUIPMENT MAINTENANCE

14.1 ZHEs are rotated so that varying ZHE vessels will be used for the blank quality control sample for each batch tumbled. A ZHE must be used as a tumble blank with 5% frequency. This is tracked via AlphaLIMS system. This will monitor cleanliness of the ZHEs and expose any possible contamination problems.

14.2 For the ZHE to be acceptable for use the piston within the ZHE should be able to move, using approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analysis and the manufacturer is contacted.

14.3 The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for one hour, and recheck the pressure. If the device does have a built-in gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be resolved, contact the manufacturer.

14.4 Before using TCLP extraction vessels, separate all parts and clean. Bake at 180° C for one hour, if required.

15.0 DETECTION LIMITS, ANALYSIS AND CALCULATIONS

15.1 Method Detection Limits will be adjusted for masses/volumes used in TCLP leachate preparation. See the limits associated with each chemistry being performed for details. Limits are adjusted by AlphaLIMS.

15.2 Analytical calculations are verified according to the procedures associated with the analytical test being performed.

16.0 INTERFERENCES

16.1 Any interferences in the method are discussed in the analytical procedures for which the TCLP extracts are prepared.

17.0 CALIBRATION AND STANDARDIZATION

17.1 pH meters are calibrated in accordance with GL-GC-E-008. When pH outside the range of pH 4 to pH 10 are read, additional buffer solutions are used to verify proper calibration. These additional buffer checks are recorded in LIMS.

17.2 Balances are calibrated in accordance with GL-LB-E-002.

18.0 SAFETY, HEALTH AND ENVIRONMENTAL HAZARDS

18.1 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

18.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

18.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for Handling Biological Materials.

18.4 If there is any question regarding the safety of any laboratory practice, stop immediately, and consult qualified senior personnel such as a Group or Team Leader.

19.0 RECORDS MANAGEMENT

19.1 Record data in AlphaLIMS extraction logbook for each sample prepared.

19.2 Test each extraction fluid for correct pH and impurities. TCLP extraction fluids are logged in LIMS after being created.

19.3 Spiking standards are recorded in the appropriate standard logbooks.

20.0 CORRECTIVE ACTIONS

20.1 Limited volume/mass of sample is the most frequent cause for departure from the method required minimum sample size of 100 grams (solid and liquid phases). When 100 grams is not available or the sample is determined to be highly contaminated, a lesser volume/mass is used as discussed in section 10.1.

21.0 REFERENCES

21.1 USEPA SW-846, Method 1311, July 1992.

21.2 USEPA, Federal Register 40 CFR Parts 261, 264, 265, 268, 271 and 302. Vol. 55, no. 126, Friday, June 29, 1990, Rules and Regulations.

21.3 USEPA, Federal Register 40 CFR Parts 261, Appendix II. (7-1-92 edition), 1992.

21.4 Larry P. Jackson, Environmental Testing and Analysis, Pp. 18-25, 9, 1993.

21.5 Operation Maintenance Instruction OM-149, Millipore Corporation, Nov. 1986.

21.6 Instruction for Use Model 3775-GTS Gas-Tight Syringe, Associated Design and Manufacturing Company, February 1990.

21.7 Nuclear Regulatory Commission, Joint NRC/EPA Guidance on Testing Requirements for Mixed Radioactive and Hazardous Waste, [7590-01], July, 1997.

22.0 HISTORY

Revision 18: Clarified spiking practices
Revision 19: Updated preparation of TCLP Extraction Fluid #1 and #2 to eliminate overnight standing. Added ZHE must be used as a tumble blank with a 5% frequency.
Revision 20: Added a NOTE to 9.14.1 for clarification sieve size method requirement.
Revision 21: Added clarification statement about difficult matrices.
Revision 22: Updated to included clarification ALARA statement for difficult sample matrices.

APPENDIX 1

Metals	Volatile Organics	Acid Extractables	Base /Neutral Extractables	Pesticides	Herbicides
Arsenic	Benzene	o-cresol	2,4 Dinitrotolune	Chlordane	2,4-D
Barium	Carbon Tetrachloride	m-cresol	Hexchloro benzene	Endrin	2,4,5-TP (Silvex)
Cadmium	Chlorobenzene	p-cresol	Hexachloro butadiene	Heptachlor	
Lead	Chloroform	Pentachloro-Phenol	Hexachloroethane	Heptachlor Epoxide	
Mercury	1,4-dichlorobenzene	2,4,5-trichlorophenol	Nitrobenzene	Lindane	
Selenium	1,2-dichloroethane	2,4,6-trichlorophenol	Pyridine	Methoxychlor	
Silver	1,1-dichloroethlyene			Toxaphene	
Chromium	Methyl ethyl Ketone Tetrachloro Ethylene Triochloro ethylene Vinyl chloride				
	1,4-Dichlorobenzene		1,4-Dichlorobenzene		

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

LABORATORY SUB-SAMPLING

(GL-LB-E-029 REVISION 0)

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1.0 STANDARD OPERATING PROCEDURE FOR LABORATORY SUB-SAMPLING

2.0 PURPOSE

2.1 This SOP covers common techniques for obtaining representative sub-samples from samples received at the laboratory for analysis. These samples may include solids, sludges, liquids, or multilayered liquids (with or without solids).

2.2 The procedures and techniques discussed in this guide depend upon the sample matrix, the type of sample preparation and analysis to be performed. The characteristic(s) of interest, and the project specific instructions or data quality objectives must also be considered. A specific aliquot amount may be identified in the laboratory standard operating procedure (SOP), in which case, the analytical or preparation SOP should be followed, rather than this guidance document.

2.3 This SOP includes several sample homogenization techniques, including mixing and grinding, as well as information on how to obtain aliquots or split laboratory samples.

3.0 DISCUSSION

3.1 This guide discusses options for taking a sub-sample aliquot of a sample submitted to the laboratory. If followed, it will minimize any bias or variance in results of interest. The laboratory must assume that the whole sample submitted by the client was correctly obtained from the environment.

3.2 This sub-sampling guide is intended for use when sub-sampling or aliquoting of the whole field sample is required for direct analysis or for sample preparation prior to analysis.

3.3 Changing the physical state of the originally submitted sample may be required. Layer separation, grinding, mixing, digesting, drying, melting or freezing may be necessary. This guide also includes cone and quartering, riffle splitting, and particle size reduction.

3.4 All sub-sampling should be performed in an area which is free from contamination, easily decontaminated, and vented to control dust and remove fumes.

4.0 DEFINITIONS

4.1 Contaminant unit—the largest particle size that contains the contaminant of interest.

4.2 Maximum allowable particle size-the largest lineal dimension of a sample's individual particles accepted for a given sample mass.

4.3 Multilayered sample-a sample consisting of two or more clearly differentiated components, determined visually.

4.4 Particle size-the controlling lineal dimension of individual particles.

4.5 Representative sub-sample- a sub-sample collected in such a manner that it reflects one or more characteristics of interest (as defined by the project objectives) of the laboratory sample from which it was collected.

4.6 Sample-a portion of material taken from a larger quantity for the purpose of estimating properties or composition of the larger/whole quantity.

4.7 Sludge-Any mixture of solids that settles out of solution. Sludges contain liquids that are not visually apparent as free liquids, which could potentially be decanted from a solid layer.

4.8 Sub-sample-a portion of a sample taken for the purpose of estimating properties or composition of the larger/whole sample.

5.0 PROCEDURES

5.1 Successful implementation of this guide depends on effective communication between the client and the laboratory staff. The selection of optimal sub-sampling procedures, techniques, and strategy by the laboratory depends on the intended use of the data. The client should submit appropriate instructions with all samples, or accept laboratory suggestions for sub-sampling.

5.1.1 The appropriate instructions must be reviewed by both the project manager and the analyst(s) or Group Leader.

5.1.2 Sample matrices and mechanisms of contamination are infinitely variable and require judgments to be made. If the client provides no instructions, it is advisable that experienced analysts decide which sub-sampling techniques are employed. For solid samples, mixing is the preferred process. See 6.6. For liquid samples without obvious layers, see instructions in section 7.0. Documentation of these two forms of sub-sampling is not required due to the frequency of their use. All other selected sub-sampling techniques should be documented.

5.2 If the sample integrity or composition does not match that anticipated by the laboratory, the client must be contacted to confirm or clarify any sub-sampling instructions. An example of a time when client direction is required can be demonstrated with the receipt of a coring sleeve. If upon opening the container, the analyst notices obvious heterogenous composition of the sample, (clay in one end of the sleeve, and sand at the other end), appropriate instructions from the client must be obtained prior to beginning analysis.

5.3 Anytime the analytical result will obviously be biased, it must be documented, and the client should be notified prior to beginning any sub-sampling technique. For example, if headspace exists in a container arriving at the laboratory, some volatile components will have partitioned into that headspace. If the client decides to proceed with the analysis, the analytical logbook and the case narrative on the final report should indicate this condition.

5.4 Sampling theory requires that sub-sample *mass* should increase as the size of the largest particle in the sample increases. If the sub-sample mass recommended by sampling theory is larger than that normally used in the sample preparation method, the sub-sample mass may be increased and the extraction/digestion procedure scaled accordingly. The standard volume of digestate/extract is then submitted for analysis. If the sub-sample mass is too large to be accommodated by the sample preparation procedure, multiple sub-samples (of equal mass) can be extracted/digested, and the extracts/digests combined and mixed prior to analysis. Another alternative is to reduce the particle size of the entire sample or sub-sample as specified by sampling theory. If the particle size is reduced

enough, a sub-sample of the mass recommended by sampling theory and the extraction/digestion method can be obtained.

5.5 Prior to sub-sampling liquids, the analyst must consider the property or characteristic requested, and the container size received. If the analyte has the ability to adsorb onto the container, the field sample should arrive at the laboratory in an appropriately sized bottle, such that the whole sample will be used. The sides of the container should then be rinsed properly to assure that all the contaminants are transferred into the analytical vessel.

5.6 Sub-sampling techniques are different when analyzing for volatile compounds than non-volatile compounds. The differences are discussed for each sample matrix.

Table 1: Limitations and Advantages of Sample Preparation Options

Instruction	Limitations	Advantages
Remove artifacts, such as rocks and twigs, from the sample prior to sub-sampling	(*1*) May bias analytical results by altering contaminant concentration, (*2*) May bias sample if results are not properly weight-averaged	(*1*) May be easier to sub-sample, (*2*) May be easier to analyze, (*3*) Appropriate if the target population is material minus artifacts.
Digest or extract the contaminant from the outside of the large particles	May bias sample if contaminant is within the large particles (may be unsuitable for volatile analyses)	(*1*) May be easier to analyze, (*2*) May prevent need for weight average calculation
Digest or extract particle sizes separately	(*1*) Separation of particle sizes may be difficult, (*2*) May bias sample if results are not properly weight-averaged, (*3*) Higher cost	(*1*) Allows some particle size consistency during analysis, (*2*) May be easier to sub-sample within portions after separation.
Separate liquid layers	(*1*) Separation of layers may be difficult, especially near the interface, (*2*) May bias sample if results are not properly weight-averaged.	(*1*) May be easier to analyze, (*2*) May be easier to sub-sample within portions after separation, (*3*) Allows different preparation methods for each layer.
Dry sample	May alter chemistry or change stability of some compounds.*	(*1*) Allows for consistency of sub-sampling for liquid/solid mixtures, (*2*) Analytes reported unbiased by moisture content.
Change the physical state, such as freeze the material so that it may be treated as a solid, or melt the material so that it may be treated as a liquid	May be difficult to achieve complete freezing or melting and maintain it long enough to get a sub-sample.*	Allows for consistency of sub-sampling.
Analyze only one layer of multilayered samples, such as analyze only the oil portion of an oil/water mixture for PCBs	May bias the sample if there is cross-contamination between layers	(*1*) Possible cost savings to customer, (*2*) May be easier to sub-sample from a single layer (*3*) May be easier to analyze.

Composite portions of the sample for volatiles analysis directly in a purge unit vs. individual analysis of these portions	(*1*) May overload gas chromatography columns if sample has high amounts of solvents in each portion, (*2*) Separation of portions may be difficult.	(*1*) May prevent losses of volatile compounds because the sample is handled only once, (*2*) Possible cost savings to customer, (*3*) May prevent need for weight-average calculation.
Reduce particle size	*(1)* Increasing surface area may effect data in some procedures with particle digestion or extraction, such as TCLP, * (*2*) May be difficult, depending on matrix.	Allows for consistency of sub-sampling.
Use standard methods for solids (for example, cone and quarter, grind, riffle, sieve)	Dependent on method * See 6.5 for more information.	Dependent on method. See 6.5 for more information.

* May be unsuitable for samples to be analyzed for volatile constituents.

6.0 SUBSAMPLING SOLIDS

Table 2 gives the relationship between the maximum particle size and sample mass to achieve a fundamental error of 15 %. If the maximum allowable particle size is greater than that listed in the table, then sampling theory would suggest particle size reduction, such as grinding, or use of a larger sample mass. For example, if granule gravel has an allowable particle size of 0.21cm, according to this table, a sub-sample mass of 10g is needed. Many digestions/extractions commonly use 1g. The 10g sub-sample would be ground to a size of 0.1 cm, and the aliquot would be taken from the ground material. Approximations were employed to construct this table. The Group Leader should be contacted for approval prior to any particle size reduction is conducted.

Table 2: Recommended Minimum Sub-sample Mass for Particulate Materials to Achieve a Fundamental Error of 15%

Recommended Minimum Sub-sample Mass, g	Recommended Allowable Particle Size[A] , cm	Size Class[B]	U.S. Standard Sieve Mesh Size
0.1	0.05	Clay to coarse sand	35
1	0.1	Coarse to very coarse sand	18
2	0.13	Very coarse sand	13
5	0.17	Very coarse sand	12
10	0.21	Granule gravel	10
30	0.31	Granule gravel	7
50	0.37	Granule gravel	6
100	0.46	Pebble gravel	5

[A]The maximum allowable particle size can be approximated for other sample masses by using the equation, allowable particle size (cm) = the cube root of 0.001 3 sample mass (g)

[B]Wentworth Size Class: These soil descriptions are added for those readers who equate particle size with the Wentworth descriptions. They are not meant to indicate that the application of this table is limited to soil particles. The table can also be used for non-soil particles such as waste.

6.1 Particle size reduction can be avoided by modifying the sample digestion/extraction methods to use large aliquot masses if allowed in the analytical procedure. Following digestion/extraction of the large aliquot, the homogeneous digestate/extract is analyzed. For example, if the contaminant of concern was a chromium solution spilled into a mixture of gravel and soil, knowing that the chromium coats the medium allows a choice of sample preparation. The analyst may totally dissolve the aliquot. He/she may digest the chromium from the outside of the particles, analyzing the digestate. Or, he/she may extract the material, and analyze the extractant. If the analyst had no information about the mechanism of contamination, he/she would have to assume that the contamination is throughout all particles of the laboratory sample.

6.2 If information is available regarding the type and mechanism of contamination, then it may be possible to avoid particle size reduction and the use of large aliquot masses. For example, if contamination occurred on a molecular level (i.e. a solvent is discharged to soil), an argument can be made to preclude large particles (i.e. rocks), since insignificant amounts of contamination will be adsorbed to the relatively small surface of the large particles. If the large particles are excluded, the appropriate mass can be based on the smaller particle sizes, which have a much larger surface area. If the decision is made to remove the large particles, the mass of both the large and small particles would be used to calculate the final concentration of the contaminant of interest.

6.3 If the desired sub-sample mass is equal to or less than the maximum allowable particle size, sub-sampling can proceed without any need for particle size reduction. If the particle size is greater than the allowable particle size in Table 2, then the sample matrix, the type and mechanism of contamination, the scale of the contaminant unit, as well as particle size reduction should be considered. These allowable particle sizes are based on the assumption that the contaminant exists as a particle or is adsorbed to particles. In those cases where the contaminant unit is on the atomic or molecular scale or is a particle much smaller than the allowable particle size of the sample, then alternative approaches can be employed with acceptable bias.

6.4 *Solid Samples for Volatile Analysis*:

6.4.1 Due to the volatility of this class of compounds, laboratory sub-sampling procedures addressing the sample's allowable particle size could result in large losses of the parameter(s) of interest, rendering the

results unrepresentative of the authentic sample. The possible exception is when cryogenic freezing conditions are maintained throughout the handling process.

NOTE: If cryogenic techniques (working with frozen samples) or other special techniques are used, the procedure should be validated on laboratory control samples (LCS) which have been spiked with known concentrates of the parameter(s) of interest. The nature of the test matrix for the LCS and the spiking solution should be chosen to allow uniform distribution of the spike in the matrix prior to sub-sampling. Regardless of the particle size reduction techniques chosen, it is advisable to carry an LCS through each preparation batch as a quality control sample. A sub-sample of the field sample without particle size reduction which is carried through the validation process will demonstrate the amount of volatile loss (from the LCS results) or increased volatiles recovery (from a comparison of the unreduced field sample with the size reduced sample) using particle size reduction.

6.4.2 When analyzing samples for low levels of volatile constituents (0.5 to 200µg/kg range), discrete samples should be placed into a container that, once sealed, is analyzed without opening. For this reason, and because sample mass is often limited by the analysis system, low level samples typically are not amenable to either particle size reduction procedures or the analysis of larger sample mass. When contaminant levels exceed 200µg/kg, discrete samples can be transferred to vessels containing an appropriate solvent, such as methanol. Because the solvent retains the volatiles in solution, and only a small portion of the solvent is removed for analysis, particle and contaminant unit size with respect to sub-sample mass requirements can be considered inconsequential.

NOTE: Current analytical guidance recommends solvent extraction only for volatile organic compounds at concentrations greater than 200 µg/kg. However, solvent extraction may be used for solvents of lower concentration levels if the solvent/solid ratio is reduced, or by using an analysis system with lower detection limits. Contact the Group Leader for further direction.

6.4.3 The following subsections discuss various sub-sampling procedures that can be used as particle size and contaminant unit vary in relationship to the allowable particle sizes listed in 6.5.1.

6.4.3.1 *Laboratory Sample Particle Size and Contaminant Unit Less Than the Allowable Particle Size*—Prepare sample vessel with the appropriate solvent and solvent volume as specified in the method. Add the appropriate mass of sample to the prepared vessel with a pre-cleaned coring tool or spatula as quickly as possible. The coring tool must be large enough to accommodate the largest sample matrix particle. After volatile extraction, analyze the appropriate volume of the solvent from the liquid portion of the aliquot.

6.4.3.2 *Laboratory Sample Particle Size Greater Than the Allowable Particle Size and the Contaminant Unit Less Than the Allowable Particle Size*—Particle size reduction cannot generally be used, since it may result in a loss of volatile contaminants. There are cases where the chemistry of the contaminant and the base sample will not allow the volatile to be lost. For these types of contaminants, see the methods in 6.5.1. Alternate approaches to sub-sampling may be viable if knowledge exists regarding the sample matrix, type and mechanism of contamination, and the contaminant unit.

6.4.3.2.1 If the contaminant unit is on a molecular scale, then the distribution of the contaminant will be a function of the absorptive properties, and the larger surface area of the smaller particles results in more contaminants being adsorbed to the smaller particles. If the client is willing to accept a biased-high concentration for the contaminant of interest, a sub-sample of only the smaller particles may be made.

6.4.3.2.2 Another method is to use a solvent appropriate for analysis, such as methanol, to extract the material. Use a 4g aliquot of the original laboratory sample in 10mL of solvent. Increase the volumes proportionally to accommodate the specified sample mass. An appropriate portion of the solvent is analyzed once the contaminant is dissolved in the solvent.

6.4.3.3 *Laboratory Sample Particle Size and Contaminant Unit Larger than the Allowable Particle Size*—When sample masses become prohibitive with regard to logistical constraints, sample extracts can be composited. An example of this is the case where soil of particle size 0.46 cm is contaminated with volatile organic compounds. The suggested sub-sample mass in this case from Table 2 is 100g, requiring a vessel with 250mL of solvent. As an alternate to a single large sample, five 20g sub-samples could be extracted. Microliter amounts of each of the five resulting extracts could be composited into the same purge chamber. Once the contaminants are dissolved in the solvent, the concern of contaminant heterogeneity is decreased and the use of small sub-samples of the extracts can be justified.

6.5 *Solid Sample for Non-Volatile Analysis*—The method of sub-sampling is dependent on the size of the allowable particle size and the size of the

contaminant unit. The following subsections discuss different sub-sampling procedures that can be used as laboratory sample particle size and contaminant unit vary in relationship to the allowable particle sizes listed in Table 2. If the laboratory sample requires mixing prior to sub-sampling, the methods in section 6.4.3.1 should be used.

6.5.1 *Laboratory Sample Particle Size and Contaminant Unit Less Than the Allowable Particle Size:*

6.5.1.1 *Transversal Sub-sampling (Rectangular Scoop) (see Fig. 1)*—One method of sub-sampling the materials is to use transversal sub-sampling. The entire laboratory sample is emptied onto a non-contaminating smooth surface. The sample is shaped into an elongated pile with a flattened top surface. Complete top-to-bottom transversal cuts are made across the pile and the extracted material is transferred into a tared container. The transversal cuts are repeated until; the appropriate mass is obtained. Cuts are made with a rectangular scoop. The width of the transversal section should be wide enough to accommodate the largest particle size, but narrow enough to require multiple transversal sections be used to obtain the appropriate mass. Two thin sheets of Teflon, metal, or polyethylene may be used to facilitate the removal of material within the transversal cut. After the removal of a few transversal sections, the pile may be reshaped to facilitate further cuts. The entire unused portion of the laboratory sample should be returned to the original sample container.

Figure 1: Transversal Sub-sampling

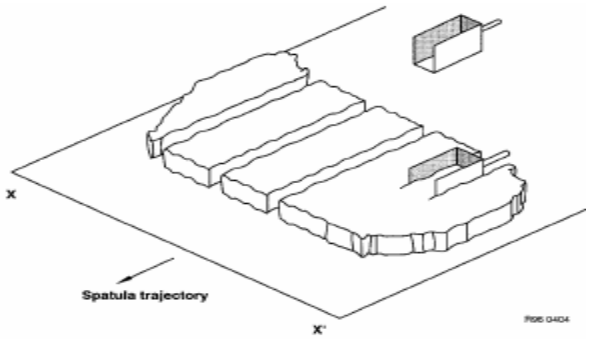
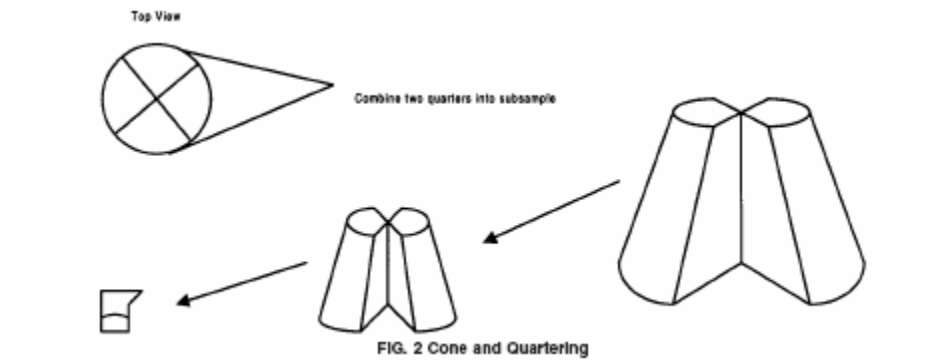


FIG. 1 Transversal Subsampling

6.5.1.2 *Cone and Quartering (see Fig. 2)*—Another method of sub-sampling materials involves cone and quartering. This method may introduce large biases from the grouping and segregation error. It is discussed here due to its widespread use, but the user should take note of its limitations (see

Table 4). The entire laboratory sample is emptied out onto a non-contaminating smooth surface. Material is piled into a cone with a flattened top surface. Two top-to-bottom cuts are made through the cone at perpendicular angles to form four equal portions, or quarters. Two opposite quarters are compiled into a new cone, and the process is repeated until the proper sample mass is achieved.

Figure 2: Cone and Quartering



6.5.1.3 *Riffle Splitter (see Fig. 3)*—A riffle splitter is a mechanical device with an equal number of narrow sloping chutes. Alternate chutes discharge the sample into opposite directions into two collection pans. Sub-sampling is achieved by pouring the entire laboratory sample into the riffle splitter. One portion is removed, and the collection pan is replaced with a clean pan. This portion is poured back through the riffle splitter so that half of the sub-sample will combine with the original material, and the other half will drop into the clean collection pan. This process is repeated until the proper sample mass is achieved. There are many types of riffle splitters available. The analyst must select the one that meets the client's needs. The riffle splitter opening should be about three times the largest particle diameter, and have an even number of chutes.

Figure 3: Riffle Splitter

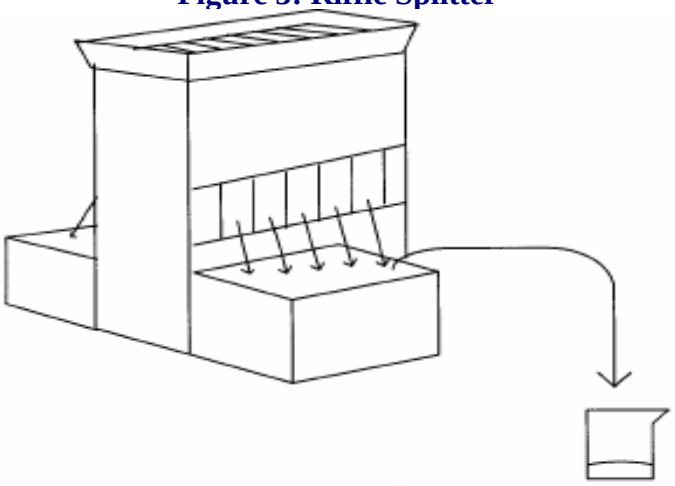


FIG. 3 Riffle Splitter

6.5.1.4 *Alternate Scoop*—Scoops of the mixed laboratory sample are either placed in the analytical vessel, or discarded. In the example in Fig. 4, three scoops are discarded for every scoop saved. Care should be taken that each scoop of material is of the same size and is taken in a consistent manner to minimize bias.

Figure 4: Alternate Scoop

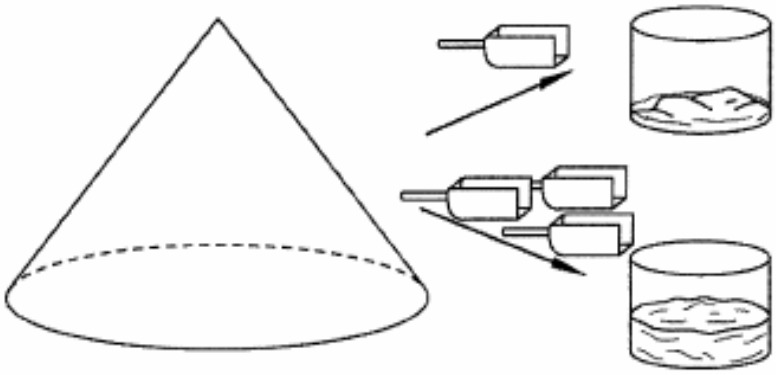


FIG. 4 Alternate Scoop

6.5.1.5 *Sectorial Splitter (Sample Divider)- (See Fig. 5)*- This is a spinning riffler-type sample divider. The sample is placed in the opening, and the material is vibrated through chutes to the spinning bottles. The aliquot may be taken directly from the bottle , or it maybe further sub-sampled by discarding

every other bottle, placing the remaining sample back in the opening, and starting the process over again.

Figure 5: Sectorial Splitter

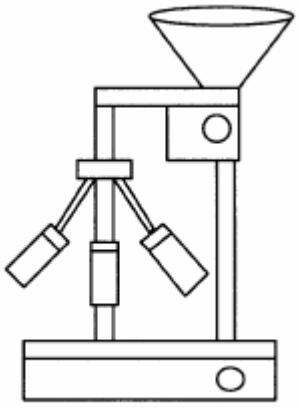


FIG. 5 Sectorial Splitter

6.5.2 *Laboratory Sample Particle Size Greater Than the Allowable Particle Size and the Contaminant Unit Less Than the Allowable Particle Size:*

6.5.2.1 If the client can accommodate worst-case, such as biased-high concentration of the parameter of interest, then sub-sampling can be performed without the need for large sample masses or particle size reduction. The procedure described in 7.1 will work, except that the particles larger than the allowable particle size are removed from the transversal section prior to addition to the sub-sample.

6.5.2.2 If the client cannot accommodate worst-case, refer to 6.5.3.1.

6.5.3 *Laboratory Sample Particle Size and Contaminant Unit Larger than the Allowable Particle Size:*

6.5.3.1 Since the contaminant is associated with the large particles in this type of laboratory sample, the option of selectively removing large particles is not viable. Optimum solutions would be to increase the sample mass, or reduce the particle size. If these methods are not practical, a multiple sub-sample approach may be employed. Ideally, enough of these sub-samples will be analyzed or extracted so that the desired sample mass is achieved. The sub-samples will then be subjected to preparation for analysis, such as solvent extraction or acid digestion. The resulting extracts or digestates can be analyzed separately and the results can be weight-averaged, or the extracts may be combined prior to analysis.

6.5.3.2 *Grinding or Milling*—An alternate method to increasing the sample mass is particle size reduction. This includes such methods as grinding or milling. Grinding can be achieved by hand methods, such as a mortar and pestle, and by using such mechanical devices as mills, grinders, or jaw crushers. Table 3 contains a list of commonly used devices that are commercially available.

Table 3: Commonly Used Particle Size Reduction Devices for Solids

Device	Manufacturer's Recommended Particle Size or Sample Mass	Reduced to	Uses
Cutting Mill	50 mm or less	Almost any size depending on mill	Foliage, grains, soils
Micro-Mill	20 to 50 mg	Almost any size depending on mill	Can be temperature controlled
Centrifugal cutting mill	3 to 100 g	40 µm	Chemicals, coal, seeds, plant stems, polypropylene or polyester.
Jar mill	pint to 2 gal	Almost any size depending on material and time	Can be used wet or dry
Horizontal and Vertical Disc Mills	5 to 20 mm particle size	250 to 1000 µm	Chemicals, clay, foods, plants, leather, cardboard
Dish and puck mill	10 g to 5 kg	10 to 100 µm	Brick, cement, chemicals, coal, coke, glass, minerals, ore, plants, rock, metals, sand, slag, soil
Mortar grinders	1 to 8 mm particle size	5 µm to 8 mm	Can be used wet or dry, organic or inorganic substances
Jar Crushers	1 to 100 mm particle size	1 to 40 mm	Medium hard, brittle, and tough materials, for example, chemicals, coke, concrete, glass, coal, gravel, quartz, slag.

6.5.3.3 Each device can be constructed out of different materials to prevent contamination of the laboratory sample.

6.5.3.4 Once particle size reduction has stopped, the laboratory sample should be poured through a sieve into a pan to demonstrate that the desired particle size has been achieved.

6.5.3.5 The sample should be reground if it doesn't go through the sieve. The sub-sample is then obtained from the sieved material using one of the methods outlined in section 6.5.1.

6.5.3.6 The limitations of each method discussed in 6.5.2 must be considered before sub-sampling begins. Table 4 discusses the limitations of each of these methods.

Table 4: Limitations and Features of Sub-sampling, mixing and Grinding Methods

Method	Type of Method	Limitations	Unique Features
Transversal Subsampling	Subsampling	(*1*) Possible sample loss due to the inability to recollect all of the soil from the underlying material, (*2*) Development of static electricity may cause a loss of fine particles, (*3*) Particle size bias if a square scoop is not used, (*4*) Method may affect sample moisture content.	(*1*) Minimizes discrimination between particle sizes, (*2*) Ease of decontamination of equipment.
Cone and Quartering	Subsampling	(*1*) Possible sample loss due to the inability to recollect all of the soil from the underlying material, (*2*) Development of static electricity may cause a loss of fine particles, (*3*) May introduce large biases from the grouping and segregation error, (*4*) Possible unequal segregation of heavy and fine particles, (*5*) Method may affect sample moisture content.	Ease of decontamination of equipment.
Alternate Scoop	Subsampling	(*1*) Possible sample loss due to the inability to recollect all of the soil from the underlying material, (*2*) Development of static electricity may cause a loss of fine particles, (*3*) Particle size bias if a square scoop is not used, (*4*) Bias may occur if each scoop is not of the same size or if not taken in a consistent manner, (*5*) Method may affect sample moisture content.	(*1*) Minimizes discrimination between particle sizes, (*2*) Ease of decontamination of equipment, (*3*) Simpler than Transversal Subsampling, since there is no need to shape the pile.
Sectorial Splitter (Sample Divider)	Subsampling	(*1*) Limited to use with small particle sizes (about 6 mm), (*2*) May be difficult to decontaminate, (*3*) Method may affect sample moisture content.	(*1*) Minimizes discrimination between particle sizes, (*2*) Proper use eliminates most biases, (*3*) Simple to use, mechanical device.
Riffle Splitting	Subsampling or Mixing	(*1*) Possible loss of fine particles due to dusting when the sample is introduced, (*2*) May introduce biases from the grouping and segregation error, (*3*) Some riffle splitters are difficult to decontaminate.	(*1*) Proper use eliminates most biases, (*2*) Many choices in size available from manufacturers, including closed or open systems.
Grinding and Sieving/Mills/Jaw Crushers	Grinding	(*1*) Development of static electricity may cause a loss of fine particles, (*2*) Possible loss of fine particles due to dusting when the sample is introduced into the grinder, or the sieve, (*3*) Increasing the surface-to-mass ratio, which may affect the leachability during partial digestion or extraction, (*4*) Grinding equipment may be difficult to decontaminate,	(*1*) Simple method to reduce particle size, (*2*) Many choices in size and type available from manufacturers.

		(*5*) Grinding and sieving may be labor intensive.	
Mixing Squares	Mixing	(*1*) Mixing sheet must not be made of material that will contaminate samples, (*2*) Development of static electricity may cause a loss of fine particles.	(*1*) Non-mechanical method of mixing, (*2*) Cost efficient, (*3*) Ease of decontamination of equipment.
Mechanical Mixers	Mixing	(*1*) Possible segregation of heavy versus light, or large versus small particles, (*2*) Some mixers are difficult to decontaminate.	Simple method to evenly distribute particles in solids that are difficult to mix by hand.

6.6 *Mixing*—To reduce heterogeneity, a sample or sub-sample must be mixed prior to removing the aliquot. However, care should be taken since mixing may actually increase the variance. For example, if a sub-sample had lead shot in soil, differences in size, shape and density may increase heterogeneity further by the development of different strata upon agitation or vibration of the sample.

6.6.1 Mixing of a sub-sample may be achieved manually, or by the use of a mechanical mixer. Manual methods can include stirring with a spatula for 2 to 3 min, until the sample appears uniform, or use of a mixing square. A mixing square is a non-contaminating square sheet, such as Teflon. The laboratory sample is poured into the middle of the sheet, and a rolling pin is used to roll the sample backward and forward while alternately lifting and releasing opposite side corners of the sheet.

6.6.2 Mixing can be attained by using a variation of the riffle splitting method. After the laboratory sample is poured through the riffle splitter, the halves are combined, and reintroduced through the riffle splitter a minimum of five times.

6.6.3 A variation of the cone and quartering method can be used to homogenize flowable solid samples. After the material is quartered, the first portions removed from the pile are re-formed into a cone. Each of the other portions is poured onto the cone, and the process is repeated a minimum of five times.

6.6.4 Mechanical methods of mixing include a spiral mixer, a cement mixer, or a twin-shell V blender, and mills.

7.0 SUBSAMPLING LIQUIDS

7.1 Some analytical methods, such as oil and grease analyses, require the analyst to use the entire laboratory sample as the aliquot. This field sample should arrive at the laboratory in a proper sized bottle. After removing the aliquot, the bottle is rinsed with an appropriate solvent to assure transfer of the entire sample from the container to the analytical vessel. Occasionally, a field sample may arrive at the laboratory in an improper container. If this happens, the client should be contacted for a resample. If the client decides to go ahead with the

inappropriately sized field sample, the analyst should remove the aliquot from the container, and the rest of the original laboratory sample should be transferred into another container. The ratio of aliquot to remaining material must be measured. The sides of the container are then rinsed with the appropriate material for the analysis being performed. The aliquot and rinsate may be either analyzed separately and weight averaged, or the ratio measured above could be used to determine the amount of rinsate to add to the aliquot and it could be analyzed directly.

7.2 Liquid Samples for Volatile Analyses:

7.2.1 Aqueous laboratory samples for volatile compounds should not be mixed prior to sub-sampling. Transfer appropriate volume for analysis using techniques that minimize loss, such as a syringe.

7.2.2 Sub-sampling of non-aqueous solutions for volatile compounds is often the first step in a sample dilution process which is necessary to prevent saturation and contamination of analytical instrumentation and to get sample concentrations within the calibrated concentration range. Due to the usually large dilution factors, an appropriate technique, such as the use of a microliter syringe, is used to obtain a sub-ample. The sub-sample is then transferred to a solvent appropriate for analysis, such as methanol, in an air-tight container.

7.3 Liquid Samples for Non-Volatile Analyses:

7.3.1 Aqueous solutions for non-volatile compounds may contain settleable materials. If the settleable materials are to be included as part of the laboratory sample, and they will remain suspended, or can easily be re-suspended and will remain so during the sub-sampling operation, the sample should be handled as a liquid sample. These laboratory samples should be gently swirled for 15 seconds or slowly inverted six or more times to reduce heterogeneity.

7.3.2 If the analyst is sub-sampling the liquid portion only, the settleable material must be allowed to sink to the bottom before withdrawing the sub-sample from the liquid portion. The liquid sub-sample or aliquot may be obtained by filtering, centrifuging, or decanting the liquid portion from the solid portion, or by pipetting only the liquid portion directly into the analytical vessel.

7.3.3 If the settleable material will not remain suspended, and is to be included in the analysis, the sample should be treated as a multilayered sample (see 8.0).

7.3.4 Single-layer aqueous laboratory samples should be gently swirled for 15 seconds or slowly inverted 6 times to reduce heterogeneity. Remove appropriate sub-sample for analysis.

CAUTION: The container should be vented periodically to release any pressure that may be developed during mixing.

7.3.5 The sub-sampling process for a non-aqueous solution used for testing non-volatile compounds is the same as the process for an aqueous solution.

8.0 SUBSAMPLING MULITLAYERED SAMPLES

8.1 Multilayered samples consist of two or more clearly differentiated components. These may include liquid/liquid layers, such as chlorinated solvents and water, or water and oil. They may be liquid/solid samples, such as sludge. They may be solid/solid samples, such as pea gravel and sand. Or they may include combinations of these materials, such as a mixture of oil, water, and sludge.

8.1.1 If the liquid portion of a sludge sample is so small that it can be re-mixed with the solid portion and will only reseparate over time, the sample should be handled as a solid sample (see 5.1).

8.1.2 If the solid portion of a sludge sample will remain suspended, or can easily be re-suspended and will remain so during the sub-sampling operation, the sample should be handled as a liquid sample. These laboratory samples may be mixed by inverting the container, or with slight shaking (see 7.0.)

8.1.3 One method of sub-sampling multilayered laboratory samples is to separate them into their component layers. Layers may be either physically separated, or individually sub-sampled from the original container. The individual layers can be analyzed separately and the weighted average calculated. Portions of the separate phases can be proportionally recombined, either in the analytical vessel for non-volatile analyses, or directly on a purge unit during volatile analysis to form a representative aliquot.

8.2 *Multilayered Samples for Volatile Analysis/Separation of Layers:*

8.2.1 For liquid/liquid layers, transfer appropriate volume for analysis using techniques that minimize loss, such as a syringe or a pipette, from each layer.

8.2.2 If laboratory samples have significant solid and liquid layers that cannot be mixed vigorously enough to suspend a solid phase without the potential of losing volatile components, materials may be separated into their component phases. The solid/liquid phase separation may be achieved by gently centrifuging the unopened container, or by allowing it to sit undisturbed until the solid portion is settled. The percentage of each phase should be determined, either by volume or weight.

8.2.3 Transfer appropriate mass for analysis using techniques that minimize loss, such as syringe or a pipette. Decant the remaining liquid into another container.

8.2.4 An aliquot of the remaining solid phase is weighed for analysis.

8.3 *Multilayered Samples for Non-Volatile Analyses/Separation of Layers:*

8.3.1 For liquid/liquid layers, separate the layers using techniques such as a separatory funnel or pipette. Each layer of the material may either be transferred into another container, or directly into the analytical vessel. Each separated portion is then handled as a homogeneous liquid sample. See 7.3 for more information.

8.3.2 For liquid/solid layers, the liquid sub-sample or aliquot may be obtained by filtering, centrifuging, or decanting the liquid portion from the solid portion, or by pipetting the liquid portion directly into the analytical vessel. The liquid portion is then handled as a homogeneous liquid sample. The solid portion is handled as a solid laboratory sample.

8.4 *Alternative Methods for Multilayered Samples for Non-Volatile Analyses—An alternative method of sub-sampling liquid/solid samples is to freeze the material*.

8.4.1 The laboratory sample is transferred into a rectangular box and the solids are allowed to settle. Dry ice or liquid nitrogen can be used to freeze the material. The container may also be placed in a freezer until frozen. Sub-samples are sliced out of the box through all the layers. This subs-ample or aliquot is then treated as a solid.

8.4.2 An alternate freezing method is to place the laboratory sample into an appropriate container. The whole sample is then frozen using dry ice of liquid nitrogen, and the sub-sample is obtained using methods described in 6.5.3.

8.4.3 An important technique in sampling liquid/solid samples is continuous agitation during the sub-sampling process. This can be applied to the sub-sampling of non-volatile compounds for laboratory samples that are pre-dominantly liquid or have liquid characteristics. This is particularly useful for laboratory samples that can form a semi-emulsified form, but only with continuous agitation. During the mixing process, remove an appropriate aliquot from the original laboratory sample for analysis.

8.5 *Solid/solid samples may be sub-sampled according to 6.0 of this SOP.*

8.5.1 One or more of the previous methods can be utilized to sub-sample multilayered samples, depending on how many layers are encountered in the sample.

9.0 SAFETY HEALTH AND ENVIRONMENTAL HAZARDS

9.1 Wear eye protection with side shields while performing procedures at the laboratory bench.

9.2 Treat all chemicals and samples as a potential health hazard, and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals in the laboratory as well as

a reference file of Material Safety Data Sheets (MSDS). These documents and individual client sample MSDS forms are maintained in the laboratory.

9.3 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

9.3.1 Wear a plastic apron over lab coat when working with radioactive samples.

9.3.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

9.3.3 Prohibit admittance to immediate work area.

9.3.4 Post signs indicating radioactive samples are in the area.

9.3.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

9.3.6 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

9.4 In the event of an accident or medical emergency, seek help immediately. When time and safety permit, file an accident report form regardless of how insignificant the injury may seem.

9.5 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

10.0 RECORDS MANAGEMENT

Standards records are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition

11.0 REFERENCES

11.1 *ASTM Standards:* D6323 (2003) Standard Guide for Laboratory Sub-sampling of Media Related to Waste Management Activities, West Conshohocken, PA.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

ACID DIGESTION OF TOTAL RECOVERABLE OR DISSOLVED METALS IN SURFACE AND GROUNDWATER SAMPLES FOR ANALYSIS BY ICP OR ICP-MS

(GL-MA-E-006 REVISION 14)

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1.0 STANDARD OPERATING PROCEDURE FOR ACID DIGESTION OF TOTAL RECOVERABLE OR DISSOLVED METALS IN SURFACE AND GROUNDWATER SAMPLES FOR ANALYSIS BY ICP OR ICP-MS

2.0 METHOD CODE

SW-846 3005A

3.0 PURPOSE

To describe the manner in which surface and groundwater samples for Inductively Coupled Plasma (ICP) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis are digested by EPA SW-846 Method 3005A. Samples digested by this procedure are applicable for analysis by SW-846 methods.

4.0 DISCUSSION

This procedure deviates from Method 3005A as follows: sample and reagent volumes are half of the method recommendations. Samples prepared by this method maybe analyze for the following analytes:

Aluminum	Hafnium	Silica	Uranium-233
Antimony	Iron	Silicon	Uranium-234
Arsenic	Lead	Sulfur	Uranium-235
Barium	Lithium	Sodium	Uranium-236
Beryllium	Magnesium	Silver	Uranium-238
Bismuth	Manganese	Strontium	Vanadium
Boron	Molybdenum	Tantalum	Zinc
Cadmium	Potassium	Tin	Zirconium
Calcium	Nickel	Thorium	
Cesium	Phosphorus	Titanium	
Chromium	Rhenium	Thallium	
Cobalt	Rhodium	Tungsten	
Copper	Selenium	Uranium	

4.1 Total Recoverable Metals - The entire sample is acidified with nitric acid at the time of collection. This sample is then refluxed with nitric acid and hydrochloric acid until the volume is reduced. The sample is diluted to a final volume, and then is ready for analysis.

4.2 Dissolved Metals - The sample is filtered at the time of collection. The liquid phase is acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested, as long as the acid concentration in the

standards matches the acid concentration in the samples. Water samples that require lab filtration are filtered from non-preserved fractions and acidified to a pH <2 with HNO_3. A filter blank is filtered with the samples for contamination QC purposes. The acidified aliquots are held at least 24 hours before digestion.

4.3 The samples are tested using pH strips to verify the correct pH values of <2 before preparation. If samples do not have the correct pH, samples are acidified to a pH <2 with HNO_3. The acidified aliquots are held at least 24 hours before digestion.

5.0 APPLICABLE MATRICES

Groundwater and surface waters.

6.0 HOLDING TIME, SAMPLE PRESERVATION, COLLECTION, STORAGE

6.1 Samples requiring filtration should be received by the laboratory chemically unpreserved. Liquid samples must be preserved prior to aliquoting for digestion. The samples are typically received chemically preserved with nitric acid to pH <2. Preservation may be performed at the time of sample collection however samples may also be submitted to the laboratory without chemical preservation. If unpreserved at the time of collection, the samples should be preserved within two weeks of collection, upon receipt at the laboratory. Following acidification, the sample should be mixed by agitation and held for 24 hrs to equilibrate. The pH of all aqueous samples should be tested immediately prior to withdrawing an aliquot for preparation to assure proper preservation. If the sample pH is >2, additional acid must be added and the sample held for 24 hrs until pH is verified as <2. If properly preserved, the sample may be held up to 6 months before analysis.

6.2 Samples may be collected in polyethylene containers.

7.0 INTERFERENCES

There are rarely any interferences with this digestion. If any are encountered, consult the Group Leader, Team Leader or Quality Assurance Officer before continuing.

8.0 METHOD PERFORMANCE

Method Detection Limit (MDL) studies are performed annually and method detection limit verification (MDLV) studies are performed quarterly. The limits are stored in the laboratory AlphaLIMS.

9.0 DEFINITIONS

9.1 Blank: Type I water that has been taken through the digestion process. The blank is used to determine the amount of background contamination.

9.2 Laboratory Control Sample (LCS): A certified reference material that has been taken through the digestion process. The LCS is used to determine digestion accuracy and to determine if the digestion process is in control.

9.3 Laboratory Control Sample Duplicate (LCS DUP): A duplicate of the LCS. The LCS DUP is used to determine reproducibility and to indicate precision.

9.4 Matrix Spike (MS): A sample that has added to it a known amount of solution containing known concentrations of analytes. The MS is used to determine the presence or absence of interferences and matrix effects in the digested sample.

9.5 Matrix Spike Duplicate (MSD): A duplicate of the MS. The MSD indicates reproducibility.

9.6 Sample Duplicate (DUP): A duplicated sample. The DUP indicates reproducibility.

9.7 Type I water: Water that conforms to the performance specifications in SOP GL-LB-E-016. Type I water is dispensed within the metals prep lab by the "MilliQ" water system.

9.8 HNO_3: Concentrated reagent grade 70.9% nitric acid.

9.9 HCl: Concentrated reagent grade 37% hydrochloric acid.

9.10 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

10.0 ANALYST VERIFICATION

Before a technician/analyst is allowed to analyze samples without supervision, he or she is trained by qualified personnel and is required to successfully analyze a proficiency sample. Training records are maintained as quality records (Refer to GL-QS-E-008).

11.0 DOCUMENTATION OF DATA

Sample preparation data are recorded in AlphaLIMS.

12.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

WARNING

CONCENTRATED HYDROCHLORIC ACID AND NITRIC ACID ARE EXTREMELY CORROSIVE AND CAN CAUSE SEVERE BURNS TO THE SKIN.

12.1 Wear eye protection with side shields while performing procedures in the lab.

12.2 Treat all chemicals and samples as potential health hazards, and reduce exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client sample MSDSs are also maintained.

12.3 Personal protective equipment

12.3.1 Disposable gloves are worn and changed frequently when working with acids, glassware, or samples. Dirty gloves pose a contamination hazard to the samples. Gloves that have holes can be dangerous to the wearer by allowing acids and toxic metals to come in contact with skin.

12.3.2 Hood doors are pulled down partially or enclosure doors are pulled together partially, while digesting samples. Acidified samples can splash and pop as they are being heated.

12.3.3 To protect clothes and skin from exposure to corrosive material, wear a lab jacket.

12.4 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

12.4.1 Protect counter tops with counter paper, or work from radioactive sample handling trays.

12.4.2 Prohibit admittance to immediate work area.

12.4.3 Post signs indicating radioactive samples are in the area.

12.4.4 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

12.4.5 Segregate radioactive wastes. Radioactive waste containers are obtained from the Waste Management.

12.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

12.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

12.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

12.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

12.7 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

13.0 SAMPLE RECEIPT FOR ANALYSIS

13.1 The analyst/technician submits the list of samples needed to the sample custodian group. The sample custodian removes the appropriate sample from the cooler and scans it using the barcode scanner to the appropriate area of the lab. The analyst then takes custody of the samples and scans them to the sample batch. The samples are now ready to be prepared or analyzed.

13.2 Analysts/technicians are responsible for retrieving their own samples when the sample custodian is unavailable.

14.0 INSTRUMENT/EQUIPMENT/GLASSWARE

14.1 Equipment

14.1.1 Air displacement pipettes

14.1.1.1 0.5-5 mL with disposable tips

14.1.1.2 100-1000 µL with disposable tips

14.1.1.3 10-100 µL with disposable tips

14.1.2 Environmental Express hot blocks or equivalent

14.1.3 Analytical balance capable of reading to three decimal places

14.1.4 Certified disposable 50 mL digestion tubes (polypropylene)

14.1.5 Ribbed disposable watch glasses (polypropylene)

14.1.6 Water resistant lab markers

14.1.7 Styrofoam trays to handle up to 25 digestion tubes

14.1.8 500 mL Nalgene squirt bottle

14.1.9 1-inch white laboratory tape

14.1.10 Borosilicate beakers (various sizes)

14.1.11 Borosilicate watch glasses (various sizes)

15.0 REAGENTS

15.1 Nitric acid (HNO_3), concentrated high purity grade 70% nitric acid

15.2 Hydrochloric acid (HCl), concentrated high purity grade 37% hydrochloric acid

15.3 Type I water, DI water (see GL-LB-E-016). Type I water is dispersed with the metals prep lab by the “Milli Q” water system.

15.4 Multi-element spiking solutions are purchased from NIST-traceable vendors.

16.0 PROCEDURES

A batch consists of samples of the same matrix and quality control (QC) samples that are digested together. Each of the quality control samples listed in section 19.2 can be included in each batch at the frequency listed or as per client request. The blank, LCS and/or LCS DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent. The MS, MSD and/or DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent, or per specific client/program requirements.

16.1 Glassware preparation:

16.1.1 Glassware that has been cleaned according to "Glassware Preparation" (GL-LB-E-003) is soaked in a water and acid mixture for at least 30 minutes.

16.1.2 After soaking, the glassware is rinsed with copious quantities of Type I water, then inverted over clean, absorbent paper or onto a rack for drying.

16.2 Label Teflon beakers or centrifuge tube with the sample numbers in the batch.

16.3 Mix the sample to achieve homogeneity. Transfer a 50 mL aliquot of sample to the appropriately labeled beaker or tube.

16.4 Quality control samples are prepared prior to digestion.

16.4.1 The beaker or tube to be used for the blank, MS, MSD and/or DUP, LCS and/or LCS DUP is labeled.

16.4.2 Unless otherwise noted, at least 50 mL of the sample is transferred to the MS, MSD and/or DUP beaker or tube.

16.4.3 Unless otherwise noted, 50 mL of Type I water is transferred to the LCS and/or LCS DUP beaker or tube.

16.4.4 The MS, MSD, LCS, and/or LCS DUP are spiked with known amounts of spiking solution.

16.4.5 The Teflon beaker or centrifuge tube to be used for the blank is labeled. 50 mL of Type I water is transferred to the beaker or tube. No spike or sample is added to the blank.

16.5 Sample digestion:

16.5.1 Add 1 mL of HNO_3 and 2.5 mL of HCl to the samples and quality control samples.

16.5.2 Cover the sample with a watchglass and heat the sample to 90 to 95° C until the sample volume is reduced to 7.5 to 10 mL or heat for 6 hours.

16.5.3 Do not allow the sample to go to dryness. Do not allow the sample to boil.

16.5.4 Remove the sample from the hot plate or block.

16.5.5 Allow the sample to cool.

16.5.6 If the sample contains particulate material that could clog the nebulizer, if necessary, you may filter or centrifuge the sample.

16.5.6.1 Be advised that filtration is a common cause of contamination. If a sample is filtered any QC associated with the sample must also be filtered. Additionally, if any sample in the batch is filtered the method blank and laboratory control sample must also be filtered.

16.5.7 Transfer the sample to a labeled centrifuge tube.

16.5.8 Dilute the sample to 50 mL with Type I water.

16.5.9 Cap the samples, organize them into a storage container, and label the storage container with the batch number of the sample group.

17.0 PREPARATION OF STANDARDS

Documentation of standards and their preparation is maintained in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

18.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

Hot plates/blocks are allowed to come to the proper temperature before digestions are started. The temperatures are documented on the data entry screens.

19.0 QUALITY CONTROL (QC) REQUIREMENTS

19.1 Frequency of QC

19.1.1 A matrix spike (MS) and a matrix spike duplicate (MSD) or a sample duplicate (DUP) and a matrix spike are prepped for every batch of $\leq$ 20 samples.

19.1.2 A method blank (MB) and a laboratory control standard (LCS) are prepped for every batch of $\leq$ 20 samples. A laboratory control standard duplicate (LCSD) is prepared if matrix QC is unavailable or upon client request.

19.2 Makeup of QC Samples

19.2.1 Sample duplicate (DUP) is a separate aliquot taken through the prep process exactly the same as the original sample.

19.2.2 Matrix spike and/or matrix spike duplicate is a separate aliquot of the sample to which appropriate spike volumes and solutions are added. The ID numbers and volumes of the spikes are recorded in the prep logbook.

19.2.3 The method blank (MB) is a reagent blank taken through the same prep process as the samples.

19.2.4 The laboratory control standard (LCS) is a fortified reagent blank taken through the same prep process as the sample. A purchased spiking solution from a certified vendor is used to fortify the LCS. (The ID number and volumes of the spikes are recorded in the prep logbook).

19.3 Handling Out-Of-Control Situations

19.3.1 If sample reactions cause popping or splattering of the digestate, discontinue the prep and contact team leader or group leader.

20.0 RUN SEQUENCE

Not applicable

21.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

The hotplates/blocks are shut off at the end of day or when device is no longer in use that day.

22.0 METHOD VARIATION

22.1 This procedure deviates from method SW-846 3005A in that sample volumes are half the method recommendations.

23.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

23.1 Upon completion of batch preparation, digestion data shall be entered into the AlphaLIMS Prep Logbook following the guidelines in GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms, and Other Recordkeeping Devices.

23.2 Data to be entered into the electronic logbook include analyst name, prep data and time, initial volume or weight with units, and final volume with units.

23.3 Standards and reagents may also be entered into the logbook and fall under the guidelines of GL-LB-E-015 for Control of Laboratory Standards and GL-LB-E-007 for Laboratory Standards Documentation.

23.4 Upon entry of prep data, obtain a printout of the logbook. The logbook page is kept with the samples with which it is associated.

23.5 The entry of correct prep data is peer reviewed (correct dates, times, weights, volumes, SOP/revision, spikes, spike amounts, and reagent information, etc.) by the analyst(s) for correctness.

24.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

25.0 LABORATORY WASTE

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

26.0 REFERENCES

26.1 Test Method for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Method 3005A, Revision 1, July 1992.

26.2 1992 Annual Book of ASTM Standards, D1193-91, “Standard Specification for Reagent Water”.

27.0 HISTORY

Revision 10: Updated to include list of analytes in discussion section. Type II water updated to type I. Format updated to reflect technical procedure.

Revision 11: Clarified wording in section 6.1, corrected reference in section 16.0, removed Appendix I.
Revision 12: Removed compounds from compound list.
Revision 13: Update several equipment changes as well as start up and shut down procedures for heating devices.
Revision 14: Extended equilibration time to 24 hrs after pH adjustment.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

ACID DIGESTION OF TOTAL METALS IN AQUEOUS SAMPLES AND EXTRACTS FOR ANALYSIS BY ICP AND ICP-MS

(GL-MA-E-008 REVISION 19)

APPLICABLE TO METHODS:
SW-846 3010A

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1.0 STANDARD OPERATING PROCEDURE FOR ACID DIGESTION OF TOTAL METALS IN AQUEOUS SAMPLES AND EXTRACTS FOR ANALYSIS BY ICP AND ICP-MS

2.0 METHOD CODE

SW-846 3010A

3.0 PURPOSE

To describe the manner in which aqueous samples and extracts for Inductively Coupled Plasma (ICP) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis are digested by EPA SW-846 Method 3010A. Samples digested by this procedure are applicable for analysis by SW-846 methods.

4.0 METHOD SUMMARY

Total Metals - The sample is refluxed with nitric acid until the color is light or the color has stabilized and the volume is reduced. The sample is refluxed with hydrochloric acid. The sample is then diluted to a final volume and is ready for analysis. This procedure deviates from method 3010A as follows: sample and reagent volumes are half of the method recommendations. GEL does not perform FLAA analysis and does not prep silver as required by Method 7760 for FLAA analysis. Samples prepared by this method may be analyzed for all the listed metals:

Aluminum	Copper	Rhodium	Thallium
Antimony	Hafnium	Selenium	Tungsten
Arsenic	Iron	Silica	Uranium
Barium	Lead	Silicon	Uranium-233
Beryllium	Lithium	Sulfur	Uranium-234
Bismuth	Magnesium	Sodium	Uranium-235
Boron	Manganese	Silver	Uranium-236
Cadmium	Molybdenum	Strontium	Uranium-238
Calcium	Potassium	Tantalum	Vandium
Cesium	Nickel	Tin	Zinc
Chromium	Phosphorus	Thorium	Zirconium
Cobalt	Rhenium	Titanium	

NOTE: All samples logged as miscellaneous liquids or samples extracted by TCLP may be diluted 10x during prep.

5.0 APPLICABLE MATRICES

Groundwaters, surface waters, wastewaters, extracts, and miscellaneous liquids.

6.0 HOLDING TIME, SAMPLE PRESERVATION, COLLECTION, STORAGE

6.1 Samples requiring filtration should be received by the laboratory chemically unpreserved. Liquid samples must be preserved prior to aliquoting for digestion. The samples are typically received chemically preserved with nitric acid to pH <2. Preservation may be performed at the time of sample collection however samples may also be submitted to the laboratory without chemical preservation. If unpreserved at the time of collection, the samples should be preserved within two weeks of collection, upon receipt at the laboratory. Following acidification, the sample should be mixed by agitation and held for 24 hrs to equilibrate. The pH of all aqueous samples should be tested immediately prior to withdrawing an aliquot for preparation to assure proper preservation. If the sample pH is >2, additional acid must be added and the sample held for 24 hrs until pH is verified as <2. If properly preserved, the sample may be held up to 6 months before analysis. Some miscellaneous liquids may be analyzed unpreserved, as they may be incompatible with preservation steps. This deviation is noted in sample prep documents.

6.2 Samples may be collected in polyethylene containers.

7.0 INTERFERENCES

There are rarely any interferences with this digestion. If any are encountered, consult the Group Leader, Team Leader or Quality Assurance Officer before continuing.

8.0 METHOD PERFORMANCE

Method Detection Limit (MDL) studies are performed annually and method detection limit verification (MDLV) studies are performed quarterly. The limits are stored in the laboratory AlphaLIMS.

9.0 DEFINITIONS

9.1 Blank: Type I water that has been taken through the digestion process. The blank is used to determine the amount of background contamination.

9.2 Laboratory Control Sample (LCS): A certified reference material that has been taken through the digestion process. The LCS is used to determine digestion accuracy and to determine if the digestion process is in control.

9.3 Laboratory Control Sample Duplicate (LCS DUP): A duplicate of the LCS. The LCS DUP is used to determine reproducibility and to indicate precision.

9.4 Matrix Spike (MS): A sample that has added to it a known amount of solution containing known concentrations of analytes. The MS is used to determine the presence or absence of interferences and matrix effects in the digested sample.

9.5 Matrix Spike Duplicate (MSD): A duplicate of the MS. The MSD indicates reproducibility.

9.6 Sample Duplicate (DUP): A duplicated sample. The DUP indicates reproducibility.

9.7 Type I water: Water that conforms to the performance specifications in SOP GL-LB-E-016. Type I water is dispensed within the metals prep lab by the “MilliQ” water system.

9.8 HNO_3: Concentrated reagent grade 70.9% nitric acid.

9.9 HCl: Concentrated reagent grade 37% hydrochloric acid.

9.10 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

10.0 ANALYST VERIFICATION

Before a technician/analyst is allowed to analyze samples without supervision, he or she is trained by qualified personnel and is required to successfully analyze a proficiency sample. Training records are maintained as quality records (Refer to GL-QS-E-008).

11.0 DOCUMENTATION OF DATA

Sample preparation data are recorded in AlphaLIMS.

12.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

WARNING

CONCENTRATED HYDROCHLORIC ACID AND NITRIC ACID ARE EXTREMELY CORROSIVE AND CAN CAUSE SEVERE BURNS TO THE SKIN.

12.1 Wear eye protection with side shields while performing procedures in the lab.

12.2 Treat all chemicals and samples as potential health hazards, and reduce exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client sample MSDSs are also maintained.

12.3 Personal protective equipment

12.3.1 Disposable gloves are worn and changed frequently when working with acids, glassware, or samples. Dirty gloves pose a contamination hazard to the samples. Gloves that have holes can be dangerous to the wearer by allowing acids and toxic metals to come in contact with skin.

12.3.2 Hood doors are pulled down partially or enclosure doors are pulled together partially while digesting samples. Acidified samples can splash and pop as they are being heated.

12.3.3 To protect clothes and skin from exposure to corrosive material, wear a lab jacket.

12.4 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

12.4.1 Protect counter tops with counter paper, or work from radioactive sample handling trays.

12.4.2 Prohibit admittance to immediate work area.

12.4.3 Post signs indicating radioactive samples are in the area.

12.4.4 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

12.4.5 Segregate radioactive wastes. Radioactive waste containers are obtained from the Waste Management.

12.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

12.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

12.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

12.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

12.7 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

13.0 SAMPLE RECEIPT FOR ANALYSIS

13.1 The analyst/technician submits the list of samples needed to the sample custodian group. The sample custodian removes the appropriate sample from the cooler and scans it using the barcode scanner to the appropriate area of the lab. The analyst then takes custody of the samples and scans them to the sample batch. The samples are now ready to be prepared or analyzed.

13.2 Analysts/technicians are responsible for retrieving their own samples when the sample custodian is unavailable.

14.0 INSTRUMENT/EQUIPMENT/GLASSWARE

14.1 Equipment

14.1.1 Air displacement pipettes

14.1.1.1 0.5-5 mL with disposable tips

14.1.1.2 100-1000 µL with disposable tips

14.1.1.3 10-100 µL with disposable tips

14.1.2 Environmental Express hot blocks or equivalent

14.1.3 Analytical balance capable of reading to three decimal places

14.1.4 Certified disposable 50 mL digestion tubes (polypropylene)

14.1.5 Ribbed disposable watch glasses (polypropylene)

14.1.6 Water resistant lab markers

14.1.7 Styrofoam trays to handle up to 25 digestion tubes

14.1.8 500 mL Nalgene squirt bottle

14.1.9 1-inch white laboratory tape

14.1.10 Borosilicate beakers (various sizes)

14.1.11 Borosilicate watch glasses (various sizes)

15.0 REAGENTS

15.1 Nitric acid (HNO_3), concentrated high purity grade 70% nitric acid

15.2 Hydrochloric acid (HCl), concentrated high purity grade 37% hydrochloric acid

15.3 Type I water, DI water (see GL-LB-E-016). Type I water is dispersed with the metals prep lab by the "Milli Q" water system.

15.4 Multi-element spiking solutions are purchased from NIST-traceable vendors.

16.0 PROCEDURES

A batch consists of samples of the same matrix and quality control (QC) samples that are digested together. Each of the quality control samples listed in section 19.2, can be included in each batch at the frequency listed or as per client request. The blank, LCS and/or LCS DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent. The MS, MSD and/or DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent, or per specified client/program requirements.

16.1 Water samples which require lab filtration are filtered from non-preserved aliquots. After filtration they are acidified to pH<2 using HNO3. A filter blank (MB) is filtered with the samples for to monitor possible contamination. The acidified aliquots are held at least 24 hours before continuing preparation for analysis.

16.2 All samples are tested for pH < 2, using pH test strips before sample preparation is initiated. If samples do not have the correct pH, samples are acidified to pH<2 using HNO_3. The acidified aliquots are held at least 24 hours prior to preparation for analysis.

16.3 Glassware preparation:

16.3.1 Glassware that has been cleaned according to "Glassware Preparation" (GL-LB-E-003) is soaked in a water and acid mixture for at least 30 mins.

16.3.2 After soaking, the glassware is rinsed with copious quantities of Type I water, then inverted over clean, absorbent paper or onto a rack for drying.

16.4 Label 150 mL or equivalent Teflon® beakers or centrifuge tubes with the sample numbers in the batch. If centrifuge tube is used, it must first be calibrated.

16.5 Mix the sample to achieve homogeneity. Transfer a 50 mL aliquot of sample to the appropriately labeled beaker or tube.

16.6 Quality control samples are prepared prior to digestion.

16.6.1 The beaker or tube to be used for the blank, MS, MSD and/or DUP, LCS and/or LCS DUP is labeled.

16.6.2 Unless otherwise noted, at least 50 mL of the sample is transferred to the MS, MSD and/or DUP beaker or tube.

16.6.3 Unless otherwise noted, 50 mL of Type I water is transferred to the LCS and/or LCS DUP beaker or tube.

16.6.4 The MS, MSD, LCS and/or LCS DUP are spiked with known amounts of spiking solution.

16.6.5 The beaker or tube to be used for the blank is labeled. 50 mL of Type I water is transferred to the beaker or tube. No spike or sample is added to the blank.

16.7 Sample digestion:

16.7.1 Add 1.5 mL of HNO_3 to the samples and quality control samples.

16.7.2 Cover the sample with a watch glass and heat the sample to near boiling, at a temperature of 90 - 95 °C, until the sample volume is reduced to a low volume (2.5 mL) or heat for 4 hours.

16.7.3 Do not allow the sample to go to dryness, or to boil.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and re-prepare.

16.7.4 Remove the sample from the hot plate or block.

16.7.5 Allow the sample to cool.

16.7.6 Add another 1.5 mL portion of HNO_3 to the samples and QC samples.

16.7.7 Cover the samples with a watch glass and return the samples to the hot plate or block. Continue refluxing, evaporating to 1-1/2 mL volume or heat 1 hour.

16.7.8 Repeat steps 16.7.1 through 16.7.7 until the digestion is complete, which is generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.

16.7.9 Remove the sample from the hot plate or block.

16.7.10 Allow the sample to cool.

16.7.11 Add 2.5 mL HCl to the sample and reflux for 15 minutes to dissolve any precipitate or residue resulting from evaporation.

16.7.12 Dilute the sample to 50 mL with Type I water.

16.7.13 Transfer the sample to a labeled centrifuge tube.

16.7.14 If the sample contains particulate material that could clog the nebulizer, if necessary, you may filter or centrifuge the sample.

16.7.15 Be advised that filtration is a common cause of contamination. If a sample is filtered any QC associated with the sample must also be filtered. Additionally, if any sample in the batch is filtered the method blank and laboratory control sample must also be filtered.

16.7.16 Cap the samples, organize them into a storage container, and label the storage container with the batch number of the sample group.

17.0 PREPARATION OF STANDARDS

Documentation of standards and their preparation is maintained in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

18.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

Hot plates/blocks are allowed to come to the proper temperature before digestions are started. The temperatures are documented on the data entry screens.

19.0 QUALITY CONTROL (QC) REQUIREMENTS

19.1 Frequency of QC

19.1.1 A matrix spike (MS) and a matrix spike duplicate (MSD) or a sample duplicate (DUP) and a matrix spike are prepped for every batch of $\leq$ 20 samples

19.1.2 A method blank (MB) and a laboratory control standard (LCS) are prepped for every batch of $\leq$ 20 samples. A laboratory control standard duplicate (LCSD) is prepared if matrix QC is unavailable or upon client request.

19.2 Makeup of QC Samples

19.2.1 Sample duplicate (DUP) is a separate aliquot taken through the prep process exactly the same as the original sample.

19.2.2 Matrix spike and/or matrix spike duplicate is a separate aliquot of the sample to which appropriate spike volumes and solutions are added. The ID numbers and volumes of the spikes are recorded in the prep logbook.

19.2.3 The method blank (MB) is a reagent blank taken through the same prep process as the samples.

19.2.4 The laboratory control standard (LCS) is a fortified reagent blank taken through the same prep process as the sample. A purchased spiking solution from a certified vendor is used to fortify the LCS. (The ID number and volumes of the spikes are recorded in the prep logbook).

19.3 Handling Out-Of-Control Situations

19.3.1 If sample reactions cause popping or splattering of the digestate, discontinue the prep and contact team leader or group leader.

20.0 RUN SEQUENCE

Not applicable

21.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

The hotplate/blocks are shut off at the end of the day or when device is no longer in use.

22.0 METHOD VARIATION

22.1 This procedure deviates from method SW-846 3010A in that sample volumes are half the method recommendations.

23.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

23.1 Upon completion of batch preparation, digestion data shall be entered into the AlphaLIMS Prep Logbook following the guidelines in GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms, and Other Recordkeeping Devices.

23.2 Data to be entered into the electronic logbook include analyst name, prep data and time, initial volume or weight with units, and final volume with units.

23.3 Standards and reagents may also be entered into the logbook and fall under the guidelines of GL-LB-E-015 for Control of Laboratory Standards and GL-LB-E-007 for Laboratory Standards Documentation.

23.4 Upon entry of prep data, obtain a printout of the logbook. The logbook page is kept with the samples with which it is associated.

23.5 The entry of correct prep data is peer reviewed (correct dates, times, weights, volumes, SOP/revision, spikes, spike amounts, and reagent information, etc.) by the analyst(s) for corrections.

24.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

25.0 LABORATORY WASTE

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

26.0 REFERENCES

26.1 Test Methods for Evaluating Solid Waste, Laboratory Manual Physical/ Chemical Methods, SW-846 Method 3010A, Revision 1, July 1992.

26.2 1992 Annual Book of ASTM Standards, Standard D 1193-91, “Standard Specification for Reagent Water.”

27.0 HISTORY

Revision 15: Updated list of analytes in method summary.
Revision 16: Clarified wording in section 6.1, corrected section 16.0, removed Appendix I (out dated and hard to read).
Revision 17: Removed discontinued elements from section 4.0 compound list.
Revision 18: Updated to current equipment in use and temperature records for hotblocks.
Revision 19: Updated to require 24 hours of equilibration after pH adjustment.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

(GL-MA-E-009 REVISION 29)

APPLICABLE TO METHODS:
EPA SW-846 3050B Modified

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1.0 STANDARD OPERATING PROCEDURE FOR ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

2.0 METHOD CODE

2.1 EPA SW-846 3050B Modified

3.0 METHOD OBJECTIVE/PURPOSE

To describe the manner in which sediments, sludges, and soils for Inductively Coupled Plasma (ICP) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis are digested by EPA SW-846 Method 3050B Modified. Samples digested by this procedure are applicable for analysis by SW-846 methods 6010 and 6020.

4.0 METHOD SUMMARY

A representative portion of sample is digested with nitric acid and hydrogen peroxide for ICP-MS analysis. A representative portion of sample is digested with nitric acid and hydrochloric acid for ICP analysis. Samples prepared by this method may be analyzed for all the listed metals. Other metals may be analyzed if they pass control standard criteria:

Aluminum	Copper	Rhodium	Thallium
Antimony	Hafnium	Selenium	Tungsten
Arsenic	Iron	Silica	Uranium
Barium	Lead	Silicon	Uranium-233
Beryllium	Lithium	Sulfur	Uranium-234
Bismuth	Magnesium	Sodium	Uranium-235
Boron	Manganese	Silver	Uranium-236
Cadmium	Molybdenum	Strontium	Uranium-238
Calcium	Potassium	Tantalum	Vanadium
Cesium	Nickel	Tin	Zinc
Chromium	Phosphorus	Thorium	Zirconium
Cobalt	Rhenium	Titanium	

This method is not a “total” digestion technique for most samples. It is a very strong acid digestion that will dissolve all elements that could become “environmentally available” by design; elements bound in silicate structures (boron, silicon, silica) are not normally dissolved by this procedure as they are not usually mobile in the environment.

5.0 APPLICABLE MATRICES

5.1 Soils

5.2 Sludges

5.3 Sediments

5.4 Solid debris/powders

5.5 Heavy oils

5.6 Filters

5.7 Paints

5.8 Ghost Wipes

6.0 HOLD TIME

Holding time is 180 days from the time and date of collection until the start of analysis unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

Solid samples are not preserved but should be stored at 0°- 6°C.

8.0 INTERFERENCES

There are rarely any interferences with this digestion. If any are encountered, consult the group leader or quality officer before continuing.

9.0 PERFORMANCE CHARACTERISTICS

Method detection limits (MDLs) and method detection limit verification (MDLVs) are performed in accordance with SOP GL-LB-E-001 the determination of method limits and a method quantitation limits.

10.0 DEFINITIONS

10.1 Blank: Type I water that has been taken through the digestion process. The blank is used to determine the amount of background contamination.

10.2 Laboratory Control Sample (LCS): A certified reference material that has been taken through the digestion process. The LCS is used to determine digestion accuracy and to determine if the digestion process is in control.

10.3 Laboratory Control Sample Duplicate (LCS DUP): A duplicate of the LCS. The LCS DUP is used to determine reproducibility and to indicate precision.

10.4 Matrix Spike (MS): A sample that has added to it a known amount of solution containing known concentrations of analytes. The MS is used to determine the presence or absence of interferences and matrix effects in the digested sample.

10.5 Matrix Spike Duplicate (MSD): A duplicate of the MS. The MSD indicates reproducibility.

10.6 Sample Duplicate (DUP): A duplicate of a sample. The DUP indicates reproducibility.

10.7 AlphaLIMS: The Laboratory Information Management System used at GEL.

10.8 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

10.9 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

11.0 ANALYST VERIFICATION

Before a technician/analyst is allowed to analyze samples without supervision, he or she is trained by qualified personnel and is required to successfully perform an Initial Demonstration of Capability (IDOC) as discussed in GL-QS-E-011. Training records are maintained as quality records (Refer to GL-QS-E-008).

12.0 DOCUMENTATION OF DATA

Sample preparation data are recorded in AlphaLIMS.

13.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

WARNING

CONCENTRATED HYDROCHLORIC ACID AND NITRIC ACID ARE EXTREMELY CORROSIVE AND CAN CAUSE SEVERE BURNS TO THE SKIN.

CONCENTRATED 30% HYDROGEN PEROXIDE IS A VIOLENT OXIDIZER. KEEP AWAY FROM OPEN FLAMES, AND RINSE WITH WATER IF SKIN CONTACT OCCURS.

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards, and reduce exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client sample MSDSs are also maintained.

13.3 Personal protective equipment

13.3.1 Disposable gloves are worn and changed frequently when working with acids, glassware, or samples. Dirty gloves pose a contamination hazard to the samples. Gloves that have holes can be dangerous to the wearer by allowing acids and toxic metals to come in contact with skin.

13.3.2 Hood doors are pulled down partially or enclosure doors are pulled together partially while digesting samples. Acidified samples can splash and pop as they are being heated.

13.3.3 To protect clothes and skin from exposure to corrosive material, wear a lab jacket.

13.4 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.4.1 Protect counter tops with counter paper, or work from radioactive sample handling trays.

13.4.2 Prohibit admittance to immediate work area.

13.4.3 Post signs indicating radioactive samples are in the area.

13.4.4 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.4.5 Segregate radioactive wastes. Radioactive waste containers are obtained from the Waste Management.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

13.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

13.7 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician submits the list of samples needed to the sample custodian group. The sample custodian removes the appropriate sample from the cooler and scans it using the barcode scanner to the appropriate area of the lab. The analyst then takes custody of the samples and scans them to the sample batch. The samples are now ready to be prepared or analyzed.

14.2 Analysts/technicians are responsible for retrieving their own samples when the sample custodian is unavailable.

15.0 INSTRUMENT/EQUIPMENT/GLASSWARE

15.1 Equipment

15.1.1 Air displacement pipettes

15.1.1.1 0.5-5 mL with disposable tips

15.1.1.2 100-1000 µL with disposable tips

15.1.1.3 10-100 µL with disposable tips

15.1.2 Environmental Express hot blocks or equivalent

15.1.3 Analytical balance capable of reading to three decimal places

15.1.4 Certified disposable 50 mL digestion tubes (polypropylene)

15.1.5 Ribbed disposable watch glasses (polypropylene)

15.1.6 Water resistant lab markers

15.1.7 Styrofoam trays to handle up to 25 digestion tubes

15.1.8 500 mL Nalgene squirt bottle

15.1.9 Teflon chips

15.1.10 1-inch white laboratory tape

15.1.11 Borosilicate beakers (various sizes)

15.1.12 Borosilicate watch glasses (various sizes)

16.0 REAGENTS

16.1 Nitric acid (HNO_3), concentrated high purity grade 70% nitric acid

16.2 Hydrochloric acid (HCl), concentrated high purity grade 37% hydrochloric acid

16.3 Hydrogen peroxide (H_2O_2), concentrated 30% hydrogen peroxide

16.4 Type I deionized (DI) water.

16.5 Multi-element spiking solutions are purchased from NIST-traceable vendors.

17.0 PREPARATION OF SAMPLES

A batch consists of samples of the same matrix and quality control (QC) samples that are digested together. Each of the quality control samples listed in steps 20.2 must be included in each batch at the frequency listed or as per client request. The blank, LCS, and/or LCS DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent. The MS, MSD, and/or DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent, or per specified client/program requirements.

17.1 Glassware preparation:

17.1.1 Glassware that has been cleaned according to GL-LB-E-003 for Glassware Preparation is soaked in a water and acid mixture for at least 30 minutes.

17.1.2 After soaking, the glassware is rinsed with copious quantities of Type I water and then inverted over clean, absorbent paper or onto a rack for drying.

17.2 Label the digestion tube with the sample numbers in the batch. If digestion tube is to be used for measuring initial and final volumes it either must be calibrated before usage or must be certified by the vendor. Refer to GL-LB-E-026 for digestion tube testing procedure.

17.3 Refer to GL-LB-E-029 for subsampling instructions. Mix the sample to achieve homogeneity. Weigh approximately 0.5 g of sample. Transfer the weighed sample to the appropriately labeled digestion tube.

17.3.1 Sample aliquots should not be taken from the top of an unmixed sample because large particles tend to rise in solid matrixes and heavy materials tend to sink in liquid matrixes.

17.3.2 Powdered samples may be homogenized by gently rocking the sample side to side. Then a representative aliquot may be taken from the center of the powder.

17.3.3 Other matrixes must be stirred, turned or mixed before sampling.

17.4 Quality control samples are prepared prior to digestion.

17.4.1 The tube to be used for the blank, MS, MSD, and/or DUP, LCS, and/or LCS DUP is labeled.

17.4.2 Weigh approximately 0.5 g of sample and transfer to the MS, MSD, and/or DUP beaker or tube.

The MS, MSD, LCS, and/or LCS DUP are spiked with known amounts of spiking solution.

17.4.3 Select a LCS. The LCS is purchased from an outside vendor and comes with a certificate of certified values and recovery ranges. The LCS is logged into the AlphaLIMS system for traceability and for the use of nominal calculations. Mix the LCS to achieve homogeneity. Weigh approximately 0.5 g of the sample and transfer to the LCS and/or LCS DUP digestion tube. For non-soil solid samples, a liquid LCS is used in combination with approximately 0.5 g of Teflon chips.

17.4.4 The blank tube is labeled and no water, spike, or sample is added to it. Approximately 0.5 g of Teflon chips is used.

17.5 If the samples are being prepared for ICP-MS analysis:

17.5.1 Add 2.5 mL nitric acid and Type I DI water to the samples and quality control samples.

17.5.2 Gently swirl the sample and acid mixture.

17.5.3 Cover the sample with a watch glass and heat the sample on a hot plate/block to 95° ± 5° C. Reflux the sample for 10 to 15 minutes.

17.5.4 Remove the sample from the hot plate or block and allow the sample to cool.

17.5.5 Add 2.5 mL of concentrated nitric acid, replace the watch glass, and reflux for 30 minutes. If brown fumes are generated indicating oxidation of the sample by nitric acid, repeat step 17.5.5 over and over until no brown fumes are given off by the sample.

17.5.6 Using a ribbed watch glass or vapor recovery system, allow the solution to evaporate to approximately 2.5 mL without boiling, or heat for 2 hours.

17.5.6.1 Remove the sample from the hot plate or block and allow the sample to cool.

17.5.6.2 Add 1.5 mL of hydrogen peroxide and 1.0 mL of Type I water. Return the sample to the hot plate or block and allow the peroxide reaction to occur. Continue to add hydrogen peroxide to the sample until the effervescence subsides. Do not add more than 5 mL hydrogen peroxide.

17.5.6.3 Cover the sample with a ribbed watchglass, heating the acid-peroxide digestate until the volume is reduced to approximately 2.5 mL, or heat at 95° ± 5° C without boiling for 2 hours.

17.5.6.4 Do not allow the sample to evaporate to dryness.

17.5.6.5 Remove the sample from step 17.5.6.3 from the hot plate or block.

17.5.6.6 Allow the sample to cool.

17.5.6.7 Dilute the sample to 50 mL with Type I water.

17.5.6.8 Cap and shake the sample.

17.5.6.9 Filter each sample with a 2.0 µm pore size plunger type filter (PTF grade) or allow to settle overnight.

17.5.6.10 Organize the samples in a storage container, and label the container with the batch number of the sample group.

17.6 If the samples are being prepared for ICP analysis:

17.6.1 Add 1.25 mL nitric acid and 10 mL hydrochloric acid to the samples and quality control samples.

17.6.2 Gently swirl to mix.

17.6.3 Cover the sample with a watch glass and heat the sample on a hotplate/block to 95° ± 5° C. Reflux the sample for 30 minutes.

17.6.4 Remove the sample from the hotplate/block and allow to cool.

17.6.5 Dilute the sample to 50 mL with Type I water.

17.6.6 Cap and shake the sample.

17.6.7 Filter each sample with 2.0 µm pore size plunger type filter (PTF grade) or allow to sit overnight.

17.6.8 Organize the samples in a storage container, and label the container with the batch number of the sample group.

17.7 If ghost wipes are being prepared for ICP or ICPMS analysis:

17.7.1 Remove ghost wipe from package and add to digestion tube.

17.7.2 Add 20 mL DI water, 10 mL Nitric Acid, and 1 mL of hydrochloric acid. Allow to sit for 30 minutes.

17.7.3 Gently swirl to mix.

17.7.4 Cover the sample with a watch glass and heat the sample on a hotblock/plate to 95 °C ± 5 °C. Reflux the sample for 30 minutes.

17.7.5 Dilute the sample to 50 mL with Type I water.

17.7.6 Cap and shake the sample.

17.7.7 Filter each sample with 2.0 µm pore size plunger type filter (PTF grade) or allow to sit overnight.

17.7.8 Organize the samples in a storage container, and label the container with the batch number of the sample group.

17.8 If the sample contains particulate material that could clog the nebulizer, you may filter or centrifuge the sample if necessary.

17.9 Be advised that filtration is a common cause of contamination. If a sample is filtered, any QC associated with the sample must also be filtered. Additionally, if any sample in the batch is filtered the method blank and laboratory control sample must also be filtered.

17.10 Filters may be prepared via this method. If the filters are small enough to fit inside the 50 mL digestion tubes, they can be treated as any solid prep materials. If the filters are too big to undergo adequate digestion using the 50 mL digestion tube, a borosilicate beaker will need to be used. All reagents and standards will need to be adjusted for any extra volumes needed. All filter analyses should be discussed and the process verified with the group/team leader prior to digestion. The group leader or project manager may have to contact the client to get the full description of what is required.

18.0 PREPARATION OF STANDARDS

Documentation of standards and their preparation is maintained in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

Hot plates/blocks are allowed to come to the proper temperature before digestions are started. The temperatures are documented on the data entry screens.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC

20.1.1 A matrix spike (MS) and a matrix spike duplicate (MSD) or a sample duplicate (DUP) and a matrix spike are prepped for every batch of $\leq$ 20 samples

20.1.2 A method blank (MB) and a laboratory control standard (LCS) are prepped for every batch of $\leq$ 20 samples. A laboratory control standard duplicate (LCSD) is prepared if matrix QC is unavailable or upon client request.

20.2 Makeup of QC Samples

20.2.1 Sample duplicate (DUP) is a separate aliquot taken through the prep process exactly the same as the original sample.

20.2.2 Matrix spike and/or matrix spike duplicate is a separate aliquot of the sample to which appropriate spike volumes and solutions are added. The ID numbers and volumes of the spikes are recorded in the prep logbook.

20.2.3 The method blank (MB) is a reagent blank taken through the same prep process as the samples. Teflon chips are used to approximate matrix weights of 0.5 g.

20.2.4 The laboratory control standard (LCS) is a standard performed two different ways. For DOE-ALB clients, a purchased SRM is used at approximately 0.5 g and is taken through the same process as the samples. For all other clients, Teflon chips weighted to approximately 0.5 g are used. The chips and acid solution is spiked with the appropriate spike volumes and solutions. The ID number and volumes of the spikes are recorded in the prep logbook.

20.3 Handling Out-Of-Control Situations

If sample reactions cause popping or splattering of the digestate, discontinue the prep and contact team leader or group leader.

21.0 RUN SEQUENCE

Not applicable

22.0 PROCEDURE

Refer to section 17.0, Preparation of Samples

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

The hotplate/blocks are shut off at the end of each day.

24.0 METHOD VARIATION

24.1 This procedure deviates from method 3050B in that sample volumes are half the method recommendations.

24.2 The ICP procedure references a modified 3050B section 7.5 procedure. The modification eliminates the use of the Whatman 41 filters, thus eliminating contamination of with some common minerals.

25.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

25.1 Upon completion of batch preparation, digestion data shall be entered into the AlphaLIMS Prep Logbook following the guidelines in GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms, and Other Recordkeeping Devices.

25.2 Data to be entered into the electronic logbook include analyst name, prep data and time, initial volume or weight with units, and final volume with units.

25.3 Standards and reagents may also be entered into the logbook and fall under the guidelines of GL-LB-E-015 for Control of Laboratory Standards and GL-LB-E-007 for Laboratory Standards Documentation.

25.4 Upon entry of prep data, obtain a printout of the logbook. The logbook page is kept with the samples with which it is associated.

25.5 The entry of correct prep data is peer reviewed (correct dates, times, weights, volumes, SOP/revision, spikes, spike amounts, and reagent information, etc.) by the analyst(s) for corrections.

26.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 LABORATORY WASTE

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

28.0 REFERENCES

28.1 Test Method for Evaluating Solid Waste; Laboratory Manual Physical/ Chemical Methods, Method 3050B, "Acid Digestion of Sediments, Sludges, and Soils," Revision 2, December 1996.

28.2 1992 Annual Book of ASTM Standards, Standard D1193-91, "Standard Specification for Reagent Water."

28.3 16 CFR Part 1303

29.0 HISTORY

Revision 24: Corrected section 17.0, and removed appendix 1 (out of date and difficult to read)

Revision 25: Removed compounds from compound list.

Revision 26: Updated to include the recording of temperatures for hotplates/blocks and shut-down processes for these devices. Updated the Analyst Verification Section.

Revision 27: Updated the reference SOP for the MDL and MDLVs.

Revision 28: Remove reference to testing of metal jewelry as a matrix.

Revision 29: Added Ghost wipe preparation to process.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR MERCURY ANALYSIS USING THE PERKIN ELMER

AUTOMATED MERCURY ANALYZER

(GL-MA-E-010 REVISION 38)

APPLICABLE TO METHODS:
EPA SW-846 Methods: 7470 and, 7471A, and 7471B
EPA Methods: 245.1 and 245.2

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1.0 STANDARD OPERATING PROCEDURE FOR MERCURY ANALYSIS USING THE PERKIN ELMER AUTOMATED MERCURY ANALYZER

2.0 METHOD OBJECTIVE AND SUMMARY

This standard operating procedure (SOP) describes the digestion and analysis procedures for the determination of mercury (Hg) in surface and saline waters, wastewaters, industrial effluents, sanitary sewage, soils, sediments, bottom deposits, sludges, oils, and TCLP extracts. This is a cold-vapor atomic absorption technique based on the absorption of radiation at 253.7 nm by mercury vapor. Samples are treated with nitric acid and sulfuric acid or hydrochloric acid in the presence of potassium permanganate and potassium persulfate to oxidize all mercury to the mercuric (Hg^{++}) form. The mercury is then reduced to its elemental state and evacuated from the sample. The mercury vapor passes through an optical cell positioned in the light source of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. This SOP is applicable for the following methods:

2.1 EPA SW-846 Methods 7470A, 7471A, and 7471B

2.2 EPA Methods 245.1 and 245.2.

3.0 METHOD APPLICABILITY

3.1 Calibration Range: The typical calibration range used for analysis of mercury is 0.2 µg/L to 10.0 µg/L.

3.2 Tested Concentration Range: The range for the method is limited by calibration and can be extended by diluting the sample.

3.3 Method Detection Limit (MDL): The MDL is calculated using the procedure described in GL-LB-E-001 for The Determination of Method Detection Limits. The MDL is verified quarterly, or whenever there is a significant change in the instrument response.

3.4 Instrument Detection Limits (IDLs) are 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 are determined by the mean of the blank results 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 a new equipment, after major instrument maintenance such as changing the detector, and/or at a frequency designated by the project.

3.5 Method Precision: Analytical precision can be determined by calculating the Relative Percent Difference (RPD) between a Laboratory Control Sample (LCS) and a Laboratory Control Sample Duplicate (LCSD) or a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD).

3.6 Method Bias (Accuracy): Accuracy can be determined by calculating recoveries of a LCS and LCSD or an MS and MSD of a similar matrix.

4.0 DEFINITIONS

4.1 Continuing Calibration Blank (CCB): An aliquot of reagent water or other blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

4.2 Continuing Calibration Verification (CCV): A solution of the method analytes used to evaluate the performance of the instrument with respect to a defined set of criteria. The CCV concentration is varied throughout the calibration range.

4.3 Initial Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination after injection of the mid-level ICV.

4.4 Initial Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of Blank or sample matrix. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

4.5 Method Detection Limit (MDL): The minimum concentration of an analyte that can be measured and reported with 99% confidence that the concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix type containing the analyte.

4.6 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

4.7 Tumble Blank (TB): TCLP extraction fluid Type 1 or 2 that has been taken through the TCLP tumbling process. The tumble blank is used to determine the amount of background contamination resulting from the tumbling process.

4.8 Contract Required Detection Limit (CRDL): The lowest level in the calibration curve.

4.9 Serial Dilution (SDILT): A 1 to 5 sample dilution used to assess matrix suppression.

4.10 Limit of Detection (LOD): An analyte, method and matrix specific estimate of the minimum amount of a substance that can be reliably detected. GEL has established LOD = 2 x MDL.

4.11 Limit of Quantitation (LOQ): An analyte, method and matrix specific estimate of the minimum amount of a substance that can be reported with a specific level of confidence. The LOQ is set at or above the concentration of the lowest initial calibration standard. The laboratory must empirically demonstrate precision and bias at the LOQ. The LOQ and associated precision and bias must meet client

requirements and must be reported. GEL uses the following guidance (LOD < LOQ):

When LOD < PQL, PQL = LOQ

When LOD > PQL, LOQ is raised to next lowest calibration standard.

4.12 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

5.0 METHOD VARIATIONS

This SOP varies from the referenced methods by utilizing a smaller sample aliquot. Reagent amounts are adjusted accordingly.

6.0 SAFETY PRECAUTIONS AND WARNINGS

WARNING

HYDROXYLAMINE HYDROCHLORIDE MAY EXPLODE WHEN HEATED TO 140º C.

MERCURY COMPOUNDS ARE TOXIC IF INHALED OR ABSORBED THROUGH THE SKIN.

ADDITION OF HYDROCHLORIC ACID AND NITRIC ACID IN THE PROPORTIONS 3 TO 1 FORMS AQUA REGIA.

ADDITION OF HYDROXYLAMINE HYDROCHLORIDE /SODIUM CHLORIDE TO AQUA REGIA CAN CAUSE THE SPONTANEOUS RELEASE OF CHLORINE GAS. PERFORM DIGESTIONS USING AQUA REGIA UNDER A HOOD.

NITRIC ACID AND SULFURIC ACID ARE HIGHLY CORROSIVE.

CONTACT WITH OXIDIZERS MAY GENERATE EXPLOSIVE MIXTURES.

NITRIC ACID IS CORROSIVE AND A POISON.

MERCURY VAPORS ARE TOXIC. DIGEST SAMPLES AND STANDARDS UNDER A FUME HOOD.

WHEN DIGESTING SOIL, OIL, AND SEDIMENT, BE CAREFUL TO AVOID INHALING TOXIC NITRATES.

WARNING

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

6.1 Wear eye protection with side shields while performing procedures in the lab.

6.2 Treat all chemicals as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and individual sample MSDS forms are maintained in the laboratory.

6.3 Personal protective equipment

6.3.1 Gloves are required when handling the chemicals in this procedure.

6.3.2 Work under a hood when using concentrated acids and bases.

6.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

6.4.1 Protect counter tops with counter paper or work from radioactive sample handling trays.

6.4.2 Prohibit admittance to immediate work area.

6.4.3 Post signs indicating radioactive samples are in the area.

6.4.4 Take swipes of the counter tops upon completion of work. Deliver those swipes to the appropriate swipe count box.

6.4.5 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

6.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

6.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

6.7 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

6.8 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

7.0 INTERFERENCES TO THE METHOD

7.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

7.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

7.3 Seawaters, brines, and industrial effluents high in chlorides may require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs at 253.7 nm.

7.4 Certain volatile organic materials that absorb at 253.7 nm may also cause interference.

8.0 APPARATUS AND MATERIALS

8.1 50 mL digestion tubes

8.2 Flask, Volumetric, (100 mL and 250 mL)

8.3 Variable and single volume pipette and micropipettes

8.4 Hot Block (Temperature controlled at 95° ± 3° for solids and 90°- 95° for liquids)

8.5 Non-mercury thermometers

8.6 Culture tubes

9.0 REAGENTS

9.1 Type I deionized water

9.2 Nitric Acid (HNO_3), Concentrated, ACS grade certified for AA use.

9.3 Sulfuric Acid (H_2SO_4), Concentrated, ACS grade certified for AA use.

9.4 Hydrochloric Acid (HCl), Concentrated, ACS grade certified for AA use.

9.5 3% HCl: Dissolve 30 mL concentrated HCl in Type I water and dilute to 1000 mL. Volume may be scaled proportionately.

9.6 Potassium Permanganate Solution ($KMnO_4$), 5%: Dissolve 5 g potassium permanganate in Type I water and dilute to 100 mL. Volume and weight may be scaled up proportionally.

9.7 Potassium Persulfate Solution ($K_2S_2O_8$), 5%: Dissolve 5 g potassium persulfate in Type I water and dilute to 100 mL. Volume and weight may be scaled up proportionally.

9.8 Sodium Chloride-Hydroxylamine Hydrochloride Solution ($NaCl\text{-}NH_2OH{\bullet}HCl$): Dissolve 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride in Type I water and dilute to 100 mL. (Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.) Volume and weight may be scaled up proportionally.

9.9 Stannous Chloride Solution ($SnCl_2$), 1.1%: Dissolve 11 g stannous chloride in 3% hydrochloric acid and dilute to1 L. Volume and weight may be scaled proportionately.

9.10 Aqua Regia: Combine 3 parts of concentrated HCl and 1 part concentrated HNO_3. Prepare fresh before use.

NOTE: Due to the inherent dangers of working with full strength aqua regia, a 1+1 solution is prepared for use with the sample preparation.

9.11 Mercury Source Standard (Hg), 1000 ppm, from an Approved Vendor. Standards are received, labeled, prepared and stored according to GL-LB-E-007 for Laboratory Standards Documentation.

9.12 Liquid Nitrogen or Compressed Nitrogen at pressures 75 to 100 psi.

10.0 INSTRUMENTATION

10.1 Perkin Elmer FIMS100 Automated Mercury Analyzers

10.2 Balance

11.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

11.1 Aqueous samples must be acidified to a pH < 2 with nitric acid. The samples are tested using pH strips to verify the correct pH values of < 2 before preparation. If samples do not have the correct pH, samples are acidified to a pH of < 2 with nitric acid. The acidified aliquots are held at least 24 hours before preparation.

The suggested maximum holding time for these samples is 28 days. When performing CLP analyses, the holding time is 26 days from verified time of sample receipt.

11.2 Non-aqueous samples shall be refrigerated and analyzed as soon as possible. The preservation required for soil/sediment samples is maintenance at 0° ≤ 6°C until analysis. Water samples that require lab filtration are filtered from non-preserved fractions and acidified to a pH < 2 with nitric acid. A filter blank is filtered with the samples for contamination QC purposes. The acidified aliquots are held at least 24 hours before preparation.

11.3 TCLP extracts have a maximum holding time of 28 days before extraction and 28 days after extraction for a total of 56 days.

12.0 SAMPLE PREPARATION TECHNIQUES

12.1 Prior to determining the concentration of mercury, all samples, calibration standards, check standards, laboratory control samples, and blanks must be digested using the following procedures:

12.1.1 For standards preparation, see the mercury recipe section of the AlphaLIMS Standards Logbook.

12.1.2 Label each digestion tube with a sample number or lab Quality Control (QC) number.

12.2 Aqueous Sample Preparation by Methods EPA SW-846 7470A, EPA 245.1 and EPA 245.2.

12.2.1 Transfer 20 mL of Type I water, 20 mL of a well mixed representative sample, or an aliquot of sample diluted to 20 mL with Type I water, to a labeled digestion tube. Record the volume of sample dispensed into the digestion tube in the Mercury Prep logbook.

12.2.2 For TCLP and MISC-L matrices, transfer 18 mL of Type I water, 2 mL of a well-mixed representative sample, or an aliquot of sample diluted to 20 mL final volume, to a labeled digestion tube. Record the volume of sample dispensed into the digestion tube in the Mercury Prep logbook.

12.2.3 The following calibration standards are required: 0.2, 0.5, 2.0, 5.0, 10.0 µg/L, ICV/CCV, ICB/CCB, and CRDL (Contract Required Detection Limit).

12.2.4 Add 0.5 mL concentrated nitric acid. Add the appropriate amount of spiking solution to each appropriate QC sample tube. Then add 1.0 mL concentrated sulfuric acid to each digestion tube and mix.

12.2.5 Add 3 mL of 5% potassium permanganate solution to each digestion tube and mix. Let sample stand for approximately 15 minutes after addition of potassium permanganate. If sample does not maintain its brown/purple color, add an additional 3 mL aliquot of the 5% potassium permanganate

to the sample and all associated QC. Record this additional aliquot on the comment section of the Mercury Prep logbook. If after the second aliquot is added, the sample is still not able to maintain its purple/brown color throughout the digestion process, then redigest the sample using an appropriate dilution.

12.2.6 Add 1.5 mL of 5% potassium persulfate solution to each digestion tube and mix. Cap each digestion tube and place in a hot block for two hours at 90° - 95°C.

12.2.7 After two hours, remove digestion tubes from the hot block and allow to cool. Cooling can be facilitated by moving samples to the walk-in cooler until they reach approximate room temperature. When the samples have been cooled to room temperature, add 2 mL of sodium chloride-hydroxylamine hydrochloride solution to each digestion tube to reduce any excess potassium permanganate. Cap tubes and shake until the samples are fully reduced. The samples are now ready for analysis.

12.3 Sediment, Oil and Soil Sample preparation by Methods EPA SW-846 7471A, 7471B.

12.3.1 Weigh 0.25 to 0.3g of a representative sample and place the aliquot into a digestion tube. The (MB) method blank and (LCS) laboratory control standard uses Teflon chips or glass beads as a solid mass. The LCS uses a liquid spike on the weighed mass. If required by client, a solid reference material (SRM) is used for the LCS. Record the weight in the Mercury Prep logbook. Refer to GL-LB-E-029 for specifics on subsampling.

12.3.2 The following calibration standards are required: 0.2, 0.5, 2.0, 5.0, 10.0 µg/L, ICV/CCV, ICB/CCB, and CRDL.

12.3.3 Add the appropriate amount of spiking solution to each QC sample tube. Add 5 mL of 1+1 aqua regia to each sample and associated QC and mix.

12.3.4 Place each digestion tube in a hot block at 95° ± 3° C for two minutes.

12.3.5 Remove digestion tubes from the hot block. Cool for at least 15 minutes. Then add 25 mL of DI water and 7.5 mL of 5% potassium permanganate solution and mix thoroughly.

12.3.6 Cap each digestion tube and again place each digestion tube in a hot block 95° ± 3° C for 30 minutes.

12.3.7 Remove tubes from the hot block and allow to cool to room temperature for at least 60 minutes.

CAUTION: This next step can cause chlorine gas to be generated. Perform the following step under a hood.

12.3.8 Uncap the digestion tubes under a hood. Add 3 mL of sodium chloride-hydroxylamine hydrochloride solution to each tube. Cap and shake until samples are fully reduced. Uncap and allow time for chlorine gas to evolve and vent from the digestates. The samples and standards are now ready for analysis.

13.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL SAMPLES

13.1 Source standard solutions

Source standard solutions are purchased from a certified vendor. These standards are traceable to National Institute of Standards and Technology (NIST) standards. The source standards are received from Purchasing. Two source standards of different lot numbers or vendors are used to prepare the curve and ICV working standards.

13.2 Intermediate and working standards must be PREPARED FRESH DAILY.

13.3 Intermediate #1 (first source) - 50µl of 1000 mg/L Hg stock #1 and 5 mL nitric acid to 250 mL with DI water.

Intermediate #2 (second source) - 50µl of 1000 mg/L Hg stock #2 and 5 mL nitric acid to 250 mL with DI water

	0.2µg/L	**0.5 µg/L**	**2.0 µg/L**	**5.0 µg/L**	**10.0µg/L**	**CCV 5.0 µg/L**	**ICV 5.0 µg/L**
Liquid Curve	20µl Int #1 to 20mL with DI Water	50µl Int #1 to 20mL with DI Water	200µl Int #1 to 20mL with DI Water	500µl Int #1 to 20mL with DI Water	1000µl Int #1 to 20mL with DI Water	500µl Int #1 to 20mL with DI Water	500µl Int #2 to 20mL with DI Water
Solid Curve	30µl Int #1 to 5mL with DI Water	75µl Int #1 to 5mL with DI Water	300µl Int #1 to 5mL with DI Water	750µl Int #1 to 5mL with DI Water	1500µl Int #1 to 5mL with DI Water	750µl Int #1 to 5mL with DI Water	750 µl Int #2 to 5mL with DI Water

13.4 For guidance on standard documentation, refer to GL-LB-E-007 for Laboratory Standards Documentation.

13.5 For Kerr-McGee Samples, reprep and reanalyze the samples if MB or CCB is greater than the reporting limit (RL) and samples are between IDL and RL. If samples are less than IDL or greater than 10 times the RL they can be reported.

14.0 INSTRUMENT CALIBRATION AND PERFORMANCE

14.1 Instrument calibration is performed using the following prepared mercury standards: 0.0, 0.2, 0.5, 2.0, 5.0 and 10.0µg/L.

14.2 Report data to the appropriate number of significant figures.

14.3 Data are reported in µg/L, mg/L, µg/kg or mg/kg Hg depending on client preference. Sample units are defined before data are input into AlphaLIMS by the analyst.

14.4 Any sample concentration less than 100% of the highest recorded calibration standard is acceptable. If sample concentrations are over 100% of the high standard, then these samples must be re-analyzed at a dilution that will bring the sample concentration within the range. Dilutions are made with digested blanks created during batch preparation.

14.5 A CRDL standard for CVAA is required to be run following calibration. The result of CRDL should be within 70%-130% of the accepted value. For DOD QSM, the CRDL should fall within 80%-120% of the accepted value or per client request.

14.6 The acceptable performance requirements for the mercury instrument are a correlation coefficient of 0.995 or better and ICV and CCV standards within the acceptance range prescribed in Section 18.2.

14.7 Proof of instrument performance during actual sample analysis is provided by records of the calibration curve, ICV, CCV, and CCB.

15.0 ANALYSIS AND INSTRUMENT OPERATION

15.1 Before actual operation, all samples, including standards and QC samples, are prepared and digested as described in Section 12. Instrument operation includes a calibration phase and a sample analysis phase. The two phases are usually run as one continuous procedure, but the instrument may be calibrated prior to loading and running samples. Also note that the analyst needs to monitor the process to ensure that the calibration is satisfactory prior to analyzing samples. If the calibration process is unsatisfactory it will need to be terminated, problems corrected, and the calibration rerun.

15.2 Turn on computer.

15.3 Input computer passwords.

15.4 Turn on Hg FIMS instrument and note that the autosampler initializes. Let it warm up for at least 30 minutes.

15.5 Prepare daily 1.1% stannous chloride reducing solution in 3% hydrochloric acid in a 2 L plastic bottle. Shake well and put in the appropriately labeled reductant reservoir bottle that feeds the instrument.

15.6 Fill other instrument reservoir bottle with 3% hydrochloric acid for instrument rinse and carrier acid.

15.7 Double-click AA WinLab Analysis icon.

15.8 Click on the applicable workspace button.

15.9 Click [Sample Info] button.

15.10 Load samples beginning in position #12. Note that samples go in the 15 mL digestion tubes. A CCV and CCB must separate each group of 10 samples. All samples must be bracketed by a satisfactory CCV and CCB.

15.11 Install dry membrane filter, rough side up (in final assembly position). Screw cap on tightly.

15.12 Hook up and clamp pump tubing. Check all pump tubing daily for proper flow and wear.

15.13 Click [FIAS] button icon.

15.14 Adjust gas flow to 40 to 70 cm^3/min.

15.15 Verify flow rates of reductant (5 to 7 mL/min, red/red tubing) and carrier (9 to 11 mL/min, blue/yellow tubing) with DI water using graduated cylinders.

15.16 Cycle [valve fill/inject] to further flush things out. Give it a minute or so in each position. Unclick all three buttons and close the window.

15.17 In the "Automated Analysis" window click on "Analyze Tab" then click on [Analyze All].

16.0 EQUIPMENT AND INSTRUMENTATION MAINTENANCE

16.1 If there are problems: During the analysis the foreground window is usually the "Results" text window that is also automatically printed, and the background window is the "Automated Analysis" window. If you need to abort a run, you must wait for the hourglass mouse cursor to change to an arrow, then click on the "Automated Analysis" window to bring it to the foreground. Then unclick the [Analyze All] button. A dialog box will come up giving you a couple of options.

16.2 For non-routine maintenance procedures, refer to Perkin Elmer manual for troubleshooting.

16.3 Whenever instrument is serviced or adjusted, an entry needs to be made in the maintenance log. The entry includes the analyst's initials, date, nature of the problem, and actions taken to correct it.

17.0 DATA RECORDING, CALCULATIONS AND DATA REDUCTION

17.1 The concentration of mercury can be determined by comparing the response obtained from analyzing the sample digestate to the calibration curve. The sample concentration of mercury is matrix specific and is calculated as follows:

Aqueous Sample

17.1.1 Concentration (µg/L) = $\frac{(C)(D)(V_t)}{V_i}$

Where:

C = Concentration (µg/L) digestate

D = Dilution Factor

V_t = Total Volume of sample digestate

V_i = Initial Volume of sample in L

17.1.2 Non-aqueous Samples

$$\text{Concentration } (\mu g/kg) = \frac{(C)(D)(V_t)}{W(\%S)}$$

Where:

C = Concentration (µg/mL) digestate

D = Dilution Factor

V_t = Total Volume of the sample digestate

W = Weight of the sample digested

%S = Percent Solids

18.0 QUALITY CONTROL REQUIREMENTS

18.1 Frequency of Quality Control Activities

18.1.1 ICV is performed immediately following each calibration and CCV is performed after every 10 analysis.

18.1.2 ICB is performed immediately following the ICV and CCB must follow each CCV.

18.1.3 A method blank is analyzed for each batch of 20 or less samples.

18.1.4 A matrix spike and matrix spike duplicate or matrix spike and a sample duplicate are analyzed for every 20 or fewer samples in a batch, or per client requirements. When performing EPA analyses, the requirement for matrix spike analysis is one per every 10 or fewer samples in a batch.

18.1.5 A LCS is analyzed with each batch of 20 or less samples. Additionally, a LCS duplicate also may be analyzed due to client specific requirements.

18.1.6 A SDILT is required with each batch of 20 or less samples, preferably the QC designated sample.

18.1.7 Linear Calibration Range (LCR) checks are performed on a 6 month basis. The high standard of the curve is read back against the calibration and must recover ± 10%. If this procedure fails, the problem must be investigated and rectified.

18.1.8 A post spike is required if the percent recovery of an MS or MSD is outside the acceptance limits or the MSD %RPD is greater than 20% RPD for all SW-846 Methods.

18.2 Acceptance Limits

18.2.1 Acceptance limits for the following methods are outlined below:

Method/ Acceptance Criteria	**SW-846 7471A SW-846 7471B**	**SW-846 7470A**	**EPA 245.1 EPA 245.2**	**DOD QSM Version 5.3**
ICV	90% - 110%	90% - 110%	95% - 105%	90-110%
ICB	-0.2 µg/L to 0.2 µg/L	-0.2 µg/L to 0.2 µg/L	-0.2 µg/L to 0.2 µg/L	± ½ LOQ
CRDL	70% - 130%	70% - 130%	70% - 130% advisory limits only	80% - 120% to investigate and recalibrate
CCV	80% - 120%	80% - 120%	90% - 110%	90% - 110%
CCB*	-0.2 µg/L to 0.2 µg/L	-0.2 µg/L to 0.2 µg/L	-0.2 µg/L to 0.2 µg/L	± ½ LOQ
Method Blank*	-0.2 µg/L to 0.2 µg/L	-0.2 µg/L to 0.2 µg/L	-0.2 µg/L to 0.2 µg/L	± ½ LOQ
LCS	80% - 120% (for non-SRM sources) certified SPC limits for SRM	80% - 120%	85% - 115%	Use QSM specified limits
Matrix Spikes	80% - 120%	75% - 125%	75% - 125%	Use QSM specified limits
Sample Duplicates	0 - 20%, when > 5 x RL, ± RL when < 5 x RL	0 - 20%, when > 5 x RL, ± RL when < 5 x RL	0 - 20%, when > 5 x RL, ± RL when < 5 x RL	0 - 20%, when > 5 x LOQ, ± LOQ < 5 x LOQ
Serial Dilution	<10% if > 25x IDL or MDL	<10% if > 25x IDL or MDL	< 10% if > 25x IDL or MDL	< 10% if > 50x LOQ
Matrix Spike Dup	0 - 20%, when > 5 x RL, ± RL when < 5 x RL	0 - 20%, when > 5 x RL, ± RL when < 5 x RL	0 - 20%, when > 5 x RL, ± RL when < 5 x RL	0 - 20%, when > 5 x LOQ, ± LOQ < 5 x LOQ
Post Spikes	80% - 120%	80% - 120%	75% - 125%	80% - 120%
Linear Calibration Range	90% - 110%	90% - 110%	90% - 110%	90% - 110%

* North Carolina sample batches require ± ½ LOQ for blanks.

18.2.2 All reported sample concentrations must be less than the highest calibration standard. Samples greater than the highest calibration standard must be diluted to bring the concentration within range.

18.2.3 The ICV is prepared from a second standard source other than the source employed for initial calibration. Generally, the concentration of the ICV is 5.0 µg/L.

18.2.4 The method blank must have an absolute value below the CRDL for CLP analyses and have an absolute value below ½ LOQ for DOD QSM analyses.

18.2.5 All LCS recoveries must fall within the stated acceptance limits. Statistical process control limits are established for LCS soils.

18.2.6 Matrix spikes, matrix spike duplicates, sample duplicates, and post spikes are indicators of method performance for a specific sample matrix. Acceptance limits are based on guidelines outlined in the specific methods and are listed in the table above.

18.2.7 The serial dilution must be < 10% difference for sample concentrations that are > 25x the IDL or the MDL or >50x the LOQ for DOD QSM, depending on client specifications.

19.0 CORRECTIVE ACTION FOR OUT OF CONTROL OR UNACCEPTABLE DATA

19.1 ICV and/or CCV failure requires recalibration of the instrument and/or preparation of new standard solutions. Samples analyzed between calibration verification that fail must be reanalyzed. An ICV or CCV that has failed may be rerun provided there is an attributable cause known to have affected the check standard only and not the previous samples. Examples of an acceptable cause may be a sample tip out of solution during analysis, no solution in the sample cup or obvious carryover in the CCV from a very high sample immediately prior to the CCV. If the CCV is reanalyzed, the data must be lined through, initialed and dated, and the reason for the rerun must be documented on the raw data. In addition, corrective action should be taken to eliminate the cause of the initial CCV failure to prevent future occurrence.

19.2 ICB or CCB failure requires recalibration of the instrument and/or repreparation of the calibration blank. When analyzing under SW-846, a CCB may be accepted above the RDL level under two conditions: 1) the CCB is acceptable if the sample value is ± RDL and 2) the CCB is acceptable if the level of analyte in the CCB is less than 1/10 the analyte value in the lowest reported sample. For DOD QSM, acceptance criteria must be the < ½ LOQ or less than 10 x the lowest value of the samples bracketed by the blank.

19.3 Method blank results higher than the RDL or ½ LOQ and greater than 10% of any sample value in that batch which has concentrations above the RDL requires that batch be redigested, reanalyzed, and/or reported with the appropriate qualifier. If the method blank results are less than -1x RDL or – ½ LOQ, there may be significant interference, calibration or contamination problems with the sample, or

instrument or calibration standards that must be resolved before the batch can be reported.

19.4 LCS results outside of the upper and lower control limits can be reanalyzed for verification. If reanalysis is still outside the limits, the batch representing the failing LCS must be reprepped for reanalysis.

20.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

20.1 The printout from the instrument is attached to the Laboratory Information Management System (AlphaLIMS) data report, original batch sheet, and the Mercury Prep Logbook.

20.2 The metals department analyst reviews mercury data by verifying that the values from the printout agree with values entered into the mercury data run logbook, and with the values that appear on computer printed data report sheets. The calibration standards, the correlation coefficient, CCV, LCS, duplicates, and spikes are also reviewed to make sure values are within the limits.

20.3 Levels of review responsibility are described below:

20.3.1 Analyst Review: Mercury data are reviewed by the analyst after the run is complete and checked once more after data are entered in AlphaLIMS.

20.3.2 Peer Analyst Review: Another analyst familiar with mercury and its data reviews all data in detail.

20.4 Review of each level

20.4.1 Analyst Review: Analyst checks his/her own data and makes necessary corrections on any errors (i.e., writing wrong numbers, checks correlation coefficient again, dilution factors, and continuous calibration standards).

20.4.2 Peer Analyst Review: Reviews all data on the printout, data reported in the Mercury Data Run Logbook, Mercury Prep Logbook, and information that are on the computer printed data report. It is important at this level to check what preparation date was entered, dilution factors, concentrations of spikes, and CCVs. The Case Narrative Report is used to standardize items checked by peer analysts.

20.5 The complete data review process requires the use of the Mercury Prep Logbook, Prep data report, batch sheet, AlphaLIMS data report, raw instrument data, auto-run sequence record if the samples were analyzed using an autosampler, and Case Narrative Report

21.0 RECORDS

21.1 Prep data are recorded in accordance with Section 12 of this SOP.

21.2 Data from an analysis are recorded on a printout from the instrument and stored in digital format on the instrument computer or on the network server.

21.3 Reported values come from one sample run if the instrument calibration and other required instrument specifications are met. The data are reported as a raw value along with any dilution factors used.

22.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

23.0 LABORATORY AND WASTE HANDLING AND DISPOSAL

23.1 Standard solutions that must be disposed of are transferred by the Waste Management Technician to be disposed of in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

23.2 Special caution must be taken when samples are radioactive. Handling, delivery, transfer, and disposal of radioactive samples and residues must follow the related SOPs. Persons handling radioactive materials must first pass the training course.

24.0 REFERENCES

24.1 Methods for the Determination of Metals in Environmental Samples, Supplement 1, EPA 600/R-94-111. Method 245.1, Revision 3.0, May 1994.

24.2 Perkin Elmer FIMS400/FIMS100 Flow Injection Mercury System.

24.3 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1A, EPA SW-846, Final Update III, June 1997. USEPA Office of Solid Waste and Emergency Response, Washington, D.C. 20460.

24.4 Method 7470A, "Mercury in Liquid Waste (Manual Cold-Vapor Technique)," Revision 1, September 1994.

24.5 Method 7471A, “Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique),” Revision 1, September 1994.

24.6 Method 7471B, "Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)," Revision 2, February 2002.

24.7 Methods for Chemical Analysis of Water and Wastes, 1983, (EPA-600/4-79/020-PB84-128677).

24.8 Method for the Determination of Metals in Environmental Samples, Method 245.2, 1974.

24.9 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM, Version 5.3, July 2019.

25.0 HISTORY

Revision 34: Added statement to clarify IEC verifications.

Revision 35: Clarification of DOD QSM criteria and method acceptance criteria.

Revision 36: Revised equilibration time to 24 after pH adjustment. Added acceptance criteria for blanks in NC sample batches.

Revision 37: Updated to volume of aqua regia used for samples and QC. Updated DoD QSM Version 5.3, July 2019. Deleted redundant sections.

Revision 38: Updated Sediment, oil and soil prep section to reflect current practices.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR DETERMINATION OF METALS BY ICP

(GL-MA-E-013 REVISION 31)

APPLICABLE TO METHODS:
EPA Method 200.7
EPA SW-846 Method 6010B
EPA SW-846 Method 6010C
EPA SW-846 Method 6010D

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR DETERMINATION OF METALS BY ICP

2.0 METHOD CODES

2.1 EPA SW-846 Method 6010B

2.2 EPA SW-846 Method 6010C

2.3 EPA SW-846 Method 6010D

2.4 EPA Method 200.7

3.0 METHOD OBJECTIVE AND PURPOSE

This standard operating procedure (SOP) describes the procedure for the determination of metals with the Perkin Elmer (PE) Optima ICPs.

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 Analytes: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, SiO_2, Sn, Sr, Ti, Tl, U, V, Zn, P, and S.

4.2 Applicable Matrices: These methods are applicable to the determinations of any of the analytes listed above for various matrices including waters, oils, soils, sludges, Toxicity Characteristic Leachate Procedure (TCLP) extracts and other more unusual types of sample which are generally classified as a miscellaneous matrix.

4.3 General Method Summary: After samples are prepared in accordance with the sample preparation SOP, they are analyzed by Inductively Coupled Plasma (ICP) as follows:

4.3.1 The instrument is calibrated with a minimum of two calibration points for each element to be analyzed. The points consist of a calibration blank solution to define the lower calibration point and at least one standard calibration solution at the analyte concentrations to define the higher calibration point(s). A correlation coefficient of 0.995 or better (0.998 or better for SW-846 Method 6010C) is required for each analyte if multiple standards are used or the instrument is recalibrated for the analyte of interest.

4.3.2 Prepared client samples, check standards, and quality control samples identified in section 21.1 are then analyzed. The check standards and quality control samples are used to determine the quality and acceptability of the analytical data.

4.3.3 Continuing Calibration Verification Samples (CCV) are analyzed a minimum of every 10 samples to ensure that the instrument is continuing to perform correctly.

5.0 METHOD SCOPE AND PERFORMANCE CHARACTERISTICS

5.1 Calibration Range: The calibration range consists of the concentrations between the calibration blank and that of the highest calibration standard for each analyte.

5.2 Tested Concentration Range: For ICP analyses, the upper limit of the linear range is determined by analyzing a linear range verification check standard, near the

expected linear range limit. The analytically determined concentration of this standard shall be within ± 10% of the true value.

5.3 Method Detection Limit (MDL) studies for each analyte are performed and/or verified at least annually. These studies are conducted and calculated in accordance with SW-846, Chapter 1, Section 5.0, and GL-LB-E-001 for The Determination of Method Detection Limits. The Reported Quantitation Limit (RQL) reflects the current MDL study. For 6010D mean recovery of the seven replicates is ± 35% of the known value with an RSD of ≤ 20%.

5.4 Instrument Detection Limits (IDLs) are useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blanks analyses to obtain a calculated concentration. IDLs are determined by the mean of blank results 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 at a frequency designated by the project.

5.5 Method Precision: To assure analytical precision of methods used, MS/MSD or sample DUP, or LCS/LCSD are analyzed with each batch or as method requires.

5.6 Method Bias (Accuracy): Determined by calculating recoveries of LCS of a similar matrix.

6.0 DEFINITIONS

6.1 Continuing Calibration Blank (CCB): An aliquot of reagent water or other blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

6.2 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample, periodically throughout the run sequence. Its purpose is to determine whether the analytical sequence is in control during sample analysis. It may be prepared from the same source as the calibration standards, and is usually of varied concentration.

6.3 Independent Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination after injection of the mid-level ICV.

6.4 Independent Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of Blank or sample matrix. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

6.5 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

6.6 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

6.7 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

6.8 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

6.9 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

6.10 Limit of Detection (LOD): An analyte, method and matrix specific estimate3 of the minimum amount of a substance that can be reliably detected. GEL has established LOD = 2 x MDL.

6.11 Limit of Quantitation (LOQ): An analyte, method and matrix specific estimate of the minimum amount of a substance that can be reported with a specific estimate of confidence. LOQ is set at or above the concentration of the lowest initial calibration standard. The laboratory must empirically demonstrate precision and bias at the LOQ. The LOQ and associated precision and bias must meet client requirements and must be reported. GEL uses the following guidance (LOD < LOQ):

When LOD < PQL, PQL =LOQ

When LOD > PQL, LOQ is raised to next lowest calibration standard

6.12 Practical Quantitation Limit (PQL): The PQL is typically at or above the lowest point on an acceptable initial calibration curve. It may also be determined by multiplying the MDL by approximately 2 to 10. Concentration of a target analyte determined to be greater than its PQL are defined as quantitative results. This limit is not used in DoD ELAP reporting.

6.13 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide use definitions.

7.0 INTERFERENCES TO THE METHOD

ICP analysis is subject to three types of interferences:

7.1 Physical interferences are those physical properties of a sample solution that prevent their introduction to the plasma with an efficiency equal to that of the calibration standards. This type of interference can be reduced through the use of an internal

standard in accordance with the instrument operating manual, or by diluting the sample in reagent blank solution until the percent recovery is acceptable.

7.2 Chemical interferences are minimal in ICP Spectroscopy because the extremely high energy of the plasma breaks chemical bonds.

7.3 Interelement Spectral Interference can be overcome by use of Interelement Correction (IEC) factors. IECs are initially calculated when a new instrument or method is brought on-line and are continually calculated on a biannual basis. To calculate IECs, single element standards are analyzed at their respective linear ranges. IEC coefficients are calculated if the element interfered with is outside ± PQL. Further calculations may be required if tighter criteria is required. IECs may be checked using single element standards (analyzed at a minimum of every 6 months) as often as needed to ensure the correct factors are being used.

7.4 The IEC coefficients are calculated if the element interfered with is outside ± PQL when analyzing a single element standard at its linear range:

7.4.1 Perkin Elmer Optima ICPs: The interfering element uses the mg/L concentration. The IEC for Cd via PE software is ¯18/490, or ¯0.03673. When verifying the IEC by analyzing the ICSA standard or the single element analysis, the non-spiked analyte concentration should be within ± 2x the PQL (6010B and 6010C), ± PQL (6010D), or ± 2x MDL for DoD QSM. IECs are calculated for all minerals and for commonly seen analytes that occur at high concentrations in environmental samples, i.e., manganese and zinc.

8.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

8.1 Sample digestates are not extremely volatile or spontaneously combustible, but they are normally acidic and should be handled with care. Small spills may generally be wiped up with paper towels that can be disposed of in the trash. Larger spills may require the use of a mop. The mop head may have to be disposed of as potentially hazardous waste in accordance with the Laboratory Waste Management Plan, GL-LB-G-001. If the spilled digestates begin any obvious fuming or reacting, pour a generous amount of the acid neutralizer, located in each lab, onto the spill before attempting to clean it up.

8.1.1 Approved gloves will be worn to avoid skin contact with the digestate during clean-up.

8.1.2 Wear eye protection with side shields while performing procedures in the laboratory. An eyewash station is located in each analysis lab.

8.1.3 Do not persist in cleaning up a spill in the presence of strong fumes. Move out of the area, attempt to isolate the area, and notify your supervisor immediately.

8.2 These instruments use high voltage electricity and therefore should be shut completely down any time electronic components may be exposed to personnel or any liquids.

8.3 Prior to handling radioactive samples, analysts must have radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

8.3.1 Protect counter tops with counter paper, or work from radioactive sample handling trays.

8.3.2 Prohibit admittance to immediate work area.

8.3.3 Post signs indicating radioactive samples are in the area.

8.3.4 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

8.3.5 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

8.3.6 For additional guidance, refer to GL-RAD-S-004 for Radioactive Material Handling, and GL-LB-G-001, the Laboratory Waste Management Plan.

8.4 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). Individual sample MSDS forms provided by the clients are also maintained.

8.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

8.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

8.6 Never leave gas cylinders unchained or untied, even when they are on moving carts.

8.7 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

8.8 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

9.0 CAUTION WARNINGS

Special care should be taken when handling hydrofluoric acid to ensure that the acid does not come into contact with the skin.

10.0 APPARATUS AND MATERIALS; REAGENTS; EQUIPMENT AND INSTRUMENTS

10.1 Apparatus and Equipment

10.1.1 Replacement glass parts for the ICP such as quartz torch bodies, purge extension windows, injector tips, nebulizers, and spray chambers may be ordered from an approved vendor through GEL's Purchasing Agent.

10.1.2 High purity argon gas is provided to the ICP instruments, via a network of pipelines, into the lab from liquid storage tanks located outside the building. The argon is purchased from a GEL approved vendor.

10.1.3 Consumable materials such as tubing are often attainable from various scientific product companies. The GEL Purchasing Agent can help to find the best prices from an approved vendor. All orders are placed through GEL's Purchasing Agent.

10.2 Reagents, Chemicals, and Standards

10.2.1 Nitric acid, reagent grade and ultra pure

10.2.2 Hydrochloric acid, reagent grade and ultra pure

10.2.3 Lithium solution, 5% or 1%

10.2.4 Scandium solution, 1000 µg/mL

10.2.5 5% Cesium

10.2.6 Yttrium solution,1000 µg/mL

10.2.7 Other Chemicals: Additional compounds, surfactants, oils, cleaning agents, etc. may be routinely ordered through GEL's Purchasing Agent.

10.3 Instrumentation

10.3.1 PE AVIO 500 with compatible PC and printer

10.3.2 PE Optima 8300DV with compatible PC and printer

10.3.3 PE Optima 7300DV with compatible PC and printer

10.3.4 ESI Autosampler

10.3.5 Polyscience6105 PE Chillers or equivalent

10.3.6 Appropriate Nebulizer (i.e., Meinhard or Burgener Mira Mist)

11.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

11.1 Aqueous samples should be preserved with nitric acid to a pH of < 2 prior to receipt by the analyst. Sediment samples should be kept at 0º ≤ 6º C prior to analysis.

11.2 Refer to GL-SR-E-001 for Sample Receipt, Login, and Storage.

12.0 SAMPLE PREPARATION TECHNIQUES

12.1 All samples, except drinking water with Turbidity <1 NTU and samples specifically exempted by contract, are prepared in accordance with the SOPs for Metals

Digestion: GL-MA-E-006 (USEPA SW-846 Method 3005A), GL-MA-E-008 (USEPA SW-846 Method 3010A), GL-MA-E-009 (USEPA SW-846 Method 3050A), and GL-MA-E-020 (NIOSH 7303). Other digestion procedures may also be used.

12.2 Additional filtration may be required to prevent clogging of sample introduction system. The method blank (MB) and laboratory control sample (LCS) must be filtered to check for contamination from the filtering process.

12.3 Sample spills should be handled as stated in Section 8.1.

13.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Routine Preventative and Special Operational (Failure)

13.1 Routine Preventative Maintenance (PM) is recommended as follows:

Frequency	Procedure
When Needed	Oil the peristaltic pump with silicon spray Replace peripump sample introduction tubing Change pump hoses on drain systems Check drain waste collection containers and empty as needed Clean/replace nebulizer Clean/replace torch. Align according to manufacturer's specifications Clean/replace air filters

13.2 Non-Routine Maintenance Procedures (Special, Operational or Failure Mode Maintenance)

13.2.1 If the instrument will not function properly, refer to the troubleshooting section in the appropriate operator's manual.

13.2.2 If the analyst is unable to fix the instrument, call the GEL Instrument Technician, and if needed, the manufacturer's Service Department.

13.3 Refer to the ICP Maintenance Logbook for routine records. Preventative maintenance and service should be recorded in the maintenance logbook.

14.0 PREPARATION OF STANDARD SOLUTION AND QUALITY CONTROL SAMPLES

14.1 Source standards records are recorded in the Metals Source Standards Logbook, which is maintained in the Metals laboratory. The preparation of working standards is fully described in the "Maintain Reference Materials" application in AlphaLIMS.

14.2 Standards are receipted, labeled, prepared and stored in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

15.0 INSTRUMENT CALIBRATION

15.1 Calibration and sample analysis are conducted automatically using the autosampler. (Samples can also be analyzed manually.)

15.1.1 Profiling: All analytical channels were aligned within specifications during initial installation or realigned after relocation of the instrument by profiling

daily, all elements will be peak-on-center. Profiling should be done after plasma warm-up prior to sample analysis and verified as needed during the day (more frequently on days with high temperature and humidity fluctuations).

15.1.1.1 Operate/Profile instrument using the procedures found in the corresponding ICP Operator's or Hardware Manual.

15.1.1.2 The PE Optima ICPs are auto-profiled using a mercury lamp.

15.1.1.3 When an acceptable profile is attained, print the graphical profile and display. An acceptable profile is defined as having the mercury peak being perfectly centered on the 253.652 nm axis. If the peak is off-centered, run the diagnostic check or have service look at the instrument.

15.1.2 Standardization: Standardization is required every twenty-four when the instrument is in use. Additionally, restandardization and/or recalibration is required when calibration checks fail.

15.2 Calculations are described in the instrument manuals.

15.3 Calibration standards may vary according to method. A minimum of a blank and standard are required, but a typical calibration uses a blank and three standards of varying concentration. For the multiple standard curve, the correlation coefficient (r) must be equal to or greater than 0.995 (0.998 for 6010C).

15.4 For typical (recommended) calibration standards, refer to Appendix 2.

15.5 For continuing calibration requirements, refer to Section 21.

15.6 For actions concerning a calibration verification failing to meet requirements, refer to Section 21.3.

16.0 INSTRUMENT PERFORMANCE REQUIREMENTS

16.1 Before samples may be analyzed, the instrument must be calibrated and verified using an Initial Calibration Verification (ICV) which is prepared from an independent source, an Initial Calibration Blank (ICB), Interference Check Sample(s) (ICS-A, ICS-AB), Practical Quantitation Limit (PQL), and a Linear Range Verification (LR). These must meet the requirements stated in Section 21.2 and Appendix 4 for each analyte being reported, unless specified otherwise by the client or contract.

16.2 The instrument calibration and all continuing verification data are maintained on the printed hard copy and electronically saved onto the computer network. The printouts are kept in chronological order by instrument. Recent files are stored in the respective metals laboratories and older records are archived in the warehouse.

17.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

17.1 Analyst training is conducted in accordance with GL-HR-E-002 for Employee Training.

17.2 Method performance is verified by conducting MDL studies in accordance with GL-LB-E-001 for The Determination of Method Detection Limits, and by the evaluation of laboratory proficiency samples (audits).

18.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

18.1 All samples are introduced to the instrument via a peristaltic pump. The amount of sample entering the instrument is dependent on the pump speed, the diameter of the pump tubing, and the nebulizer efficiency.

18.2 Run Sequence

18.2.1 Calibration sequence (may vary slightly under different autosampler files/see Appendix 2 also).

18.2.1.1 S0 (reagent blank, 3% HCl/1%HNO_3)
18.2.1.2 S0.1 (100 ppb standard)
18.2.1.3 S0.5 (500 ppb standard)
18.2.1.4 SCAL (1000 ppb standard)
18.2.1.5 S10 (20 to 50 ppm standard)

18.2.2 The calibration verification steps include:

18.2.2.1 ICV
18.2.2.2 ICB
18.2.2.3 PQL (low level ICV for 6010C)
18.2.2.4 ICS-A
18.2.2.5 ICS-AB
18.2.2.6 LR1
18.2.2.7 LR2
18.2.2.8 CCV
18.2.2.9 CCB

18.2.3 Samples (10 samples or less)

18.2.4 Continuing Calibration Verification (CCV), Low Level Calibration Verification (PQL) required for SW-846 6010C, and Continuing Calibration Blank (CCB)

18.2.5 Repeat steps 18.2.3 and 18.2.4 through the end of the run or until applicable verification is out of specifications.

18.2.6 Final verification steps in order:

18.2.6.1 ICS-A (required for 200.7)
18.2.6.2 ICS-AB (required for 200.7)
18.2.6.3 CCV
18.2.6.4 PQL (required for SW-846 6010C)
18.2.6.5 CCB

NOTE: 6010C only requires there to be a closing low level continuing calibration standard (PQL). For ease of analysis, the PQL standard can be analyzed every 10 samples.

18.2.7 ICS-A and ICS-AB are analyzed at least every 8 hours or after the analytical batch for 200.7 analyses.

18.3 For data storage see section 23 and 24.

18.4 General operation of the instrument

The Perkin Elmer Optima 7300V, 8300DV and AVIO500 and are simultaneous, dual view, inductively coupled, argon plasma emission spectrometers. As configured for GEL, it is capable of analyzing 32 substances: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, SiO_2, Sr, Ti, Sn, Tl, U, V, and Zn. The operating software of the system is a menu driven type.

18.4.1 Typical Analytical Challenges

18.4.1.1 Sample Over-range: If an analyte is above the working linear range of the instrument, even if this element is not required, dilute the sample to an acceptable range and reanalyze, especially if the over ranged element is an interferant of the reported analyte. Dilutions are required if the value of an analyte exceeds 100% of the working linear range when the element of interest is being reported, or is interfering with an element that will be reported. Dilution factors must be taken into account when reporting final values. Additionally, further rinse and/or an acidified rinse solution may be required before continuing with the next sample.

18.4.1.2 Torch/Sample Introduction Drift: Various changes in torch plasma conditions, sample introduction, or other external factors can have a great effect on the analysis.

18.4.1.2.1 If sample introduction drift is suspected several items should be reviewed. Check the peristaltic pump tubing for wear and replace as needed. Check the internal standard to make sure it is being introduced to the instrument at a constant rate. Check the nebulizer to ensure that it's free of clogs and that the spray is a continuous mist.

18.4.1.2.2 Profile drift may mimic torch/sample introduction drift. Re-profiling should be done routinely. Profile drift is a function of temperature and should be checked more frequently when large temperature swings are observed. During an analytical run profile drift is evident when a clean

blank shows significant deviation from zero. As suggested by the manufacturer, two elements to track for this problem are Na and Al.

18.4.1.2.3 Tubing connections may become loose, allowing air to bubble into the sample path. Tighten or replace tubing connection as necessary.

18.4.1.3 Sample Matrix: The internal standard technique is used to correct for physical interferences. Each ICP has a Scandium (Sc) internal standard that is continuously fed through the sample introduction system via a peristaltic pump. Scandium is used as the internal standard. It is used at 10 ppm both radially and axially on the Optimas. In addition, the Optimas run yttrium at 2 ppm to reprocess as an internal standard if Sc is suspected in the sample.

18.5 Power switches and auxiliaries are addressed in detail in the appropriate operator's manual and/or hardware guide.

18.6 Start-up and shutdown procedures are addressed in detail in the appropriate operator's manual and/or hardware guide.

18.7 Sample quantity requirements vary based on several different factors such as nebulizer type, diameter of tubing, and pump rate.

18.8 Autosampler can be used with various nebulizers by attaching the sample introduction tube to the autosampler sample tube. The autosampler rinse should be setup by connecting the autosampler rinse tubing to the peristaltic pump in the instrument.

19.0 CALCULATIONS AND DATA REDUCTION METHODS

19.1 Any dilutions, concentrations, or preparation factors must be taken into account prior to reporting data to a client. The appropriate factors are entered into AlphaLIMS.

19.2 Care must be taken that the correct units are being employed. Analytical results originating from the ICPs are reported in ppb or µg/L.

20.0 DATA RECORDING

20.1 The Optima data are stored on the Network as a CSV file and printed at the instrument as each sample is analyzed.

20.2 ICP samples and standards are generally analyzed in three replicates (minimum of 2), and the reported value is the average of the replicates. At times, one replicate may be removed due to an attributable cause. This attributable cause should be documented on the hard data (i.e. third replicate ran out of volume). The average of the two remaining replicates is subsequently recalculated prior to reporting the data to the client.

20.3 Data are retrieved by the data entry personnel where unused data can be eliminated, dilution factors entered, and conversions made prior to uploading to AlphaLIMS.

21.0 QUALITY CONTROL REQUIREMENTS

21.1 Frequency of Quality Control Activities (refer to Appendix 3)

21.1.1 The Initial Calibration Verification (ICV) is performed following each calibration. The Continuing Calibration Verification (CCV) is performed following every ten or fewer samples. Any quality control samples excluding the CCV and CCB are counted as samples no more than two hours should pass between analyzing successive CCVs that bracket reportable data.

21.1.2 An Initial Calibration Blank (ICB) is performed immediately following the ICV, and Continuing Calibration Blanks (CCB) must follow each CCV.

21.1.3 The PQL standard is analyzed after each calibration and recommended for analysis at least every 10 samples, between the CCV and CCB analyses for SW-846 Method 6010C. Method 6010C requires analysis at the end of every batch and only recommends analysis every 10 samples. This standard may also be labeled as a CRDL standard.

21.1.4 An Interference Check Standard is analyzed after the calibration. For 200.7 analysis, an ICSA and ICSAB must be performed before the final CCV, CCB. Interference check standards are analyzed at least every 8 hours per Method 200.7.

21.1.5 A method blank (MB) is performed for each batch of twenty or fewer samples, or more frequently per client contract requirement.

21.1.6 A matrix spike (MS) and a sample duplicate (DUP), or a matrix spike (MS) and a matrix spike duplicate (MSD) are analyzed for each batch of 20 or fewer samples or per client or method requirements. For a matrix spike recovery to be applicable the sample value may not exceed four times the nominal concentration of the spike.

21.1.7 A laboratory control sample (LCS) is analyzed with each batch of twenty or fewer samples. A LCS Duplicate (LCSD) is performed at the same frequency as the LCS when required by a specific program or client.

21.1.8 Serial dilutions are analyzed to indicate the presence or absence of interferences. The analyte concentrations must be greater than 50 times the detection limit for 200.7, 6010B, and 6010C. The analyte concentrations must be greater than 25 times the reporting limit for 6010D for a serial dilution to be applicable. The serial dilution is generally performed at a 5x dilution of the test sample or requested by client contracts.

21.1.9 A serial dilution will be performed for each SDG of up to twenty samples.

21.1.10 When performing 6010C and 6010D analyses, a post-spike must be performed on the original sample when the matrix spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added. Otherwise, post spikes are analyzed per client request.

21.1.11 Linear Range standards are analyzed after each calibration. These standards are labeled LR1 and LR2.

21.2 Acceptance Limits (refer to Appendix 4)

ICV and CCV results must fall between 90% to 110% of the true values for work under EPA SW-846 Method 6010B/6010C/6010D. ICV must be between 95% to 105% of the true value for work under EPA Method 200.7. The ICV/CCV Relative Standard Deviation (RSD) (minimum of 2 replicates) must be < 5% for all methods, **NOTE:** The ICV is a second source standard and may be used as the CCV to show calibration verification.

21.2.1 ICV and/or CCV failure requires a recalibration of the instrument and/or repreparation of standard solutions. Samples bracketed by calibration verifications that are not acceptable for required analytes must be reanalyzed. An ICV or CCV that has failed may be reanalyzed provided there is an attributable cause known to have affected the check standard only and not the previous samples. Examples of an acceptable cause may be a sample tip out of solution during analysis, an incorrectly prepared CCV, or obvious carryover in the CCV from a very high sample immediately prior to the CCV. If a CCV is reanalyzed, the data must be lined through, initialed and dated, and the reason for the reanalysis must be documented on the raw data. In addition, corrective action should be taken to eliminate the cause of the initial CCV failure to prevent future occurrence.

21.2.2 The ICB and CCB results for the various methods are displayed in Appendix 4. ICB and CCB failure requires recalibration of the instrument and/or repreparation of the calibration blank. When analyzing under SW-846, a CCB may be accepted above the PQL level under two conditions: 1) the CCB is acceptable if the sample value is below the PQL and 2) the CCB is acceptable if the level of analyte in the CCB is less than 1/10 the analyte value in the lowest reported sample. For DoD QSM, the ICB and CCB must have an absolute value less than ½ LOQ or less than 10x value of the samples bracketed by the blank.

21.2.3 The PQL recovery requirements are displayed in Appendix 4. This includes the low level continuing calibration verification standard analyzed every 10 samples or at the end of the analytical batch. For all methods, sample results can be evaluated for reporting if they are at least 2x the PQL for a

given analyte. For 6010B or 200.7 analysis no specific acceptance criteria have been established for the PQL, however an unofficial range of 70% to 130% has been set for guidance purposes. PQL failure should be evaluated, but no action is required if the results are outside of the 70% to 130% range for all methods unless otherwise specified by the client. DoD QSM analysis must have passing PQL recoveries or the instrument needs recalibration. Further failures need to be communicated to the client for guidance.

21.2.4 The analytes for the ICS-AB results typically must fall between 80% and 120% of the true value. The requirements for analytes for the ICS-A are displayed in Appendix 4.

21.2.5 Method blank results should be less than the PQL but no less than the negative PQL or ± ½ LOQ for DOD QSM. Additionally, the method blank may exceed the PQL provided that the blank value is insignificant relative to the lowest value of the samples in the batch. Specific method requirements are displayed in Appendix 4. All failures require reprep of the samples in the batch..

21.2.6 The LCS and LCSD are used for indicators of sample digestion validity. LCS and LCSD recoveries and RPDs must fall within process control limits as established by Statistical Process Control, manufacturer's certification, or method requirements (See Appendix 4). LCS and/or LCS duplicate results outside of established acceptance limits require the batch to be redigested and reanalyzed.

21.2.7 Matrix spike and matrix spike duplicates recoveries are applicable to those sample values that do not exceed four times the nominal concentration of the spike. Recoveries of one or more of the matrix spikes that fall outside recommended ranges (as displayed in Appendix 4) may indicate an improper sample digestion, sample in homogeneity, or matrix interference.

21.2.8 The relative percent difference (RPD) between an MS and MSD or a sample and DUP must fall within ≤ 20% if the analyte level is sufficiently high (5x the PQL). See Appendix 4 for method requirements for the DUP.

21.2.9 Serial dilution results that agree within the method limits displayed in Appendix 4 suggest the absence of interference. Failures of a serial dilution should be noted, but are not considered pass/fail criteria. A criterion of greater than 50 times the MDL may be requested by some clients. The criterion of greater than 50 times the LOQ is used for DoD QSM.

21.2.10 The LR1 and LR2 standards must fall within 90-110% of the known value. If any analyte fails to meet the 10% criteria, the working linear range is then defined as the high standard concentration used in the calibration curve.

21.2.11 Post spike recovery requirements are displayed in Appendix 4. Acceptable recoveries suggest the absence of interferences.

21.3 Out-of-Control situations

21.3.1 ICS failure requires that the interferences be corrected, by recalculation, of Interelement Correction Factors or selection of background correction factors so that the ICS can be read within the required limits before samples are analyzed. ICS failure at the end of an analysis period will require that the samples run for the affected analyte(s) during that period to be reanalyzed

21.3.2 Matrix spikes, duplicates, post spikes, and spike duplicates are used only as indicators of method effectiveness on that sample and will not be used as acceptability criteria for the process, unless this is a client-specific requirement.

21.3.3 When analytical results suggest the presence of interference, the serial dilution test discussed in Section 21.1.8 must be employed.

21.3.4 The intensity and percent recovery of the internal standard are monitored per sample. There is no acceptance criterion per SW-846 and 200.7; however, the laboratory has adopted a ± 50% recovery criterion. If the internal standard fails to meet the criteria, reprocess the data using a different internal standard if available or dilute the sample within acceptable parameters.

21.4 Analytical data are evaluated for conformance with the requirements stated in Section 21.2 by the analyst during and/or after the analysis but before the data are entered into AlphaLIMS. Data may be accepted or rejected by the analyst at this point or by the data reviewer(s) as stated in Section 22.

21.5 Corrective actions taken for data not conforming to the requirements in Section 21.2 are stated in Section 21.3. If these corrective actions can be taken by the analyst prior to the acceptance of the data, then no nonconformance documentation is required. However, if these corrective actions include redigestion of the batch or sample and if the data have already been accepted, then a nonconformance/ corrective action report should be completed. This report includes the date, person requesting the action, sample(s) or batch(es) affected, and action requested, all provided by the requester. The person taking the action will provide any pertinent comments, a signature, and the date the action is completed. The disposition of the nonconformance will then be verified by the Group Leader and Quality Assurance Officer if pertinent. These reports will be kept on file in AlphaLIMS. Refer to GL-QS-E-004 for Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items.

22.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

22.1 The AlphaLIMS Data Report and the original batch sheet are provided to the ICP reviewer.

22.2 A knowledgeable person other than the originating analyst shall review the data within the day or specified time limit. When this review is completed and all of the data are found to be acceptable, the reviewer signs and dates the batch data report. If the reviewer determines that the reviewed data are not acceptable and requires additional work or correction, they are returned to the Group Leader or representative with an appropriate explanation.

22.3 Listed below are the data review responsibilities at the Analyst, Peer Review and Validator levels:

22.3.1 Analyst Review is performed by the analyst who generated the data before the data are submitted for entry into AlphaLIMS. The analyst uploads the data to AlphaLIMS and completes the batch data report.

22.3.2 Peer Analyst Review is performed by an individual who did not perform the analysis but is familiar with the analytical method used and the reporting requirements. This person reviews the complete data report after all data are entered and ensures that any data entry corrections are made before the data are approved, and then signs the batch data report. If the data do not meet the necessary quality requirements and need further analysis, they are returned to the analyst.

22.3.3 Data Validation: For data requiring forms packages, the forms are generated per contract requirements and validated per GL-MA-E-017.

22.4 Specific items that are reviewed at each level include the following:

22.4.1 Analyst Review: Before data are submitted for entry into AlphaLIMS.

22.4.1.1 All analyses in the batch are completed with explanations of exceptions.

22.4.1.2 Any corrections and comments on the data are properly initialed and dated.

22.4.1.3 Proper standard identification numbers appear on the runlog to ensure traceability from the data to original source standards.

22.4.1.4 Data acceptance limit criteria identified in Section 21.2 and Appendix 4 are met or an explanation given.

22.4.2 Peer Analyst Review: before Data are statused to DONE in AlphaLIMS:

22.4.2.1 All data are complete and accurate in the AlphaLIMS Data Report.

22.4.2.2 Any exceptions or shortcomings have been sufficiently explained or corrected.

22.4.2.3 Data are reported in the proper units, or an explanation is given.

22.4.2.4 Prep factor and dilution calculations by AlphaLIMS are present in the data report and AlphaLIMS calculations are correct.

22.4.2.5 LCS and Spike Recoveries and RPD calculations by AlphaLIMS are correct and are within control limits.

22.4.3 Validation: Before data are reported out of the lab:

22.4.3.1 Analyst and Peer Level reviews have been completed and any corrections or comments made.

22.4.3.2 Preparation data have been entered and reviewed by a peer.

22.4.3.3 Analytical data are present for all analyses.

22.4.3.4 Weight/Volume, dilution, spike recovery, RPD, and LCS recoveries appear to be calculated correctly.

22.4.3.5 All forms, raw data, and log sheets requested by the client are present.

22.4.3.6 Results are accurate on forms (refer to GL-MA-E-017).

22.5 Documentation and review process are reflected in the Data Review Flow Chart in Appendix 1.

23.0 DATA REPORT

23.1 To report data after the initial review process has been completed:

23.1.1 Enter the AlphaLIMS program through GEL home page and click on AlphaLIMS application.

23.1.2 Click on MAINTAIN BATCHES and type in the queue at SELECT A QUEUE (ICP for the analytical).

23.1.3 Select batch number at SAMPLE ID column, and the run status will show whether data are ready to calculate.

23.1.4 When data are ready to calculate, click on CAL.

23.1.5 Click on SAVE to save the data.

23.1.6 Send data to review at STATUS column for quality purposes.

23.1.7 Print data, and initial and date for final review.

23.2 The Final Reviewer is responsible for changing the batch status to DONE in AlphaLIMS and initialing and dating the data report.

24.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

25.0 LABORATORY WASTE HANDLING AND DISPOSAL

All Laboratory wastes are handled and disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

26.0 METHOD VARIATION

SW-846 requires that ICB and CCB results must agree within three standard deviations of the mean blank value. GEL uses the absolute value of the PQL for evaluating ICB and CCB results. The acceptance limits are further discussed in Appendix 4.

27.0 REFERENCES

27.1 Perkin Elmer Optima 7300DV, 8300DV and AVIO500 Operator's Manual

27.2 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1A, SW-846, 3rd Edition, Nov. 1986. Method 6010B, "Inductively Coupled Plasma-Atomic Emission Spectroscopy," Rev 2, Sept. 1994. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

27.3 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1A, SW-846, 3rd Edition, Nov. 1986. Method 6010C, "Inductively Coupled Plasma-Atomic Emission Spectroscopy," Rev 3, February. 2007. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

27.4 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1A, SW-846, Update V, Revision 4, Method 6010D "Inductively Coupled Plasma - Optical Emission Spectrometry"

27.5 EPA Method 200.7, Revision 4.4.

27.6 Department of Defense (DoD), Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, Version DoD 5.1 and DOE 3.1, January 2017.

28.0 HISTORY

Revision 31: Updated to remove retired and add new instrumentation.

Revision 30: Removed readback statements for methods no longer performed, clarified should vs. must in several sections.

Revision 29: Clarification of DOD QSM criteria and method acceptance criteria.

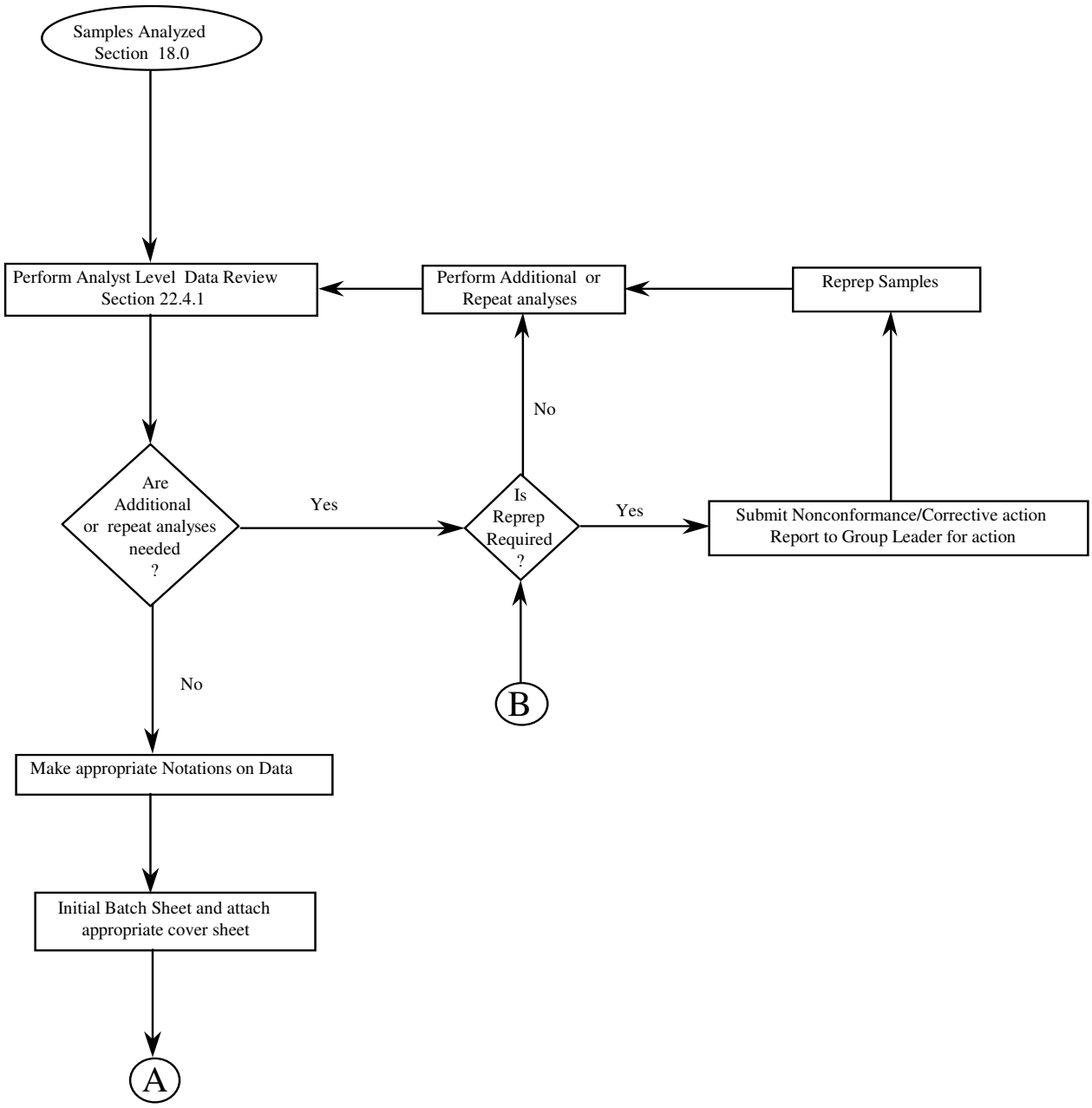
Revision 28: Add statements to clarify the IEC verifications.

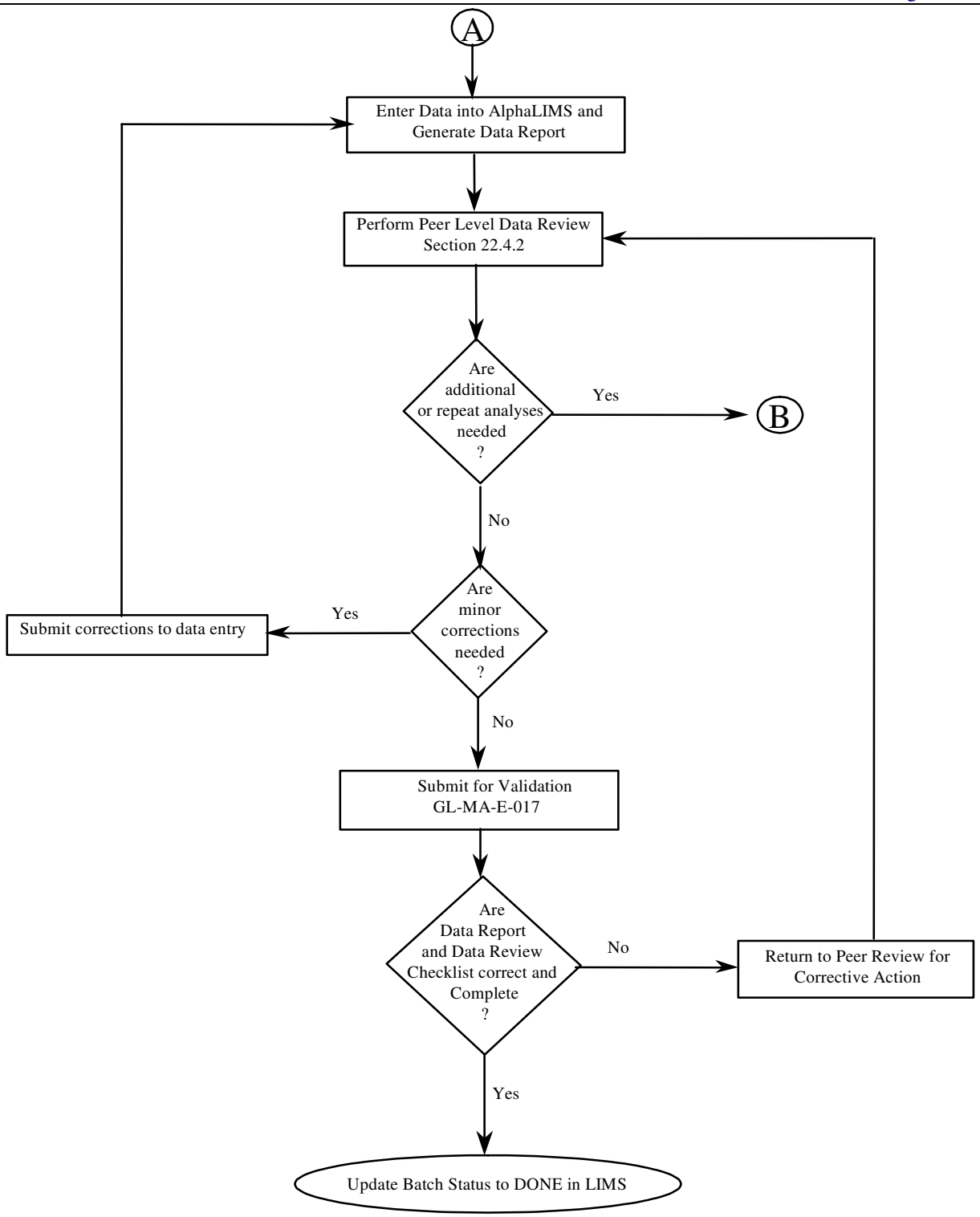
Revision 27: Added method requirement for IEC verification performed on a quarterly basis.

APPENDIX 1: PRODUCTION FLOW CHART

(For Illustrative Purposes Only)

Data Review Flow Chart




A
Enter Data into AlphaLIMS and Generate Data Report
Perform Peer Level Data Review Section 22.4.2
Are additional or repeat analyses needed ?
Yes
B
No
Are minor corrections needed ?
Yes
Submit corrections to data entry
No
Submit for Validation GL-MA-E-017
Are Data Report and Data Review Checklist correct and Complete ?
No
Return to Peer Review for Corrective Action
Yes
Update Batch Status to DONE in LIMS

APPENDIX 2: CALIBRATION STANDARDS FOR TRACE

(For Illustrative Purposes Only)

S0 reagent blank (3% HCl / 1% HNO_3)

S0.1 0.1 ppm (100 ppb) As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Sr, Tl, U, V, Zn Sb, Mo, Ag, Sn, Ti

0.2 ppm (200 ppb) S

0.5 ppm (500 ppb) Si, P

1 ppm (1000 ppb) Al, Ca, Mg, K, Na

S0.5 0.5 ppm (500 ppb) As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Sr, Tl, U, V, Zn Sb, Mo, Ag, Sn, Ti

1 ppm (1000 ppb) S

2.5 ppm (2500 ppb) Si, P

5 ppm (5000 ppb) Al, Ca, Mg, K

SCAL 1 ppm (1000 ppb) As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Sr, Tl, U, V, Zn Sb, Mo, Ag, Sn, Ti

2 ppm (2000 ppb) S

5 ppm (5000 ppb) Si, P

10 ppm (10000 ppb) Al, Ca, Mg, K, Na

S10 50 ppm (50000 ppb) Ca, Al, Mg
20 ppm (20000 ppb) Fe, Na

(Analytes and concentrations may change with further method development)

APPENDIX 3: FREQUENCY OF QUALITY CONTROL ACTIVITIES

(For Illustrative Purposes Only)
Frequency of Quality Control Activities

Method/ Frequency	**SW-846 6010B and 6010D**	**EPA 200.7**	**SW-846 6010C**
Linear Range Std	Per calibration	Per calibration	Per calibration
ICV	Per calibration	Per calibration	Per calibration
ICB	Per calibration	Per calibration	Per calibration
PQL/CRI (CLP)	Per calibration	Per calibration	Per calibration and at end of each analytical batch.
ICSA	Per calibration	Per calibration; every 8 hours after or end of analytical run	Per calibration
ICSAB	Per calibration	Per calibration; every 8 hours after or end of analytical run	Per calibration
CCV	Every 10 instrument runs	Every 10 instrument runs	Every 10 instrument runs
CCB	Every 10 instrument runs	Every 10 instrument runs	Every 10 instrument runs
Method Blank	5% or per batch	5% or per batch	5% or per batch
LCS - liquid LCS - soil	5% or per batch	5% or per batch	5% or per batch
Matrix Spikes	5% or per request	10% or per request	5% or per request
Sample Duplicates	5% or per request	5% or per request	5% or per request
Serial Dilutions	5% or per request	5% or per request	5% or per request
Matrix Spike Duplicates	5% or per request	10% or per request	5% or per request
Post Digestion Spikes	5% or per request	5% or per request	5% or per request

APPENDIX 4: ACCEPTANCE LIMITS

Method/ Acceptance Criteria	SW-846 6010B	EPA 200.7	DOD QSM Version 5.1	SW-846 6010C	SW-846 6010D
Linear Range Std	± 10% of true value	± 10% of true value	± 10% of the true value	± 10% of true value	± 10% of true value
ICV	90% - 110%	95% - 105%	90%-110%	90% - 110%	90% - 110%
ICB	< absolute value of PQL	< absolute value of PQL *	< ± ½ LOQ	< absolute value of PQL	<absolute value of ½ PQL
PQL	70% - 130% advisory limits only	70% - 130% advisory limits only	80%-120% or investigate and recalibrate	70% - 130% or investigate and recalibrate	80%-120% or investigate and recalibrate
ICSA	80-120% for major components, ±2XPQL for non-spiked	80-120% for major components, ±2XPQL for non-spiked	80%-120% for major components, < ± ½ LOQ for non-spiked	80-120% for major components, ±2XPQL for non-spiked	80%-120% for major components, ±PQL for non-spiked
ICSAB	80%-120%	80%-120% (may be requested)	80%-120%	80%-120%	Not Required
CCV	90% - 110%	90% - 110%	90%-110%	90% - 110%	90% - 110%
CCB	± PQL	±PQL *	± ½ LOQ	± PQL	± PQL
Method Blank	± PQL	± PQL *	± ½ LOQ , except for Al, Fe, Ca, Mg, Na and K	± PQL	± ½ PQL
LCS - liquid LCS - soil	80% - 120% current SPC limits	85% - 115% current SPC limits	Use QSM Specified limits	80% - 120% current SPC limits	80% - 120% current SPC limits
Matrix Spikes	75% - 125%, when applicable	75% - 125%, when applicable	Use QSM Specified limits	75% - 125%, when applicable	75% - 125%, when applicable
Sample Duplicates	0% - 20% when greater than 5X PQL, +/-PQL when less than 5X PQL	0% - 20% when greater than 5X PQL, +/-PQL when less than 5X PQL	0% - 20% when greater than 5X PQL, +/-PQL when less than 5X PQL	0% - 20% when greater than 5X PQL, +/-PQL when less than 5X PQL	0% - 20% when greater than 5X PQL, +/-PQL when less than 5X PQL
Serial Dilutions	0% - 10% of initial raw value, when applicable	0% - 10% of initial raw value, when applicable	0% - 10% of initial raw value, when > 50X LOQ	0% - 10% of initial raw value, when applicable	0% - 20% of initial raw value, when applicable
Post Digestion Spikes	75%-125%, when applicable	75%-125%, when applicable	80%-120%	80%-120%, for all	75%-125%; when applicable
Internal Standards	50%-150%, then evaluate dilution	50%-150%, then evaluate dilution	50%-150%, then evaluate dilution	50%-150%, then evaluate dilution	50%-150%, then evaluate dilution
Matrix Spike Duplicate	0% - 20%	0% - 20%	0% - 20%	0% - 20%	0% - 20%

*North samples require ½ the PQL

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

DETERMINATION OF METALS BY ICP-MS

APPLICABLE TO METHODS:
EPA Method 200.8
EPA SW-846 Method 6020
EPA SW-846 Method 6020A
EPA SW-846 Method 6020B

(GL-MA-E-014 REVISION 33)

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1.0 STANDARD OPERATING PROCEDURE FOR DETERMINATION OF METALS BY ICP-MS

2.0 METHOD CODES

2.1 EPA Method 200.8

2.2 EPA SW-846 Method 6020

2.3 EPA SW-846 Method 6020A

2.4 EPA SW-846 Method 6020B

3.0 METHOD OBJECTIVE AND PURPOSE

This standard operating procedure (SOP) describes the determination of metals using a Perkin Elmer ICP-MS Model ELAN 9000 Spectrometer and Perkin Elmer ICP-MS NexION 300x and 350x. Prior to analysis, samples must be digested using appropriate sample preparation methods (such as Methods 3005, 3010, 3050, or 200.2) and other applicable requests.

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 Refer to Appendix 3 for analyte lists and masses.

4.2 Applicable Matrices: These methods are applicable to the determinations of any of the analytes listed above for various matrices including waters, oils, soils, sludges, biological tissues, Toxicity Characteristic Leaching Procedure (TCLP) extracts and other more unusual types of sample which are generally classified as a miscellaneous matrix.

4.3 General Method Summary: After the samples are prepared in accordance with the sample preparation SOP, they are analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) as follows:

4.3.1 The instrument is calibrated with a minimum of two calibration points for each element to be analyzed. The points consist of a calibration blank solution to define the lower calibration point and at least one standard calibration solution at the analyte concentrations to define the higher calibration point(s). A correlation coefficient of 0.995 or better (0.998 or better for SW-846 Method 6020A) is required for each analyte if multiple standards are used or the instrument is recalibrated for the analyte of interest.

4.3.2 Prepared client samples and numerous check standards and quality control samples, identified in Section 22.1 are then analyzed. The check standards and quality control samples are used to determine the quality and acceptability of the analytical data.

4.3.3 Continuing Calibration Verification standards (CCV) and Continuing Calibration Blanks (CCB) are analyzed a minimum of every 10 samples to ensure that the instrument is continuing to perform correctly. For 6020A, low level continuing calibration verification standards are analyzed in conjunction with the CCVs and CCBs.

4.4 Method Codes: Analyses must conform to EPA Method 200.8, SW-846 Method 6020, SW-846 Method 6020A, SW-846 6020B and/or customer contract specifications.

4.5 Radiochemistry conversion calculations for the uranium isotopes are included in Appendix 4.

5.0 METHOD SCOPE AND PERFORMANCE CHARACTERISTICS

5.1 Calibration Range: The range of concentrations between the calibration blank, typically 0, and that of the highest calibration standard for each analyte. Calibration standards vary according to method and equipment. A minimum of two, a blank and value standard, are required.

5.2 Linear Dynamic Range standards (LRS) are analyzed with each calibration. The linear calibration range that may be used for the analysis of samples should be judged by the analyst from the resulting data. The instrument is calibrated. The target linear range should be prepared and analyzed. The LRS results must fall within ± 10% of the target value. This LRS value is entered into the instrument's software. Any hits below this value will be valid. Hits at or above this value will be flagged by the system and must be diluted to fall within the linear dynamic range. If a linear range standard is not used for a specific calibration, the highest calibration standard becomes the upper limit of reporting.

5.3 Instrument Detection Limits (IDLs) are 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 are determined by the mean of blank results 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 should be 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 at a frequency designated by the project.

5.4 Method Detection Limit (MDL) studies for each analyte are performed and/or verified at least annually. These studies are conducted and calculated in accordance with SW-846, Chapter 1, paragraph 5.0, and GL-LB-E-001 for the Determination of Method Detection Limits. The relevant quantitation limits are established based on the most current MDL study. The current MDLs are maintained and can be found in the AlphaLIMS database. For 6020B mean recovery for the seven replicates is ± 35% of the known value with RSD of ≤ 20%.

5.5 Method Precision: To assure analytical precision of methods used, Laboratory Control Samples (LCS) are analyzed with each batch. LCS duplicates are analyzed with each batch when requested.

5.6 Method Bias (Accuracy) is determined by calculating recoveries of LCS of a similar matrix.

5.7 If uncertainty and total propagated uncertainty measurements are needed, they may be determined using GL-QS-E-014 for Quality Assurance Measurement Calculations and Processes.

6.0 DEFINITIONS

6.1 Continuing Calibration Blank (CCB): An aliquot of reagent water or other blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

6.2 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The CCV is analyzed exactly like a sample, periodically throughout the run sequence. Its purpose is to determine whether the analytical sequence is in control during the sample analysis. It may be prepared from the same source as the calibration standards, and is usually of varied concentrations.

6.3 Contract Required Detection Limit (CRDL): Minimum level of detection acceptable under the client project requirements.

6.4 Correlation Coefficient: A number (r) that indicates the degree of dependence between two variables (concentration-absorbance). The more dependent they are, the closer the value to one. Determined on the basis of the least squares line.

6.5 Data Qualifiers: The following qualifiers should be used in order to identify analytical situations that might need additional information stated in narrative before the release of the data.

U - Non-Detect. Below the Instrument or Method Detection Limit (depending upon specific project requirements)

B - Sample concentration value is between the MDL (or IDL) and the CRDL or analyte was detected in the Method Blank (Client Specific)

J - Sample concentration is between the MDL (or IDL) and the CRDL-client specific qualifier.

Blank - Concentration value is above the CRDL

* - An RPD value in the duplicate sample is out of criteria

N - A percent recovery value in the spike sample is out of criteria

E - A percent difference in the serial dilution sample is out of criteria because of the presence interference.

6.6 Initial Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination.

6.7 Initial Calibration Verification (ICV): A solution of method analytes of known concentrations. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

6.8 Instrument Performance Check Solution (IPC): A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

6.9 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

6.10 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

6.11 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

6.12 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified measured and reported with 99% confidence that the analyte concentration is greater than zero.

6.13 Spike (Matrix Spike or Post Spike): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or PS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or PS corrected for background concentrations.

6.14 Limit of Detection (LOD): An analyte, method and matrix specific estimate of the minimum amount of a substance that can be reliably detected. GEL has established LOD = 2 x MDL.

6.15 Limit of Quantitation (LOQ): An analyte, method and matrix specific estimate of the minimum amount of a substance that can be reported with a specific level of confidence. The LOQ is set at or above the concentration of the lowest initial calibration standard. The laboratory must empirically demonstrate precision and bias at the LOQ. The LOQ and associated precision and bias must meet client requirements and must be reported. GEL uses the following guidance (LOD < LOQ):

When LOD < PQL, PQL = LOQ

When LOD > PQL, LOQ is raised to next lowest calibration standard.

6.16 Practical Quantitation Limit (PQL): The PQL is typically at or above the lowest point on an acceptable initial calibration curve. It may also be determined by multiplying the MDL by approximately 2 to 10. Concentrations of a target analyte

determined to be greater than its PQL are defined as quantitative results. This limit is not used in DoD ELAP reporting.

6.17 10% Frequency: A frequency specification during an analytical sequence allowing for not more than 10 analytical samples between required calibration verification measurement, as specified by the EPA methodology.

6.18 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

7.0 INTERFERENCES TO THE METHOD

7.1 Chemical interferences are minimal in ICP-MS Spectroscopy because the extremely high energy of the plasma breaks nearly all the chemical bonds. However, ICP-MS analysis is subject to the following three types of interferences:

7.1.1 Physical interferences are those physical properties of a sample solution that prevent their introduction to the plasma with efficiency equal to that of the calibration standards. This type of interference can be corrected via the bias correction calculation in SW-846, Chapter 1, paragraph 5.0, through the use of an internal standard in accordance with the instrument operating manual or by diluting the sample in reagent blank solution until the percent recovery falls with method guidelines.

7.1.2 Isobaric elemental interferences are caused by isotopes of different elements that form singly or doubly charged ions of the same nominal mass-to-charge ratio and that cannot be resolved by the mass spectrometer. If analytical isotopes are selected that may have an isobaric interference, then all data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest.

7.1.3 Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom that have the same nominal mass-to-charge ratio as the isotope of interest, and that cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified and are listed in Method 200.8, Table 2 together with the method elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes or sample prep procedures, appropriate corrections must be made to the data.

8.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

8.1 PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

8.2 WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

8.3 Sample digestates are not extremely volatile or spontaneously combustible, but they are normally acidic and should be handled with care. Small spills may generally be wiped up with paper towels that can be disposed of in the trash. Larger spills may require the use of a mop, and the mop head may have to be disposed of as potentially hazardous waste in accordance with the Laboratory Waste Management Plan (GL-LB-G-001). If the spilled digestates begin any obvious fuming or reacting, pour a generous amount of the acid neutralizer, which is located in each lab, onto the spill before attempting to clean it up.

8.3.1 Gloves should be worn to avoid skin contact with digestate during clean-up.

8.3.2 Eye protection is required when handling samples and an eyewash station is located in each analysis lab.

8.3.3 Do not persist in cleaning up a spill in the presence of strong fumes. Move out of the area, try to isolate the area and notify your supervisor immediately.

8.4 Handling radioactive samples requires the use of gloves, a lab coat or an apron in addition to eye protection. Refer to GL-RAD-S-004 for Radioactive Material Handling

8.5 These instruments use high voltage electricity and therefore, should be shut completely down any time electronic components may be exposed to personnel or any liquids.

8.6 Wear eye protection with side shields while performing procedures in the lab.

8.7 All chemicals and samples should be treated as potential health hazards, and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents are maintained in the laboratory. Individual sample MSDS forms provided by the clients are kept in Login.

8.8 Personal protective equipment

8.8.1 Gloves are required when handling the chemicals in this procedure.

8.8.2 Work under a hood when using concentrated acids.

8.9 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

8.9.1 Wear a lab coat when working with radioactive samples.

8.9.2 Prohibit admittance to immediate work area.

8.9.3 Protect counter tops with counter paper or work from radioactive sample handling trays.

8.9.4 Post signs indicating radioactive samples are in the area.

8.9.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the nearest swipe count box.

8.9.6 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

8.10 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.10.1 Segregate solid wastes from liquid wastes in the satellite area containers.

8.10.2 Segregate oil wastes from water-soluble wastes in the satellite area containers

8.11 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

8.12 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

8.13 Fire escape routes are posted in the lab; all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

9.0 CAUTION WARNINGS

9.1 Because they can be health hazards, the exhaust gases from the plasma and vacuum systems must be eliminated through the laboratory's ventilation duct, which is attached to the instrument's exhaust vent. If inadequate ventilation occurs, pump-fluid vapor, ozone, and other toxic products of combustion can accumulate in the laboratory and cause bodily harm. Hydrofluoric acid (HF) fumes, if inhaled, extensively burn lung tissue. Ensure that the exhaust system established at installation continues to operate effectively.

9.2 Prepare sample and transfer acids using a hood to avoid fumes.

9.3 Store and prepare sample away from the instrument to minimize corrosion.

9.4 Clean up any spills quickly.

9.5 The drain vessel contains the spray chamber's effluent, which can be toxic. Corrosion of the vessel and connecting tube can result in leaks that damage the instrument or cause bodily harm.

9.5.1 Use the capped plastic drain vessel that was provided with the instrument. Never use glass.

9.5.2 Place the drain vessel on the instrument table below the peristaltic pump where the container is easy to check.

9.5.3 Check the drain vessel frequently. Empty it before it is three-fourths full.

9.5.4 Check the tubing and vessel for deterioration. If the tubing becomes brittle or cracked, replace it. Organic solvents cause more rapid deterioration than aqueous solutions.

9.6 The torch and interface remain hot after the plasma is turned off. Do not touch the torch box or interface cones for 10 minutes after the plasma has been shut off.

9.7 High voltages and radio frequencies are potential hazards of the ICP-MS. Shut the instrument down completely before removing any of the outside panels (to clean air filters, replace a fuse, etc.).

9.8 When changing the rotary pump oil, remember that the pump oil may be hot. The oil can cause a burn if allowed to contact the skin.

10.0 APPARATUS, MATERIALS, REAGENTS, EQUIPMENT, AND INSTRUMENTS

10.1 Apparatus and Equipment

10.1.1 Replacement special glass parts for the ICP-MS such as quartz torch bodies, injector tips and spray chambers may be ordered from a qualified vendor through the GEL Purchasing Agent.

10.1.2 Replacement ICP-MS interface parts such as sampling cones, skimmer cones and ion-optics can be purchased from a qualified vendor through the GEL Purchasing Agent.

10.1.3 Consumable materials such as tubing are often attainable from various scientific product companies. The GEL Purchasing Agent can help to find the best prices. These items may also be ordered from the instrument manufacturer if necessary. All orders must be placed through the GEL Purchasing Agent.

10.2 Reagents, Chemicals, and Standards

10.2.1 Reagents: Refer to Reagent Logbook

10.2.2 Standards: Refer to GL-LB-E-007 for Laboratory Standards

10.2.3 Other Chemicals: Additional compounds, surfactants, oils, cleaning agents, etc., may be routinely ordered through the GEL Purchasing Agent.

10.3 Instrumentation

10.3.1 Perkin Elmer ICP-MS ELAN Model 9000 with PC monitor and printer.

10.3.2 Perkin Elmer ICP-MS NexION 300x and 350x with PC, monitor and printer

10.3.3 ESI SC4 DX

10.3.4 CETAC Model ASX-510 Autosampler with accessory autodiluter (PE 9000).

10.3.5 Neslab CFT75 recirculating bath or equivalent provides cooling to the ICP-MS.

11.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

11.1 Aqueous samples should be preserved with nitric acid to a pH of < 2 prior to receipt by the analyst. Solid samples should be kept at 0° ≤ 6° C prior to digestion.

11.2 Refer to GL-SR-E-001 for Sample Receipt, Login and Storage.

12.0 SAMPLE PREPARATION TECHNIQUES

12.1 All samples except drinking water with Turbidity < 1 NTU and samples specifically exempted by contract, are prepared in accordance with the following SOPs:

12.1.1 GL-MA-E-016 for Sample Preparation for Total Recoverable Elements by EPA Method 200.2 (USEPA Method 200.2)

12.1.2 GL-MA-E-006 for Acid Digestion of Total Recoverable or Dissolved Metals in Surface and Groundwater Samples for Analysis by ICP or ICP-MS (USEPA SW-846 Method 3005A)

12.1.3 GL-MA-E-008 for Acid Digestion of Total Metals in Aqueous Samples and Extracts for Analysis by ICP or ICP-MS (USEPA SW-846 Method 3010A)

12.1.4 GL-MA-E-009 for Acid Digestion of Sediments, Sludges and Soils (USEPA SW-846 Method 3050B)

12.1.5 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM, Version 5.1, January 2017 and DOE QSAS Version 3.1 January 2017.

12.2 Additional filtration may be required to prevent clogging of sample introduction system.

12.3 All sample preparation records are stored in AlphaLIMS.

12.4 Sample spills should be handled as stated in Section 8.3.

13.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

13.1 Routine Preventative and Special Operational (Failure)

13.2 Routine Preventative Maintenance (PM) Procedures are done as follows:

Frequency	Procedure
When Needed	Clean nebulizer tip after use. Replace peripump sample introduction tubing. Change pump hoses on drain systems. Check drain waste collection containers, and empty as necessary. Check Neslab water level and add water if required. Clean/replace interface cones. Clean/replace nebulizer. Clean/replace torch. Check/replace water filter.
Quarterly	Change oil in interface rotary pump (or as needed). Clean ion lenses 4-6 months (or as needed).
6 Months	Clean air filters.
12 months	Change pump oil in backing rotary pump. Evaluate/replace EM (electron multiplier)

13.3 Non-Routine Maintenance Procedures (Special, Operational or Failure Mode Maintenance)

13.3.1 If the instrument will not function properly see the trouble shooting section in the appropriate Maintenance Manual.

13.3.2 If the analyst is unable to determine cause/fix instrument, the GEL Service Engineer is called, and if needed, the manufacturer's customer support number may be found in the owner's maintenance manuals.

13.4 Refer to ICP-MS Maintenance Logbook for routine records. Service call records are also available.

14.0 PREPARATION OF STANDARD SOLUTION AND QUALITY CONTROL SAMPLES

14.1 Source standards records are recorded in AlphaLIMS.

14.2 Recommended Suppliers: Refer to source log and use Approved Vendors List maintained in Procurement.

14.3 Standards are receipted, labeled, prepared and stored in accordance with the GL-LB-E-007 for Laboratory Standards Documentation.

14.4 Acid Screens and ICSA Standard Screens are performed prior to use.

14.4.1 Prior to use, new lots of nitric acid, hydrochloric acid, and 30% hydrogen peroxide are screened to test for contamination. If an analyte is detected above ½ RL, the acid is re-screened. If the re-screen is also ½ RL, the resulting lot is transferred to another area of the lab where this low-level contamination doesn't affect the analysis. New lots are then screened until a suitable lot is obtained. Copies of the acid screens by lot number are kep on file. The following concentrations are submitted for analysis.

14.4.1.1 3% solution of 30% hydrogen peroxide (per SW-846 3050B prep volumes)

14.4.1.2 10% solution of nitric acid (per SW-846 3050B prep volumes)

14.4.1.3 5% solution of hydrochloric acid (per SW-846 3010A prep volumes)

14.4.1.4 20% solution of hydrochloric acid is analyzed via ICP for Sulfur determination only (per SW-846 3050B prep volumes)

14.4.2 Prior to use, new lots of ICSA standards are screened to document low-level inherent concentrations of non-target analytes. Typically 20 analyses of the ICSA are averaged and the average concentration is then used to assess the ICSA and ICSAB interferent and recovery data.

15.0 INSTRUMENT CALIBRATION

15.1 Samples may be analyzed manually or automatically.

15.1.1 Tuning for each instrument is performed daily according to the following directions and criteria.

15.1.2 Aspirate a tuning solution consisting of 10 µg/L each of ^{9}Be, ^{24}Mg, ^{59}Co, ^{115}In and ^{208}Pb. Perform 5 replicates. Manufacturer's recommended tune criteria are as follows:

Parameter	Starting Point
^{9}Be	± 0.10 amu
^{24}Mg	± 0.10 amu
^{59}Co	± 0.10 amu
^{115}In	± 0.10 amu
^{208}Pb	± 0.10 amu
Ba^{++} net intensity mean	< 0.05 or 5%
CeO net intensity mean	< 0.03 or 3%
Be, Mg, Co, In, Pb net intensity RSD	< 5%
Resolution at 10% peak height	< 0.9 amu

15.1.3 Conduct additional tuning procedures as specified by client contract or other methodology.

15.1.4 If any of the preceding tune criteria does not meet the recommended requirements, investigate the problem, correct the situation, and reanalyze the tune sequence.

15.1.5 Standardization: Standardization is required on a daily basis.

15.2 Internal standards are used as appropriate for the analytes of interest. The internal standards are made in the appropriate acid and contain varying concentrations of such elements as ^{45}Sc, ^{74}Ge, ^{115}In, ^{175}Lu, and/or ^{181}Ta. The internal standard solution is mixed in-line with the sample stream using a dedicated channel of the peristaltic pump. Internal standards may be added at the time of analysis as an alternative to in-line mixing. Alternate internal standards may be used to meet client needs.

15.3 Calculations are described in the instrument manual.

15.4 Calibration standards vary according to method and equipment. A minimum of two, a blank and value standard, is required.

15.5 For required quality control standards refer to Section 21.0.

15.6 For continuing calibration requirements refer to Section 21.0.

15.7 For what to do when initial or continuing calibrations fail to meet requirements, refer to Section 21.0.

16.0 INSTRUMENT PERFORMANCE REQUIREMENTS

16.1 Before samples may be analyzed to generate reportable data, the instrument must have been tuned and calibrated. Also, the Initial Calibration Verification (ICV), which is prepared from an independent source, Initial Calibration Blank (ICB), the Reportable Detection Limit (CRDL), the Interference Check Standards (ICS-A, ICS-AB), and the Linear Range Standards (LRS) must meet the requirements stated in Section 21.2 for each analyte being reported, unless otherwise required by methodology, clients or contracts.

16.2 The instrument calibration and all continuing verification data is maintained in the printed hard copy file. The printouts are kept in chronological order by instrument. Recent files are in the metals laboratory; older records are archived in short or long-term storage.

17.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

17.1 Analyst training is conducted and certified in accordance with the GL-HR-E-002 for Employee Training.

17.2 Method performance is verified by the conductance of MDL studies in accordance with GL-LB-E-001 for The Determination of Method Detection Limits, and by the evaluation of LCS and LCS duplicates for each batch of samples.

18.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

18.1 All samples are introduced in a set measured quantity, via a peristaltic pump, through a nebulizer into a spray chamber and carried with argon gas through the Radio Frequency (RF) field to generate analyte ions that are selected and measured by the quadruple mass spectrometer.

18.2 Run Sequence

18.2.1 Instrument Calibration executed in accordance with Section 16.

18.2.2 Initial Calibration Verification steps include:

18.2.2.1 ICV

18.2.2.2 ICB

18.2.2.3 CRDL (low level ICV for 6020A)

18.2.2.4 ICS-A

18.2.2.5 ICS-AB

18.2.2.6 CCV

18.2.2.7 CCB

18.2.2.8 LRS

18.2.2.9 CCV

18.2.2.10 CCB

18.2.3 Sample Run (10 samples or less)

18.2.4 Continuing Calibration Verification:

18.2.4.1 CCV

18.2.4.2 CRDL (for SW-846 Method 6020A only and analyzed at end of batch).

18.2.4.3 CCB

18.2.5 Repeat steps 18.2.3 and 18.2.4 until end of run or verification is out of specification. When the latter occurs, repeat step 18.2.1 and continue with steps 18.2.2 and 18.2.3.

18.2.6 Repeat steps 18.2.3 through 18.2.5 until the end of the run or verification is out of specification. When latter condition occurs, repeat 18.2.1 and continue sequentially through 18.2.7.

18.2.7 Final Verification Steps

18.2.7.1 ICS-A (if required)

18.2.7.2 ICS-AB (if required)

18.2.7.3 CCV

18.2.7.4 CRDL (for SW-846 Method 6020A only)

18.2.7.5 CCB

NOTE: Method 6020A only requires there to be a closing low level continuing calibration standard (CRDL). For ease of analysis, the CRDL standard can be analyzed every 10 samples.

18.3 For data storage refer to Section 24.1.

18.4 General operation of the instrument.

18.4.1 The Perkin Elmer ICP-MSs are inductively-coupled argon plasma mass spectrometers. The ICP-MS is capable of determining analytes from m/z =

6 (Li) through m/z = 238 (U). The operating software of the system is based on Microsoft Windows.

18.4.2 Set-up

18.4.2.1 Attach the nebulizer argon line to the quick-connect on the nebulizer's argon tube and ensure that it is tightly in place.

18.4.2.2 Attach the nebulizer and endcap to the spray chamber.

18.4.2.3 Attach sample pump tubing to the front peristaltic pump (various sizes may be used depending on need), and attach feed end to endcap.

18.4.2.4 If running manually, place the suction end of the sample tubing in acidified rinse water; otherwise attach it to the autosampler.

18.4.2.5 Ensure that drain hose is connected to the spray chamber and properly plumbed through the drain peristaltic pump.

18.4.3 Run Procedure

18.4.3.1 Refer to the respective owner's manuals for specific instructions for tuning, sequence loading, and method development on each instrument; ELAN 9000 software guide, NexION 300x/350x software guide.

18.4.3.2 The owner's manual for each instrument is located in the ICP-MS laboratory.

18.4.4 Typical Analysis Problems

18.4.4.1 Sample Overrange: If a requested element is overrange for a sample, it is necessary to dilute the sample and rerun. Dilution factors must be taken into account when reporting final values.

18.4.4.2 Interferences: Although the ICP-MS can compensate for many interferences with appropriate correction factors, unpredicted interferences may still occur. If the analyst suspects this, then the sample should be diluted and rerun. Dilution factors must be taken into account when reporting final values.

18.4.4.3 Torch/Sample Introduction Drift: Various changes in torch plasma conditions or sample introduction can have a great effect on the detector counts. They must be corrected or the instrument must be re-standardized.

18.4.4.3.1 If oils or solid samples have been run, and the CCV is not acceptable, allow the instrument to rinse 15 to 20 minutes. If CCV is then acceptable, reanalyze

the samples and continue. If the CCV again fails its requirements, re-standardize as necessary.

18.4.4.3.2 If sample introduction drift is suspected, check peristaltic pump tubing for collapse and replace as needed.

18.4.4.3.3 Tubing connections may become loose allowing air to bubble into the sample path. Tighten or replace tubing. If necessary, seal with Parafilm.

18.4.4.4 Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 100 times above the MDL, 25x PQL for 6020B and 50 x the LOQ for DoD QSM in the original sample), an analysis of a five fold (1 + 4) dilution should agree within 10% (20% for 6020B) of the original determination. If not, a chemical or physical interference effect should be suspected.

18.5 Power switches and auxiliaries

18.5.1 Each instrument has one main power switch. Refer to the respective maintenance manuals for the location. This switch remains on except while servicing the instrument.

18.5.2 The computer system has 3 power cords all connected to a switchable power strip: the computer main, the monitor and the printer power cords. The power to these is left on while the instrument is not in use for short times (e.g. overnight).

18.5.2.1 The main computer switch is on the front of the CPU.

18.5.2.2 The ***monitor switch*** is on the front of the monitor itself.

NOTE: If the computer is left in use without an analyst present for an extended period of time, turn the monitor off to prevent screen burn-in.

18.5.2.3 The ***printer switch*** is on the lower front of the printer. Refer to printer manual for operating instructions.

18.5.3 Argon gas is provided through a manifold from the storage tank. Under normal conditions a constant argon flow is available.

18.5.4 Start-up

18.5.4.1 Before starting, ensure that the power is on and the vacuum system is switched on.

18.5.4.2 The owner's manual for each instrument provides specific instructions for ignition of the plasma (refer to Section 18.5.1 for software manuals).

18.5.4.3 The plasma should be steady and should not flicker.

18.5.4.4 Once ignition has occurred, levels may be adjusted; it is best to set levels appropriate to the method by loading or editing an appropriate tune file and allow 30 minutes for warm-up.

18.5.5 Shutdown

18.5.5.1 When the plasma is off, the instrument is either in Standby or Shutdown mode. The ICP-MS should be completely shut down only in case of major maintenance, relocation of the instrument, or when the lab is closed for an extended time.

18.5.5.2 Daily shutdown (if required): Refer to the respective owner's manual shutdown procedures (Refer to Section 18.5.1 for software manuals.)

18.6 Sample quantity requirements are approximately 5 mL for each run with the nebulizer. If out of specification or range, further sample may be necessary for reruns.

18.7 The autosampler can be used by attaching introduction tube to sample introduction system, and rinsing tubing to peristaltic pump and following autosampler table set-up and procedures. To define a sequence, refer to the appropriate software manual (refer to Section 18.5.1).

19.0 CALCULATIONS AND DATA REDUCTION METHODS

19.1 Any dilutions, concentrations, or preparation factors must be taken into account prior to reporting data to a client.

$$\text{Relative Percent Difference} = \frac{100 * |\text{Sample 1 Value} - \text{Sample 2 Value}|}{\frac{(\text{Sample 1 Value} + \text{Sample 2 Value}}{2}}$$

$$\text{Matrix Spike Recovery} = \frac{100 * (\text{Spike Value} * \text{DF} * \text{PF} - \text{Sample Value} * \text{DF} * \text{PF})}{\text{Spike Nominal Concentration} * \text{DF} * \text{PF}}$$

$$\text{Post Spike Recovery} = \frac{100 * (\text{Spike Value} - \text{Sample Value})}{\text{Spike Nominal Concentration}}$$

$$\text{LCS Recovery} = \frac{100 * (\text{Sample Value} * \text{DF} * \text{PF})}{\text{Nominal Concentration} * \text{DF} * \text{PF}}$$

Where: Sample Value = instrument reading for the sample
Spike Value = instrument reading for the spiked sample

DF = Dilution Factor

PF = Preparation Factor

Relative Error Ratio (RER) 2 sigma equation:

$$RER = \frac{|\text{Sample Activity} - \text{Duplicate Activity}|}{\sqrt{(\text{Sample 2 sigma TPU}/1.96)^2 + (\text{Duplicate 2 sigma TPU}/1.96)^2)}} = \leq 3$$

NOTE: Activity calculations can be found in Appendix 4 of this SOP. Two sigma TPU calculations can be found in SOP GL-QS-E-014.

19.2 Care must be taken that the correct units are being employed.

20.0 DATA RECORDING

20.1 ICP-MS data are generally stored to the hard disk drive of the ICP-MS computer system and printed at the instrument as each sample is analyzed.

20.2 ICP-MS samples are analyzed in three replicates and the reported value is the average of the replicates. The data for individual replicates is stored in the computer.

20.3 Data are processed locally by manual or programmable procedures to eliminate unused data, to enter dilution factors, and to enter relevant conversion factors prior to uploading to AlphaLIMS.

21.0 QUALITY CONTROL REQUIREMENTS

21.1 Frequency of Quality Control Activities (also refer to Appendix 1)

21.1.1 Initial Calibration Verification (ICV) is performed immediately following each calibration and Continuing Calibration Verification (CCV) is performed after at least every 10 samples.

21.1.2 Initial Calibration Blank (ICB) is performed immediately following the ICV and Continuing Calibration Blanks (CCB) must run with each CCV.

21.1.3 An Interference Check Standard (ICS) is analyzed at the beginning of each analytical run and at least once every twelve hours (if required). Additional requirements may be specified by client contract or methodology.

21.1.4 The PQL standard is analyzed after each calibration and recommended at least every 10 samples between the CCV and CCB analyses for SW-846 Method 6020A. Method 6020A requires analysis at the end of every batch and only recommends analysis every 10 samples. This standard may also be labeled as a CRDL standard.

21.1.5 A method blank (MB) is performed for each batch of 20 or fewer samples or per client requirement.

21.1.6 A matrix spike (MS) and a duplicate (DUP), or matrix spike (MS) and matrix spike duplicate (MSD) are analyzed for each batch of 20 or fewer

samples or per client requirements (5% frequency). For EPA 200.8, the same QC are analyzed for each batch of 10 or fewer samples (10% frequency).

21.1.7 A laboratory control sample (LCS) is analyzed with each batch of 20 or fewer samples. An LCS duplicate (LCS DUP) may be added if required by the client.

21.1.8 Serial dilutions or analytical spikes are analyzed to confirm the presence or absence of interferences when analyzing a new matrix type. The serial dilution is generally performed at a 5x of the test sample.

21.1.9 A post spike (PS) is required for DoD-QSM, SW-846 6020A, or SW-846 6020B if the matrix spike (MS) or matrix spike duplicate (MSD) recoveries fall outside of the limits in section 21.2.8. Post spikes can also be performed at client request.

21.2 Acceptance Limits (also refer to Appendix 2)

21.2.1 ICV results must be between 90% and 110% of the true values for all methods.

NOTE: The ICV is the second source standard and may be used as the CCV as it also will show calibration verification.

21.2.2 ICB and CCB results must have an absolute value less than PQL for 200.8, SW-846 6020 and SW-846 6020A . For DoD QSM analysis, the absolute value must be less than the ½ LOQ. The ICB results must have an absolute value less than or equal to ½ PQL for 6020B and less than or equal to the PQL for the CCB for 6020B. If this is not the case, the reason for the out-of-control condition must be found and corrected, or any data reported must be 10 times greater than the absolute value for the element or less than the PQL.

21.2.3 Interference Check Sample results must be monitored at the beginning of an analytical run or once every 12 hours, whichever is more frequent, for work under SW-846. The ISCA and ICSAB must recover 80-120% the reporting level for the spiked analysis and must have an absolute value less that 2x the reporting level for the non-spiked analyte. For DoD QSM, the ICSA must have an absolute value of less than ½ LOQ for the non-spiked analytes.

21.2.4 The Linear Range Standard (LRS) is analyzed within the calibration verification read back and must fall between 90% and 110% of the true values. Meeting these criteria allows target analyte concentration to be reported up to the LRS concentration thus extending the calibration range of the instrument. Any sample concentrations above the LRS concentration will be diluted to fall below the concentration of the linear calibration range standard.

21.2.5 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30% and 120% (or 70% and 130% for SW-846 Method 6020A and 6020B) of the intensity of that internal standard in the initial calibration then the sample must be diluted five fold (1 + 4) and reanalyzed with the addition of appropriate amounts of internal standards. The intensity levels of the internal standards for the calibration blanks (ICB and CCB) and instrument check standards (ICV and CCV) must agree within ± 20% of the intensity level of the internal standard of the original calibration solution. For work done under EPA Method 200.8, the internal standard responses of any one internal standard must not deviate more than 60% to 125% of the original response in the calibration blank. Five internal standards (^{45}Sc, ^{74}Ge, ^{115}In, ^{175}Lu, and/or ^{181}Ta) are used to cover the mass ranges reported. Refer to Appendix 3 for list of internal standard/ analyte associations. Other exotic analytes may be used as needed. Refer to Section 15.2.

21.2.6 Method blank results must be lower than the PQL (SW-846 6020 and 6020A), lower than ½ the PQL (SW-846 6020B), or less than 10% of the determined value of all samples in the batch. When performing work under EPA Method 200.8, if LRB (laboratory reagent blank) values are 10% or more of the analyte level determined for a sample or are 2.2 times the analyte MDL, then fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained. For DoD QSM work, the absolute value must be less than ½ LOQ or less than 10% of the determined value of all samples in the batch. Al, Fe, Mg, Ca, Na, and K must be less than the PQL.

21.2.7 LCS results, and LCS duplicate (if performed), must be within process control limits as established by Statistical Process Control, manufacturer's certification, or method requirements.

21.2.8 Matrix spikes with recoveries between 75% and 125% suggest the absence of interference for work under EPA Method 200.8. Matrix spikes with recoveries between 75% and 125% suggest the absence of interference for work under SW-846 Method 6020 and SW-846 Method 6020A. Matrix spikes with recoveries between 80% and 120% suggest the absence of interferences for work under DoD QSM.

21.2.9 The relative percent difference (RPD) between a sample and a sample duplicate must be within ± 20% if the analyte concentration in the sample or duplicate is greater than 5 times the PQL. If either the sample or duplicate concentration is less than 5 times the PQL, the results should agree within the absolute value of the PQL. Results less than the MDL or IDL are not evaluated. The relative error ratio (RER) between a sample and a sample duplicate should be ≤ 3%.

21.2.10 Serial dilution results that agree within 10% of the original analytical results, if the original results are greater than 100 times the instrument detection limit or greater than 50 times the LOQ, suggest the absence of interference. For SW-846 6020B, results that agree within 20% of the original analytical results are greater than 25 x the PQL, suggest the absence of interference.

21.2.11 Post spikes with recoveries between 75% and 125% under EPA Method 200.8 and SW-846 Method 6020 and 6020B, and between 80% and 120% under SW-846 6020A and DOD QSM suggest the absence of interference.

21.3 Out-of-Control Situations

21.3.1 ICV and/or CCV failure requires recalibration of the instrument and/or preparation of new standard solutions. Samples analyzed prior to or after calibration verifications that are not acceptable for required analytes must be reanalyzed. An ICV or CCV that has failed may be rerun once only if there is an attributable cause known to have affected the CCV only and not the previous samples. Examples of an acceptable cause may be a sample tip out of solution during analysis, an incorrectly prepared CCV, or obvious carryover in the CCV from a very high sample immediately prior to the CCV. If a CCV is reanalyzed, the data must be lined through, initialed and dated, and the reason for the rerun must be documented on the raw data. In addition, corrective action should be taken to eliminate the cause of the initial CCV failure to prevent future occurrence.

21.3.2 ICB and CCB failure requires recalibration of the instrument and/or calibration blank solution to be remade. The CCB is acceptable if the level of analyte in the corresponding sample(s) is 10 times greater or less than the PQL for the failing element. For DoD QSM work, the absolute values must be less than the ½ the LOQ or less than 10% of the determined value of all samples in the batch.

21.3.3 ICS failure requires that the instrument be re-calibrated or the interferences be corrected, via recalculation, of Interelement Correction Factors so that the ICS can be read within the required limits before samples are analyzed. ICS failure at the end of an analysis period will require that the samples' ICSA run for the affected analyte(s) during that period to be reanalyzed. The ICSA and ICSAB must recover 80-120% for the spiked analytes and must have an absolute value less than 2x the reporting level for the non-spiked analytes. For DoD QSM, the ICSA must have an absolute value of less than ½ LOQ for the non-spiked analytes.

21.3.4 LRS failures limit the reportable calibration range to the high standard in the calibration curve. Any sample concentration that falls above the high calibration standard will be diluted to fall within the calibration range.

21.3.5 Internal Standard failure requires one or more of the following: five-fold dilution of the sample, correction of the problem, termination of analysis, recalibration of the instrument, and/or reanalysis of the affected samples depending on whether the failure is due to the samples or the instrumental drift.

21.3.6 Method blank results higher than the limits in 21.2.6 and greater than 10% of any sample value in that batch that has concentrations above the PQL require that batch be redigested and reanalyzed. For DoD QSM work, the absolute value must be less than ½ LOQ or less than 10% of the determined value of all samples in the batch. Al, Fe, Ca, Mg, Na, and K must be less than PQL.

21.3.7 Matrix spikes, duplicates and spike duplicates are used only as indicators of method effectiveness on that sample and will not be used as acceptability criteria for the process, unless a special requirement of the client.

21.3.8 LCS and/or LCS duplicate results outside of established acceptance limits require the batch to be redigested and reanalyzed.

21.3.9 When analytical results suggest the presence of interference, one of the methods listed in Section 18.4.4.2 should be employed.

21.3.10 The CRDL standard should be evaluated, but no action is required if the results fall outside of the 70-130% advisory window for SW-846 6020 and EPA 200.8. For DoD QSM and SW-846 6020B, the CRDL standard must be 80-120% of the true value or recalibration is required. For SW-846 Method 6020A, the CRDL standard must be 70-130% of the true value or recalibration is required. This also includes the low level continuing calibration verification standard analyzed every 10 samples. Sample results can be evaluated for reporting if they are at least 2x the PQL for a given analyte.

21.4 Corrective actions taken for data not conforming to the requirements in Section 21.2 are stated in Section 21.3. If these corrective actions can be taken by the analyst prior to the acceptance of the data, then no nonconformance documentation is required. However, if these corrective actions include redigestion of the batch or sample, if the data have already been accepted, or if the corrective action requires an instrument service call, then a nonconformance and/or corrective action report should be completed. This report includes the date, person requesting the action, sample(s) or batch(s) affected, and action requested, all provided by the requester. The person taking the action will provide any pertinent comments, their signature, and the date the action is completed. The disposition of the nonconformance will then be verified by the Quality Systems specialist. These reports will be kept on file. Refer to GL-QS-E-002 for Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items.

21.5 Analytical data are evaluated for conformance with the requirements stated in Section 21.2 by the analyst during and/or after the analysis, but before the data are entered into AlphaLIMS. Data may be accepted or rejected by the analyst at this point or by the data reviewer(s) as stated in Section 22.0.

22.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

22.1 After samples are analyzed, the data must go through the review process before it can be reported out of the lab. The analyst who performed the analysis will review the raw data prior to uploading it into AlphaLIMS. The upload process may be handled by the analyst or by a data entry clerk.

22.2 After the upload is complete, an AlphaLIMS data report is generated that will be passed (along with the batch sheet, data review checklist, and the raw data) to another analyst for a peer review. Discrepancies found in this review will be resolved before the batch data are passed and the status updated.

22.3 When this peer review is completed and all of the data are found to be acceptable, the reviewer signs and dates the batch data report and updates the status of the batch to done. If the reviewer determines that the reviewed data are not acceptable and requires additional work or correction, data are returned to the analyst or representative with an appropriate explanation.

22.4 Listed below are the data review responsibilities of the Analyst and Peer Reviewer:

22.4.1 Analyst Review is performed by the analyst who generated the data before the data are submitted for entry into AlphaLIMS. Analyst completes and attaches the run data cover sheet to the printout.

22.4.2 Peer Analyst Review is performed by an individual who did not perform the analysis but is familiar with the analytical method used and the reporting requirements. This person will review the complete data report after all data are entered, will ensure that any data entry corrections are made before data are approved, and will complete the reviewer portion of the data review check list. If the data do not meet the necessary quality requirements and need further analysis, they are returned to the analyst or representative.

22.5 A Third Review is performed for Data Packages (level 3 to level 6 CLP-Like) and/or by client requirement. This review is by the Metals Team Validator or other qualified person.

22.6 Specific items that are reviewed at each level include the following:

22.6.1 Analyst Review: Before data is submitted for entry into AlphaLIMS.

22.6.1.1 All analyses in the batch are completed.

22.6.1.2 Any corrections and comments on the data are properly initialed and dated.

22.6.1.3 Proper standard identification numbers appear on the runlog to ensure traceability from the data to original source standards.

22.6.1.4 All data are complete and accurate in the AlphaLIMS data report.

22.6.1.5 Data acceptance limit criteria identified in Section 21.2 are met or an explanation given.

22.6.2 Peer Analyst Review: Before data are submitted for further review or update:

22.6.2.1 All data are complete and accurate in the AlphaLIMS Data Report.

22.6.2.2 Any exceptions or shortcomings have been sufficiently explained or corrected.

22.6.2.3 Data are reported in the proper units or an explanation is given.

22.6.2.4 Prep factor and dilution calculations by AlphaLIMS are present in the data report and AlphaLIMS calculations are correct.

22.6.2.5 LCS and Spike Recoveries and RPD calculations by AlphaLIMS are correct, and the values are within control limits.

22.7 When the data review is completed and the data have been reported out of the lab, they are bound with the batching sheet and kept on file in the lab.

22.8 The complete data review process requires the use of the Prep Log Book, Prep data report, batch sheet, AlphaLIMS data report, raw instrument data, and runlog.

23.0 DATA REPORTING

23.1 To report data after the review process has been completed:

23.1.1 Enter the AlphaLIMS program through an available terminal and select DATA MENU, BATCH ITEMS, CHANGE BATCH STATUS.

23.1.2 Enter the Batch Number and “Submit.”

23.1.3 Use the down arrow key to move the cursor down the new status column to the end. Change status from REVW to DONE and “Save.”

24.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

25.0 LABORATORY WASTE HANDLING AND DISPOSAL: SAMPLES, EXTRACTS, DIGESTATES, AND REAGENTS

25.1 Standard solutions that must be disposed are taken to the Waste Disposal coordinator for disposal in accordance with Laboratory Waste Management Plan, GL-LB-G-001.

25.2 Sample digestates are stored in the lab for a specified period of time following analysis. At this time, they are composited into a waste container that is picked up by the Waste Management Technician for proper disposal.

25.3 Radioactive Waste:

25.3.1 Samples returned to sample storage

25.3.2 Drain waste collected in the radioactive waste carboy is dumped when full into the appropriate 55 gallon drum sitting outside the ICPMS laboratory. Ultimate disposal of liquid radioactive waste done by waste management department.

25.3.3 Implements, vials, gloves, etc., are wrapped and labeled with radioactive tape and placed in the radioactive waste container in high bay area.

25.3.4 Expired Standard Solutions: Refer to Section 25.1.

26.0 REFERENCES

26.1 Perkin Elmer ELAN 9000 Hardware Guide

26.2 Perkin Elmer ELAN 9000 Software Guide

26.3 Perkin Elmer NexION 300x/350x Hardware

26.4 Perkin Elmer NexION 300x/350 Software Guide.

26.5 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods. Volume 1A, USEPA SW-846, Third Edition, Revision 2, September 1994.

26.5.1 Method 6020A, "Inductively Coupled Plasma – Mass Spectrometry," Revision 1, February 2007.

26.5.2 Method 6020, "Inductively Coupled Plasma – Mass Spectrometry," Revision 0, September 1994.

26.5.3 Method 6020B, "Inductively Coupled Plasma – Mass Spectrometry," Revision 2, July 2014.

26.5.4 Method 3005A, "Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy", Revision 1, July 1992.

26.5.5 Method 3010A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy," Revision 1, July 1992.

26.5.6 Method 3050B, "Acid Digestion of Sediments, Sludges, and Soils", Revision 2, December 1996.

26.6 USEPA Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry," Revision 5.4, May 1994.

26.7 Conversion Constants for Uranium Isotopes, Dr. Robert Litman, April 2009.

26.8 Department of Defense (DoD), Department of Energy (DoE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, DoD QSM Version 5.1, DoE QSAS Version 3.1, January 2017.

27.0 HISTORY

Revision 33: Replace "IDL for non DOE Clients, 100 x the MDL for DOE Alb Clients" with MDL

Revision 32: Updated for clarification for ICP-MS replicates. Updated the Appendices 1 and 2 to remove readback requirements no longer needed.

Revision 31: Clarification of DOD QSM criteria and method acceptance criteria.

Revision 30: Removed reference to obsolete SOP. Updated reference to current DOD/DOE QSM version 5.1 and 3.1. Added section 14.4 for clarification on Acid Screens.

Revision 29: Added statement to clarify the IEC verifications

APPENDIX 1: FREQUENCY OF QUALITY CONTROL ACTIVITIES

(For illustrative purposes only)

Frequency of Quality Control Activities

Method/ Frequency	**SW-846 6020 and 6020B**	**EPA 200.8**	**SW-846 6020A**
ICV	Per calibration	Per calibration	Per calibration
ICB	Per calibration	Per calibration	Per calibration
PQL	Per calibration	Per calibration	Per calibration and at end of each analytical batch.
ICSA	Per calibration	Per calibration	Per calibration
ICSAB	Per calibration; every 12 hours after	Per calibration	Per calibration; every 12 hours after
Linear Range Standard (LRS)	Per calibration, if applicable	Per calibration, if applicable	Per calibration, if applicable
CCV	Every 10 instrument runs	Every 10 instrument runs	Every 10 instrument runs
CCB	Every 10 instrument runs	Every 10 instrument runs	Every 10 instrument runs
Method Blank	5% or per batch	5% or per batch	5% or per batch
LCS – liquid LCS – soil	5% or per batch	5% or per batch	5% or per batch
Matrix Spikes	5% or per request	10% or per request	5% or per request
Sample Duplicates	5% or per request	5% or per request	5% or per request
Serial Dilutions	5% or per request	5% or per request	5% or per request
Matrix Spike Duplicates	5% or per request	10% or per request	5% or per request
Post-Digestion Spikes	5% or per request	10% or per request	5% or per request

APPENDIX 2: ACCEPTANCE LIMITS

Method/ Acceptance Criteria	SW-846 6020	EPA 200.8	DoD QSM Version 5.1	SW-846 6020A	SW-846 6020B
ICV	90% - 110%	90% - 110%	90%-110%	90% - 110%	90% - 110%
ICB	< absolute value of PQL	< absolute value of PQL *	< ± ½ LOQ	< absolute value of PQL	< absolute value of ½ PQL
PQL/CRI (CLP)	70% - 130% advisory limits only	70% - 130% advisory limits only	80%-120% or investigate and recalibrate	70% - 130% or investigate and recalibrate	80%-120% or investigate and recalibrate
ICSA	80-120% for major components; ± 2x PQL for non-spiked	80-120% for major components; ± 2x PQL for non-spiked	80%-120% for major compounds; < ± ½ LOQ for non-spiked	80-120% for major components; ± 2x PQL for non-spiked	80-120% for major components; ± 2x PQL for non-spiked
ICSAB	80%-120%	80%-120% (may be requested)	80%-120%	80%-120%	80%-120%
Linear Range Standard (LRS)	90%-110%, or up to the high calibration standard	90%-110%, or up to the high calibration standard	90%-110%, or up to the high calibration standard	90%-110%, or up to the high calibration standard	90%-110%, or up to the high calibration standard
CCV	90% - 110%	90% - 110%	90%-110%	90% - 110%	90% - 110%
CCB	± PQL	± PQL *	± ½ LOQ	± PQL	± PQL
Method Blank	± PQL	± PQL *	± ½ LOQ, except for Al, Fe, Mg, Ca, Na, and K	± PQL	± ½ PQL
LCS - liquid LCS - soil	80% - 120% current SPC limits	85% - 115% current SPC limits	Use QSM specified limits	80% - 120% current SPC limits	80% - 120% current SPC limits
Matrix Spikes	75% - 125%, when applicable	75% - 125%, when applicable	Use QSM specified limits	75% - 125%, when applicable	75% - 125%, when applicable
Sample Duplicates	0% - 20% when greater than 5X PQL, ± PQL when less than 5X PQL	0% - 20% when greater than 5X PQL, ± PQL when less than 5X PQL	0% - 20% when greater than 5X PQL, ± PQL when less than 5X PQL	0% - 20% when greater than 5X PQL, ± PQL when less than 5X PQL	0% - 20% when greater than 5X PQL, ± PQL when less than 5X PQL
Serial Dilutions	0% - 10% of initial raw value, when applicable	0% - 10% of initial raw value, when applicable	0% - 10% of initial raw value, when applicable (> 50x LOQ)	0% - 10% of initial raw value, when applicable	0%-20% of initial raw value, when applicable
Post-digestion spikes	75%-125%, when applicable	75%-125%, when applicable	80%-120%	80%-120%, when applicable	75%-125%, when applicable
Internal Standards	30%-120%, samples 80%-120% for ICB, ICV, CCV, CCB	60%-125% for all	30%-120%	70%-130%, for all	70%-130%, for all

APPENDIX 2: CONT'D

Method/ Acceptance Criteria	SW-846 6020	EPA 200.8	DoD QSM Version 5.1	SW-846 6020A	SW-846 6020B
Matrix Spike Duplicate	0% - 20%	0% - 20%	0% - 20%	0% - 20%	0% - 20%
Sample Duplicates RER activity	≤ 3%	≤ 3%	≤ 3%	≤ 3%	≤ 3%

* North Carolina requires ½ the PQL

APPENDIX 3: INTERNAL STANDARDS WITH ASSOCIATED ANALYTES/ISOTOPES

IS ^{45}Sc	IS ^{74}Ge	IS ^{115}In	IS ^{175}Lu ^{181}Ta
^{7}Li	^{66}Zn	^{88}Sr	^{133}Cs
^{9}Be	^{67}Zn (calc)	^{90}Zr	^{135}Ba (calc)
^{11}B	^{68}Zn (calc)	^{98}Mo	^{137}Ba
^{23}Na	^{75}As	^{103} Rh	^{178}Hf
^{24}Mg	^{77}Se (calc)	^{107}Ag	^{181} Ta
^{27}Al	^{82}Se	^{111}Cd	^{184}W
^{31}P	^{83}Kr (calc)	^{114}Cd (calc)	^{187}Re
^{39}K		^{120}Sn	^{205}Tl
^{43}Ca		^{121}Sb	^{208}Pb
^{47}Ti		^{123}Sb (calc)	^{209}Bi
^{51}V			^{232}Th
^{52}Cr			^{233}U
^{53}Cr(calc)			^{234}U
^{55}Mn			^{235}U
^{57}Fe			^{236}U
^{59}Co			^{238}U
^{60}Ni			
^{63}Cu(calc)			
^{65}Cu			

*(calc) – isotope used in calculations

APPENDIX 4: RADIOCHEMISTRY CONVERSION CALCULATIONS FOR URANIUM ISOTOPES

Conversion for liquids (µg/L x CF = pCi/L)

^{233}U (µg/L to pCi/L) = 9640.6
^{234}U (µg/L to pCi/L) = 6224.9
^{235}U (µg/L to pCi/L) = 2.1615
^{236}U (µg/L to pCi/L) = 64.698
^{238}U (µg/L to pCi/L) = 0.33627

Conversion for solids (mg/kg x CF = pCi/g)

^{233}U (mg/kg to pCi/g) = 9640.6
^{234}U (mg/kg to pCi/g) = 6224.9
^{235}U (mg/kg to pCi/g) = 2.1615
^{236}U (mg/kg to pCi/g) = 64.698
^{238}U (mg/kg to pCi/g) = 0.33627

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

(GL-OA-E-009 REVISION 45)

APPLICABLE TO METHODS:
EPA SW-846 Methods 625.1, 8000D, 8270C, 8270D and 8270E

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1.0 STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

2.0 METHOD CODES

2.1 EPA Method 625.1

2.2 EPA SW-846 Methods 8270C, 8270D, 8270E

2.3 EPA SW-846 Methods 8000D

3.0 METHOD OBJECTIVE AND PURPOSE

This standard operating procedure (SOP) covers the determination of semivolatile organic compounds in a wide variety of solid waste matrices, soil, and water according to USEPA methods 8270C, 8270D, 8270E and 625.1. Other analytical protocols such as Department of Defense (DOD) and Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental laboratories are also covered. Please refer to Appendix 8 for a summary of these requirements.

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 Applicable matrices include, but are not limited to, groundwater, wastewater, surface water, leachate, soil, oil, and other miscellaneous matrices.

4.2 Methods 8270C, 8270D, 8270E and 625.1 may be used to quantitate many neutral, acidic, and basic organic compounds that are soluble in methylene chloride. The compounds are separated using a gas chromatograph (GC) and detected using a mass selective detector (MSD). Such compounds include polynuclear aromatic hydrocarbons (PAH), chlorinated hydrocarbons, phthalate esters, pesticides, nitrosamines, haloethers, aldehydes, ketones, pyridines, and phenols. Appendix 1 lists the analytes typically analyzed using these methods. Please note that the list may change as new compounds are added or existing compounds are removed. Appendix 1 includes internal standards and surrogates.

4.3 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation method. The semivolatile compounds are introduced into a GC equipped with a narrow-bore fused silica capillary column. The GC column is temperature programmed to separate the analytes, which are then detected by the MSD. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of standards. Quantitation is accomplished by comparing the response of the quantitation ion relative to an internal standard using an appropriate calibration curve.

4.4 Appendix 5 outlines the procedure for dioxin screen analysis.

4.5 Appendix 6 outlines the procedure for SIM (Selective Ion Monitoring) analysis. Please note that SIM analysis is performed for some PAH analytes and the list may change as new compounds are added or existing compounds are removed.

4.6 Methods associated with this SOP may include USEPA SW-846 methods 8270C, 8270D, 8270E and USEPA method 625.1, as well as others not listed.

4.7 The practical quantitation limit (PQL) is the lowest level in the calibration curve. The PQL is the lowest level at which compounds may be accurately quantitated and is compound dependent. The calibration curve typically ranges from 10 µg/mL to 120 µg/mL. These ranges reflect instrument readings which are in µg/mL (ppm). The required detection limit (RDL) may be different from the PQL if a prep procedure is performed on the sample. It should be noted that the calibration range may vary between calibrations and instruments. Some compounds may have PQLs that are slightly higher or lower than those listed above. Additionally, newer instrumentation may make it possible to achieve even lower quantitation limits in the future.

4.8 Method detection limit studies (MDLs) are performed on an annual basis. MDLs are done for liquid and solid matrices. For more information regarding MDLs, refer to The Determination of Method Detection Limits, GL-LB-E-001.

5.0 METHOD SCOPE AND PERFORMANCE CHARACTERISTICS

Various performance characteristics associated with this method should be given special consideration. Benzidine and 3,3'-dichlorobenzidine can be subject to oxidative losses during solvent concentration. In addition, these two compounds often break down quickly when prepared in a mixture with other compounds. Hence, they may need to be prepared separately. Some of the pesticides are particularly prone to decomposition in the injection port if the temperature is too high or the liner becomes dirty. Various substituted phenols, in particular 4-nitrophenol, 2,4-dinitrophenol, and 4,6-dinitro-2-methylphenol are susceptible to breakdown and erratic chromatography. 2-nitroaniline, 3-nitroaniline, and 4-chloroaniline should be watched closely for poor responses and decomposition. Care should be taken when installing a new guard column to look for degradation and subsequent loss of pentachlorophenol. The guard column may need to be rinsed or cut prior to installation to prevent this from happening. Please see Appendix 7 for additional information on poor responders.

6.0 DEFINITIONS

6.1 Definitions specific to this SOP include:

6.2 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample periodically throughout the run sequence. Its purpose is to determine whether the analytical sequence is in control during sample analysis. It may be prepared from the same source as the calibration standards and is usually of varied concentration.

6.3 Limit of Detection (LOD): The lowest concentration level that can be determined by a single analysis and with a defined level of confidence to be statistically different from a blank. The LOD verification is typically spiked at two times the MDL.

6.4 Limit of Quantitation (LOQ): The lowest concentration level of the initial calibration curve used to quantitate an analyte. The LOQ verification is typically spiked at the PQL.

6.5 Lower Limit of Quantitation (LLOQ): The lowest concentration at which a target analyte can be reliably measured and reported. The LLOQ is ≥ the lowest point in the

calibration curve and represents a concentration at which both quantitative and qualitative requirements can be consistently demonstrated. The LLOQ is verified at least annually, but typically quarterly, as the LOQ verification. The verifications performed by extracting and analyzing an LCS spiked at 0.5 to 2 times the LOQ. The LLOQ verification is carried through the same preparation and analytical procedures as environmental samples and QC. It is recommended to analyze the LLOQ on every instrument where data are reported and this is the laboratory's normal protocol. Recovery of target analytes in the LLOQ are compared to in-house-statistically-derived limits. Concentrations in samples reported below the LLOQ and above the MDL are qualified as estimated.

6.6 Practical Quantitation Limit (PQL): The lowest level in the calibration curve. With the prep factor applied, the PQL is referred to as the effective PQL. The PQL is equivalent to the LOQ and the LLOQ.

6.7 Lab-wide used definitions can be found in GL-QS-B-001 the Quality Assurance Plan.

7.0 INTERFERENCES TO THE METHOD

7.1 Contaminants found in extraction glassware, solvents, and other sample processing hardware may jeopardize the integrity of this method.

7.2 Glassware must be scrupulously cleaned as soon as possible after extraction.

7.3 Contamination may also occur in the GC/MS system. High boiling materials tend to build up in the injection port and the front end of the column. The analyst should maintain a thorough working knowledge of keeping the injection port free of contamination, including changing out the septum, injection port liner, O-ring, ferrule, and gold seal. To eliminate build-up of high boiling material in the front end of the column, a guard column can be connected between the injection port and the analytical column and cut periodically. Guard columns typically have no phase and are typically 5 to 10 meters long.

7.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed between samples with solvent. If carryover is suspected, potentially impacted samples should be re-analyzed after any needed maintenance or cleaning has been done.

8.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

METHYLENE CHLORIDE IS A SUSPECTED CARCINOGEN AND A KNOWN SKIN IRRITANT.

CONTACT WITH OXIDIZERS MAY GENERATE EXPLOSIVE MIXTURES.

PYRIDINE IS A FLAMMABLE COMPOUND AND IS TOXIC UPON INHALATION. PREVENT INHALATION BY USING PYRIDINE UNDER A HOOD.

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

8.1 Eye protection should be worn when handling samples, reagents, or standards.

8.2 Treat all chemicals and samples as potential health hazards and reduce exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and individual sample MSDS provided by clients are maintained in the laboratory.

8.3 Personal Protective Equipment (PPE)

8.3.1 Gloves should be worn when handling chemicals, solvents, and samples.

8.3.2 Analysts should prepare samples and standards under the hood.

8.4 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

8.4.1 Proper PPE should be worn at all times when handling radioactive samples. Gloves, safety glasses, and a lab coat should be worn when handling radioactive samples. In addition, a disposable lab apron may be worn over the lab coat.

8.4.2 Protect counter tops with counter paper, or work from radioactive sample handling trays.

8.4.3 Post signs indicating radioactive samples are in the area.

8.4.4 Swipes of the counter tops should be taken upon completion of work. Deliver those swipes to the designated swipe count box.

8.4.5 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

8.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.6 Radioactive and non-radioactive wastes are segregated in the waste satellite area.

8.7 Never leave gas cylinders unchained or untied.

8.8 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed.

8.9 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

8.10 Refer to SOP GL-LB-N-001 the Safety, Health and Chemical Hygiene Plan for additional general safety and health information pertaining to the laboratory.

9.0 CAUTION WARNINGS

The analyst must use care when operating and assembling instrumentation. Use caution when handling samples and reagents. Check to see that the gas chromatograph equipment is properly assembled and hooked up to the proper gas cylinder and power, by referencing appropriate reference manual.

10.0 APPARATUS AND MATERIALS; REAGENTS; EQUIPMENT AND INSTRUMENTS

10.1 Equipment associated with this method includes:

10.1.1 Gas tight syringes

10.1.2 Volumetric flasks

10.1.3 40 mL vials

10.1.4 Refrigerator and freezer

10.1.5 Mininert vials

10.1.6 2 mL autosampler vials

10.1.7 250 µL clear glass vial inserts

10.1.8 Teflon crimp tops

10.1.9 Crimper

10.1.10 Columns

10.1.11 Glass injection port liners

10.1.12 O-rings

10.1.13 Ferrules

10.1.14 Column cleaving tool

10.1.15 Septa

10.1.16 Guard column connectors

10.2 Reagents, chemicals, and standards

10.2.1 Source Standards: Source Standards are purchased directly from vendors and may be diluted to make stock, intermediate, or working standards. Source standards expire per the vendor expiration date or after one year from the date opened, whichever is shorter. Please reference GL-LB-E-007 for further information regarding standards and their preparation.

10.2.2 Internal Standard Solutions: The recommended internal standards are: 1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12. Internal standard solutions are prepared from pure standard materials or purchased as certified solutions.

10.2.3 GC/MS Tuning Standard: A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/µL of pentachlorophenol, benzidine and 4,4'-DDT to verify injection port inertness and GC column performance.

10.2.4 Calibration Standards: Calibration standards are prepared at a minimum of five concentration levels. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the expected range of compounds found in samples. Calibration standards may be purchased pre-mixed as source standards or may be prepared in the laboratory from certified source standards.

Calibration standards expire after a maximum of six months or the shortest vendor expiration date (whichever is sooner) and should be monitored frequently for signs of degradation.

10.2.5 Surrogate Standards: Surrogate recoveries are used to monitor unusual matrix effects, sample processing errors, and extraction efficiency. The recommended base/neutral surrogates are: 2-fluorobiphenyl, nitrobenzene-d5, and terphenyl-d14. These surrogates are added at a concentration of 50 µg/mL. The recommended acid surrogates are: 2-fluorophenol, 2,4,6-tribromophenol, and phenol-d5. These surrogates are added at a concentration of 100 µg/mL. Surrogates are added to each blank, laboratory control sample (LCS), matrix spike (MS), matrix spike duplicate (MSD) and sample during the extraction. Surrogate concentrations may vary, depending on the prep method. For example, method 3580 (waste dilution) requires surrogates at ten times the normal concentration. The surrogate typically used for the SIM PAH analysis is 5-alpha-androstane.

10.2.6 Laboratory Control Sample (LCS) and Matrix Spike (MS) Standards: The LCS and MS standards contain a representative list of target compounds. Depending on client and contract requirements, some or all of the spiking compounds may be monitored for recovery. In addition, some analytical protocols such as QSM, require that every target analyte be spiked and monitored. For TCLP samples, the matrix spiking standards are: hexachloroethane, nitrobenzene, hexachlorobutadiene, 2,4-dinitrotoluene, hexachlorobenzene, pyridine, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, and pentachlorophenol, and 1,4-dichlorobenzene. When method 625.1. is referenced, the matrix spike should contain all target 625.1 compounds of interest. Both the acid and base compounds are typically added at 50 µg/mL, however spike concentrations may vary, depending on the prep method. Waste dilution prep (method 3580) requires elevated spike and surrogate concentrations to account for the dilution in the prep step.

10.2.7 Calibration Verification Standards (CCV): The CCV is prepared at a concentration that is near to the midpoint of the calibration curve. A CCV may be purchased as a source standard or prepared from other source standards.

10.3 Instrumentation

10.3.1 Gas Chromatograph: A gas chromatograph (GC) should be capable of temperature programming and suitable for split/splitless injections. Electronic pressure control (EPC) is recommended but not required. In most cases, an autosampler is used for injections. The laboratory utilizes Agilent 6890 and 7890 GCs and 5973, 5975 and 5977 MSDs. Agilent Chemstation/Enviroquant software is used for data processing and evaluation.

10.3.2 Suggested parameters for the autosampler:

Sample volume – 0.5 µL to 1 µL

Number of sample washes - 1

Solvent washes - 6

Sample viscosity wait - 0

Number of sample pumps - 6

Injection mode is 'Fast'.

10.3.3 The mass selective detector (MSD) should be capable of scanning from 35 to 500 AMU every 1 second or less, using a recommended electron energy of 70 volts in the electron impact ionization mode. The MSD must be capable of producing a mass spectrum that meets the criteria established by the EPA. A slightly polar fused silica capillary column, such as a J&W DB-5MS column or its equivalent, is recommended for use with this method.

A suggested temperature program follows:

Temperature 1	50° C
Time	1 min.
Rate	15° C/min.
Temperature 2	120° C
Rate	20°/min
Temperature 3	280° C
Rate	2° C/min
Temperature 4	295 ° C
Rate	20° C/min
Final Temperature	325° C
Time	4.5 min
Run Time:	Approximately 27 minutes or until Benzo (a,e) pyrene elutes.
Scan Start Time:	2.0 (or prior to 2-ethoxyethanol)
Splitless Valve Time:	1.0
Number of A10 Samples:	2
MS Threshold:	100 counts
Mass Range:	35 - 500 AMU

NOTE: These instrument conditions and rates are guidelines which may change.

11.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

11.1 Sample extracts have a 40-day holding time from the date of extraction.

11.2 Sample extracts are delivered from the prep lab to the semivolatiles lab and are stored in a freezer at approximately -10° C or less. QSM requires -10° to -20° C. The extracts are usually grouped according to batches and are accompanied by the batch pull sheet and other pertinent paperwork.

11.3 Custody of samples is monitored using the AlphaLIMS sample tracking system. Each analyst should scan the samples he/she plans to run into his/her custody prior to analysis.

11.4 All sample extracts should be treated with caution as potential health hazards. Refer to Section 8.0 on safety.

12.0 SAMPLE PREPARATION TECHNIQUES

12.1 Before extracts can be analyzed on the instrument, they must first be transferred to an autosampler vial and have internal standards added. A determination must also be made as to whether the extract should be diluted. The decision to dilute a sample extract is based on a number of factors: sample screening, historical data about the sample or sample site, the appearance of the extract (color, viscosity, odor, turbidity, etc.), or regulatory considerations. The experience of the analyst is invaluable in making this determination.

NOTE: Sample extracts may contain extraneous material, multiple layers or sediment. Sediment or other extraneous material cannot be injected into a GC column, and therefore, is excluded from the aliquot taken from the vial. Multiple layers are treated on a case-by-case basis. If the extract can be homogenized, then a uniform sample is achieved. If the extract remains bi-phasic, the PM and client are contacted for further guidance.

12.2 If a sample is to be analyzed without dilution ('neat'), internal standard solution is added to the autosampler vial with sample at a ratio of 1:50. For example, if 5 µL of a 2000 µg/mL internal standard solution is added to an autosampler vial using a syringe, 250 µL of the sample extract is then added to the same vial. A cap is then placed on the vial and secured by crimping. This procedure may vary slightly depending on the specific analytical protocol being used (i.e. CLP).

12.3 If samples are diluted, the dilution is made using methylene chloride or appropriate solvent. Again, 5 µL of the 2000 µg/mL internal standards solution is added to the autosampler vial. If the sample were being diluted 1:5, 50 µL of the sample extract would be added along with 200 µL of methylene chloride.

12.4 Once samples are prepped, they are ready to be injected onto the GC/MS. Usually, an autosampler, such as the Agilent 7683, is used to inject standards and extracts on the instrument.

12.5 Some samples cannot be extracted and concentrated using typical prep procedures. Oils and solvents that are miscible in methylene chloride are common examples. In these cases, method 3580 (waste dilution) may be used.

13.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

13.1 Preventative maintenance on a GC/MS system involves the following basic areas:

13.1.1 Vacuum pumps for the analyzer need a change of oil about every year or when system performance indicates it is needed.

13.1.2 The GC injection port is cleaned as needed, usually every day or every other day. It is recommended that the septum (if there is one) and injection port liner be replaced at the time of cleaning. A guard column is often used to prevent high boiling contaminants from reaching the analytical column. A loop or two of the guard column should be cleaved off when cleaning. Additionally, the gold plated seal should be cleaned.

13.1.3 Analyzer maintenance is usage dependent. The type and quantity of samples that have been injected determine the frequency of ion source cleaning and electron multiplier replacement.

13.1.4 Autosampler maintenance is primarily that of cleanliness. Most autosamplers need their moving parts to be clean and lightly lubricated. The most frequent corrective maintenance is that of changing the syringe.

13.1.5 Instrument maintenance logs are kept with each instrument and serve as a record of all the maintenance that has been done on the instrument.

13.2 Non-Routine Maintenance Procedures (Special, Operational or Failure Mode Maintenance)

13.2.1 Service is provided to the instrument via the analyst, the in-house instrument service engineer, or a technical support specialist from the manufacturer. When instrument failure occurs, different parts of the instrument are isolated to determine the root cause. For example, the injection port may be capped off if a leak is suspected to prove the leak is/is not coming from that source. Instrument maintenance logbooks are kept for each instrument detailing the type of maintenance performed on the instrument and when it was performed.

13.2.2 Analytical columns are replaced when the existing column shows signs of excessive degradation or the inability to properly resolve chromatographic peaks. Excessive peak tailing, poor responses, and baseline disturbances may also indicate that the column needs to be replaced. When the analytical column is replaced, the instrument is recalibrated.

14.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL SAMPLES

14.1 Source standards are purchased as certified mixtures or as neat chemicals. Documentation of the standard's quality and traceability should be provided from the vendor. This documentation is scanned and linked to the standard in the LIMS database. Standards may be purchased from certified vendors.

14.2 Source standards are assigned a unique code number for the purposes of traceability. The standard, along with its code, is recorded in AlphaLIMS. AlphaLIMS can be used to generate a label that is affixed to the standards container. Source standards are good for one year after opening or from the vendor’s expiration date, whichever is shorter.

14.3 Intermediate, and working standards are likewise assigned a unique code number and recorded in AlphaLIMS. These standards are valid for six months, or from the vendor's expiration date, whichever is shorter.

15.0 INSTRUMENT CALIBRATION

15.1 Initial Calibration. Prior to running a multi-level calibration, take precautions to ensure that the instrument is clean and functioning properly. An instrument blank should be analyzed with each ICAL tune window. A minimum of five calibration levels is run for each analyte. Typically, the calibration levels range from 10 µg/mL to 120 µg/mL. However, these levels may vary among compounds. Special care is taken to ensure that saturation or overloading is not taking place in the higher level standards. If saturation is noted, take appropriate corrective action, such as manually re-tuning the instrument or lowering the multiplier voltage.

15.2 In some cases the upper level(s) of the calibration may be removed in order to meet method criteria for single compounds. This practice results in a narrower calibration range. Individual calibration levels may be analyzed within the same tune window if no samples have yet been analyzed. Target analytes detected above the highest calibration level are re-analyzed at a dilution to bring the elevated concentrations within the instrument's calibration range. The low standard representing the PQL is not dropped. Please note that this practice does not represent "cherry picking," which is acknowledged as an unacceptable laboratory practice.

15.3 Because some of the target analytes may decompose or react when mixed with other analytes, several calibration mixes are used. These mixes are prepared at differing concentrations. The various mixes are used to prevent chemical degradation. All of the mixes are analyzed at the same time. The analytical sequence may lapse over two days.

15.4 Each instrument should be hardware-tuned to meet EPA criteria for DFTPP before any analyses, including the initial calibration, can begin.

15.4.1 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 is the internal standard that has a retention time closest to the compound being measured. The RF is calculated as follows:

$$RF = (A_X C_{is}) / (A_{is} C_X)$$

Where:

A_X = Area of the characteristic ion for the compound being measured.

A_{is} = Area of the characteristic ion for the specific internal standard.

C_{is} = Concentration of the specific internal standard.

C_X = Concentration of the compound being measured.

15.4.2 The average RF must be calculated for each compound. A system performance check should be made before this calibration curve is used. Four compounds

(System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol. The minimum acceptable average RF for these compounds is 0.0500. These compounds typically have RFs of 0.05 to 0.10. These compounds are used to check for standard degradation, system cleanliness, and active sites in the system. Methods 8270D and 8270E do not designate SPCCs. Rather, it is recommended that a minimum RF for the most common target analytes be demonstrated for each calibration level (refer to Appendix 9 for a list of RFs) as a means to ensure that these compounds are recovering as expected. These methods also note that meeting the minimum RF criteria for the lowest calibration standard is critical to demonstrating appropriate sensitivity. Due to the large number of analytes that may be analyzed by these method, some analytes will fail to meet these criteria. In those cases, data may still be reported if the compounds are not project-critical. Otherwise, the data are qualified as estimated or the sample is re-analyzed on an instrument that passes the response factor criteria. Results should not be reported if any compounds of interest for a project fail the minimum response factor criteria for South Carolina samples. All compounds should have a minimum RF of at least 0.01 and the failures should be addressed in the case narrative.

15.5 The percent relative standard deviation (%RSD) should be less than 15% for each compound in method 8270C and 35% for method 625.1. However, the %RSD for each individual Calibration Check Compound (CCC) must be less than 30%, in method 8270C.

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

Where:

RSD = relative standard deviation

$\bar{x}$ = mean of 5 or more initial RFs for a compound

SD = standard deviation of average RFs for a compound

$$SD = \sqrt{\sum_{c=1}^{n} \frac{\left(x_1 - \bar{x}\right)^2}{N-1}}$$

The following compounds are CCCs: phenol; 1,4-dichloro-benzene; 2-nitrophenol; 2,4-dichlorophenol; hexachlorobutadiene; 4-chloro-3-methylphenol; 2,4,6-trichlorophenol; acenaphthene; diphenylamine; pentachlorophenol; fluoranthene; di-n-octylphthalate; and benzo(a)pyrene. Methods 8270D and 8270E do not designate CCCs. Rather, all target analytes should have calculated RSDs of ≤ 20%. If more than 10% of the compounds included in the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99), then the chromatographic system is

considered too reactive for analysis to begin and maintenance and re-calibration may be required.

15.6 If the %RSD of any compound is 15% or less (20% for 8270D and 8270E), then the relative response factor is assumed to be constant over the calibration range and the average relative response factor may be used for quantitation. If the %RSD for any compound is greater than 15% (20% for 8270D and 8270E), a calibration curve of area ratio (A/A_{IS}) versus concentration using the first regression fit should be constructed. Certain compounds are known poor responders and may prove to be difficult to calibrate. Please refer to Appendix 7 for a list of these analytes.

15.7 If the analyst chooses to use linear regression, he/she must not force the calibration line through the origin.

15.7.1 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response

a = slope of line (also called the "coefficient of x")

x = concentration of the calibration standard

b = the intercept

15.7.2 The analyst should not force the line through the origin, but have the intercept calculated from the five or more data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0, 0) as a sixth calibration point.

15.7.3 The regression calculation will generate a coefficient of determination (r^2) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r^2 should be not less than 0.99. (The correlation coefficient is r and must be greater than 0.990.) The calculated intercept value needs to be evaluated before reporting sample results.

15.7.4 A positive value for the intercept indicates that there is some threshold instrument response that is the limiting factor in establishing linearity. A negative intercept value can be transformed into an x-intercept value that represents a threshold concentration that is the limitation. If the intercept is positive, then as a general rule, results where the instrument response is less than three times (3x) the intercept value may be unreliable. This will afford some protection against false positive results. If the intercept is negative, results below the concentration of the lowest concentration calibration standard may be unreliable.

Some clients require further evaluation when an analyte is calibrated using a linear regression curve. In these cases, the intercept value is multiplied by the ISTD concentration. This value is then compared to the MDL (the lower of the soil and water MDLs is used). If the calculated value is > 3x the MDL, then the curve is changed to weighted linear; r^2 should still be > 0.99.
When calculating the calibration curves using the linear regression model in 8270D and 8270E, a minimum quantitation check of the lowest calibration standard should be performed. The lowest calibration standard is re-quantitated as sample and evaluated. The re-calculated concentration of the low calibration point should be within 30% of the standard's true concentration for method 8270D and 50 % for method 8270E. Other recovery criteria may be applicable depending on the project-specific criteria or QAP. If the minimum quantitation check criteria are not met the analyst may take corrective action by re-defining the lower limit of quantitation and/or reporting the "out of control" target analytes as estimated when the concentration is at or near the lowest calibration point. The laboratory must be aware that raising the lower limit of quantitation may not be suitable to meet the project data quality objectives or permit limits where applicable. Other corrective actions, such as instrument maintenance and re-calibrating may be used instead of raising the quantitation limit or qualifying data for all samples analyzed after the calibration curve.

15.7.5 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y - b)}{a}$$

15.7.6 Method 8000D outlines two procedures that may be used to determine calibration function acceptability for linear and non-linear curves. The calibration data are refitted back to the calibration model. % Error and Relative Standard Error (RSE) evaluate the difference between the measured amount and the true amount (or concentration). % Error is determined as follows:

$$\%\,Error = \frac{x_i - x'_i}{x_i} \times 100$$

Where:

x'_i = Measured amount of analyte at calibration level *i*, in mass or concentration units

x_i = True amount of analyte at calibration level *i*, in mass or concentration units.

15.7.7 Percent error between the calculated and expected amounts of an analyte should be ≤30% for all standards and ≤ 50% for the lowest calibration level.

15.7.8 Relative Standard Error is calculated as follows:

$$RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x_i' - x_i}{x_i} \right]^2 \Big/ (n-p)}$$

Where:

x_i = True amount of analyte in calibration level i, in mass or concentration units.

x'_i = Measured amount of analyte in calibration level i, in mass or concentration units.

p = Number of terms in the fitting equation
(average = 1, linear 2, quadratic =3, cubic =4)

n = Number of calibration points

15.7.9 The RSE acceptance limit criterion is the same as the RSD Limit for CF or RF in the determinative method. If the RSD limit is not defined in the determinative method, the limit should be set at ≤20% for well performing compounds and ≤30% for poor responders. Please see the Appendix for a list of demonstrated poor responders.

15.8 Following calibration, an initial calibration verification (ICV) standard is analyzed. If available, the ICV should be made using standards from a vendor other than the one used for the calibration standards. If not available, a second lot from the same vendor may be used for verification. The criteria for the ICV are the same in 8270C and 625.1 as for the daily CCV (refer to section below). 8270D and 8270E requires that the ICV should recover within 30% of the expected concentration. An alternative recovery limit may be appropriate based on the project-specific data quality objectives. Quantitative sample analysis should not proceed for those analytes that fail the second source standard ICV. Any results reported for these compounds would be considered estimated values.

15.9 Calibration Check Standards

15.9.1 The initial calibration curve for each compound of interest must be checked and verified once every 12 hours of analysis time for all methods. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS.

15.9.2 System Performance Check Compounds (SPCCs): A system performance check for 8270C must be made every 12 hours. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same

check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. The minimum response factor for semivolatile SPCCs is 0.05. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. Methods 8270D and 8270E do not designate SPCCs. Rather, minimum response factor (RF) criteria should be met. See Appendix 9 for RF criteria.

15.9.3 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs are used to check the validity of the initial calibration in method 8270C. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\left|\overline{RF}_i - RF_c\right|}{\overline{RF}_i} \times 100$$

Where:

$\overline{RF}_i$ = average response factor from initial calibration

RF_C = response factor from current verification check standard

15.9.3.1 If the percent difference for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (>20% difference), for any one CCC, corrective action should be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new calibration may need to be generated. This criterion must be met before quantitative sample analysis begins. For method 625.1 analyses, the %D for all requested compounds of interest listed in Table 6 of the method must be 20% or less.

15.9.3.2 If one or more of the CCCs fail to meet criteria corrective action should be taken. This may require analyzing another calibration verification standard, or the instrument may require cleaning or additional maintenance. If the CCV continues to fail, a new calibration may have to be analyzed. When CCC criteria are not met, samples may still be analyzed, providing that all of the target compounds have a %D value ≤ 20%. Target analytes that are not CCCs should have a %D of ≤ 60 % in the daily check standard. If these criteria are not met, another CCV should be analyzed. In some cases, client specific criteria may be used provided they are tighter than the %D of ≤ 60% criteria. Exceptions may be taken to this and include cases where the analyte is biased high and there are no detects in the associated samples. Also, some analytes are known poor responders and may have to be evaluated on a case by

case basis. These analytes include benzoic acid, 2,4-dinitrophenol, the substituted anilines, benzidine, 3,3'-dichlorobenzidine, p-phenylenediamine, hexachlorophene, p-benzoquinone, n-decane, n-octadecane, atrazine, and others. In these cases, the high %D values need to be clearly documented and communicated to the client.

15.9.3.3 For 8270D and 8270E evaluation of the CCV, each of the target analytes in the calibration verification standard should meet the minimum response factor criteria as noted in Appendix 9. These criteria are particularly important when the common target analytes are also project-required compounds. This is the same check that is applied during the initial calibration.

15.9.3.4 If the minimum response factors are not met, the system should be evaluated, and corrective action should be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

15.9.3.5 Problems similar to those listed under initial calibration could affect the ability to pass the calibration verification standard analysis. If the problem cannot be corrected by other measures, a new initial calibration should be generated. The calibration verification criteria must be met before sample analysis begins.

15.9.4 The internal standard (ISTD) responses and retention times in each calibration check verification standard (CCV) should be evaluated against the mid-level standard from the calibration curve of the corresponding mix. The responses in the CCV should be within +100% and -50% of the responses in the mid-level calibration standard. The retention times should be within a half-minute of those in the mid-level standard.

15.10 If continuing calibration fails, the analyst determines why the check failed (i.e., instrument or standards) and makes the appropriate corrective action. Samples cannot be analyzed until the validity of the calibration has been verified.

15.11 For method 8270D and 8270E, if the %D (difference or drift) for a target analyte is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large number of compounds that may be analyzed by this method, it is expected that some compounds will fail to meet the criterion. If more than 20% of the compounds included in the initial calibration do not meet the criterion, then corrective action must be taken prior to analysis of samples. In cases where compounds fail (total less than 20% in the calibration) they may still be reported as nondetects provided that it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. Low level sensitivity may be evaluated by examining the lowest calibration level and the daily

CCV response factors. Depending on client requirements and regulatory agencies, the data may be reported as estimated or the sample may need to be re-analyzed for those compounds not meeting the 20 % criteria on a passing instrument. It is not acceptable to report estimated results for compliance samples.

15.12 The GC/MS should meet certain performance requirements, including DFTPP tune, initial calibration, calibration check standard, internal standard response factors, retention times, surrogate recoveries, and correct ion spectra, as well as others. These criteria are outlined in other parts of this SOP. When samples or QC fail to pass, it is important to verify whether the instrument has successfully passed all of the performance criteria. In this way, it can be determined if the samples or QC in question need to be re-extracted or if corrective action needs to be taken with the instrument.

15.13 Resolution of closely eluting structural isomers with similar mass spectra should be evaluated for the mid-point calibration standard and subsequent continuing calibration standards. The height of the valley between two isomer peaks must be less than 50% of the average of the two peak's heights (i.e. percent valley greater than 50%) for Method 8270C if closely eluting isomers are to be reported. For Method 8270D and 8270E, the percent valley must be greater than 75%.

16.0 ANALYST AND METHOD VALIDATION REQUIREMENTS

16.1 To establish the ability to generate acceptable accuracy and precision, the analyst should perform an "analyst validation study", Initial Demonstration of Proficiency, or QC Startup. Four LCS standards are extracted and analyzed. Calculate the average recovery and the standard deviation of the recovery for each analyte of interest using the four results. Table 6 of method 8270C (Appendix 2) may be used for comparison. If the validation study fails for one or more of the compounds, then the study must be repeated for those compounds which failed. For method 8270D and 8270E, SPC derived limits will be used.

16.2 For method 625.1, a quality control check sample concentrate is required containing each parameter of interest at a concentration of 100 ug/mL. Multiple solutions may be required. Calculate the average recovery in ug/L and the standard deviation of the recovery in ug/L and the standard deviation of the recovery(s) in ug/L for each parameter using the four results. For each parameter compare s and x with the corresponding acceptance criteria precision and accuracy, respectively, found in Table 6. If s and x meet the acceptance criteria, analysis of samples can begin. If an individual analyte does not meet the acceptance limits, the test must be repeated for that analyte.

17.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

17.1 DFTPP tune.

During each tune period, the GC/MS system is checked to see if acceptable performance criteria are achieved. For methods 8270C, 8270D and 625.1 the tune frequency is defined per 12 hours. Method 8270E requires that a tune be analyzed

with each calibration. A sample of 50 ng of decafluorotriphenylphosphine (DFTPP) is injected into the GC/MS system. (Refer to Appendix 3.) Compounds benzidine and pentachlorophenol are included in the DFTPP tune, and the tailing factor is calculated and checked daily. For method 8270C, DDT breakdown should be ≤ 20% and the tailing factors for pentachlorophenol and benzidine should be < 5 and < 3 respectively. The tailing factor criteria for 625.1 is <2 benzidine and pentachlorphenol. For Methods 8270D and 8270E, DDT breakdown should be ≤ 20% and the tailing factors for both pentachlorophenol and benzidine should be < 2.

$$\% \text{ breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD + DDE)}}{\text{sum of all peak areas (DDT + DDE + DDD)}} \times 100$$

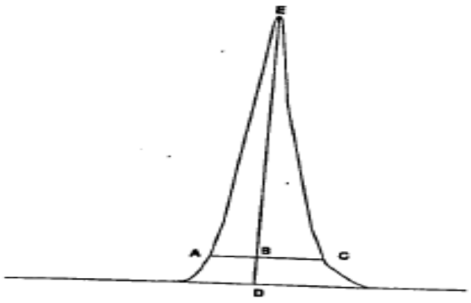
Tailing = BC/AB

Peak Height = DE

10% Peak Height = BD

Peak Width at 10% Peak Height = AC

Apex = E



17.1.1 If the tune does not pass, the GC/MS may need to be manually tuned to achieve the appropriate abundance. The suggested relative abundances are:

Mass 69	100%
Mass 219	35-45%
Mass 502	> 0.8%, but < 2%

These suggestions are meant to serve as guidelines only. Analysts should consult the manufacturer's guidelines and specifications.

17.2 Data Interpretation

17.2.1 Qualitative Analysis

17.2.1.1 The qualitative identification of compounds using this SOP is based on retention time and the comparison of the sample mass spectrum with the mass spectrum of a standard reference of the suspected compound. The characteristic ions from the reference mass

spectrum are defined as the three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. At least two ions (m/z) must be present to qualitatively identify a compound.

17.2.1.2 The relative retention time (RRT) of the sample component should be within ± 0.06 RRT units of the RRT of the standard component. Particular attention should be paid to the following compounds for possible coelution and misidentification: 1,2-, 1,3-, 1,4-dichloro-benzene, 2,4,5- ,2,4,6- trichlorophenol , benzo(b)fluoranthene, and benzo(k)fluoranthene, phenanthrene and anthracene, fluoranthene, benzo(a) anthracene, chrysene, and pyrene, as well as others.

17.2.1.3 The relative intensities of the characteristic ions should agree within 30% of the relative intensities of these ions in the reference spectrum. When analytes of different m/z ratios coelute, the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

17.2.1.4 For samples containing components not associated with the calibration standards, a library search may be performed for the purpose of tentative identification. **NOTE:** Non-requested calibrated analytes detected in a client sample may be reported on the Form 1 or certificate of analysis as TICs. A library search of a blank for that day must be performed for contamination check. Guidelines for tentative identification procedures are found in Appendix 4.

18.0 CALCULATIONS AND DATA REDUCTION METHODS

18.1 Quantitative Analysis

18.1.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given compound.

18.1.2 The concentration of each identified compound ion in the sample is calculated as follows if using a response factor:

Liquid Matrix:

Concentration

$$(\mu g/L) = \{[(Ax)(Is)(Vt)]/[(Ais)(\overline{RF})(Vo)(Vi)]\}$$

Where:

Ax = Area of characteristic ion for compound being measured

Is = Amount of internal standard injected (ng).

Vt = Volume of total extract, taking into account dilutions (i.e., a 1 to 10 dilution of a 1 mL extract will mean Vt = 10,000 µL.)

Ais = Area of characteristic ion for the internal standard.

RF = Average response factor for compound being measured.

Vo = Volume of water extracted (mL).

Vi = Volume of extract injected (µL).

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis):

Concentration

$$(\mu g/kg) = \{[(Ax)(Is)(Vt) / [(Ais)(RF)(Vi)(Ws)(D)]\}$$

Where:

Ax, Ix, Vt, Ais, RF, Vi = Same as for water matrix

Ws = Weight of sample extracted or diluted in grams.

D = (100% moisture in sample)/100, or 1 for wet-weight basis.

18.1.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: the areas Ax and Ais should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

18.1.4 Quantitation of multicomponent compounds (i.e. Aroclors, toxaphene, and chlordane) is beyond the scope of methods associated with this SOP.

18.2 When a target analyte is detected at a concentration above the calibration range, the sample is diluted to bring the concentration within the calibration range. All efforts are made to analyze samples undiluted or at the lowest possible dilutions. If a sample is initially diluted and no target analytes are detected, the lab will try to re-analyze the sample at a lower dilution or undiluted. In some cases, matrix interference or the presence of non-target analytes may prevent analysis at low or undiluted concentrations.

19.0 DATA RECORDING

19.1 Data are evaluated qualitatively and quantitatively as above using analytical software program such as Chemistation/Environquant.

19.2 Data are reviewed initialed, and annotated electronically in LIMS. Reasons for manual integrations or removal if false positives are documented as well.

19.3 Additional supporting documentation, LCS, MS/MSD, and surrogate recovery reports; ISTD recovery report; run logs; calibration summary; calibration history; and TIC search data are with the data.

20.0 QUALITY CONTROL REQUIREMENTS

20.1 Blanks:

20.1.1 A blank is extracted with each analytical batch or every 20 samples to demonstrate that interferences from the analytical system, glassware, and reagents are under control. Blanks are carried through all stages of sample preparation and analysis.

20.1.2 Typically, a blank, laboratory control sample (LCS), matrix spike (MS), and matrix spike duplicate (MSD) are extracted and analyzed with each prep batch. However, this may vary depending on such factors as sample availability and client requirements. Other client requirements may include a laboratory control sample duplicate (LCSD).

20.2 Laboratory Control Samples and Matrix Spikes

20.2.1 The lab typically spikes the analytes listed in the TCL list. In other cases, clients may require that every target analyte be spiked. Usually compounds are spiked at a concentration of 50 µg/mL. Concentrations may vary depending on the specific method or client requirements. Method 625.1 requires that all analytes of interest are spiked. Refer to Method 625.1 for a complete list of these compounds and concentrations. TCLP spiking compounds are:

1,4-dichlorobenzene
pyridine
o-cresol
hexachloroethane
m,p-cresols
nitrobenzene
hexachlorobutadiene
2,4,6-trichlorophenol
2,4,5-trichlorophenol
2,4-dinitrotoluene
hexachlorobenzene
pentachlorophenol

20.2.2 To determine recovery limits for LCSs, MSs, and MSDs, the following procedure is used. For each LCS, MS, and MSD, the percent recovery is calculated. Once a minimum of twenty data points is obtained, the average percent recovery (P) and the standard deviation (s) are calculated for each

spiking analyte. For a given matrix, upper and lower control limits are calculated as follows:

Upper Control Limit (UCL) = P + 3s

Lower Control Limit (LCL) = P - 3s

Control limits, also referred to as SPC or Statistical Process Control limits are typically generated semi-annually. For method 625.1, the LCS, MS/MSD recoveries must pass the "P1", "P2" and "RPD" criteria found in table 6 of that method.

20.2.3 If recovery is not within these limits, the data may need to be re-checked for errors, or the LCS, MS, MSD may be re-analyzed or re-extracted. In addition, the instrumentation may be checked for performance problems or the QC extracts may be checked to insure that the final volume was accurately measured and recorded. If the LCS fails to meet acceptance criteria due to low recovery, the associated samples may have to be re-extracted and re-analyzed when possible. If one or more recoveries are high in the LCS and these analytes are not detected in the samples, the event should be documented and data may be reported. If the MS and MSD both fail due to matrix interference and/or dilution, data may be reported provided the associated LCS passes acceptance criteria.

NOTE: Many clients have contract specific criteria that must be considered when evaluating recovery of the Quality Control samples.

20.2.4 The recovery limits are entered into the laboratory information management system (AlphaLIMS) at the time of certification.

20.2.5 Surrogates are added to all samples and QC at the time of prep. The method recommended surrogates are:

2-fluorophenol
phenol-d6
nitrobenzene-d5
2-fluorobiphenyl
2,4,6-tribromophenol
p-terphenyl-d14

Acid surrogates are usually spiked at a concentration of 100 µg/mL and base surrogates at a concentration of 50 µg/mL. The concentration may vary depending on the matrix and historical information of samples. Other analytical protocols, such as CLP, may require the use of different or additional surrogates.

20.2.6 The percent recovery of each surrogate is calculated. In cases where a sample or QC sample is diluted, the surrogates may be diluted out of the calibration range, and a calculation need not be performed. Periodically, a minimum of

twenty data points is collected in order to trend and update surrogate recovery limits. The average percent recovery (P) and the standard deviation of the percent recovery (s) are calculated for each of the surrogates. For solid and liquid matrices, the upper and lower control limits are calculated as follows:

Upper control limit (UCL) = P + 3s

Lower control limit (LCL) = P - 3s

20.2.7 The internal standard responses (ISTD) and retention times in the daily check standard are compared with those in the midpoint standard of the most recent calibration curve. ISTD responses must agree within + 100% and – 50% of those found in the midpoint standard. The retention times must agree within ± 0.5 minutes. Subsequent daily runs (check standards, QC and samples) are compared to the daily CCV and must meet the same criteria. For QSM samples, compare the ISTD for samples and QC to the mid-level calibration standard.

20.3 Handling Non-Compliant Data

While every attempt is made to satisfy all method and client requirements, instances when non-compliant data are reported. For example, it may not be possible to re-extract a sample due to lack of availability or a re-extraction may yield non-compliant results or holding times may be exceeded. Samples analyzed by methods 8270C, 8270D, 8270E and 625.1, in particular, are subject to non-compliance due to the extensive list of possible target analytes and the great variability in their chemistries. These methods, along with other analytical protocols and programs, such as QSM describe how to handle, qualify and report non-compliant data. Appendix 8 of this SOP outline some of the more common methodologies and their requirements for reporting non-compliant data. Analysts should approach these appendices for guidance, along with the body of this SOP, client-specific contracts, QSM, as well as the methods (such as SW-846). Analysts are also encouraged to seek guidance from other analysts, senior chemists, data validators, group leaders and the quality department as circumstances may dictate.

21.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

21.1 A review process is used to insure the quality of the data. Raw data are peer reviewed by a second analyst or a validator. When the analyst is satisfied that the data have been entered correctly, a data report is generated from AlphaLIMS. The AlphaLIMS report along with the raw data and supporting documentation, such as a run log and case narrative, are submitted for review to the data validator or another experienced analyst. The reviewer goes through the raw data as if he/she was working it up for the first time and verifies that they are correct. In addition, he/she must make sure that the data have been correctly entered into AlphaLIMS. AlphaLIMS reports may be self-reviewed. If errors are discovered in either the raw data or the AlphaLIMS report, then the two analysts should discuss the differences and how best to resolve them. Other analysts may be called upon to offer their advice or opinions as well. In some cases, the peer review

process may uncover errors that lead to a sample being re-extracted or re-run. All anomalies must be discussed in the case narrative.

21.2 Once the data review has been completed by the reviewer, the batch is returned to the analyst for corrections (if applicable) and the status is updated from REVW to DONE in AlphaLIMS.

22.0 DATA TRANSMITTAL

Data may be transmitted automatically to AlphaLIMS. This automatic "upload" procedure may be activated prior to data review or after data review is complete. In either case, the data recorded in AlphaLIMS are checked by the analyst for accuracy and completeness.

23.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

23.1 Run logs are generated for each instrument each day that the instrument is run. These run logs serve as records of what is run on the instrument, including samples, QC, calibrations, tunes, etc. Additional information is provided in the run log, including the analyst's initials, run date and time, and file name.

23.2 Raw data are stored electronically. Data are archived daily onto a serve.

24.0 LABORATORY WASTE HANDLING AND DISPOSAL

Sample extracts that have been run are temporarily stored in case they have to be reanalyzed. Once space is no longer available to keep them in the lab, they are moved to Waste Disposal where they are handled and disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

25.0 REFERENCES

25.1 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1B, SW-846, 3rd Edition, Nov. 1986. Method 8270C, "Semivolatile Organic Compounds by Gas Chromatograph/ Mass Spectroscopy (GC/MS): Capillary Column Technique," Rev. 3, Dec. 1996. USEPA, Office of Solid Waste and Emergency Response, Washington, DC 20460.

25.2 Federal Register, 40 CFR Part 136, December 22, 2000, 81295, contains Attachment 1 to Method 625.1.

25.3 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1B, SW-846, 3rd Edition, Feb 2007. Method 8270D, "Semivolatile Organic Compounds by Gas Chromatograph/ Mass Spectroscopy (GC/MS): Capillary Column Technique," Rev. 4, Feb. 2007. USEPA, Office of Solid Waste and Emergency Response, Washington, DC 20460.

25.4 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1B, SW-846, 3rd Edition, Feb 2007. Method 8270E, "Semivolatile Organic Compounds by Gas Chromatograph/ Mass Spectroscopy (GC/MS): Capillary Column Technique," Rev 6, June 2018. USEPA, Office of Solid Waste and Emergency Response, Washington, DC 20460.

25.5 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) Version 5.3, May 2019.

25.6 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1B, SW846 Update V, Revision 4, Method 8000D, July 2014.

26.0 HISTORY

Revision 45: Prometon and Sulfolane were added to the compounds in Appendix 1
Revision 44: Updated DoD QSM to version 5.3, July. Added Appendix 11.
Revision 43: Updated for clarification of methods.
Revision 42: Updated to include new updated SW-846 Method 8270E. Corrected grammatical errors. Updated to DoD QSM Version 5.2, December 2018.
Revision 41: deleted sentence for standard used for 625.1.
Revision 40: Update for new 600 methods.

APPENDIX 1: METHOD ANALYTES

Analyte	CAS Number	Analyte	CAS Number
1,1'-Biphenyl	92-52-4	4-Bromophenylphenylether	101-55-3
1,2,4,5-Tetrachlorobenzene	95-94-3	4-Chloro-3-methylphenol	59-50-7
1,2,4-Trichlorobenzene	120-82-1	4-Chloroaniline	106-47-8
1,2-Dichlorobenzene	95-50-1	4-Chlorophenylphenylether	7005-72-3
1,2-Diphenylhydrazine	122-66-7	4-Nitrophenol	100-02-7
1,3,5-Trinitrobenzene	99-35-4	4-Nitroquinoline-1-oxide	56-57-5
1,3-Dichlorobenzene	541-73-1	5-Methylchrysene	3697-24-3
1,4-Dichlorobenzene	106-46-7	5-Nitro-o-toluidine	99-55-8
1,4-Dinitrobenzene	100-25-4	7,12Dimethylbenz(a)anthracene	57-97-6
1,4-Dioxane	123-91-1	Acenaphthene	83-32-9
1,4-Naphthoquinone	130-15-4	Acenaphthylene	208-96-8
1-Hexanol	111-27-3	Acetophenone	98-86-2
1-Methylnaphthalene	90-12-0	Aniline	62-53-3
1-Naphthylamine	134-32-7	Anthracene	120-12-7
2,2'-Dichlorobenzil	21854-95-5	Aramite	140-57-8
2,3,4,6-Tetrachlorophenol	58-90-2	Atrazine	1912-24-9
2,3-Dichloroaniline	608-27-5	Benzaldehyde	100-52-7
2,4,5-Trichlorophenol	95-95-4	Benzidine	92-87-5
2,4,6-Tribromophenol (surr)	118-79-6	Benzo(a)anthracene	56-55-3
2,4,6-Trichlorophenol	88-06-2	Benzo(a)pyrene	50-32-8
2,4-Dichlorophenol	120-83-2	Benzo(b)fluoranthene	205-99-2
2,4-Dimethylphenol	105-67-9	Benzo(ghi)perylene	191-24-2
2,4-Dinitrophenol	51-28-5	Benzo(k)fluoranthene	207-08-9
2,4-Dinitrotoluene	121-14-2	Benzoic acid	65-85-0
2,6-Dichlorophenol	87-65-0	Benzyl alcohol	100-51-6
2,6-Dinitrotoluene	606-20-2	Biphenyl	
2-Acetylaminofluorene	53-96-3	Butylbenzylphthalate	85-68-7
2-Butoxyethanol	111-76-2	Caprolactam	105-60-2
2-Chloronaphthalene	91-58-7	Carbazole	86-74-8
2-Chlorophenol	95-57-8	Chlorobenzilate	510-15-6
2-Ethoxyethanol	110-80-5	Chrysene	218-01-9
2-Fluorobiphenyl (surr)	321-60-8	Cresols (total)	1319-77-3
2-Fluorophenol (surr)	367-12-4	Di-n-butylphthalate	84-74-2
2-Methyl-4,6-dinitrophenol	534-52-1	Di-n-octylphthalate	117-84-0
2-Methylnaphthalene	91-57-6	Diallate	2303-16-4
2-Naphthylamine	91-59-8	Dibenzo(a,e)pyrene	192-65-4
2-Nitrophenol	88-75-5	Dibenzo(a,h)anthracene	53-70-3
2-Picoline	109-06-8	Dibenzo(a,h)pyrene	189-64-0
3,3'-Dichlorobenzidine	91-94-1	Dibenzofuran	132-64-9
3,3'-Dimethylbenzidine	119-93-7	Diethylphthalate	84-66-2
3-Methylcholanthrene	56-49-5	Dimethoate	60-51-5
4,4'-Methylenebis(2-chloroaniline)	101-14-4	Dimethylphthalate	131-11-3
4-Aminobiphenyl	92-67-1	Dinoseb	88-85-7

Analyte	CAS Number
Diphenylamine	122-39-4
Disulfoton	298-04-4
Ethyl Methanesulfonate	62-50-0
Ethyl methacrylate	97-63-2
Famphur	52-85-7
Fluoranthene	206-44-0
Fluorene	86-73-7
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Hexachlorophene	70-30-4
Hexachloropropene	1888-71-7
Indeno(1,2,3-cd)pyrene	193-39-5
Isodrin	465-73-6
Isophorone	78-59-1
Isosafrole	120-58-1
Kepone	143-50-0
Methapyrilene	91-80-5
Methoxychlor	72-43-5
Methyl methacrylate	80-62-6
Methyl methanesulfonate	66-27-3
Methyl parathion	298-00-0
N-Methyl-N-nitrosomethylamine	62-75-9
N-Nitrosodi-n-butylamine	924-16-3
N-Nitrosodiethylamine	55-18-5
N-Nitrosodipropylamine	621-64-7
N-Nitrosomethylethylamine	10595-95-6
N-Nitrosomorpholine	59-89-2
N-Nitrosopiperidine	100-75-4
N-Nitrosopyrrolidine	930-55-2
Naphthalene	91-20-3
Nitrobenzene	98-95-3
Nitrobenzene-d5 (surr)	4165-60-0
Parathion	56-38-2
Pentachlorobenzene	608-93-5
Pentachloroethane	76-01-7
Pentachloronitrobenzene	82-68-8
Pentachlorophenol	87-86-5
Phenacetin	62-44-2
Phenanthrene	85-01-8
Phenol	108-95-2
Phenol-d5 (surr)	4165-62-2

Analyte	CAS Number
Phorate	298-02-2
Prometon	1610-18-0
Pronamide	23950-58-5
Pyrene	129-00-0
Pyridine	110-86-1
Sulfolane	126-33-0
Safrole	94-59-7
Sulfotepp	3689-24-5
Thionazin	297-97-2
Tributylphosphate	126-73-8
Triethylphosphorothioate	126-68-1
a,a-Dimethylphenethylamine	122-09-8
alpha-Terpineol	98-55-5
bis(2-Chloro-1-methylethyl)ether	108-60-1
bis(2-Chloroethoxy)methane	111-91-1
bis(2-Chloroethyl) ether	111-44-4
bis(2-Ethylhexyl)phthalate	117-81-7
m,p-Cresols	65794-96-9
m-Dinitrobenzene	99-65-0
m-Nitroaniline	99-09-2
m-Toluidine	108-44-1
n-Decane	124-18-5
n-Octadecane	593-45-3
o-Cresol	95-48-7
o-Nitroaniline	88-74-4
o-Toluidine	95-53-4
p-(Dimethylamino)azobenzene	60-11-7
p-Benzoquinone	106-51-4
p-Nitroaniline	100-01-6
p-Phenylenediamine	106-50-3
p-Terphenyl-d14 (surr)	1718-51-0
p-Toluidine	106-44-1

APPENDIX 2: QC ACCEPTANCE CRITERIA

Table 6 – QC Acceptance Criteria – Method 625.1					
Analyte	**Range for Q (%)**	**Limit for s (%) [3]**	**Range for $\bar{X}$ (%)[3]**	**Range for P_s (%) [3]**	**Limit for RPD (%)**
Acenaphthene	70-130	29	60-132	47-145	48
Acenaphthylene	60-130	45	54-126	33-145	74
Aldrin	7-152	39	7-152	D-166	81
Anthracene	58-130	40	43-120	27-133	66
Benzo(a)anthracene	42-133	32	42-133	33-143	53
Benzo(b)fluoranthene	42-140	43	42-140	24-159	71
Benzo(k)fluoranthene	25-146	38	25-146	11-162	63
Benzo(a)pyrene	32-148	43	32-148	17-163	72
Benzo(ghi)perylene	13-195	61	D-195	D-219	97
Benzyl butyl phthalate	43-140	36	D-140	D-152	60
beta-BHC	42-131	37	42-131	24-149	61
delta -BHC	D-130	77	D-120	D-120	129
bis(2-Chloroethyl)ether	52-130	65	43-126	12-158	108
bis(2-	52-164	32	49-165	33-184	54
bis(2-Chloroisopropyl)	63-139	46	63-139	36-166	76
bis(2-Ethylhexyl)	43-137	50	29-137	8-158	82
4-Bromophenyl phenyl	70-130	26	65-120	53-127	43
2-Chloronaphthalene	70-130	15	65-120	60-120	24
4-Chlorophenyl phenyl	57-145	36	38-145	25-158	61
Chrysene	44-140	53	44-140	17-168	87
4,4'-DDD	D-135	56	D-135	D-145	93
4,4'-DDE	19-130	46	19-120	4-136	77
4,4'-DDT	D-171	81	D-171	D-203	135
Dibenz(a,h)anthracene	13-200	75	D-200	D-227	126
Di-*n*-butyl phthalate	52-130	28	8-120	1-120	47
3,3'-Dichlorobenzidine	18-213	65	8-213	D-262	108
Dieldrin	70-130	38	44-119	29-136	62
Diethyl phthalate	47-130	60	D-120	D-120	100
Dimethyl phthalate	50-130	110	D-120	D-120	183
2,4-Dinitrotoluene	53-130	25	48-127	39-139	42
2,6-Dinitrotoluene	68-137	29	68-137	50-158	48
Di-*n*-octyl phthalate	21-132	42	19-132	4-146	69
Endosulfan sulfate	D-130	42	D-120	D-120	70
Endrin aldehyde	D-189	45	D-189	D-209	75
Fluoranthene	47-130	40	43-121	26-137	66
Fluorene	70-130	23	70-120	59-121	38
Heptachlor	D-172	44	D-172	D-192	74

Heptachlor epoxide	70-130	61	71-120	26-155	101
Hexachlorobenzene	38-142	33	8-142	D-152	55
Hexachlorobutadiene	68-130	38	38-120	24-120	62
Hexachloroethane	55-130	32	55-120	40-120	52
Indeno(1,2,3-cd)pyrene	13-151	60	D-151	D-171	99
Isophorone	52-180	56	47-180	21-196	93
Naphthalene	70-130	39	36-120	21-133	65
Nitrobenzene	54-158	37	54-158	35-180	62
N-Nitrosodi-*n*-	59-170	52	14-198	D-230	87

Analyte	**Range for Q (%)** [2]	**Limit for s (%)** [3]	**Range for $\bar{X}$ (%)** [3]	**Range for P, P_s (%)** [3]	**Limit for RPD (%)**
PCB-1260	19-130	77	19-130	D-164	128
Phenanthrene	67-130	24	65-120	54-120	39
Pyrene	70-130	30	70-120	52-120	49
1,2,4-Trichlorobenzene	61-130	30	57-130	44-142	50
4-Chloro-3-methylphenol	68-130	44	41-128	22-147	73
2-Chlorophenol	55-130	37	36-120	23-134	61
2,4-Dichlorophenol	64-130	30	53-122	39-135	50
2,4-Dimethylphenol	58-130	35	42-120	32-120	58
2,4-Dinitrophenol	39-173	79	D-173	D-191	132
2-Methyl-4,6-	56-130	122	53-130	D-181	203
2-Nitrophenol	61-163	33	45-167	29-182	55
4-Nitrophenol	35-130	79	13-129	D-132	131
Pentachlorophenol	42-152	52	38-152	14-176	86
Phenol	48-130	39	17-120	5-120	64
2,4,6-Trichlorophenol	69-130	35	52-129	37-144	58

1 Acceptance criteria are based upon method performance data in Table 7 and from EPA Method 625.1. Where necessary, limits for recovery have been broadened to assure applicability to concentrations below those used to develop Table 7.
2 Test concentration = 100 µg/mL
3 Test concentration = 100 µg/L

Q = Calibration verification (Sections 7.3.1 and 13.4)
s = Standard deviation for four recovery measurements in the DOC test (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements in the DOC test (Section 8.2.4).
P, Ps = MS/MSD recovery (Section 8.3.2, Section 8.4.2).
RPD = MS/MSD relative percent difference (RPD; Section 8.3.3).
D = Detected; result must be greater than zero.

APPENDIX 3: ABUNDANCE CRITERIA

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA (8270C, 625.1)

MASS	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% of mass 198
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

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA (8270D)

MASS	ION ABUNDANCE CRITERIA
51	10 - 80% of Base Peak
68	< 2% of mass 69
70	< 2% of mass 69
127	10 - 80% of Base Peak
197	< 2% of mass 198
198	Base peak or > 50% of mass 442
199	5 - 9% of mass 198
275	10 - 60% of Base Peak
365	> 1% of mass 198
441	Present but < 24% of mass 442
442	Base peak or > 50% of mass 198
443	15 - 24% of mass 442

APPENDIX 3: ABUNDANCE (continued)

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA (8270E)

MASS	ION ABUNDANCE CRITERIA
68	<2% of m/z 69
69	Present
70	<2% of m/z 69
197	<2% of m/z 198
198	Base peak or present
199	5-9% of m/z 198
365	>1% of Base Peak
441	<150% of m/z 443
442	Base peak or present
443	15-24% of m/z 442

APPENDIX 4: TENTATIVE IDENTIFICATION PROCEDURES

1. Relative intensities of major ions (> 10%) in the reference spectrum should be present in sample spectrum. This equates to detects of TICs ≥ 4 ppb concentration (10% of 40 ppb internal standard concentration).

2. Relative intensities of the major ions should agree within ± 30% (i.e., for an ion with an abundance of 50% of the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)

3. Molecular ion present in reference spectrum should be present in sample spectrum.

4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

5. If no valid identification can be made, the compound should be reported as "unknown." If an additional classification can be given to the unknown (unknown hydrocarbon, aromatic, chlorinated, etc.) it should be listed as such.

6. Peaks that are detected in the sample and analytical blank should be flagged as such on the report.

7. TIC detects with “fit” value < 85 will be identified with J qualifier. Detects with “fit” value > 85 will be identified with NJ qualifier and parameter name.

8. Peaks that are suspected as aldol-condensation reaction products should be flagged as such on the report.

9. The CAS for calibrated compounds not included on the client requested list of parameters will be the true CASRN, while the CASRN for non-calibrated compounds will be reported with leading zeros (000) in front of the probable CASRN.

10. GEL’s policy for reporting calibrated compounds when requested by the client as TICs only is to follow TIC reporting from National Functional Guidelines and report only ≥ 4 ppb for SVOA with J or NJ qualification.

APPENDIX 5: DIOXIN SCREENS

Dioxin Screens may be analyzed as a part of EPA Method 625.1. This appendix outlines the steps for preparing extracts and conducting the analysis. A dioxin screen is used for qualitative characterization only and may not be used to generate quantitative results. The presence of 2,3,7,8-TCDD is indicated as either 'yes" or "no."

Liquid or solid samples are extracted and concentrated according to routine prep procedures (refer to applicable SOPs). The sample extracts and the associated blank extract are evaporated to dryness under a hood. The extracts are then re-constituted with 100 µL of methylene chloride. Approximately 50 µL of the extract is then placed in an autosampler vial and injected on the GC/MS.

Prior to analyzing samples and blanks, an appropriate 2,3,7,8-TCDD standard is analyzed on the instrument. This standard is used for qualitative purposes and to determine the retention time. No acceptance criteria apply. The compound merely needs to be detected.

Dioxin screens are analyzed using a Selective Ion Monitoring (SIM) method. One window is used for the duration of the entire run and three ions are monitored: m/z 257, 320, and 322.

After a samples is analyzed, the analyst checks to see if a peak is present at the appropriate retention time and exhibiting all three ions. If such a peak is detected, a "yes" result is reported.

APPENDIX 6: SIM PAH ANALYSIS

Selected ion monitoring (SIM) allows for specific ion fragments to be monitored and detected by the mass spectrometer. Lower detection limits can be achieved with SIM since the instrument is only looking at a small number of mass fragments during each scan and more scans can take place each second. Since only a few mass fragments of interest are being monitored, matrix interferences can also be minimized.

SIM is ideally suited for smaller target compound lists when lower detection limits are critical. The analysis of polynuclear aromatic hydrocarbons (PAHs) is therefore a common application of SIM.

The criteria outlined in this SOP for tuning, initial calibrations, calibration verification standards, and quality control samples also apply to SIM analyses. Please refer to those sections for acceptance criteria and guidance. This appendix provides an overview of SIM and SIM PAH in particular.

SIM PAH samples are extracted and prepped for analysis in the same manner as regular 8270C or 8270D, 8270E samples using methods 3510C, 3550C and 3541. Quality control samples include a method blank (MB), laboratory control sample (LCS), laboratory control sample duplicate (LCSD) if appropriate, matrix spike (MS), and matrix spike duplicate (MSD). All samples and QC are spiked with a surrogate standard as well. For SIM PAH, the surrogate is 5-alpha-Androstane (CAS 438-22-2).

The SIM PAH initial calibration is subject to the same acceptance criteria as an 8270C or 8270D, 8270E calibration (See pertinent sections in this SOP). The typical SIM PAH calibration range is from 0.1 ng/uL to 20 ng/uL (on-column concentration), although this may vary depending on project requirements.

Some clients may request SIM analysis for additional compounds for liquid matrices using prep method 3510C (sometimes referred to as SIM PLUS).

The following compounds may be analyzed using SIM PAH:

Compound	Target Ions (m/z)
Naphthalene	128, 129
2-Methylnaphthalene	142, 141
1-Methylnaphthalene	142, 141, 115
2-Chloronaphthalene	162, 164
Acenaphthylene	152, 151, 153
Acenaphthene	154, 153, 152
Fluorene	166, 165
Phenanthrene	178, 179
Anthracene	178, 179
Fluoranthene	202, 203
Pyrene	202, 200
Benzo(a)anthracene	228, 226, 229
Chrysene	228, 229, 226
Benzo(b)fluoranthene	252, 253
Benzo(k)fluoranthene	252, 253

Benzo(a)pyrene	252, 253
Indeno(1,2,3-cd)pyrene	276, 138
Dibenzo(a,h)anthracene	278, 138
Benzo(ghi)perylene	276, 138
N-Methyl-N-nitrosomethylamine	74, 42
Bis(2-Chloroethyl)ether	93, 63
N-Nitrosodipropylamine	70, 42
N-Nitrosodiethylamine	102, 42, 57
N-Nitrosoprrolidine	101, 41, 68
N-Nitrosidi-n-butylamine	84, 57, 41
Benzidine	184, 92
3,3'-Dichlorobenzidine	252, 254

APPENDIX 7: POOR RESPONDERS

The following compounds may require special treatment when being determined by this method. As documented poor responders, these compounds do not extract or recover well. As a result, low recoveries are to be expected in LCS, MS, and MSD.

Benzidine may be subject to oxidative losses during the solvent concentration.

p-Phenylenediamine belongs to a class of amine compounds that are very unstable at higher pHs and will readily oxidize under basic conditions. p-Phenylenediamine has been a historically difficult compound to extract in water matrices due to the solubility and the solvent extraction efficiency.

N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from Diphenylamine.

1,2-Diphenylhydrazine is unstable even at ambient temperature and readily converts to Azobenzene.

Benzoic acid may recover poorly in spiked samples if the pH is not acidic enough (liquid) and is subject to erratic chromatography.

Pentachlorophenol, 2,4-Dinitrophenol, 4-Nitrophenol, 4,6-Dinitro-2-methylphenol, 4-Chloro-3-methylphenol, 2-Nitroaniline, 3-Nitroaniline, 4-Nitroaniline and Benzyl alcohol are subject to erratic chromatography behavior, especially if the GC system is contaminated.

p-Benzoquinone is a poor responder and typically has a very low RF.

Kepone is susceptible to degradation associated with active sites and GC system contamination.

Hexachlorocyclopentadiene is subject to thermal decomposition and chemical reaction in acetone solution.

APPENDIX 8: BNA Method Comparison

SVOA Method Comparison Table
Last Updated: July 2019

	8270C	8270D	8270E	QSM 5.3	625.1
IDOC	Analyze four LCS replicates. Evaluate average and standard deviation of replicates with method limits (Table 6 for 8270C and 625). Generate QC Summary and training certificate.	Analyze four LCS replicates. Evaluate average and standard deviation of replicates with method limits (Table 6 for 8270C and 625). Generate QC Summary and training certificate.	Analyze four LCS replicates. Evaluate average and standard deviation of replicates with method limits (Table 6 for 8270C and 625). Generate QC Summary and training certificate.	Analyze four LCS replicates. Evaluate average and standard deviation of replicates with method limits (Table 6 for 8270C and 625). Generate QC Summary and training certificate.	Analyze four LCS replicates. Evaluate average and standard deviation of replicates with method limits (Table 6 for 8270C and 625). Generate QC Summary and training certificate.
MDL LOD/LOQ LLOQ	Following initial set-up, MDLs are determined using points from each quarter. Q1: 1/2x, 1x, LOD, LOQ, MDL. Q2, Q3, Q4: LOD, LOQ, MDL. Analyzed on every instrument. LOD = 2x MDL LOQ = LLOQ=PQL	Following initial set-up, MDLs are determined using points from each quarter. Q1: 1/2x, 1x, LOD, LOQ, MDL. Q2, Q3, Q4: LOD, LOQ, MDL. Analyzed on every instrument. LOD = 2x MDL LOQ = LLOQ=PQL	Following initial set-up, MDLs are determined using points from each quarter. Q1: 1/2x, 1x, LOD, LOQ, MDL. Q2, Q3, Q4: LOD, LOQ, MDL. Analyzed on every instrument. LOD = 2x MDL LOQ = LLOQ=PQL	Following initial set-up, MDLs are determined using points from each quarter. Q1: 1/2x, 1x, LOD, LOQ, MDL. Q2, Q3, Q4: LOD, LOQ, MDL. Analyzed on every instrument. LOD = 2x MDL LOQ = LLOQ=PQL .	Following initial set-up, MDLs are determined using points from each quarter. Q1: 1/2x, 1x, LOD, LOQ, MDL. Q2, Q3, Q4: LOD, LOQ, MDL. Analyzed on every instrument. LOD = 2x MDL LOQ = LLOQ=PQL
Tune	Analyze every 12 hours. Criteria in method 8270C. Breakdown ≤ 20% for DDT; PCP tailing factor < 5; Benzidine tailing factor < 3	Analyze every 12 hours. Criteria in method 8270D. Breakdown ≤ 20% for DDT; PCP tailing factor < 2; Benzidine tailing factor < 2	Analyze with ICAL. Daily tune is optional. Meet ion ratio criteria for DFTPP in Table 3. Breakdown ≤ 20% for DDT; PCP tailing factor < 2; Benzidine tailing factor < 2	Analyze every 12 hours. Use 8270C or 8270D criteria depending on how samples are logged. Breakdown ≤ 20% for DDT. PCP tailing factor < 2; Benzidine tailing factor < 2.	Analyze every 12 hours. Criteria in method 8270C. Breakdown ≤ 20% for DDT; PCP tailing factor < 2; Benzidine tailing factor < 2
ICAL	Minimum of five levels. SPCCs: minimum RF is 0.05. CCCs: RSD ≤ 30%.	Minimum of five levels. RSD ≤ 20% for all targets or linear regression R^2 ≥ 0.99. Due to large number of diverse analytes, 8270D allows up to	Minimum of five levels. RSD ≤ 20% for all targets or linear regression R^2 ≥ 0.99. Due to large number of diverse analytes, 8270E allows up to	Minimum of five levels. There are no CCCs or SPCCs. RSD ≤ 15% for all targets or linear regression R^2 ≥ 0.99.	Minimum of three levels. RSD for each target analyte ≤ 35%. No linear curves.

	RSD for each target analyte ≤ 15% or linear regression for each target analyte R^2 ≥ 0.99. Some documented poor responders may not meet criteria. Qualitative analysis may proceed, but if these compounds are detected, re-analysis on a passing ICAL is required. %Error: ± 50% for low level and ± 30% for all other levels. RSE: criteria same as RSD for the method. If %Error or RSE fail, consult validator or GL. If adequate sensitivity has been established, ICAL may be acceptable for qualitative analysis.	10% outliers. If there are > 10% outliers, then re-calibration is required. Recommended minimum RFs (see Table 4) should be met for each level (With new ISTD approach, RF failures should be few if any). For outliers, non-detects do not require qualification, providing adequate sensitivity has been demonstrated with LLOQ level check standard (see CCV section). Analytes using a linear curve require evaluation of the intercept. The low level standard is re-evaluated as a sample. Recoveries must be within ± 30% of the true concentration. %Error: ± 50% for low level and ± 30% for all other levels. RSE: criteria same as RSD for the method. If %Error or RSE fail, consult validator or GL. If adequate sensitivity has been established, ICAL may be acceptable for qualitative analysis.	10% outliers. If there are > 10% outliers, then re-calibration is required. Recommended minimum RFs (see Table 4) should be met for each level (With new ISTD approach, RF failures should be few if any). For outliers, non-detects do not require qualification, providing adequate sensitivity has been demonstrated with LLOQ level check standard (see CCV section). Analytes using a linear curve require evaluation of the intercept. ICAL standards are re-evaluated as samples. Recoveries must be within ± 50% of the true concentration for LLOQ and ± 30% for other levels. Or, RSE ≤ 20%.	Analytes that do not meet either option may not be analyzed per QSAS. If criteria are not met, analyze sample(s) and QC on passing instrument for those compound(s).	
ICV	Second source. Same acceptance criteria as CCV.	Second source. All targets should recover within ± 30%.	Second source. All targets should recover within ± 30%.	Second source. All targets should recover within ± 20%.	Second source. All targets should recover within ± 20%.

		Minimum RFs should be met as outlined in Table 4 of the method. Per 8270D, *quantitative* analysis should not proceed for those analytes that fail ICV. Qualitative analysis may still be allowed.	Minimum RFs should be met as outlined in Table 4 of the method. Per 8270E, *quantitative* analysis should not proceed for those analytes that fail ICV. Qualitative analysis may still be allowed.	If a compound fails with a positive bias and there are no detects, results may be reported (with Q qualifier). Otherwise, re-analyze failing target compound(s) on a passing instrument.	
CCV	Analyze every 12 hours. CCC %D or %Drift ≤ 20%. SPCC RF ≥ 0.05. All targets RF ≥ 0.01. All targets %D or %Drift within ± 60% (source: DOE-AL SOW). Some exceptions may be made for documented poor performing compounds (see SOP) or target compounds with a positive bias if there are no detects. Note exceptions in narrative and DER. If the CCCs are not included in the target list, all analytes must pass 20% (section 7.4.5.2 of method).	Analyze every 12 hours. No CCCs or SPCCs. All targets should recover within ± 20% of the expected value. Method 8270D allows for up to 20% outliers (compared to target list of analytes). If more than 20% of analytes do not meet recovery criteria, then corrective action is required prior to analysis of samples. Recommended minimum RFs should be met as outlined in Table 4 of the method. If an outlier target compound is detected, the sample should be re-analyzed on a passing instrument. Non-detects may be reported, provided adequate sensitivity is demonstrated via a passing LLOQ standard. If a compound fails ± 20% in the CCV low, a LLOQ standard is analyzed. If the compound	Analyze every 12 hours. No CCCs or SPCCs. All targets should recover within ± 20% of the expected value. Method 8270E allows for up to 20% outliers (compared to target list of analytes). If more than 20% of analytes do not meet recovery criteria, then corrective action is required prior to analysis of samples. Recommended minimum RFs should be met as outlined in Table 4 of the method. If an outlier target compound is detected, the sample should be re-analyzed on a passing instrument. Non-detects may be reported, provided adequate sensitivity is demonstrated via a passing LLOQ standard. If a compound fails ± 20% in the CCV low, a LLOQ standard is analyzed. If the compound	Analyze every 12 hours and at end of tune window. All targets within ± 20%. All targets within ± 50% for ending CCV(s). For ending CCV(s), the first CCV must be injected within tune window. If target(s) fail, inject two additional CCVs within one hour. If both CCVs pass for the failing target(s), data may be reported. If either fails, corrective action must be taken (i.e. rerun with passing CCV). If a compound fails with a positive bias and there are no detects, results may be reported (with Q qualifier). Otherwise, re-analyze failing target compound(s) on a passing instrument.	Analyze every 12 hours. All targets within ± 20%.

		recovers within ± 30% (or high), the non-detect may be reported with no qualification. If it does not pass, the sample should be rerun.	recovers within ± 30% (or high), the non-detect may be reported with no qualification. If it does not pass, the sample should be rerun.		
ISTDs	Samples and QC: RT within ± 30 seconds from RT in CCV. EICP areas within -50% to +100% of the CCV. ISTD failures must be confirmed by re-analysis.	Samples and QC: RT within ± 30 seconds from RT in CCV. EICP areas within -50% to +100% of the CCV. ISTD failures must be confirmed by re-analysis.	Samples and QC: RT within ± 30 seconds from RT in CCV. CCV is compared to mid-level of ICAL. EICP areas within -50% to +100% of the CCV. ISTD failures must be confirmed by re-analysis.	CCV, Samples, and QC: RT within ± 10 seconds from RT in the midpoint of the ICAL. EICP areas within -50% to +100% of the midpoint in the ICAL. ISTD failures must be confirmed by re-analysis.	Samples and QC: RT within ± 30 seconds from RT in CCV. EICP areas within -50% to +100% of the CCV. ISTD failures must be confirmed by re-analysis.
MB	Detects of target analytes in MB acceptable if not detected in samples or if detects in samples are 10x higher than in MB. Apply B qualifier.	Detects of target analytes in MB acceptable if not detected in samples or if detects in samples are 10x higher than in MB. Apply B qualifier.	Detects of target analytes in MB acceptable if not detected in samples or if detects in samples are 10x higher than in MB. Apply B qualifier.	No target analytes detected >1/2 LOQ or >1/10 the amount measured in any sample or >1/10 the regulatory limit, whichever is greater. Common contaminants must not be detected > LOQ.	Detects of target analytes in MB acceptable if not detected in samples or if detects in samples are 10x higher than in MB. Apply B qualifier.
LCS	Evaluate with SPC limits. Re-extract samples if LCS fails (can fail high if there are no detects of those analytes in samples). Over-range analytes should be diluted to bring them within the calibration range. When samples are out of holding: consult with validator or GL for industrial clients (re-extraction may not be required); for others, re-extract if within 2x holding. Narrate and DER any failures.	Evaluate with SPC limits. Re-extract samples if LCS fails (can fail high if there are no detects of those analytes in samples). Over-range analytes should be diluted to bring them within the calibration range. When samples are out of holding: consult with validator or GL for industrial clients (re-extraction may not be required); for others, re-extract if within 2x holding. Narrate and DER any failures.	Evaluate with SPC limits. Re-extract samples if LCS fails (can fail high if there are no detects of those analytes in samples). Over-range analytes should be diluted to bring them within the calibration range. When samples are out of holding: consult with validator or GL for industrial clients (re-extraction may not be required); for others, re-extract if within 2x holding. Narrate and DER any failures.	Evaluate with QSM 5.0 limits in Appendix C. If analyte is not listed in the table, use SPC limits. If LCS fails, re-extract samples (can fail high if there are no detects of these analytes). Spike with ALL target analytes. If there are failures and samples cannot be re-extracted, narrate and DER. Identify compounds and validator will apply Q flag.	Evaluate with SPC limits (DHEC requires 625 method limits). Re-extract samples if LCS fails (can fail high if there are no detects of those analytes in samples). Over-range analytes should be diluted to bring them within the calibration range. When samples are out of holding: consult with validator or GL for industrial clients (re-extraction may not be required); for others, re-extract if within 2x holding. Narrate and DER any failures.

MS/MSD	Evaluate with SPC limits for recovery and RPD. Confirmed failures may be attributed to matrix interference.	Evaluate with SPC limits for recovery and RPD. Confirmed failures may be attributed to matrix interference.	Evaluate with SPC limits for recovery and RPD. Confirmed failures may be attributed to matrix interference.	Evaluate with QSM 5.0 limits in Appendix C for recovery and RPD (same limits used for LCS). Confirmed failures may be attributed to matrix interference.	Evaluate with SPC limits (DEHEC requires method 625 limits) for recovery and RPD. Confirmed failures may be attributed to matrix interference.
Surrogates	Evaluate with SPC limits. If surrogates fail low, re-extract the sample for confirmation. If there is obvious matrix interference, dilution and re-analysis may be appropriate and re-extraction may not be required. If surrogates fail high with no detects, data may be reported.	Evaluate with SPC limits. If surrogates fail low, re-extract the sample for confirmation. If there is obvious matrix interference, dilution and re-analysis may be appropriate and re-extraction may not be required. If surrogates fail high with no detects, data may be reported.	Evaluate with SPC limits. If surrogates fail low, re-extract the sample for confirmation. If there is obvious matrix interference, dilution and re-analysis may be appropriate and re-extraction may not be required. If surrogates fail high with no detects, data may be reported.	Evaluate with QSM 5.0 limits. If surrogates fail low, re-extract the sample for confirmation. If there is obvious matrix interference, re-extraction may not be required. Failures are Q qualified.	Evaluate with SPC limits. If surrogates fail low, re-extract the sample for confirmation. If there is obvious matrix interference, dilution and re-analysis may be appropriate and re-extraction may not be required. If surrogates fail high with no detects, data may be reported.

APPENDIX 9: 8270D MINIMUM RFs

RECOMMENDED MINIMUM RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION USING THE SUGGESTED IONS FROM TABLE 1

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800

Semivolatile Compounds	Minimum Response Factor (RF)
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800

Semivolatile Compounds	Minimum Response Factor (RF)
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

APPENDIX 10: CALIBRATION CONCENTRATIONS

	Level 1 (ng/uL)	Level 2 (ng/uL)	Level 3 (ng/uL)	Level 4 (ng/uL)	Level 5 (ng/uL)	Level 6 (ng/uL)	Level 7 (ng/uL)	Level 8 (ng/uL)	Level 9 (ng/uL)	Level 10 (ng/uL)
1,4-Dichlorobenzene-d4 (INTERNAL STANDARD)										
Naphthalene-d8 (INTERNAL STANDARD)										
Acenaphthene-d10 (INTERNAL STANDARD)										
Phenanthrene-d10 (INTERNAL STANDARD)										
Chrysene-d12 (INTERNAL STANDARD)										
Perylene-d12 (INTERNAL STANDARD)										
2-Fluorophenol (SURROGATE)		10	20	40	50	80	100	120	30	60
Phenol-d5 (SURROGATE)		10	20	40	50	80	100	120	30	60
Nitrobenzene-d5 (SURROGATE)		10	20	40	50	80	100	120	30	60
2-Fluorobiphenyl (SURROGATE)		10	20	40	50	80	100	120	30	60
2,4,6-Tribromophenol (SURROGATE)		10	20	40	50	80	100	120	30	60
p-Terphenyl-d14 (SURROGATE)		10	20	40	50	80	100	120	30	60
N-Nitrosodimethylamine	1**	10	20	40	50	80	100	120	30	60
Pyridine		10	20	40	50	80	100	120	30	60
Aniline		10	20	40	50	80	100	120	30	60
Phenol		10	20	40	50	80	100	120	30	60
bis(2-Chloroethyl)ether		10	20	40	50	80	100	120	30	60
2-Chlorophenol		10	20	40	50	80	100	120	30	60
n-Decane		10	20	40	50	80	100	120	30	60
1,3-Dichlorobenzene		10	20	40	50	80	100	120	30	60
1,4-Dichlorobenzene		10	20	40	50	80	100	120	30	60
Benzyl Alcohol		10	20	40	50	80	100	120	30	60
1,2-Dichlorobenzene		10	20	40	50	80	100	120	30	60
bis(2-Chloro-1-methylethyl)ether		10	20	40	50	80	100	120	30	60

o-Cresol (2-Methylphenol)		10	20	40	50	80	100	120	30	60
N-Nitrosodipropylamine		10	20	40	50	80	100	120	30	60
m,p-Cresols (3-Methylphenol & 4-Methylphenol)		10	20	40	50	80	100	120	30	60
Hexachloroethane		10	20	40	50	80	100	120	30	60
Nitrobenzene		10	20	40	50	80	100	120	30	60
Isophorone		10	20	40	50	80	100	120	30	60
2-Nitrophenol		10	20	40	50	80	100	120	30	60
2,4-Dimethylphenol		10	20	40	50	80	100	120	30	60
bis(2-Chloroethoxy)methane		10	20	40	50	80	100	120	30	60
2,4-Dichlorophenol		10	20	40	50	80	100	120	30	60
Benzoic Acid			20	40	50	80	100	120	30	60
1,2,4-Trichlorobenzene		10	20	40	50	80	100	120	30	60
Naphthalene	1	10	20	40	50	80	100	120	30	60
alpha-Terpineol		10	20	40	50	80	100	120	30	60
4-Chloroaniline		10	20	40	50	80	100	120	30	60
Hexachlorobutadiene		10	20	40	50	80	100	120	30	60
4-Chloro-3-methylphenol		10	20	40	50	80	100	120	30	60
2-Methylnaphthalene	1	10	20	40	50	80	100	120	30	60
1-Methylnaphthalene	1	10	20	40	50	80	100	120	30	60
Hexachlorocyclopentadiene		10	20	40	50	80	100	120	30	60
2,3-Dichloroaniline		10	20	40	50	80	100	120	30	60
2,4,6-Trichlorophenol		10	20	40	50	80	100	120	30	60
2,4,5-Trichlorophenol		10	20	40	50	80	100	120	30	60
2-Chloronaphthalene	1	10	20	40	50	80	100	120	30	60
o-Nitroaniline		10	20	40	50	80	100	120	30	60
m-Nitroaniline		10	20	40	50	80	100	120	30	60
Dimethylphthalate	1	10	20	40	50	80	100	120	30	60
2,6-Dinitrotoluene		10	20	40	50	80	100	120	30	60
Acenaphthylene	1	10	20	40	50	80	100	120	30	60

Acenaphthene	1	10	20	40	50	80	100	120	30	60
2,4-Dinitrophenol			20	40	50	80	100	120	30	60
Dibenzofuran		10	20	40	50	80	100	120	30	60
2,4-Dinitrotoluene		10	20	40	50	80	100	120	30	60
Diethylphthalate	1	10	20	40	50	80	100	120	30	60
4-Nitrophenol		10	20	40	50	80	100	120	30	60
Fluorene	1	10	20	40	50	80	100	120	30	60
4-Chlorophenyl phenyl ether		10	20	40	50	80	100	120	30	60
2-Methyl-4,6-dinitrophenol		10	20	40	50	80	100	120	30	60
p-Nitroaniline		10	20	40	50	80	100	120	30	60
Diphenylamine		10	20	40	50	80	100	120	30	60
1,2-Diphenylhydrazine		10	20	40	50	80	100	120	30	60
4-Bromophenyl phenyether		10	20	40	50	80	100	120	30	60
Hexachlorobenzene		10	20	40	50	80	100	120	30	60
Pentachlorophenol		10	20	40	50	80	100	120	30	60
n-Octadecane		10	20	40	50	80	100	120	30	60
Phenanthrene	1	10	20	40	50	80	100	120	30	60
Anthracene	1	10	20	40	50	80	100	120	30	60
Di-n-butylphthalate	1	10	20	40	50	80	100	120	30	60
Fluoranthene	1	10	20	40	50	80	100	120	30	60
Pyrene	1	10	20	40	50	80	100	120	30	60
Butylbenzylphthalate	1	10	20	40	50	80	100	120	30	60
Benzo(a)anthracene	1	10	20	40	50	80	100	120	30	60
Chrysene	1	10	20	40	50	80	100	120	30	60
bis (2-Ethylhexyl) phthalate	1	10	20	40	50	80	100	120	30	60
Di-n-octylphthalate	1	10	20	40	50	80	100	120	30	60
Benzo(b)fluoranthene	1	10	20	40	50	80	100	120	30	60
Benzo(k)fluoranthene	1	10	20	40	50	80	100	120	30	60
Benzo(a)pyrene	1	10	20	40	50	80	100	120	30	60
Indeno-(1,2,3-cd)pyrene	1	10	20	40	50	80	100	120	30	60

Dibenzo(a,h)anthracene	1	10	20	40	50	80	100	120	30	60
Benzo(ghi)perylene	1	10	20	40	50	80	100	120	30	60
m-Dinitrobenzene		10	20	40	50	80	100	120	30	60
2,3,4,6-Tetrachlorophenol		10	20	40	50	80	100	120	30	60
Dinoseb		10	20	40	50	80	100	120	30	60
Carbazole	1	10	20	40	50	80	100	120	30	60
p-Benzoquinone		10	20	40	50	80	100	120	30	60
Methoxychlor		10	20	40	50	80	100	120	30	60
p-Toluidine		10	20	40	50	80	100	120	30	60
m-Toluidine		10	20	40	50	80	10	120	30	60
1,4-Dinitrobenzene		10	20	40	50	80	100	120	30	60
2-Ethoxyethanol		10	20	40	50	80	100	120	30	60
Phthalic anhydride		10	20	40	50	80	100	120	30	60
Methylenebis(2-chloroaniline)		10	20	40	50	80	100	120	30	60
Dibenzo(a,e)pyrene		10	20	40	50	80	100	120	30	60
Benzaldehyde		10	20	40	50	80	100	120	30	60
Acetophenone		10	20	40	50	80	100	120	30	60
Caprolactam		10	20	40	50	80	100	120	30	60
1,1'-Biphenyl		10	20	40	50	80	100	120	30	60
Atrazine		10	20	40	50	80	100	120	30	60
Benzidine		10	20	40	50	80	100	120	30	60
3,3'-Dichlorobenzidene		10	20	40	50	80	100	120	30	60
1,4-Dioxane		10	20	40	50	80	100	120	30	60
Methyl methacrylate		10	20	40	50	80	100	120	30	60
Ethyl methacrylate		10	20	40	50	80	100	120	30	60
2-Picoline		10	20	40	50	80	100	120	30	60
N-Nitrosomethylethylamine		10	20	40	50	80	100	120	30	60
Methyl methanesulfonate		10	20	40	50	80	100	120	30	60
N-Nitrosodiethylamine		10	20	40	50	80	100	120	30	60
Ethyl methanesulfonate		10	20	40	50	80	100	120	30	60

Pentachloroethane		10	20	40	50	80	100	120	30	60
N-Nitrosopyrrolidine		10	20	40	50	80	100	120	30	60
N-Nitrosomorpholine		10	20	40	50	80	100	120	30	60
o-Toluidine		10	20	40	50	80	100	120	30	60
N-Nitrosopiperidine		10	20	40	50	80	100	120	30	60
a,a-Dimethylphenethylamine		10	20	40	50	80	100	120	30	60
2,6-Dichlorophenol		10	20	40	50	80	100	120	30	60
Hexachloropropene		10	20	40	50	80	100	120	30	60
N-Nitrosodi-n-butylamine		10	20	40	50	80	100	120	30	60
Safrole		10	20	40	50	80	100	120	30	60
1,2,4,5-Tetrachlorobenzene		10	20	40	50	80	100	120	30	60
Isosafrole		10	20	40	50	80	100	120	30	60
1,4-Naphthoquinone		10	20	40	50	80	100	120	30	60
Pentachlorobenzene		10	20	40	50	80	100	120	30	60
1-Naphthylamine		10	20	40	50	80	100	120	30	60
2-Naphthylamine		10	20	40	50	80	100	120	30	60
5-Nitro-o-toluidine		10	20	40	50	80	100	120	30	60
1,3,5-Trinitrobenzene		10	20	40	50	80	100	120	30	60
Phenacetin		10	20	40	50	80	100	120	30	60
Diallate		10	20	40	50	80	100	120	30	60
cis-Diallate		1.5	3	6	7.5	12	15	18	4.5	9
trans-Diallate		8.5	17	34	42	68	85	102	25.5	51
4-Aminobiphenyl		10	20	40	50	80	100	120	30	60
Pentachloronitrobenzene		10	20	40	50	80	100	120	30	60
Pronamide		10	20	40	50	80	100	120	30	60
4-Nitroquinoline-1-oxide		10	20	40	50	80	100	120	30	60
Methapyrilene		10	20	40	50	80	100	120	30	60
Isodrin		10	20	40	50	80	100	120	30	60
Aramite		10	20	40	50	80	100	120	30	60
Kepone		10	20	40	50	80	100	120	30	60

p-(Dimethylamino)azobenzene		10	20	40	50	80	100	120	30	60
Chlorobenzilate		10	20	40	50	80	100	120	30	60
3,3'-Dimethylbenzidine		10	20	40	50	80	100	120	30	60
2-Acetylaminofluorene		10	20	40	50	80	100	120	30	60
7,12-Dimethylbenz(a)anthracene		10	20	40	50	80	100	120	30	60
3-Methylcholanthrene		10	20	40	50	80	100	120	30	60
Hexachlorophene		500	1000	1250	1500	1750	2000			
p-Phenylenediamine		500	1000	1250	1500	1750	2000			
bis(Chloromethyl)ether		10	20	40	50	80	100	120	30	60
Tributylphosphate		10	20	40	50	80	100	120	30	60
Triethylphosphorothioate		10	20	40	50	80	100	120	30	60
Thionazin		10	20	40	50	80	100	120	30	60
Sulfotepp		10	20	40	50	80	100	120	30	60
Phorate		10	20	40	50	80	100	120	30	60
Dimethoate		10	20	40	50	80	100	120	30	60
Disulfoton		10	20	40	50	80	100	120	30	60
Methyl parathion		10	20	40	50	80	100	120	30	60
Famphur		10	20	40	50	80	100	120	30	60
Parathion		10	20	40	50	80	100	120	30	60
bis(Chloromethyl)ether		10	20	40	50	80	100	120	30	60
4-Chlorothiophenol		10	20	40	50	80	100	120	30	60
4-Chlorothioanisole		10	20	40	50	80	100	120	30	60
Phthalic acid		10	20	40	50	80	100	120	30	60
Hydroxymethyl phthalimide		10	20	40	50	80	100	120	30	60
Diphenyl sulfide		10	20	40	50	80	100	120	30	60
Diphenyl disulfide		10	20	40	50	80	100	120	30	60
Phenyl sulfone		10	20	40	50	80	100	120	30	60
Octachlorostyrene		10	20	40	50	80	100	120	30	60
Thiophenol		10	20	40	50	80	100	120	30	60
2,2'-Dichlorobenzil		10	20	40	50	80	100	120	30	60

bis(p-Chlorophenyl)disulfide		10	20	40	50	80	100	120	30	60
bis(p-Chlorophenyl)sulfone		10	20	40	50	80	100	120	30	60
SIM PLUS PAH										
5-alpha-Androstane (SURROGATE)	0.1	0.2	0.5	1	2	5	10	20		
N-Methyl-N-nitrosomethylamine		0.2	0.5	1	2	5	10	20		
bis(2-Chloroethyl)ether	0.1	0.2	0.5	1	2	5	10	20		
N-Nitrosodipropylamine	0.1	0.2	0.5	1	2	5	10	20		
Naphthalene	0.1	0.2	0.5	1	2	5	10	20		
2-Methylnaphthalene	0.1	0.2	0.5	1	2	5	10	20		
1-Methylnaphthalene	0.1	0.2	0.5	1	2	5	10	20		
2-Chloronaphthalene	0.1	0.2	0.5	1	2	5	10	20		
Acenaphthylene	0.1	0.2	0.5	1	2	5	10	20		
Acenaphthene	0.1	0.2	0.5	1	2	5	10	20		
Fluorene	0.1	0.2	0.5	1	2	5	10	20		
Phenanthrene	0.1	0.2	0.5	1	2	5	10	20		
Anthracene	0.1	0.2	0.5	1	2	5	10	20		
Fluoranthene	0.1	0.2	0.5	1	2	5	10	20		
Pyrene	0.1	0.2	0.5	1	2	5	10	20		
Benzo(a)anthracene	0.1	0.2	0.5	1	2	5	10	20		
Chrysene	0.1	0.2	0.5	1	2	5	10	20		
Benzo(b)fluoranthene	0.1	0.2	0.5	1	2	5	10	20		
Benzo(k)fluoranthene	0.1	0.2	0.5	1	2	5	10	20		
Benzo(a)pyrene	0.1	0.2	0.5	1	2	5	10	20		
Indeno-(1,2,3-cd)pyrene	0.1	0.2	0.5	1	2	5	10	20		
Dibenzo(a,h)anthracene	0.1	0.2	0.5	1	2	5	10	20		
Benzo(ghi)perylene	0.1	0.2	0.5	1	2	5	10	20		

APPENDIX 11: 1,4-Dioxane Analysis in Water Samples by 8270 SIM

1. Due to the high solubility and polarity of 1,4-Dioxane, multiple analytical approaches may be used for this compound. These include Method 8270 Full Scan Mode, Method 522, and Method 8270 SIM Mode. This appendix addresses the unique method variations employed when analyzing 1,4-Dioxane using Method 8270 SIM Mode.
2. Many of the procedures used for extracting and analyzing samples by Method 522 are followed for 8270 SIM. As such, SOP GL-OA-E-073 should be consulted for details concerning this procedure. This appendix primarily addresses key differences when using Method 8270 instead of Method 522.
3. Method 8270 requires that water samples be extracted within seven days of collection and analyzed within 40 days. 100 mL of sample are extracted using solid phase extraction (SPE) by Method 3535 following the procedure outlined in section 15.4 of SOP GL-OA-E-073.
4. While Method 522 uses BFB for tuning the mass spec, Method 8270 uses DFTPP. As such, for this analysis, 10 uL of a 5 ng/uL DFTPP tuning solution are used to tune the instrument. Samples must then be analyzed within twelve hours of the DFTPP standard.
5. The analytical column used with this analysis is a Restek Rtx-624, 30 m x 0.25 mm x 1.4 um film thickness (catalog# 10968) or equivalent. Other columns may be used, such as a DB-5MS column. However, MDL studies and other method performance evaluations must be analyzed with the new column prior to submitting sample results.
    a. Calibration standards are made to encompass the desired calibration range of 1,4-dioxane and the surrogate, 1,4-dioxane-d8. A minimum of five calibration levels are used. The typical calibration range for 1,4- dioxane is from 10 ug/L to 500 ug/L (on-column). Using a standard SPE extraction (100 mL to 2 mL), the final reporting concentration range is from 0.2 ug/L to 10 ug/L. Some states, such as North Carolina, have an action level of 0.4 ug/L.

6. Per the recommendation in Method 8270E, 1,4-Dioxane-d8 is used as the surrogate standard to monitor extraction efficiency. The surrogate recovery limits are set at 70-130% until statistically derived control limits can be generated. The internal standard employed in this SIM analysis is Tetrahydrofuran-d8 (THF-d8). The peak area of the IS must be monitored in all injections during each analysis day. The IS response must not deviate from the response in the most recent CVS by more than 30%. All samples and quality control samples are fortified with surrogate and internal standard.
    a. The specifications and run conditions described in this appendix were used during method development and may be changed if QC criteria outlined in the method are met. Note that a large volume injection (LVI) is used in order to achieve maximum sensitivity.

APPENDIX 11: 1,4-Dioxane Analysis in Water Samples by 8270 SIM (Continued)

Injection: 10 uL
Inlet: large volume splitless, 120 ºC, split delay of 0.5 min Pressure pulse: 30 psi, 0.4 min
MS Conditions: This SOP is written for SIM analysis, although method 522 does allow for SCAN analysis.
Window 1: m/z 46, 78, and 80 are scanned for the ISTD (tetrahydrofuran-d8) at a rate of 19.27 cycles/sec.
Window 2: m/z 58 and 88 are scanned for the target (1,4-dioxane) as well as m/z 62, 64, and 96 for the SURR (1,4-dioxane-d8) at 13.6 cycles/sec.
The SIM windows should be set so that no peak elutes within 5 seconds of the beginning or end of the window.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR

ANALYSIS OF CHLOROPHENOXY ACID HERBICIDES BY ECD

(GL-OA-E-011 REVISION 25)

APPLICABLE TO METHODS:
EPA SW-846 METHODS 8000D, 8151A

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1.0 STANDARD OPERATING PROCEDURE FOR ANALYSIS OF CHLOROPHENOXY ACID HERBICIDES BY ECD

2.0 METHOD CODES

EPA SW-846 Method 8000D, and 8151A

3.0 METHOD OBJECTIVE AND PURPOSE

This standard operating procedure provides the necessary instructions to conduct the analysis of samples for chlorophenoxy acid herbicides.

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 This is a gas chromatographic procedure for quantitatively determining certain chlorophenoxy acid herbicides. The following compounds can be quantitatively and qualitatively determined by this procedure:

Compound	
Pentachlorophenol	
2,4-D	Dalapon
2,4-DB	Dicamba
2,4,5-T	Dichlorprop
2,4,5-TP(Silvex)	Dinoseb
MCPP	MCPA

4.2 This method describes the analysis of chlorophenoxy acid herbicides by gas chromatography. Samples are extracted with diethyl ether and then esterified with either diazomethane or pentafluoro-benzyl bromide. The derivatives are determined by gas chromatography with dual columns and dual electron capture detectors (ECD).

4.3 The method code for chlorophenoxy acid herbicides is SW-846 Method 8151A.

5.0 METHOD SCOPE AND PERFORMANCE CHARACTERISTICS

5.1 The calibration concentration ranges vary per analyte. The typical tested concentration ranges follow. These concentrations reflect on-column values and do not include prep factors.

Compound	Concentration Range µg/L
Pentachlorophenal	25-400
Dalapon	500 - 4000
Dicamba	25 - 400
MCPP	5000 - 40000
MCPA	5000 - 40000
Dichlorprop	25 - 400
2,4 - D	25 - 400
2,4,5-T	25 - 400
Dinoseb	25 - 400

2,4-DB	25 - 400
2,4-DCAA (surr)	62.5 – 1000
2,4,5-TP	25 - 400

5.2 Method Detection Limits (MDL) for herbicides are performed annually.

5.3 Precision is determined by the Relative Percent Difference (RPD) between the Laboratory Control Sample (LCS) and the Laboratory Control Sample Duplicate (LCSD) or a Matrix Spike (MS) and Matrix Spike Duplicate (MSD). The RPD is determined through Statistical Process Control (SPC).

5.4 Accuracy is determined by the percent recovery on LCSs, and the control ranges are determined through Statistical Process Control (SPC). For South Carolina samples, the LCS must pass within 70-130%.

6.0 DEFINITIONS

6.1 Definitions specific to this SOP include:

6.2 Limit of Detection (LOD): The lowest concentration level that can be determined by a single analysis and with a defined level of confidence to be statistically different from a blank. The LOD verification is typically spiked at two times the MDL.

6.3 Limit of Quantitation (LOQ): The lowest level in the calibration curve. With the prep factor applied, the LOQ is referred to as the effective LOQ. The LOQ is equivalent to the PQL and LLOQ.

6.4 Lower Limit of Quantitation (LLOQ): The lowest concentration at which a target analyte can be reliably measured and reported. The LLOQ is the lowest point in the calibration curve and represents a concentration at which both quantitative and qualitative requirements can be consistently demonstrated. The LLOQ is verified quarterly, as the LOQ verification. The verifications performed by extracting and analyzing an LCS spiked at the LOQ. The LLOQ verification is carried through the same preparation and analytical procedures as environmental samples and QC. The LLOQ is analyzed on every instrument where data are reported and this is the laboratory's normal protocol. Recovery of target analytes in the LLOQ are compared to in-house-statistically-derived limits. Concentrations in samples reported below the LLOQ and above the MDL are qualified as estimated.

6.5 Practical Quantitation Limit (PQL): The lowest level in the calibration curve. With the prep factor applied, the PQL is referred to as the effective PQL. The PQL is equivalent to the LOQ and the LLOQ.

6.6 Relative Percent Difference (RPD): The difference between two duplicate samples, such as a MS/MSD, LCS/LCSD, or sample/sample DUP. It is determined by taking the difference between the two results and dividing by the average.

6.7 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

6.8 Lab-wide definitions can be found in GL-QS-B-001 the Quality Assurance Plan.

7.0 REFERENCES

7.1 Test Methods for Evaluating Solid Wastes: Laboratory Manual Physical/Chemical Methods, Volume 1B, SW-846, 3rd Edition, June 1997. Method 8151A, "Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization: Capillary Column Technique," Revision 1, December 1996.

7.2 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.0, July 2013 and Version 5.1, January 2017; DOE QSAS 3.0, July 2013 and Version 3.1 January 2017.

8.0 INTERFERENCES TO THE METHOD

8.1 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurements of chlorinated acid herbicides. Sample clean-up procedures are generally required. However, they may result in the loss of certain herbicides.

8.2 Organic acids, especially chlorinated acids, cause the most direct interference with this determination process. Phenols, including chlorophenols, will also interfere with the analysis.

8.3 Alkaline hydrolysis and subsequent extraction eliminates many of the predominant chlorinated insecticides that may otherwise interfere with the analysis.

8.4 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Glassware and glass wool should be acid rinsed, and the sodium sulfate should be muffled and acidified to avoid the possibility.

9.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

HEXANE IS MODERATELY TOXIC. PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

9.1 Wear eye protection with side shields while performing procedures in the lab.

9.2 Treat all chemicals and samples as potential health hazards and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and individual sample MSDSs are maintained in the laboratory.

9.3 Gloves are required when handling the chemicals and samples in this procedure. Latex or nitrile gloves may be used.

9.4 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Follow these general guidelines:

9.4.1 A plastic apron may be worn over lab coat when working with radioactive samples.

9.4.2 Protect counter tops with counter paper or work from radioactive sampling trays.

9.4.3 Prohibit admittance to immediate work area.

9.4.4 Post signs indicating radioactive samples are in the area.

9.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

9.4.6 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

9.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

9.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

9.7 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report should be completed and turned in to the safety committee.

9.8 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment, such as fire extinguishers, is located in the lab. Training is available on the proper operation of this equipment.

10.0 CAUTION WARNINGS

Hexane is moderately toxic. It should be used in a well-ventilated area.

11.0 APPARATUS AND EQUIPMENT, REAGENTS, AND INSTRUMENTS

11.1 Apparatus and Equipment

11.1.1 2 mL amber autosampler screw cap vials with Teflon-lined septa

11.1.2 Supelco Thermogreen 12.5 mm GC septa or equivalent

11.1.3 Pasteur pipets

11.1.4 Microliter syringe

11.1.5 Diverter valve (8”)

11.1.6 Capillary cleaving tool

11.1.7 Septum penetrating tool

11.1.8 0.32 mm ferrules

11.1.9 MXTY Connector

11.2 Reagents, Chemicals, and Standards

11.2.1 Standards can be bought from a certified vendor able to produce documentation tracing it to a certified source.

11.2.2 Hexane (C_6H_{14}), pesticide quality or equivalent

11.2.3 Diazomethane (CH_2N_2)

11.2.4 Silicic acid (H_2SiO_5)

11.3Instrumentation

GC: HP6890 (or equivalent)

HP7673 GC/SFC auto sampler (or equivalent)

Recommended Columns:

J&W Scientific DB-XLB	30 m x 0.25 mm x 0.2 µm
J&W Scientific DB17MS	30 m x 0.25 mm x 0.2 µm
Restek CLP Pest I	30 m x 0.25 mm x 0.2µm
Restek CLP Pest II	30 m x 0.25 mm x 0.2µm

It should be noted that the instrumentation and columns listed above are merely the recommended instrumentation and columns for use with this method.

12.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

12.1 Samples are collected in an amber glass bottle with a Teflon-lined cap. The collection containers are bought precleaned from a certified vendor.

12.2 All liquid samples have a holding date of seven days from the time of collection to be extracted, while all solid samples have fourteen days from the collection date to be extracted. Samples are protected from light and stored at 0° ≤ 6° C in amber vials with Teflon-sealed screw caps.

13.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

13.1 In order to maintain the gas chromatograph's columns and detectors, the gases should be changed when the tank pressure is below 250 psi. The gas chromatograph's septum in the injection port should be changed as needed. The splitter should be changed and column maintenance performed when baseline rise is present or the column becomes contaminated.

13.2 Routine Maintenance

Component	As Needed	Semi-Annually
Gases	X	
SiltekMXT or other connector	X	
Column Maintenance	X	
Detector Wipe Test		X
Detector Cleaning	X	
Injector Cleaning	X	

13.3 Non-routine Maintenance

13.3.1 When a check standard fails, column maintenance may need to be performed. One loop of each column should be cleaved and the Siltek MXT connector changed. The instrument is then baked out at 270º C overnight or until a straight baseline is obtained. If a straight baseline is

not obtained, the column is leaking or bleeding too badly to use and column maintenance must be performed again.

13.3.2 When contamination occurs, first replace/clean the autosampler syringe. If contamination is still present, column maintenance should be performed. If contamination is still present, replace the column. The column must then be leak checked and baked overnight. The instrument is then to be checked to determine if the problem is solved and if the instrument is stable. If not, the in-house service technician is called.

13.3.3 When maintenance is done on the instrument, it must be documented in the AlphaLIMS system.

14.0 PREPARATION OF STANDARD SOLUTION AND QUALITY CONTROL SAMPLES

14.1 Standard Solutions

14.1.1 Source standard solutions are purchased form Chem-Service, Protocol, Accu-Standard, and other certified vendors as organic acids and then esterified in the lab prior to use. The standards are traceable to National Institute of Standards and Technology (NIST) standards. The standards are given a unique identifying number for that day and is recorded in AlphaLIMS. Refer to Appendix 1 for detailed instructions on herbicide standards and ICAL preparations.

14.1.2 For guidance on standard documentation and traceability, refer to GL-LB-E-007 for Laboratory Standards Documentation.

15.0 INSTRUMENT CALIBRATION

15.1 The instrument should be checked for cleanliness and stability prior to analyzing calibration standards. The standards are loaded onto the auto sampler with the lowest standard being analyzed first to prevent carryover.

15.2 An external standard technique is used to calibrate the instrument. Calibration is obtained by analyzing the standards using the same method used for samples. Each standard must contain the same analytes, but at different concentration levels. The area counts of each peak along with the concentration of that particular analyte can then be used to plot a calibration curve. All standards are purchased in acid form and are esterified in the laboratory. (Herbicide standards in the acid form are good for two months after date opened. Esterified herbicide standards are good for six months). The typical calibration range is from 25 ug/L to 400 ug/L. MCPP and MCPA are calibrated from 5,000 ug/L to 40,000 ug/L and Dalapon is calibrated from 500 ug/L to 4,000 ug/L. The lowest calibration level corresponds to the LLOQ (PQL). Refer to Appendix 1 for calibration concentrations. The MDL, LOD, and LLOQ (LOQ) are verified quarterly. The MDL verification is spiked at the MDL concentration (approximately one third of the LLOQ). The LOD is spiked at two times the MDL. And the LLOQ is spiked at the lowest calibration level (the PQL) . Verification samples are extracted using the same methods and processes used for samples and analyzed on each

instrument used for that analysis. Statistical Process Limits (SPC) are calculated for the LLOQ using historical data from the lab and are used to evaluate the LLOQ recoveries.

15.3 The calibration standards are introduced into the gas chromatograph using a syringe. Calculate the Calibration Factor (CF) and the relative standard deviation for each analyte at each standard concentration using the formula below.

NOTE: Both columns should meet acceptance criteria for each analyte of interest before analyzing samples.

15.3.1 Calculate the calibration factor for each analyte at each concentration as:

$$\text{CF} = \frac{\text{Peak Area of the Compound in the Standard}}{\text{Mass of Compound injected (in nanograms)}}$$

The CF can also be calculated using the concentration of the standard rather than the mass in the denominator of the equation above. However, the use of the concentration will require changes to the equations that are used to calculate sample concentration.

15.3.2 Calculate the mean calibration factor for each analyte as:

$$\text{CF} = \frac{\sum_{i-1}^{n} \text{CF}_i}{n}$$

Where n = the number of standards analyzed

15.3.3 Calculate the standard deviation and the RSD of the calibration factor for each analyte as:

$$SD = \sqrt{\frac{\sum_{I=1}^{N}(CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{CF} X\ 100$$

If the percent relative standard deviation (%RSD) of the calibration factor is $\leq$ 20% over the working range, linearity through the origin can be assumed, and the mean calibration factor can be used to quantitate sample results. When this is not the case, linearity cannot be assumed and the analyst must use a calibration curve.

15.4 If the analyst chooses to use linear regression, he/she must not force the calibration line through the origin.

15.4.1 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response

a = slope of line (also called the "coefficient of x")

x = concentration of the calibration standard

b = the intercept

15.4.2 The analyst should not force the line through the origin, but have the intercept calculated from the data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0,0) as a sixth calibration point.

15.4.3 The regression calculation will generate a correlation coefficient (R) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, R must be $\geq$ 0.99. The calculated intercept value needs to be evaluated before reporting sample results. If the system you are using calculates the coefficient of determination (R^2), the value must still meet the 0.99 criteria. Please note that second order curve types (i.e. quadratic fit) cannot be used to meet the acceptance criteria.

15.4.4 In calculating the sample concentrations, the regression equation is rearranged to solve for concentration (x) as shown below:

$$x = \frac{(y-b)}{a}$$

15.5 A minimum number of five calibration standards is required by the method.

15.5.1 Method 8000D outlines two procedures that may be used to determine calibration function acceptability for linear and non-linear curves. The calibration data are refitted back to the calibration model. % Error and Relative Standard Error (RSE) evaluate the difference between the measured amount and the true amount (or concentration).

15.5.2 % Error is determined as follows:

$$\%Error = \frac{x_i - x'_i}{x_i} x100$$

Where:

x'_i = Measured amount of analyte at calibration level *i*, in mass or concentration units

x_i = True amount of analyte at calibration level *i*, in mass or concentration units.

Percent error between the calculated and expected amounts of an analyte should be ≤30% for all standards and ≤50% for the lowest calibration level.

15.5.3 Relative Standard Error is calculated as follows:

$$RSE = 100 \times \sqrt{\sum_{i-1}^{n} \left[\frac{x'_i - x_i}{x_i} \right]^2 \Big/ (n-p)}$$

Where:

x_i = True amount of analyte in calibration level *i*, in mass or concentration units.

x'_i = Measured amount of analyte in calibration level *i*, in mass or concentration units.

p = Number of terms in the fitting equation (average = 1, linear 2, quadratic =3, cubic =4)

n = Number of calibration points

15.5.4 The *RSE* acceptance limit criterion is the same as the RSD Limit for $\overline{CF}$ or $\overline{RF}$ in the determinative method. If the RSD limit is not defined in the determinative method, the limit should be set at ≤ 20% for well performing compounds.

15.6 Continuing Calibration

15.6.1 The initial calibration curve for each compound of interest must be checked and verified prior to conducting any sample analysis. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC. The initial calibration verification standard must be from a second vender if available or a second lot from the same vendor. If a second lot is used, it should be from a different source than the ICAL. The standard must also be injected at intervals of once every ten samples and at the end of the analysis sequence. The continuing calibration check standard may be from the same source as the initial calibration. This will determine the validity of the initial calibration on a daily basis. These standards are prepared using acids which go through the same esterification process as the samples.

15.6.2 Calibration verification for linear curves involves the calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference.

$$\%\ \text{Drift} = \frac{\text{Calculated Concentration - Theoretical Concentration}}{\text{Theoretical Concentration}} \times 100$$

Where the calculated concentration is determined using the calibration factor or response factor from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

Where:

CF_v = response factor from current verification check standard

15.6.3 The CVS should recover within ± 15% (8151 A) or ± 20% (DoDQSM) of the known concentration. If this criterion is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration will be generated. This criterion must be met before quantitative sample analysis begins. If a bracketing CVS recovers with a positive bias and there are no detects in the samples, the data may be reported. If there are detects, the samples must be reanalyzed for confirmation. If the bracketing CVS fails with a negative bias on both columns, the samples in the bracket must be reanalyzed. If the CVS fails low on only one column and there are no detects, data may be reported.

16.0 INSTRUMENT PERFORMANCE REQUIREMENTS

16.1 Gas Chromatography Recommended Conditions:

Detector Temperature: 325º C

Injector Temperature: 215º C

Column A: DB-17MS or CL Pest I

Column B: DB-XLB or CLP Pest II

Column Flow = 2.0 mL/minute

Carrier Gas: Helium or Hydrogen

Make-up Gas: Nitrogen

1st Temperature: 50º C

Hold = 30 sec.

1st Ramp = 25.00° C/minute

2nd Temperature = 190º C

Hold = 1 minute

2nd Ramp = 11.00 º C/minute

3rd Temperature: 300º C

Hold = 0 minute

3rd Ramp = 20.00° C /minute

Final Temperature = 320º C

Hold = 3 minutes

Run Time = 21.10 minutes

NOTE: Slight variations may be needed as column length changes.

16.2 Before samples can be analyzed, the baseline must be stable with little or no background noise or baseline rise, and the continuing calibration check standard must be within ± 15% of the true value (± 20% for DoD QSM).

17.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

17.1 To establish that an analyst can perform the procedures in an acceptable manner and that the method generates data of acceptable bias and precision, the following operations are performed:

17.1.1 A Quality Control (QC) check standard must be prepared containing each analyte of interest. It must be prepared from pure standard material or purchased as a certified solution. It must be made from a source independent of that used for calibration.

17.1.2 Four aliquots should be prepared and analyzed by the same procedures used to prepare and analyze actual samples.

17.1.3 Calculate the average recovery in µg/L, and the standard deviation of the recovery (S) in µg/L, for each analyte of interest using the four results.

17.1.4 For each analyte compare S with the corresponding acceptance criteria for precision and accuracy, respectively, given in the quality control table at the end of the method. If the S for all analytes of interest meets the acceptance criteria, the systems performance is acceptable and analysis of actual samples can begin. If any individual S exceeds the precision limits or fall out of the range for accuracy, the system's performance is unacceptable for that analyte and a check standard for that analyte must be prepared and reanalyzed.

17.2 Method Detection Limits are also determined and documented annually.

17.3 Analysts are given continual performance evaluation samples as an ongoing assessment of their ability to perform the procedure.

18.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

18.1 Standards, samples, blanks, and Quality Control samples are introduced to the instrument via direct injection. Daily retention time windows must be centered for each analyte. Refer to GL-OA-E-001 for Establishing Retention Time Windows for GC and HPLC Analysis as to when and how often retention time windows should be established.

18.2 Samples are analyzed in a set referred to as analysis sequence or run sequence. The sequence begins with the instrument blank, followed by the sample extracts. A mid-level calibration check standard must be analyzed after every ten extracts

and at the end of each run sequence. The sequence ends when all extracts have been injected and analyzed.

18.3 The data are entered into the computer and a data report is generated. A run log is created by the analyst on the computer. It lists every injection made by the instrument in order, for a given date.

18.4 Before the instrument is used, a highly concentrated standard may be analyzed to prime the columns.

18.5 1.0 µl of the extract is injected into the instrument.

18.6 The autosampler is used to inject extracts sequentially. It can be set to run from any given starting position to a specific ending position. The digital integrator converts the analog signal from the instrument to digital information that is processed into a graphic format showing concentration based on peak area.

18.7 Samples containing target analyte concentrations that exceed the linear range of the analyte calibration curve must be diluted. The dilution level should be performed to place the highest analyte concentration between the middle and high points of the calibration curve (on column). If a sample is initially diluted, and target analytes are not detected and non-target analytes are not interfering with the analysis, the sample must be reanalyzed at a lower dilution. Analysts should be aware that diluting samples will increase the detection limits for undetected analytes. Random dilutions without due cause are not acceptable. Samples should undergo appropriate clean up methods prior to diluting for observed matrix problems.

18.8 The automated sequence is initiated by programming the autosampler to start at the first sample to be analyzed.

19.0 CALCULATIONS AND DATA REDUCTION METHODS

The concentration of each analyte in extract can be determined by comparing the response obtained from analyzing the extract to calibration curve.

20.0 DATA RECORDING

Data are recorded and calculated by the Chemstation data acquisition system. Data are stored on a chem server. The data are also input into AlphaLIMS.

21.0 QUALITY CONTROL REQUIREMENTS

21.1 Before analysis of any Quality Control samples, the instrument calibration must be verified. A continuing calibration check standard must be analyzed, before any QC or client samples, to verify instrument calibration and must be ± 15% of its true value.

21.2 A Method Blank (MB) is used to determine background concentrations of analytes of interest that have the potential to interfere with sample analysis. These MBs are analyzed with every analytical batch that has a maximum number of twenty samples. The criteria for acceptance are that there are no target analytes of interest present above the Lower Limit of Quantitation (LLOQ).

21.2.1 If the analyte of interest is present at a concentration between the MDL and LLOQ, all data are qualified with a “B” flag and reported. If the

analyte of interest is present at a concentration above the LLOQ and the samples contain the analyte of interest at a concentration of greater than 10 times the concentration found in the MB, the data are qualified with a "B" flag and reported. If the concentration found in the sample is less than 10 times that found in the MB and greater than the LLOQ, the samples must be re-extracted.

21.3 A Laboratory Control Sample (LCS) is analyzed with every batch. The accuracy and precision of the extraction and analysis are monitored with these samples. Sample spikes and sample duplicates are also used for this purpose. The criterion for acceptance is that the recoveries must be within the fixed range given for any given analyte for a specific matrix. Refer to sections 5.3 and 5.4. In addition to a LCS, a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) are typically extracted and analyzed with each batch of samples. If not enough sample aliquot is available for a MS and MSD, a LCSD may be extracted and analyzed.

21.4 For Method 8151A, the surrogate 2,4-DCAA is used. Its acceptance is based on SPC limits and is matrix specific.

21.5 The Retention Time (RT) window should be established using the initial calibration check standard. Refer to GL-OA-E-001 for Establishing Retention Time Windows for GC and HPLC Analysis for instructions. In order to report a concentration from the external standards table, the retention time must be within the established window. If not, the concentration is not reported.

21.6 Nonconformance

21.6.1 If the continuing check standard fails any criteria in section 15.6, the analyst must take action to correct the situation. This may be performing any of the maintenance steps described in section 13.0 to get the instrument to meet its daily calibration. If all attempts fail, the analyst must analyze a new series of calibration standards, thus obtaining a new calibration curve.

21.6.2 If the percent recovery in the MS or MSD falls outside the established SPC limits for recovery, the analyst should evaluate the LCS recoveries and MB analyses. If the LCS and MB analyses do not indicate a problem with the preparation procedures, the MS recoveries may be attributed to matrix effect. Surrogate recovery data should also be used to evaluate the data. Recoveries of both MS compounds and surrogates that are outside the acceptance limits suggest more pervasive analytical problems than problems with the recoveries of either MSs or surrogates alone. Analysts are not required to reanalyze the MSs for failing recoveries; however they should seek additional technical support before deciding not to reanalyze MS samples. Acceptance limits are determined semi-annually using Statistical Process Control (SPC). The limits are maintained in the Quality Department. SPC limits are generated for surrogates, LCSs, MSs, MSDs, and RPDs.

21.6.3 When a Method Blank fails, the acceptance criteria as described in section 21.2, the analytical batch may be re-extracted.

21.6.4 If a surrogate in a sample falls outside of the acceptable range, the sample should be re-extracted. However, if the recovery is above the acceptance range and no target analytes are detected in the sample, the result may be reported. A DER must be generated and the failure documented in the Case Narrative. If the surrogate fails the second time, the failure is attributed to matrix interference.

21.6.5 If retention time is out of the window, the concentration for that analyte cannot be reported. However, if the continuing check standard falls outside the established window, all the samples bracketed by that standard must be re-injected.

21.7 Any positive identification and quantitation of an analyte of interest must be confirmed on a separate column. Qualitative confirmation is presence within the RT window on each column. Quantitation of an analyte of interest must be taken from a column whose daily check standards, bracketing that sample set, have met the acceptable Quality Control criteria.

21.7.1 Since the same method criteria and instrument calibration specified in section 15.0 are applied uniformly to both columns, either column can be selected to serve as the primary or confirmatory column. The lab's standard practice is to report the lower column result.

21.7.2 The determination of MDLs is also applied to both columns. Refer to The Determination of Method Detection Limits, GL-LB-E-001.

22.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

22.1 Upon completion of a batch, the analyst enters data. A data report is generated and is placed in a file folder along with the batch sheet and all the raw data (chromatograms). This folder is given to a Data Review person for reviewing.

22.2 Levels of Review

22.2.1 First level review: It is the responsibility of the analyst to ensure that the check standard passes and that the Quality Control results were within acceptance ranges. The analyst makes sure that all necessary paperwork is given to the data reviewer.

22.2.2 Second level review: The data reviewer reviews all of the raw data making sure that the check standard passed and that the QC results are within acceptance ranges. The data reviewer makes sure that the correct result, date, and time were uploaded by the analyst, as well as any dilutions or comments. He/she is to compare the data entry report with the raw data, initialing and dating each hard copy. He/she also ensures that the calibration curves being used are acceptable and that the standards have not expired. Once the reviewer determines that everything is correct or that corrections need to be made, he/she returns the data to

the analyst, who makes the necessary corrections and/or sends the batch to "Done" status.

23.0 DATA TRANSMITTAL

After the review process is complete, Data Management generates the appropriate report.

24.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

All raw data along with the run sequence, batch sheet, and data entry report must be stored together. After a time, it is boxed and stored off-site.

25.0 LABORATORY WASTE HANDLING AND DISPOSAL: SAMPLES, EXTRACTS, DIGESTATES AND REAGENTS

Samples, extracts, solvent wastes, and expired standards are stored in a hazardous waste can. Once the can is full, it is emptied by the waste disposal specialist.

26.0 HISTORY

Revision 21: Removed reference to retired procedure GL-OA-E-002.
Revision 22: Updated Section 21 for compliance with 8000C and 8000D.
Revision 23: Updated to include Method 8000D requirements.
Revision 24: Revised definitions and instrument calibration sections for clarification of LLOQ. Added DOD/DOE QSM version 5.1.
Revision 25: Added statement for SC Samples, the LCS must pass within 70-130%.

APPENDIX 1

Herbicide Standard
Need two **10 mL** volumetric flasks for Initial Calibration Curve (ICAL) and Check Standards. Rinse clean with ether.

ICAL Intermediate Standard
1. Add 500 µL of surrogate standard to ICAL flask.
2. Add 200 µL of herbicide mix #1 to ICAL flask.
3. Add 200 µL of herbicide mix #2 to ICAL flask.
4. Add 200 µL of herbicide mix #3 to ICAL flask.

Dilute to the 10 mL mark with Ether.

Continuing Calibration Intermediate Standard
Same as above, but different lot numbers, serving as a second source.

Initial Calibration Curve (ICAL) Preparation
1. Need 7- 15 mL centrifuge tubes, rinsed clean with hexane.
2. Label each tube with the different concentrations 25 ppb, 50 ppb, 100 ppb, 150 ppb, 200 ppb, 300 ppb, 400 ppb.
3. 25 ppb add 62.5 µL of ICAL standard
4. 50 ppb add 125 µL of ICAL standard
5. 100 ppb add 250 µL of ICAL standard
6. 150 ppb add 375 µL of ICAL standard
7. 200 ppb add 500 µL of ICAL standard
8. 300 ppb add 750 µL of ICAL standard
9. 400 ppb add 1000 µL of ICAL standard

Continuing Calibration Curve Preparation
1. Need 4- 15 mL centrifuge tubes
2. The check standard is the same as the 200 ppb level 5 ICAL
3. Add 500 µL of Check Standard to each tube

To each tube add **0.5 mL of isooctane** and **0.25 mL methanol** to extract. Dilute to a volume of **4 mL of hexane**.

Add 1 mL of **diazomethane** and swirl. Cover rack with aluminum foil. Extract should stay yellow after 30 minutes. If it does not stay yellow add more diazomethane.

Add approximately 10 mg silicic acid which will destroy excess diazomethane. This does not need to be weighed on a balance. Let stand for 15 minutes. Bring to a final volume of 10 mL with **hexane**.

Pipet the standard from the centrifuge tube, taking care to avoid the silicic acid, and transfer to a clean 10 mL volumetric flask. (Intermediate herbicide standards are good for two months. Esterified herbicide standards are good for six months).

NOTE: Too much diazomethane will cause low recoveries of Dinoseb.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR EXTRACTION OF SEMIVOLATILE AND NONVOLATILE ORGANIC COMPOUNDS FROM GROUNDWATER, WASTEWATER, AND OTHER AQUEOUS SAMPLES

(GL-OA-E-013 REVISION 34)

APPLICABLE TO METHOD:
EPA SW-846 3510C

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR EXTRACTION OF SEMIVOLATILE AND NONVOLATILE ORGANIC COMPOUNDS FROM GROUNDWATER, WASTEWATER, AND OTHER AQUEOUS SAMPLES

2.0 METHOD REFERENCE

EPA SW-846 3510C

3.0 METHOD, PURPOSE, AND OBJECTIVE

To describe the manner in which groundwater, wastewater, and other aqueous samples are extracted using SW-846 Method 3510C for organic analysis methods 8270C, 8270D, 8081, 8081A, 8081B, 8082, 8082A, 8015A, 8015B, 8015C, 8015D, 8310, 625, and 608. The extraction processes Alaska AK102, AK103, Washington Method for the Determination of Extractable Petroleum Hydrocarbons (WA EPH), and the Method for the Determination of Extractable Petroleum Hydrocarbons (EPH) by the Massachusetts Dept. of Environmental Protection are also included in this procedure. Analytes listed in the above-referenced methods are partitioned from water matrices using separatory funnels for a liquid/liquid extraction. The extract is concentrated using Kuderna-Danish techniques coupled with nitrogen gas blowdown. These techniques prepare the sample such that analytes of interest are in solvent and at concentrations suitable for analysis using gas or liquid chromatography.

4.0 INTERFERENCES TO THE METHOD

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all glass systems may be necessary.

4.2 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

4.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

4.4 Soap residue (e.g., sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, Aldrin, Heptachlor, and most organophosphorous pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500 mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

5.0 DEFINITIONS

5.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

5.2 Blank: Organic-free reagent water used to determine that no background contaminants are present in the extraction process.

5.3 Laboratory Control Sample (LCS): Organic free reagent water containing the spiking solution to indicate the process is in control and to indicate accuracy.

5.4 Laboratory Control Sample Duplicate (LCS DUP): A duplicate of the LCS to indicate reproducibility and to indicate precision.

5.5 Lower Limit of Quantitation (LLOQ): The lowest concentration at which a target analyte can be reliably measured and reported. The LLOQ is the lowest point in the calibration curve and represents a concentration at which both quantitative and qualitative requirements can be consistently demonstrated. The LLOQ is verified quarterly, as the LOQ verification. The verification is performed by extracting and analyzing an LCS spiked at the lowest level of initial calibration curve. The LLOQ verification is carried through the same preparation and analytical procedures as environmental samples and QC. The LLOQ is analyzed on every instrument where data are reported and this is the laboratory's normal protocol. Recovery of target analytes in the LLOQ are compared to in-house-statistically-derived limits. Concentrations in samples reported below the LLOQ and above the MDL are qualified as estimated.

5.6 Matrix Spike (MS): A sample to which the spiking solution is added. The recovery of matrix spike compounds indicates the presence or absence of matrix interferences. This may be duplicated (MSD) at a client's request and if enough sample is provided.

5.7 Sample Duplicate: A duplicate of a sample indicating reproducibility.

5.8 Surrogate: A solution added to each sample and quality control sample to monitor the efficiency of the extraction process. It contains compounds similar to those being analyzed. For compounds and concentrations, refer to the Create/Edit/View Reference Materials section of AlphaLIMS. Surrogate solutions purchased as source standards expire by vendor expiration date or one year from receipt, whichever comes first. Surrogate solutions created as working standards expire six months from the date opened or the date prepared, whichever comes first. All standards are screened prior to use in extractions.

5.9 Spike: A solution added to the laboratory control samples and matrix spikes that contain compounds defined by the referenced method. For compounds and concentrations, refer to the Create/Edit/View Reference Materials section of AlphaLIMS. Spiking solutions purchased as source standards expire by vendor expiration date or one year from receipt, whichever comes first. Spiking solutions created as working standards expire six months from the date opened or the date prepared, whichever comes first.

5.10 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

6.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

WARNING

METHYLENE CHLORIDE IS A POSSIBLE CARCINOGEN. HEXANE IS FLAMMABLE AND TOXIC. ACETONITRILE IS FLAMMABLE AND TOXIC.

SODIUM HYDROXIDE CAUSES SEVERE BURNS AND MAY BE FATAL IF SWALLOWED.

CARBON DISULFIDE IS TOXIC.

SULFURIC ACID IS CORROSIVE, CAUSES SERIOUS BURNS, AND MAY BE FATAL IF SWALLOWED.

WARNING

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

6.1 Wear eye protection with side shields while working in the laboratory.

6.2 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and client sample MSDS forms are maintained in the laboratory.

6.3 Personal protective equipment

6.3.1 Gloves are required when working with solvents, standards and samples. Solvents, and any solute in them, can absorb easily through the skin.

6.3.2 Work under a hood when using concentrated acids.

6.3.3 To protect clothes and skin from exposure to corrosive material, wear a lab coat.

6.4 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

6.4.1 Wear a dosimeter at all times while working in the lab to monitor radioactive exposure.

6.4.2 Wear a lab coat when working with radioactive samples.

6.4.3 Protect counter tops with counter paper, or work from radioactive sample handling trays.

6.4.4 Prohibit admittance to immediate work area.

6.4.5 Post signs indicating that radioactive samples are in the area.

6.4.6 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

6.4.7 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

6.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

6.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

6.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

6.6 Solvent in a closed separatory funnel creates excessive pressure, so always vent immediately when beginning to shake.

6.7 When venting a separatory funnel, point stopcock end toward fume hood and always away from other people working in the area to minimize solvent fumes.

6.8 Hood doors should be pulled down partially while K-D apparatus is on the bath. Snyder columns may shoot off due to pressure inside the K-D.

6.9 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

6.10 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

7.0 APPARATUS AND MATERIALS

(Unless otherwise indicated, all apparatus and materials are suggested only.)

7.1 Glassware

7.1.1 Separatory funnel, 2000 mL with Teflon stopcock or equivalent

7.1.2 Concentrator tube, Kuderna-Danish 10 mL graduated (Kontes K570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test.

7.1.3 Evaporative flask, Kuderna-Danish 500 mL (Kontes K570001-0500 or equivalent). Attach to concentrator tube with clips.

7.1.4 Snyder column, Kuderna-Danish three ball macro (Kontes K503000-0121 or equivalent). Rotary evaporation setup may be used alternatively.

7.1.5 Two mL glass vials with Teflon-lined cap (autosampler vials).

7.1.6 Disposable pipettes, 1-10 mL

7.1.7 Graduated cylinders, 250-1000 mL.

7.1.8 Glass or Teflon funnels

7.1.9 Erlenmeyer flask, 250 mL

7.1.10 Vials, 2 mL glass with PTFE-lined screw caps or crimp tops

7.2 Boiling chips, solvent rinsed, approximately 10/40 mesh (silicon carbide or equivalent).

7.3 Water bath, heated with concentric ring cover, capable of temperature control (± 5° C). The bath should be used in a hood.

7.4 Nitrogen evaporator with high purity (grade 4.5 or equivalent) nitrogen gas source.

7.5 pH indicator paper, range bracketing desired extraction pH

7.6 Erlenmeyer flask, 250 mL

7.7 Syringe, 1 mL

7.8 Glass wool: Rinse with extraction solvent prior to use.

7.9 Top Loading Balance

8.0 REAGENTS AND STANDARDS

8.1 Reagents should meet ACS Analytical criteria. Reagents should not be stored in plastic containers.

8.2 Solvents should be screened prior to use. All solvents must be pesticide quality or equivalent. Refer to GL-OA-E-065 for Reagent/Solvent/Standards Screening for Organic Prep.

8.2.1 Organic-free reagent water

8.2.2 Methylene chloride (CH_2Cl_2), pesticide grade or equivalent

8.2.3 Acetone (CH_3COCH_3), pesticide grade or equivalent

8.2.4 Hexane (C_6H_{14}), pesticide grade or equivalent

8.2.5 Acetonitrile (CH_3CN), pesticide grade or equivalent

8.2.6 1:1 Sulfuric acid (H_2SO_4): Slowly add 100 mL of sulfuric acid to 100 mL of organic-free reagent water in an Erlenmeyer flask.

8.2.7 10 N Sodium hydroxide: Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

8.2.8 Anhydrous sodium sulfate (Na_2SO_4): Muffle granular Na_2SO_4 at 400º C for 4 hours, and rinse with extraction solvent prior to use.

8.2.9 LLOQ standard solutions are purchased directly from a certified vendor and may be diluted from the source to make working standards.

9.0 EQUIPMENT MAINTENANCE

Maintenance to these devices are recorded in LIMS in an electronic logbook.

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Sample containers should be glass or Teflon with Teflon-lined screw cap. To prevent phthalate or hydrocarbon contamination, plastic containers must not be used.

10.2 Sample containers should be amber bottles for some samples that are light sensitive.

10.3 Samples are to be maintained at 0 ≤ 6º C until extraction begins.

10.4 Samples must be extracted within seven days from collection. PCB samples must be extracted within the one year of collection.

10.5 If samples are not in appropriate containers or holding time has expired, notify the group Leader or Project Manager for further instructions.

11.0 SAMPLE PREPARATION

11.1 Rinse all glassware with methylene chloride (CH_2Cl_2). Label glassware with sample number.

11.2 A tally of available containers for Organic Prep is shown in AlphaLIMS during the batching process. If enough sample containers are not available for the extraction process contact the Project Manager immediately.

11.3 Using a 1-Liter graduated cylinder measure 1L of sample. If the entire contents of the sample bottle are to be extracted, mark the meniscus on sample bottle. A smaller sample volume may be taken and diluted to 1L with organic free reagent water. Sample final volume can be determined by using the computer calculation of weight to volume. This information is recorded and generated in AlphaLIMS.

NOTE: If sample volume is full to the rim of the bottle, proceed as follow:

(1) Mark meniscus on sample bottle.

(2) Pour some of the sample into the clean designated separatory funnel allowing space in the sample bottle for addition of surrogates/spike.

(3) Proceed to step 11.4.

11.4 Check the pH of the sample with wide- range pH indicator strip and record the initial pH.

NOTE: All pH measurements require the use of a pre-rinsed, 1 mL disposable pipet to deliver a small aliquot of sample to a wide-range pH indicator strip.

11.5 Record volume to nearest 5 mL

11.6 In graduated cylinder or sample bottle, add appropriate surrogate to all samples and quality control samples. Add appropriate spiking solution to quality control samples to be spiked and mix well. For appropriate surrogate and spiking solution refer to Appendix 2. For volume of surrogate and spike added refer to Appendix 2. Peer witnessing is practiced during this process.

11.7 Transfer sample from the graduated cylinder or sample bottle to the separatory funnel and adjust the pH if necessary to pH indicated in Appendix 1.

11.8 Add 60 mL of methylene chloride to the graduated cylinder or sample bottle transfer to separatory funnel.

12.0 EXTRACTION PROCEDURE

WARNING: METHYLENE CHLORIDE CREATES EXCESSIVE PRESSURE VERY RAPIDLY, POTENTIALLY CAUSING SEPARATORY FUNNEL TO EXPLODE.

12.1 Extraction

12.1.1 Shake vigorously for two minutes. Vent often. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If emulsion interface between layers is more than 1/3 the size of solvent layer, employ one of the following mechanical techniques to break emulsion: stirring, quantitative filtration through glass wool, centrifugation, or other physical procedures.

12.1.2 Drain methylene chloride layer through pre-rinsed thistle funnel containing prepped glass wool and muffled anhydrous sodium sulfate (Na_2SO_4) into a K-D with 10 mL concentrator tube.

12.1.3 Add 60 mL of methylene chloride and repeat steps 12.1.1 through 12.1.2 for a total of three extractions using the appropriate volume of methylene chloride.

12.1.4 Adjust pH if additional extractions are required, and adjust the pH of the aqueous phase to the desired pH indicated in Appendix 1. Repeat steps 12.1.1 through 12.1.2. Collect and combine the extracts and label the combined extract appropriately.

12.1.5 Rinse thistle funnel with 20 to 30 mL of methylene chloride. Add this rinse to the K-D.

NOTE: The use of a solvent-rinsed graduated cylinder is required by specific clients (i.e., Navy).

12.2 Concentration and Packaging

CAUTION: ANALYTES OF INTEREST MAY BE LOST IF SAMPLES ARE CONCENTRATED TOO LOW.

12.2.1 Add small prepped boiling chip and Snyder column to K-D. Pre-wet column with 1 to 2 mL of methylene chloride for safety and place the K-D apparatus on a hot water bath heated to 65° to 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 in hot vapor. (At proper distillation rate, balls will chatter, but chambers will not flood.)

12.2.2 If a solvent exchange is required, place on a heated water bath at 80° to 90° C to maintain proper distillation. Refer to Appendix 1 for extraction conditions.

12.2.3 At approximately 1 to 5 mL, remove from water bath and allow to cool for at least 10 minutes.

CAUTION: ANALYTES OF INTEREST MAY BE LOST IF SOLVENT IS NOT MIXED PROPERLY AND PRESSURE FORCES SOLVENT THROUGH TOP OF SNYDER COLUMN.

CAUTION: ANALYTES OF INTEREST MAY BE LOST IF SAMPLES ARE CONCENTRATED TOO LOW OR TOO FAST.

12.2.4 Using a gentle stream of nitrogen, concentrate just below (not below 0.5 mL) desired final volume and reconstitute with final solvent. If solvent exchange was necessary, concentrate to approximately 1 mL, reconstitute with final solvent to 2 mL, and then concentrate to desired final volume. Refer to Appendix 2 for appropriate volumes.

12.2.5 Proceed with clean-up if necessary. Refer to Appendix 1 for appropriate clean-up.

12.2.6 Using GENTLE stream of nitrogen, concentrate to appropriate volume.

12.2.7 Transfer to 2 or 4 mL amber vial with Teflon-lined screw cap using a 1 mL disposable pipet or syringe. Record final volume. Label with AlphaLIMS-generated barcoded label. Mark the meniscus. Store PCBs, pesticides, herbicides and DRO extracts at 0° ≤ 6° C. For BNA and Alaska DRO, store at -10º C to -20° C.

12.2.8 Rinse glassware with ChemSolve solution before having glassware washed.

13.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL SAMPLES

13.1 Source standards are purchased as certified mixtures. Documentation of the standard's quality and traceability should be provided by the vendor. This documentation is scanned and uploaded to Reference Materials in AlphaLIMS. Standards may be purchased from outside vendors, including o2si, AccuStandard, Inc., NSI Solutions, Inc., and Supelco. Other vendors on GEL's Approved Vendors list may be also used.

13.2 Source standards are assigned a unique code number for the purpose of traceability. The standard, along with its code, is recorded in AlphaLIMS. AlphaLIMS can be used to generate a label that is affixed to the standard's container, or a handwritten label may be created.

13.3 Stock, intermediate and working standards are likewise assigned a unique code number and recorded in AlphaLIMS.

14.0 SAFETY AND POLLUTION PREVENTION

Follow all laboratory safety rules for preparation, analysis, and handling of the reagents of interest. Refer to method SOPs and the GEL safety plan for guidance.

15.0 QUALITY CONTROL REQUIREMENTS

Typically, the blank, laboratory control sample (LCS), matrix spike (MS) and matrix spike duplicate (MSD) are extracted and analyzed for each matrix with up to 20 samples in the same batch. For method 608, a matrix spike must be performed for 10 % of the

samples. For method 625, a matrix spike must be performed for 5 % of the samples. In addition, a laboratory control sample (LCS) and its duplicate (when requested) are analyzed with each sample batch (up to 20 samples of the same matrix). The LCS consists of an aliquot of clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentration as the matrix spike. When the results of the matrix analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. LCS recoveries are statistically generated using at least 20 results of the same matrix type. SPC limits are updated semi-annually.

Method Detection Limit studies are performed annually for each analytical method associated with this SOP. Refer to GL-LB-E-001 for The Determination of Method Detection Limits.

16.0 RECORDS MANAGEMENT

16.1 Documentation of Training

16.1.1 Extraction technicians must be properly trained to perform the contents of this SOP. Personnel must extract four laboratory control samples for each analytical SOP referenced within this SOP as training commences. Training documentation is maintained per GL-HR-E-002 for Employee Training.

16.1.2 LCS/LCS DUP demonstrates on a continuing basis that personnel are properly trained.

16.2 Documentation of Extraction

16.2.1 Record initial volume of sample, final volume of extract, the volume of surrogate and spikes added, the concentration of surrogate and spiking solutions, and any comments about the extraction process. Also, record all reagent lot numbers such as the surrogate, spike, and solvent lot numbers in AlphaLIMS. Note any deviations from this standard operating procedure in the comment section.

16.2.2 Complete Data Review Sheet (Appendix 3).

16.2.3 These documents are stored in AlphaLIMS. A copy is also maintained with the analytical data.

16.3 Documentation of Standards

16.3.1 Refer to the following SOPs for standards documentation:

16.3.1.1 Laboratory Standards Documentation (GL-LB-E-007)

17.0 DATA, REVIEW, APPROVAL, AND TRANSMITTAL

A review process is used to insure that quality of the data. Extraction logs are peer reviewed by a second technician or Group Leader. When the reviewer is satisfied that the data have been entered correctly, a data report is generated from AlphaLIMS. The report

along with the batch sheets are copied and submitted to the appropriate analytical area for analysis.

18.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

19.0 REFERENCES

19.1 Test Methods for Evaluating Solid Waste: Laboratory Manual: Physical/ Chemical Methods, Volume 1B, SW-846, Third Edition, November 1986. Method 3510C, "Separatory Funnel Liquid-Liquid Extraction," Revision 3, December 1996.

19.2 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act: Final Rule and Interim Final Rule and Proposed Rule, Friday, October 26, 1984, Methods 625 and 608.

19.3 Method AK 102, “Determination of Diesel Range Organics,” Version 3-1-99.

19.4 Analytical Methods for Petroleum Hydrocarbons, ECY 97-602, June 1997 Washington State Dept. of Ecology

19.5 Method for the Determination of Extractable Hydrocarbons (EPH), May 2004, Revision 1.1, Massachusetts Dept. of Environmental Protection.

19.6 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.3 July, 2019.

20.0 HISTORY

Revision 34: Added Top loading balance to list of equipment. Added clarification about final volume calculation in section 11.3. Update for DOD QSM version 5.3, July 2019.
Revision 33: Updated section references. Updated DOD QSM reference for version 5.1.1, February, 2018
Revision 32: Updated for clarification on process of contacting PM or Client if there is insufficient sample container(s) or if hold time has expired.
Revision 31: Added LLOQ in definitions section. Added reference to new DoD/DoE QSM version 5.1, January 2017.
Revision 30: Updated section 11.0 to include the process if more sample is needed for analysis but limited is available.

APPENDIX 1: EXTRACTION CONDITIONS

Extraction Conditions for Various Water Analyses

Prep	Analysis	Surrogate/Spike[a]	Extraction pH	pH Change	Solvent Exchange	Clean up Required
BNA	8270D	BNA Surrogate/ BNA Spike	< 2	> 11	None	
Pesticide/ PCB[c]	8081B	Pesticide Surrogate/ Pesticide Spike	5 to 9	None	Hexane	Florisil
PCB	8081B 8082A	PCB H_2O Surrogate/ PCB H_2O Spike	5 to 9	None	Hexane	$KMnO_4$/ H_2SO_4
DRO	8015C 8015D WA EPH MADEP EPH	DRO Surrogate/ DRO Spike WA EPH Surrogate/ WA EPH Spike MADEP EPH Surrogate/ MADEP EPH Spike	< 2	None	None	
PAH	8310	PAH Surrogate/ PAH Spike	5 to 9	None	Acetonitrile	
BNA	625.1	BNA Surrogate/ 625 Spike	< 2	> 11	None	
Pesticide/ PCB	608.3	Pesticide Surrogate/ 608 Spike	5 to 9	None	Hexane	Florisil
PCB	608	PCB H_2O Surrogate/ PCB H_2O Spike	5 to 9	None	Hexane	$KMnO_4$/ H_2SO_4
BNA	TCLP	BNA Surrogate/ TCLP BNA Spike	< 2	> 11	None	
Pesticide[b]	TCLP	Pesticide Surrogate/TCLP Pesticide Spike/ Toxaphene/ Chlordane	5 to 9	None	Hexane	
AK102	TPH	TPH Surrogate AK102 Spike	< 2	NONE	None	

a: Other spiking compounds may be used if client requests non-regulated compounds.

b: Due to chromatography of pesticide compounds regulated by TCLP, extract separately a TCLP spike, a Toxaphene spike, and a Chlordane spike for each spiked sample.

c: GEL has defined Method 8081/8081A into two classes of compounds: Pesticides and Pesticides/PCBs. When a batch consists of samples requesting Pesticides and/or Pesticides/PCBs, use Pesticide Surrogate and Pesticide Spike.

NOTE: For recipes, concentrations, analytes and diluents generally used, refer to the Create/Edit/View Reference Materials section of AlphaLIMS.

APPENDIX 2: SURROGATE AND SPIKE VOLUMES

Typical Volumes: Initial, Final, Surrogate/Spike, and Solvent

Prep	Analysis	Initial Volume[a]	Final Volume	Surrogate/ Spike Volume
BNA	8270C 8270D	1000 mL	1 mL	1 mL
Pesticide/ PCB	8081A 8081B	1000 mL	5 mL	1 mL
PCB	8081A 8081B 8082 8082A	1000 mL	1 mL	1 mL
DRO	8015B 8015C 8015D WA MADEP EPH	1000 mL	1 mL	1 mL
PAH	8310	1000 mL	1 mL	1 mL
BNA	625.1	1000 mL	1 mL	1 mL
Pesticide/ PCB	608.3	1000 mL	1 mL	1 mL
PCB	608	1000 mL	1 mL	1 mL
BNA	TCLP	200 mL	1 mL	1 mL
Pesticide	TCLP	20 mL	1 mL	1 mL
AK102	TPH	1000 mL	1 mL	1 mL

a: These volumes are guidelines. Due to the nature of sample or amount of sample collected, other volumes may be used if diluted to 1000 mL with organic free water. Surrogate, spikes, and final volumes should be adjusted to maintain reporting limits.

b: Sample extract is concentrated to 1.0 mL in methylene chloride and brought to a final volume of 2.0 mL with carbon disulfide.

c: All spike and surrogate solutions are stored at 0˚ ≤ 6˚ C except for Alaska DRO. Alaska DRO and BNA standards are stored in a frost-free freezer at -10˚ C to -20˚ C.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE
FOR
THE EXTRACTION OF HERBICIDES
FROM
GROUNDWATER, WASTEWATER, AND OTHER AQUEOUS SAMPLES

(GL-OA-E-015 REVISION 20)

APPLICABLE TO METHOD:
EPA Method 8151A for Herbicides

PROPRIETARY INFORMATION

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APPENDIX 1: GENERATION OF DIAZOMETHANE USING DIAZALD KIT 14

1.0 STANDARD OPERATING PROCEDURE FOR THE EXTRACTION OF HERBICIDES FROM GROUNDWATER, WASTEWATER, AND OTHER AQUEOUS SAMPLES

2.0 METHOD REFERENCE

EPA SW-846 8151A

3.0 PURPOSE

To describe the manner in which aqueous samples are extracted for selected herbicides listed in EPA Method 8151A.

4.0 DISCUSSION

Analytes listed in the above-referenced method are partitioned from aqueous matrices using separatory funnel extraction. An acid-base cleanup is integrated into the procedure prior to concentration using Kuderna-Danish (K-D) techniques. This solvent concentrate is esterified so that analytes are in a form that is suitable for analysis, using a gas chromatography technique that employs an electron capture detector.

5.0 INTERFERENCE TO THE METHOD

5.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

5.2 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Separatory funnels are kept in the open lab. Immediately prior to use, glassware and separatory funnels should be rinsed with the next solvent to be used. Refer to GL-LB-E-003 for instructions.

5.3 The use of high purity reagents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

5.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

5.5 Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure.

5.6 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of

dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

5.7 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid washed and then rinsed with organic-free reagent water. Sodium sulfate must be acidified.

5.8 Sample extracts should be dry prior to methylation or else poor recoveries will be obtained.

5.9 Method Detection Limit studies are performed annually for each analytical method associated with this SOP. Refer to GL-LB-E-001 for instructions.

6.0 DEFINITIONS

6.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

*6.2 Herbicide Spike: A solution added to the laboratory control sample, laboratory control sample duplicate, matrix spike, and matrix spike duplicate that contains all compounds of interest. These standards expire two months from date prepared. Please refer to the Maintaining Reference Material section of AlphaLIMS for analyte names and concentrations.

*6.3 Herbicide Surrogate: A compound with properties that mimic the analytes of interest, but that is unlikely to be found in environmental samples. The surrogate is added to each sample and quality control sample to monitor the extraction efficiency. 2,4-Dichlorophenyl acetic acid is used as the surrogate for this method. This standard expires two month from date prepared or the expiration date of the parent, which ever comes first.

6.4 Laboratory Control Sample (LCS): Organic free reagent water containing herbicide spiking solution to indicate the process is in control and to indicate accuracy.

6.5 Laboratory Duplicate (DUP, LCSD, MSD or PSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

6.6 Matrix Spike and Matrix Spike Duplicate (MS and MSD): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or MSD is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or MSD corrected for background concentrations.

6.7 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other

samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

6.8 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. Typically, the MDL is two to three times less than the PQL.

6.9 Sample Duplicate: A duplicate of a sample indicating reproducibility.

6.10 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

6.11 Lower Limit of Quantitation (LLOQ): The lowest concentration at which a target analyte can be reliably measured and reported. The LLOQ is the lowest point in the calibration curve and represents a concentration at which both quantitative and qualitative requirements can be consistently demonstrated. The LLOQ is verified quarterly, as the LOQ verification. The verification is performed by extracting and analyzing an LCS spiked at the lowest level of initial calibration curve (see the appropriate analytical SOP for calibration concentrations). The LLOQ verification is carried through the same preparation and analytical procedures as environmental samples and QC. The LLOQ is analyzed on every instrument where data are reported and this is the laboratory's normal protocol. Recovery of target analytes in the LLOQ are compared to in-house-statistically-derived limits. Concentrations in samples reported below the LLOQ and above the MDL are qualified as estimated.

6.12 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide definitions.

(*) All herbicide surrogate and spike compounds are added in the free acid form. The free acid is used so that not only are you monitoring extraction efficiency, but also the derivitization efficiency. All standards are screened prior to use in extractions.

7.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

WARNING

METHYLENE CHLORIDE IS A POSSIBLE CARCINOGEN.

DIETHYL ETHER IS EXTREMELY FLAMMABLE.

HEXANE IS FLAMMABLE AND TOXIC.

ISOOCTANE IS EXTREMELY FLAMMABLE.

METHANOL IS TOXIC.

SODIUM HYDROXIDE CAUSES SEVERE BURNS AND MAY BE FATAL IF SWALLOWED.

SULFURIC ACID IS CORROSIVE, CAUSES SERIOUS BURNS, AND MAY BE FATAL IF SWALLOWED.

DIAZOMETHANE IS A CARCINOGEN.

DIAZOMETHANE IS EXTREMELY EXPLOSIVE.

7.1 Wear eye protection with side shields while working in the laboratory.

7.2 Treat all chemicals as potential health hazards, and limit exposure to them to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals used in this SOP. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this SOP via GEL's Intranet. If necessary, contact the safety coordinator for specific MSDS sheets.

7.3 Personal protective equipment

7.3.1 Gloves are required when working with solvents, standards and samples. Solvents, along with any solute in them, can absorb easily through the skin.

7.3.2 Work under a hood when using concentrated acids.

7.3.3 To protect clothes and skin from being exposed to corrosive material, wear a lab coat.

7.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

7.4.1 Wear a dosimeter at all times while working in the lab to monitor radioactive exposure.

7.4.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

7.4.3 Prohibit admittance to immediate work area.

7.4.4 Post signs indicating radioactive samples are in the area.

7.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

7.4.6 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

7.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

7.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

7.5.2 Segregate oil wastes from water soluble wastes in the satellite area containers.

7.6 Solvent in a closed separatory funnel creates excessive pressure, so always vent immediately when beginning to shake.

7.7 When venting a separatory funnel, point stopcock end toward fume hood to minimize solvent fumes and always away from other people working in the area.

7.8 Hood doors should be pulled down partially while K-D apparatus are on the bath. Snyder columns may shoot off due to pressure inside the K-D. Always wet

Snyder column with 1 to 2 mL of the extraction solvent to help minimize a pressure build up.

7.9 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

7.10 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

8.0 APPARATUS AND MATERIALS

8.1 Glassware

8.1.1 Separatory funnel, 2000 mL with Teflon stopcock or equivalent.

8.1.2 Concentrator tube, Kuderna-Danish 10 mL graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test.

8.1.3 Evaporative flask, Kuderna-Danish 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with clips.

8.1.4 Snyder column, Kuderna-Danish three ball macro (Kontes K-503000-0121 or equivalent). Rotary evaporation set-up may be used alternatively.

8.1.5 Two mL glass vials with Teflon-lined cap (autosampler vials).

8.1.6 Disposable pipettes, Pasteur

8.1.7 Graduated cylinders, 1000 mL

8.1.8 Glass or Teflon funnels.

8.1.9 Vials 10 mL, glass with PTFE-lined screw caps.

8.2 Volumetric flasks, Class A,10 mL to 1000 mL.

8.2.1 Glass wool, Pyrex, acid washed.

8.2.2 Beaker, 400mL, thick-walled.

8.2.3 Erlenmeyer flasks, 250 mL and 2000 mL with a ground-glass joint at the neck

8.2.4 Centrifuge

8.2.5 Balance, analytical, capable of accurately weighing to 0.0001 g.

8.2.6 Diazald kit, recommended for the generation of diazomethane (Aldrich Chemical Co., No. 201,025-0, or equivalent)

8.2.7 Boiling chips, solvent rinsed, approximately 10/40 mesh (silicon carbide or equivalent)

8.2.8 Water bath, heated with concentric ring cover, capable of temperature control (± 5° C). The bath should be used in a hood.

8.2.9 Nitrogen evaporator with high purity (grade 4.5 or equivalent) nitrogen gas source.

9.0 REAGENTS AND STANDARDS

9.1 Reagents should meet ACS analytical criteria. Reagents should not be stored in plastic containers. Refer to GL-OA-E-065 for instructions.

9.1.1 Organic-free reagent water

9.1.2 12 N Sulfuric acid (H_2SO_4): Slowly add 335 mL of sulfuric acid to 665 mL of organic free reagent water in Erlenmeyer flask.

9.1.3 6 N Sodium hydroxide: Dissolve 216 g NaOH in 900 mL organic free reagent water.

9.1.4 Anhydrous sodium sulfate (Na_2SO_4), muffled at 400˚ C for 4 hours.

9.1.5 Acidified sodium sulfate: Cover anhydrous (Na_2SO_4) with ether. Carefully add 0.1mL concentrated sulfuric acid (H_2SO_4) per 100 g Na_2SO_4. Use a Buchner funnel to dry. Test pH of Na_2SO_4 by adding 1g to 5 mL deionized H_2O. pH of Na_2SO_4 must be < 4. Store at 130˚ C.

9.1.6 Sodium chloride (NaCl): Muffle salt at 400˚ C for 4 hours

9.1.7 Diazomethane (CH_2N_2): Refer to Appendix 1 for generation of diazomethane using Diazald kit. Reagents for generation include ether, potassium hydroxide, organic free reagent water, 2-(2-ethoxyethoxy) ethanol and Diazald.

9.1.8 Silicic Acid, (H_2SiO_5), 100 mesh powder, store at 130˚ C.

9.2 Solvents – should be screened prior to use. Refer to GL-OA-E-065 for instructions.

9.2.1 Methylene chloride (CH_2Cl_2), pesticide quality or equivalent

9.2.2 Diethyl ether ($C_2H_5OC_2H_5$), pesticide quality or equivalent. Check each bottle of ether for peroxides with peroxide strips. Do not use if peroxides are present.

9.2.3 Hexane (C_6H_{14}), pesticide quality or equivalent

9.2.4 Isooctane ($(CH_3)_3CH_2CHC(CH_3)_2$), pesticide quality or equivalent

9.2.5 Methanol (CH_3OH), pesticide quality or equivalent

9.2.6 LLOQ standard solutions are purchased directly from a certified vendor and may be diluted from the source to make working standards.

10.0 EQUIPMENT MAINTENANCE

Maintenance to these devices are recorded in LIMS in an electronic logbook.

11.0 SAMPLE HANDLING AND PRESERVATION

11.1 Sample Handling and Preservation

11.1.1 Sample containers should be glass or Teflon with a Teflon-lined screw cap. Plastic containers must not be used to prevent phthalate or hydrocarbon contamination.

11.1.2 Sample containers should be protected from light, for some analytes are light sensitive.

11.1.3 Samples are to be maintained at $0^{\circ} \leq 6^{\circ}$ C until extraction begins.

11.1.4 Samples must be extracted within seven days from collection.

11.1.5 If samples are not in appropriate containers or holding time has expired, notify the Group Leader or Project Manager for further instructions.

12.0 SAMPLE PREPARATION

12.1 All batches (up to 20 samples) will be extracted with a blank, LCS, MS, and MSD. Additional QC may be required by specific clients and/or contracts. If insufficient sample is provided, the MS/MSD will be substituted with a LCS DUP.

12.2 Rinse all glassware with solvent. Label glassware with sample number.

12.3 Check sample pH and record.

NOTE: All pH measurements require the using a clean, 1 mL serological glass pipet to deliver a small aliquot of sample onto a wide-range pH indicator strip.

12.4 Pour sample into a solvent rinsed 2 L separatory funnel. When sufficient sample is provided, use entire 1 L amber bottle and mark water meniscus on sample container. Sample volume may be adjusted due to limited volume. Use 5 mL of sample for TCLP leachates. This sample volume meets TCLP limits.

12.5 Add 50 µL of surrogate to each separatory funnel. Add 1 mL spike to the appropriate separatory funnel (LCS, LCSD, MS, MSD). Surrogate and spike volumes may be adjusted in accordance to sample volume extracted. Peer witnessing is practiced during this process.

12.6 Add approximately 250 g sodium chloride to each sample separatory funnel. Sodium chloride amount may be adjusted in accordance to sample volume extracted. Seal and shake the sample to dissolve the salt.

12.7 Hydrolysis

12.7.1 Adjust sample pH to $\geq$ 12 with 17 mL 6N sodium hydroxide. Add 17 mL of 6 N sodium hydroxide to the sample, seal, and shake. Check the pH of the sample with pH paper. If the sample does not have a pH greater than or equal to 12, adjust the pH by adding more 6 N sodium hydroxide. Let the sample sit at room temperature until the hydrolysis step is completed (usually 1 to 2 hours), shaking the separatory funnel and contents periodically.

WARNING

METHYLENE CHLORIDE CREATES EXCESSIVE PRESSURE VERY RAPIDLY, POTENTIALLY CAUSING SEPARATORY FUNNEL TO EXPLODE.

12.7.2 Rinse the sample bottle by adding 60 mL of methylene chloride.

12.7.3 Transfer the rinsate to the appropriate 2 L separatory funnel. Seal, invert and vent immediately. Swirl sample to allow pressure release.

12.7.4 Shake vigorously for 2 minutes. Vent often. Allow layers to separate for a minimum of 10 minutes. If emulsion interface between layers is more than 1/3 size of solvent layer, employ one of the following mechanical techniques to break emulsion: stirring, filtration through glass wool, centrifugation, or other physical procedures.

12.7.5 Discard the methylene chloride phase.

12.7.6 Add a second 60 mL volume of methylene chloride to the separatory funnel, and repeat the extraction procedure a second time, discarding the methylene chloride layer.

12.7.7 Repeat step 12.7.6.

13.0 EXTRACTION

13.1 Adjust sample pH to ≤ 2 with 17 mL of cold (0˚ ≤ 6˚ C) 12 N sulfuric acid.

13.2 Add 120 mL of diethyl ether to sample, shake vigorously for 2 minutes.

13.3 Allow layers to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than 1/3 the size of the solvent layer, analyst must employ one of the following mechanical techniques to complete separation: swirl, stir with clean glass rod, quantitatively pass filtrate through acid-washed glass wool, or centrifugation.

13.4 Drain the sample (aqueous phase) into a 2 L Erlenmeyer flask.

13.5 Collect the diethyl ether extract in a rinsed 250 mL wide mouth Erlenmeyer flask containing approximately 10 g of acidified sodium sulfate.

13.6 Return the aqueous phase to the separatory funnel.

13.7 Repeat extraction two more times using 60 mL of ether each time combining the three extracts in the same Erlenmeyer.

13.8 If necessary, add more acidified sodium sulfate to the diethyl ether extract until there is no residue of water in the ether.

13.9 Allow extract to dry for at least two hours. Periodically, vigorously swirl the extract and drying agent. If not finishing after the two hours, place this extract in a refrigerator (0˚ ≤ 6˚ C) to keep the diethyl ether from evaporating.

NOTE: The drying step is critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all

the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate and again test by swirling. The 2-hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

13.10 Concentration

13.10.1 Set-up K-D and concentrator tube with a solvent rinsed boiling stone. Use a glass stirring rod to break up the sodium sulfate in the dried extract. If water is present, add more acidified sodium sulfate.

13.10.2 Pour the extract through a funnel containing pre-rinsed acidified glass wool, and collect in a K-D apparatus. Use a glass rod to crush any caked sodium sulfate during the transfer.

13.10.3 Rinse the flask with 20 to 30 mL of diethyl ether, transfer rinse to K-D through drying funnel if used. Add a Snyder column to K-D. Wet column for safety with 1 to 2 mL of ether.

13.10.4 Concentrate the diethyl ether to about 5.0 mL on a water bath with temperature between 60 - 70 °C. Remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

13.10.5 Concentrate to approximately 2 mL using the N-EVAP.

13.10.6 Transfer to 15 mL centrifuge tube or sample concentrator tube.

13.11 Esterification

13.11.1 Add 1.0 mL isooctane and 0.5 mL methanol to extract. Dilute to a final volume of 4 mL with diethyl ether.

WARNING

DIAZOMETHANE IS EXTREMELY EXPLOSIVE. USE COLD AND RETURN TO FREEZER WHEN FINISHED USING.

13.11.2 Add 2 mL diazomethane (refer to Appendix 1 for diazomethane generation) and swirl. Extract should stay yellow for a duration of 10-15 minutes. If it does not stay yellow, add more diazomethane.

13.11.3 Allow extract to evaporate in a hood to remove excess diazomethane until colorless (at least 6 hours or overnight), or add 10 mg of silicic acid, which will destroy excess diazomethane. Bring to a final volume of 10 mL with hexane in a 10 mL volumetric flask. The fizzing of the silicic acid should be finished before transferring to sample vials.

13.11.4 The sample is ready for analysis. Cap tightly. Store at $0^{\circ} \leq 6^{\circ}$ C immediately.

14.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL SAMPLES

14.1 Source standards are purchased as certified mixtures. Documentation of the standard's quality and traceability should be provided by the vendor. This documentation entered into the Reference Materials table in LIMS. Standards may be purchased from outside vendors, including o2si smart solutions,

AccuStandard, NSI, Inc., and Supleco. Other vendors on GEL's Approved Vendors list may be also used. Herbicides standards are esterified. Refer to section 13.11. Refer also to GL-OA-E-065 for Reagent/Solvent/Standards Screening for Organic Prep.

14.2 Source standards are assigned a unique code number for the purpose of traceability.

14.3 The standard, along with its code, is recorded in AlphaLIMS. AlphaLIMS can be used to generate a label which is affixed to the standards container, or a handwritten label may be created.

14.4 Stock, intermediate, and working standards are likewise assigned a unique code number and recorded in AlphaLIMS.

15.0 SAFETY AND POLLUTION PREVENTION

Follow all laboratory safety rules for preparation, analysis and handling of the reagents of interest. Reference method SOPs and the GEL safety plan for guidance.

16.0 QUALITY CONTROL REQUIREMENTS

Typically, blank, laboratory control sample (LCS), matrix spike (MS) and matrix spike duplicate (MSD) are extracted and analyzed with each prep batch. However, this may vary depending on such factors as sample availability and client requirements. Other client requirements may include a laboratory control sample duplicate (LCSD). They are carried through all stages of sample preparation, extraction, and analysis.

17.0 DETECTION LIMIT

Method Detection Limit studies are performed annually for each analytical method associated with this SOP. Refer to GL-LB-E-001 for instructions.

18.0 RECORDS MANAGEMENT

18.1 Documentation of Training

18.1.1 Extraction technicians must be properly trained to perform the contents of this SOP. Personnel will extract four laboratory control samples for each analytical SOP referenced within this SOP as training commences. Training records are maintained as quality records.

18.1.2 LCS/LCS DUP will demonstrate on a continuing basis that personnel are properly trained.

18.2 Documentation of Extraction

18.2.1 Complete sample tracker form. Record initial volume of sample, final volume of extract, amount of surrogate and spikes added, and any comments about the extraction process. Record all reagent lot numbers like surrogate, spike and solvent lot numbers. Note any deviations from this standard operating procedure in the comment section. Also, note all discrepancies about sample handling and preservation.

18.2.2 Enter initial volume and final volume of each sample into AlphaLIMS and print a hard copy.

18.2.3 These documents are stored in AlphaLIMS. A copy is also maintained with the analytical data.

19.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

A review process is used to ensure quality of the data. Extraction logs are peer reviewed by a second technician or group leader. When the reviewer is satisfied that the data have been entered correctly, a data report is generated from AlphaLIMS. The report along with the batch sheets are copied and submitted to the appropriate analytical area for analysis.

20.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

21.0 REFERENCES

21.1 Test Methods for Evaluating Solid Waste; Laboratory Manual Physical/ Chemical Methods, Volume 1B, SW-846, 3rd Edition, 1990. Method 8151A, "Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivation," Revision 1, December 1996.

21.2 AL-180 Technical Bulletin, "Aldrich, Diazald, MNNG and Diazomethane Generators." Sigma-Aldrich, Milwaukee, WI.

21.3 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.1.1, February, 2018.

22.0 HISTORY

Revision 20: Updated QSM version, and clarified use of volumetric glassware in section 13.11

Revision 19: Updated to equipment used in process. Updated the time to process diazomethane. Updated the DOD QSM reference to 5.1.1, February, 2018.

Revision 18: Updated for clarification on process of contacting PM or Client if there is insufficient sample container or if hold time has expired.

Revision 17: Added LLOQ to definitions section. Updated standards section on how LLOQ standards and used in lab. Updated reference with current DOD/DOE QSM. Version 5.1, January, 2017

Revision 16: Changed concentration of diethyl ether from 1 mL to 2 mL.

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APPENDIX 1: GENERATION OF DIAZOMETHANE USING DIAZALD KIT

WARNING

DIAZOMETHANE IS A CARCINOGEN.

DIAZOMETHANE IS EXTREMELY EXPLOSIVE:

AVOID GRINDING SURFACES, GROUND GLASS JOINTS, SLEEVE BEARINGS, GLASS STIRRERS

DO NOT HEAT ABOVE 90˚C

STORE AWAY FROM ALKALI METALS

SOLUTIONS OF DIAZOMETHANE DECOMPOSE RAPIDLY IN THE PRESENCE OF SOLID MATERIALS SUCH AS COPPER POWDER, CALCIUM CHLORIDE AND BOILING CHIPS

1. Wash glassware in Diazald kit from Wheaton. This glassware is specially fitted without using ground glass joints. Do not use brushes. Rinse glassware with ether.

2. In the reaction vessel dissolve 2 g of potassium hydroxide in 4 mL DI water. Add 14 mL 2-(2-ethoxyethoxy) ethanol and 8 mL diethyl ether to the potassium hydroxide solution.

3. Attach condenser to chiller. Check chiller for water level. Add water if needed.

4. Attach receiving vessel to condenser and cool in ice bath.

5. Attach diethyl ether trap containing 1 to 2 mL diethyl ether and cool in ice/salt bath.

6. Fill the separatory funnel with a solution of 5 g Diazald in 45 mL diethyl ether and place over the reaction vessel.

7. Heat the reaction vessel at 65 ˚C ± 5˚ and add the Diazald solution at the rate of distillation.

8. Continue adding Diazald solution. When it is used, slowly add 10 mL of diethyl ether and continue distilling until the distillate is colorless.

9. Diazomethane is ready to use. Place diazomethane in Teflon-lined screw top bottle and store in freezer. Diazomethane may be stored as long as yellow color persists

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR VOLATILE ORGANIC COMPOUNDS (VOC) BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

(GL-OA-E-038 REVISION 28)

APPLICABLE TO METHODS:

EPA SW-846 Method 8000D	EPA SW-846 Method 5030A
EPA SW-846 Method 8260B	EPA SW-846 Method 5030B
EPA SW-846 Method 8260C	EPA SW-846 Method 5035
EPA SW-846 Method 8260D	EPA SW-846 Method 5035A
Standard Methods 6200	EPA SW-846 Method 3585

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1.0 STANDARD OPERATING PROCEDURE FOR VOLATLE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETER

2.0 METHOD OBJECTIVES, PURPOSE, AND CODE

2.1 This procedure is used to determine purgeable organic compounds. The compounds are purged out of a solvent and absorbed onto a trap, separated via the gas chromatograph, and detected using a mass spectrometer. The Mass Selective Detector analyzes minute amounts of material by fragmenting the sample into charged ions, separating them on the basis of molecular weight-to-charge ratio, and then counting the ions as they enter the detector. The counted ions identified by mass can be plotted on a graph with the mass on the x-axis and the counted ions or abundances on the y-axis.

2.2 The procedure can be used to quantify most volatile organic compounds that:

2.2.1 Have a boiling point below 200°C.

2.2.2 Are insoluble or slightly soluble in water.

2.3 Method Codes for this procedure are EPA SW-846 Methods 8000D, 8260B, 8260C, 8260D, 5030A, 5030B, 5035A, 3585 and Standard Methods 6200.

NOTE: For South Carolina samples, only 8260B is applicable.

3.0 APPLICABLE MATRIX AND MATRICES

3.1 Applicable matrices for this method include groundwater, aqueous sludges, caustic liquids, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filtercakes, spent carbons, spent catalysts, soils, tissues, wastewaters, and sediments.

4.0 METHOD SCOPE, DETECTION LIMITS, AND PRECISION/ACCURACY MEASUREMENTS

4.1 Calibration Range: Can be as low as 0.5 ppb up to 100 ppb for most analytes. The range for those analytes with poorer purging efficiencies can be as low as 5.0 ppb up to 5000 ppb.

4.2 Tested Concentration Range: The tested concentration will be the same as the linear calibration range, with no upper limit if dilutions are performed.

4.3 Method Detection Limits (MDL) and Practical Quantitation Limit (PQL):

4.3.1 Method detection limit studies are performed annually.
See GL-LB-E-001 for requirements.

4.3.2 The practical quantitation limit is defined as the lowest concentration level used to standardize the instrument.

4.4 Method precision is measured using a Statistical Process Control (SPC). The SPC limits are generated annually for surrogate, laboratory control samples, and matrix spike analyses.

4.5 Method accuracy is measured using spiked samples of known concentration.

5.0 METHOD VARIATIONS

There are no significant variations to the method procedures described in this SOP. It should be noted that method 8260C requires method-specific criteria in addition to the criteria listed

in the body of this SOP. Specific criteria are outlined in Appendix 4 and Appendix 5. Method 6200 requires method-specific criteria in addition to the criteria listed in the body of this SOP. Specific criteria are outlined in Appendix 8. For 8260D method specified criteria is outlined in Appendix 9-11.

6.0 DEFINITIONS

6.1 Calibration Standard (CAL): A solution prepared from the primary dilution, standard solution, or stock standard solutions, and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

6.2 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample, at the beginning of the analytical sequence. Its purpose is to determine whether the instrument calibration is in control prior to sample analysis. It may be prepared from the same source as the calibration standards, and is usually of varied concentration. For SC samples the CCV must come from the same source standard that is used to prepare the initial calibration curve.

6.3 Holding Times (Maximum Allowable Holding Time): The maximum times that samples may be held prior to analysis and still be considered valid or not compromised. (SW-846, Table 2-40A)

6.4 Initial Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of blank or sample matrix. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to validate an initial calibration curve with externally prepared test materials.

6.5 Initial Standard (ISTD): A known amount of standard added to a portion of the sample extract as a reference for evaluating and controlling the precision and bias of the applied analytical method.

6.6 Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, it must be a separate source standard from the initial calibration): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes of a matrix containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

6.7 Limit of Detection (LOD): The lowest concentration level that can be determined by a single analysis and with a defined level of confidence to be statistically different from a blank.

6.8 Limit of Quantitation (LOQ): The lowest level in the calibration curve. With the prep factor applied, the LOQ is referred to as the effective LOQ. The LOQ is equivalent to the PQL and LLOQ.

6.9 Lower Limit of Quantitation (LLOQ): The lowest concentration at which a target analyte can be reliably measured and reported. The LLOQ is the lowest point in the calibration curve and represents a concentration at which both quantitative and qualitative requirements can be consistently demonstrated. The LLOQ is verified quarterly, as the LOQ verification. The verification is performed by extracting and analyzing an LCS spiked at the lowest level of initial calibration curve (see Appendix 3 for concentrations). The LLOQ verification is carried through the same preparation and analytical procedures as environmental samples and QC. The LLOQ is analyzed on every instrument where data are reported and this is the laboratory's normal protocol. Recovery of target analytes in the LLOQ are compared to in-house-statistically-derived limits. Concentrations in samples reported below the LLOQ and above the MDL are qualified as estimated.

6.10 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

6.11 Method Detection Limit (MDL): The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined for analysis for a sample in a given matrix containing the analyte. (40 CFR Part 136 Appendix B)

6.12 Practical Quantitation Limit (PQL): The lowest level in the calibration curve. With the prep factor applied, the PQL is referred to as the effective PQL. The PQL is equivalent to the LOQ and the LLOQ.

6.13 Quantitation Limit (DoD clarification): The value at which an instrument can accurately measure an analyte at a specific concentration (i.e., a specific numeric concentration can be quantified). These points are established by the upper and lower limits of the calibration range.

6.14 Relative Percent Difference (RPD): The difference between two duplicate samples, such as a MS/MSD, LCS/LCSD, or sample/sample dup. It is determined by taking the difference between the two results and dividing by the average.

6.15 Statistical Process Control (SPC) Limits: Statistically derived limits, which establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS, PSD and surrogate standards.

6.16 Target Analytes: Identified on a list of project specific analytes of which laboratory analysis is required.

6.17 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

7.0 INTERFERENCES TO THE METHOD

7.1 Potential contaminants for this procedure include common laboratory solvents, typically ketones, methylene chloride, toluene, freons, and carbon disulfide. These compounds are used frequently in other areas of the laboratory and care must be taken to seclude the volatile organics lab and personnel from the other areas.

7.2 To minimize the contamination, use organic-free deionized water or equivalent for all analyses.

7.3 Cross contamination by carry-over can occur during sequential analyses. If cross-contamination is suspected, the affected sample or samples are reanalyzed.

7.4 The trap and other parts of the system, such as the column, are subject to contamination; therefore frequent bake out and purging of the system are required.

7.5 Sample vials are purchased as EPA Level 2 (pre-cleaned) or Level 3 (certified) and are certified free of organic contaminants. Glassware should be baked in an oven until needed. DO NOT USE HOT GLASSWARE. Wait until the glassware has cooled to room temperature before use.

8.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

8.1 Treat all chemicals and samples as potential health hazards. Exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals as well as a reference file of Material Safety Data Sheets (MSDS). These documents are maintained in the laboratory. Individual sample MSDS forms provided by the clients are kept in Login.

8.2 Personal protective equipment

8.2.1 Approved gloves are required when handling standards and samples in this procedure.

8.2.2 Work under a hood when using concentrated acids, bases, and stock solutions or if samples are suspected of having high VOC contents.

8.2.3 Safety glasses and lab coats are required when handling samples and reagents.

8.3 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling.

8.4 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.5 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

8.6 In the event of an accident or medical emergency, seek help immediately. When time and safety permit, file an accident report form regardless of how insignificant the injury may seem.

8.7 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

8.8 The analyst must use great care when operating and assembling instrumentation and when handling samples and reagents. Check to see that the equipment is properly assembled and connected to gas and power, etc.

8.9 In an effort to maintain instrument integrity, take care to avoid running samples that contain over-range hits of analytes, especially hydrocarbons. Observe samples for foaming. Use caution when analyzing oils, multiphasic samples or samples suspected of containing high concentrations of VOC analytes.

8.10 Refer to SOP GL-LB-N-001 the Safety, Health and Chemical Hygiene Plan for additional general safety and health information pertaining to the laboratory.

9.0 APPARATUS AND MATERIALS; REAGENTS; EQUIPMENT AND INSTRUMENTS

9.1 Apparatus and Equipment

9.1.1 5 mL or 10 mL glass syringes

9.1.2 Gas Tight syringes: 10, 25, 50, 100, 250, 500, 1000 µL

9.1.3 Purge vessels, 40 mL glass vials, EPA certified level 2 or higher.

9.1.4 Drying oven

9.1.5 Refrigerator and freezer

9.1.6 Columns

9.1.7 Reactor vials with mininert valves

9.1.8 Centrifuge

9.1.9 Disposable pipets

9.1.10 Balance

9.1.11 2 mL vials with screw cap lids for storage of sample extracts (soil)

9.1.12 Scintillation vials with screw cap lids for storage of sample aliquots (liquids)

9.2 Instrumentation

9.2.1 Purge and trap system for water, soil, and waste samples. This system consists of an autosampler with a heater assembly and a concentrator.

9.2.2 The concentrator contains a trap which holds various types of adsorbent materials. Traps are obtained from OI Analytical and are type “10”. Equivalent traps may be used from alternate vendors.

9.2.3 The heater assembly is used to maintain samples at 40°C.

9.2.3.1 Recommended Parameters (example only)

9.2.3.2 Standby: 30° C

9.2.3.3 Preheat: 1.0 minute

9.2.3.4 Purge: 11.0 minutes

9.2.3.5 Prepurge: 0.00

9.2.3.6 Sample: 40° C

9.2.3.7 Dry Purge: 0.00

9.2.3.8 Desorb preheat: 150° C (or the recommended temperature per manufacturer for the type of trap installed).

9.2.3.9 Desorb: 0.6 minutes at 180° C

9.2.3.10 Bake: 10.00 minutes at 220° C

9.2.3.11 Purge flow: 25 mL/min to 40 mL/min depending upon each instrument

9.2.3.12 Valve: 120° C, Line: 120° C, Mount: 120° C

9.3 GC/MS System

9.3.1 This device consists of a Gas Chromatograph and Mass Selective Detector, capable of scanning from 35 to 300 amu every two seconds or less. A computerized data system is used to control or assist in instrument tuning, data acquisition, data reduction, report production, and automation.

9.3.2 The laboratory utilizes Agilent 5890, 6890 and 7890 and 7890B Gas Chromatographs and 5972, 5973, 5975 and 5977A Mass Selective Detectors. Agilent Chemstation/Enviroquant Software is used for data processing and evaluations.

9.4 Columns

9.4.1 J & W DB-624 or Restek RTX-624 or equivalent fused silica capillary. column 0.25 mm ID x 60 m, 1.4 µm film thickness.

9.4.2 Temperature Limits: (-20° C to 260° C).

9.4.3 Temperature Program: used to achieve optimal analyte separation.

10.0 REAGENTS AND STANDARDS

10.1 The water used for volatile organic analysis must be high quality organic free water or equivalent.

10.2 Methanol: Spectrum high purity solvent for purge and trap analysis or equivalent. Each lot of methanol is screened for contaminants prior to use. See GL-OA-E-065 Reagent/Solvent/Standard Screening for Organic prep.

10.3 Source Standard Solutions: Most source standard solutions are purchased from approved vendors. Source standards are used to make stock, intermediate, and working standards. The primary source standards used for calibrating the instrument are listed below. The names in parentheses are an alternate description for the compound.

Calibration Short List:

Acrylonitrile	cis-1,4-Dichloro-2-butene
Acrolein	Isopropyl alcohol
Allyl chloride (3-Chloropropene)	tert-Butyl alcohol
Cyclohexanone	Isopropyl ether (Diisopropyl ether)
Ethyl methacrylate	Ethyl-tert-butyl ether (ETBE)
Isobutyl alcohol (2-Methyl-1-propanol)	Methyl-tert-amyl ether (TAME)
Methacrylonitrile	Ethyl acetate
Methyl methacrylate	Benzyl chloride
Trichlorotrifluoroethane (Freon 113)	1-Chlorohexane
Pentachloroethane	2-Nitropropane
Tetrahydrofuran (THF)	bis(2-Chloro-1-methylethyl)ether
Propionitrile (Ethyl cyanide)	1,4-Dioxane
trans-1,4-Dichloro-2-butene	2-Chloro-1,3-Butadiene (chloroprene)

Calibration Long List:

Acetone	Methyl acetate
Acetonitrile	1,2-Dichloropropane
Benzene	2,2-Dichloropropane
Bromobenzene	1,3-Dichloropropane
Bromochloromethane	cis-1,2-Dichloroethene
Bromodichloromethane	cis-1,3-Dichloropropene
Bromoform	trans-1,2-Dichloroethene
Bromomethane (Methyl Bromide)	trans-1,3-Dichloropropene
2-Butanone (Methyl Ethyl Ketone, MEK)	Ethylbenzene
Toluene-d8(surr)	Ethyl ether (Diethyl ether)
n-Butylbenzene	Hexachlorobutadiene
sec-Butylbenzene	2-Hexanone
tert-Butylbenzene	Iodomethane
Carbon disulfide	Isopropylbenzene (Cumene)
Carbon tetrachloride	p-Isopropyltoluene (p-Cymene)
Chlorobenzene	4-Methyl-2-pentanone (MIBK)
Chloroethane	Naphthalene
Chloroform	n-Propylbenzene
Chloromethane (Methyl Chloride)	n-Butyl alcohol
Cyclohexane	Styrene
Cyclohexene	Tetrachloroethylene (Perchloroethylene) (PCE)
2-Chloroethylvinyl ether	Trichlorofluoromethane (Freon II)
2-Chlorotoluene	1,1,1,2-Tetrachloroethane
4-Chlorotoluene	1,1,2,2-Tetrachloroethane
Dibromochloromethane	tert-Butyl methyl ether (MTBE)
Methylene chloride(Dichloromethane)	Toluene
1,2-Dichloroethane-d4 (surr)	Trichloroethene (TCE)
1,2-Dibromoethane (EDB) (Ethylene dibromide)	1,2,3-Trichlorobenzene
Dibromomethane	1,2,4-Trichlorobenzene
1,2-Dichlorobenzene	1,1,2-Trichloroethane
1,3-Dichlorobenzene	Methylcyclohexane
1,4-Dichlorobenzene	1,2,4-Trimethylbenzene
1,1-Dichloroethane	1,3,5-Trimethylbenzene (Mesitylene)
1,1,1-Trichloroethane	o-Xylene
1,1-Dichloroethene	1,2-Dibromo-3-Chloropropane (DBCP)
1,1-Dichloropropene	m,p-Xylene
1,2-Dichloroethane	Vinyl acetate

Dichlorodifluoromethane (Freon 12)	Vinyl chloride
4-Bromofluorobenzene (surr)	1,2,3-Trichloropropane (TCP)

10.4 Surrogates: Toluene-d8, 4-Bromofluorobenzene and 1,2-Dichloroethane-d4. Other compounds may be used as surrogates, depending upon the analysis requirements. Final concentrations of the surrogates should be 50 µg/L. Surrogate analytes are calibrated in the Calibration Long List.

10.5 Internal standards: Fluorobenzene, Chlorobenzene-d5, and 1,4-Dichlorobenzene-d4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by the GC/MS. Final concentration of internal standards should be 50 µg/L.

10.6 BFB Tune (4-Bromofluorobenzene): Prior to sample analysis, a 5 to 50 ng BFB solution must be analyzed. The BFB solution is 50 µg/L. One microliter of this solution is placed into 5 mL of deionized water. The tune is evaluated against the criteria in Appendix 2.

10.7 Calibration Standards: A minimum of five calibration standards must be used to establish instrument linearity. Each standard is prepared in a 10 mL or 5 mL syringe. The lowest concentration level used to standardize the instrument is considered the practical quantitation limit for the compound of interest. (Refer to Appendix 3 for calibration levels)

10.8 Matrix Spiking/LCS Standards: The spiking solution is a separate source standard from the calibration standards. A set of representative compounds is used to spike sample matrices. Each compound spiked into the sample is reviewed to evaluate the effect of matrix on the spiked compounds. Refer to client specific requirements for spiking list to be reported.

10.9 Volatile organic standards are stored at -10° to -20° C.

10.10 Non-gas standards have an expiration of one month from opening. Standards for the permanent gases must be replaced after one week of opening. Intermediate standards containing gases have a one week expiration date from the day that they are made, or the vendor expiration date if sooner. Volatile working standards are made on a daily basis and are never reused the following day.

10.11 AlphaLIMS software is used to inventory and document standard traceability. For guidance on standard documentation, refer to GL-LB-E-007 for Laboratory Standards Documentation.

11.0 PRESERVATION AND SAMPLE HANDLING REQUIREMENTS

11.1 Aqueous Samples

11.1.1 Aqueous samples must be stored at 0° ≤ 6° C from the time of collection until analysis. The samples should be collected and stored with no headspace, however, pea-size bubbles are acceptable. Large volumes of sediment and any headspace should be noted in the case narrative.

NOTE: Large volumes of headspace indicate that the sample was improperly collected. Notify the Project Manager, who is responsible for contacting the client and requesting that the sample be recollected. If recollection is not possible, flag the report to indicate that the samples were improperly collected. In either case, nonconformance to proper sample collection should be noted in the case narrative.

11.1.2 Water samples should not contain any headspace and should have pH checks with pH paper strips immediately prior to analysis. Aqueous samples are preserved with hydrochloric acid to a pH less than 2 and have a 14-day holding time. Unpreserved waters have a holding time of 7 days from collection. If samples are analyzed after the 7 days with a pH above 2 the nonconformance is documented in the case narrative, the client is notified and the results are flagged accordingly. Samples that request Acrolein and Acrylonitirile must be preserved to a pH of 4-5 and analyzed with 7 days unless the applicable sampling and analysis plan or QAPP specifies otherwise.

11.1.3 Upon obtaining the aliquot for analysis, waters shall be checked for residual chlorine. The residual chlorine check is similar to the pH measurement, using a chlorine test strip. The presence of residual chlorine is documented in the runlog as “Yes” or “No”. If residual chlorine is present in samples, the analyst should document the information on the runlog, in the case narrative, and notify the project manager.

11.2 Soil Samples

11.2.1 Soil samples collected for SW-846 8260 should be unpreserved or preserved in the field with specific collection kits or collected in EnCore samplers. EnCore samplers must be sent to the lab and preserved within 48 hours of collection. Preservation can be client specific however, refer to GL-OA-E-039 (SW-846 5035/SW-846 5035A, collection and preservation) for laboratory standard procedures. Method 5035 list two preservatives-sodium bisulfate and methanol. The laboratory does not analyze samples preserved in sodium bisulfate.

11.2.1.1 Low Level Soil Sample Prep

11.2.1.1.1 Using a sampling device (such as an EnCore), three sets of approximately 5 g of soil are collected per sampling site. Two are prepared for Low Level and one for High Level analysis.

11.2.1.1.2 Transfer the soil from each EnCore device to a tared 40 mL vial. Reweigh the vial (now containing the soil) and record the weight in the Soil Prep Logbook as well as on the sample label. Add 5 mL of organic free water and a magnetic stir bar before sealing the vial. Store unpreserved (water only)

samples in the freezer until analysis. Sample weights are recorded in the soil prep logbook, in AlphaLIMS in the sample prep batch and on the instrument runlog.

11.2.1.2 High Level Soils Collected in EnCore Samplers

11.2.1.2.1 Transfer the soil (approximately 5 g) from the sampling device to a tared 40 mL vial. Record the soil weight in the soil prep logbook. Add 10 mL of purge and trap grade methanol. The volume of methanol added during the extraction process can vary from 5 mL to greater than 10 mL depending on client requirements or matrix. Replace the cap and gently shake for 2 minutes. Allow the soil to settle. Centrifuge if necessary. Transfer an aliquot of the methanol extract to a 2.0 mL vial with minimum headspace, label appropriately, and store in the refrigerator until analysis. Discard the remaining soil/extract in appropriate manner for solvent/solid waste per GL-LB-G-001 for Laboratory Waste Management Plan. Sample weights are recorded in the soil prep logbook, in AlphaLIMS in the sample prep batch and on the instrument runlog.

11.2.1.2.2 A methanol solvent blank (HB) is prepared by placing a portion of the methanol used for sample extractions into a 2.0 mL vial with minimal headspace. The labeled vial is stored with the soil extracts at 0° C ≤ 6° C until the time of analysis. It is analyzed under the same conditions as the associated samples. Methanol used in the laboratory is screened by lot prior to use.

11.3 Solids or liquid waste and oils should not be acid preserved. These types of samples should be stored at 0° ≤ 6° C from the time of collection until analysis.

11.4 Analysts receive the samples directly from the storage cooler. Samples must be tracked into the analyst's custody, then tracked back to the cooler or archive upon completion of the analysis.

11.5 If samples are analyzed out of holding or the correct preservation was not performed, the analyst must immediately notify the Project Manager. Additional information for the nonconformance should be indicated in the batch and/or fractional case narrative.

12.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

12.1 Low Level Soil Sample Preservation (SW-846 5035/SW-846 5035A)

12.1.1 Preserved samples received from the field are wiped to remove any extraneous material from the exterior of the vial. The vial is weighed to the nearest 0.1 g and the weight is recorded in the soil prep logbook. The weights are entered into the AlphaLIMS system in the sample prep batch. The analyst should observe the vial for any indication for leaks or cracks. If any significant observations are detected, the project manager is notified and the appropriate action is taken.

12.1.2 Allow the sample to warm to room temperature. Shake the vial gently to ensure that the contents move freely and that stirring will be effective. Place the vial in the autosampler and ensure the autosampler will add the appropriate volumes of organic-free water, surrogates, and internal standards to all vials. All samples, blanks, and calibration standards are analyzed with the same final volume.

12.1.3 When low level soil analysis produces target analyte results with concentrations higher than the calibration range of the instrument, the sample is reanalyzed using the prepared aliquot from the High Level Soil Sample Prep (11.2.2). Such reanalysis need only address those analytes for which the concentration exceeded the calibration range of the Low Level Method. The maximum volume of methanol analyzed is 100 µL.

12.1.4 Analysts should never open a 5035 preserved low level soil vial from the field or EnCore sampler. All spiking must be performed through the vial septum with a syringe or autosampler needle.

12.1.5 Results are to be reported on a dry weight basis unless otherwise specified by the client.

NOTE: Low level soil samples originating in South Carolina must be collected and analyzed using EPA Methods 5035.

12.2 High Level Soil Sample Preparation (SW-846 5035/SW-846 5035A)

12.2.1 High Level soils collected in EnCore samplers

12.2.1.1 To analyze the methanol extract, transfer 100 µL of the extract to a 5 mL syringe containing 4.9 mL of organic-free water. Transfer the fortified water to an autosampler vial (40 mL vial with septum cap). Place the vial in the autosampler. If concentrations of analytes exceed the calibration range, the sample is reanalyzed using a smaller volume of sample aliquot.

12.2.1.2 For high level soils preserved in the field, this aliquot may or may not be analyzed depending on the concentration of the analytes present in the sample. Prior to analysis, allow the soil/methanol extract to reach room temperature. Withdraw 100 µL or the desired volume from the vial. Transfer the methanol extract to a syringe containing 4.9 mL of organic-free water.

Transfer the fortified water to an autosampler vial (40 mL volatiles vial). Place vial in autosampler.

12.2.1.3 All sample analyses for high level soils using the methanol extract procedure require the preparation and analysis of a methanol blank (HB) if the samples are prepared at the laboratory. Field prepared samples may or may not include a methanol aliquot for analysis. Place 100 µL of the methanol in a syringe containing 4.9 mL of organic-free water. Transfer the water to an autosampler vial (40 mL volatiles vial). Place the vial in the autosampler. The acceptance criteria applied to the HB should be the same as method blank criteria outlined in 17.2.3.

12.3 Low Level Soil analysis: Allow samples to reach room temperature. Weigh approximately 5 g (± 0.1 g) of sample into a 40 mL autosampler vial. Document the weight used in the soil preparation logbook and on the instrument runlog. The weights are also entered into AlphaLIMS system in the sample prep batch. Add 5 mL of organic-free water to the vial and a stir bar. Gently shake the sample vial to ensure the magnetic stir bar moves freely. Place the sample vial in the appropriate position and complete the autosampler sequence as desired to purge each sample.

NOTE: The sample may be diluted by weighing less sample. Do not analyze less than 1.0g of the solid sample. If a higher dilution is required, use the high level soil sample preparation method.

12.4 High Level Soil Preparation (SW-846 5035/SW-846 5030C)

12.4.1 Solid samples that contain concentrations of analytes greater than the highest concentration level in the calibration or samples with high viscosity, are extracted with methanol, and then diluted in water. Approximately 5 g of sample is weighed out and extracted with 10 mL of methanol. The methanol extract is gently shaken for two minutes then allowed to settle until distinct layers form. Centrifuge if necessary. An aliquot of the methanol layer is then transferred to a 2.0 mL vial. The extract is then analyzed immediately or the vial is stored in the sample refrigerator until analysis. The dilution factor is 1:50 if 100 µL of sample is used. The minimum amount of soil that can be used is 1 gram.

12.4.2 Oily waste samples or samples of unknown solid matrix are extracted following SW 846 Method 3585 with some modifications. SW 846 Method 3585 suggests n-Hexadecane or another appropriate solvent be used as the extraction solvent when performing waste dilutions on oily matrices. The laboratory uses purge and trap methanol as the extraction solvent for these types of sample preparations. The samples are prepared by weighing a 1 g aliquot into a VOA vial and adding an appropriate volume of purge and trap methanol to meet the client's detection limit requirements if possible.

This volume is usually 5 to 10 mL but can be as high as 20 mL. The methanol extract is gently shaken for two minutes then allowed to settle until distinct layers form. Centrifuge if necessary. An aliquot of the methanol layer is then transferred to a 2.0 mL vial. The methanol volume may be increased if the matrix absorbs the initial volume of methanol used. The total volume of methanol used is documented in the soil prep logbook and AlphaLIMS. Care should be taken with any oily or unknown matrix to avoid contamination to the analytical system from high concentrations of targets or non-target analytes. Methanol is screened by lot prior to use.

12.5 Aqueous analysis (5030B)

12.5.1 Allow samples to reach room temperature. Invert each sample vial to check for headspace. Gently pour approximately 6 mL of the aqueous sample into a 10 mL syringe. Place the plunger in the syringe and invert, allowing any bubbles to escape through the end fitting. Adjust the sample volume 5.0 mL by depressing the plunger to the mark. The extraneous sample volume may be added back to the original sample vial. Transfer the 5.0 mL of sample to a clean 40 mL autosampler vial and place the vial in the appropriate autosampler position. Complete the autosampler sequence as desired.

12.5.2 After obtaining that aliquot for analysis, the pH of the sample is checked using wide range pH paper. Samples should be preserved to a pH <2. Document pH on instrument run log. Notify project manager of samples with a pH >2 if not analyzed within 7 days from collection. Analysts should always obtain their sample aliquots before taking pH. If sample volumes are limited (one vial per sample) the analyst should transfer a sample aliquot to a smaller container with no headspace (scintillation vial) if additional testing may be required. For limited volume samples, the analyst should obtain the pH of the sample by pipetting a small volume of the sample across the pH strip into a waste container, otherwise the pH strip may be dipped in the sample vial and the vial discarded.
NOTE: Make a note of any sample discrepancies, i.e. unpreserved sample, any headspace, and excessive sediment in the batch case narrative and on the instrument runlog.

12.5.3 After obtaining the aliquot for analysis, waters shall be checked for residual chlorine. Residual chlorine check is similar to the pH measurement, using a chlorine test strip. Additional sample aliquots cannot be taken from the vial once the residual chlorine test has been performed. For limited sample volumes the steps outlined in 12.5.2 may be necessary to preserve sample aliquots for future testing. The presence of residual chlorine is documented in the run log as “Yes” or “No”. If

residual chlorine is present in samples, the analyst should document the information in the case narrative, and notify the project manager.

12.5.4 TCLP extracts and Tumble blanks are diluted prior to analysis for a total 5 mL prep. Transfer the 5 mL of sample to a clean 40 mL autosampler vial and place the vial in the appropriate autosampler position. Complete the autosampler sequence as desired. The batch QC requirements are a tumble blank, method blank, LCS, post spike and post spike duplicate.

13.0 QUALITY CONTROL SAMPLE FOR SOLID AND AQUEOUS SAMPLES

13.1 After preparing and prior to purging, fortify the appropriate samples for matrix spike purposes using an amount of MS/LCS spike solution needed to achieve the desired concentration.

13.2 Preserved soils (5035) should be fortified by inserting the syringe needle into the vial septum and injecting the spike solution into the liquid. Tilt the vial during this process to ensure that the spike solution enters the liquid phase of the sample.

13.3 Aqueous and/or 5035A solid samples can be fortified in the syringe prior to transferring the aqueous sample or organic free water to the autosampler vial.

13.4 Prepare the Laboratory Control Sample (LCS) for solids and liquids by injecting the appropriate amount of spike solution needed to achieve the desired concentration into a gas tight syringe containing 5 mL organic free water. Transfer the syringe contents to an empty 40 mL autosampler vial or one containing 5 g of sand.

13.5 Prepare aqueous method blanks by transferring 5 mL organic free water to an empty 40 mL autosampler vial. Prepare solid method blanks by transferring 5 mL of organic free water to a 40 mL autosampler vial containing a stir bar and 5 g of sand.

13.6 Quality control samples for solids should contain 5 g of sand and a stirbar.

14.0 OVERALL QUALITY CONTROL REQUIREMENTS

14.1 Prior to any quality control or sample analysis, the analyst must perform an instrument check by injecting 5 to 50 ng of Bromofluorobenzene (BFB). The BFB tune check must be performed prior to each analytical sequence. A new BFB check must be performed after 12 hours of analysis.

14.2 Prior to any sample analysis the instrument must be calibrated. Initial calibration standards are analyzed if the calibration verification standards do not meet the acceptance criteria or if instrument maintenance was performed (i.e., source cleaning, new column, replacing source parts).

14.3 The initial calibration must be verified in each 12-hour sequence by purging a mid-level calibration verification standard. For SC samples the calibration verification standard must come from the same source standard that is used to prepare the initial calibration curve.

14.4 A laboratory control sample must be analyzed during each 12-hour sequence by purging a second source mid-level standard.

14.5 A method blank must be analyzed during each 12-hour sequence by purging organic free water.

14.6 Matrix spike and matrix spike duplicate samples are analyzed in each batch of up to 20 samples of the same matrix. Many clients require their sample to be used for matrix spike purposes. Refer to client specifications in AlphaLIMS for this information.

14.7 A laboratory control sample duplicate should be analyzed if matrix volumes are limited.

14.8 Surrogate compounds and internal standards are added to each sample and all quality control samples.

15.0 INSTRUMENT CALIBRATION, STANDARDIZATION AND PERFORMANCE

15.1 Prior to the analysis of calibration standards, inject or introduce 5 to 50 ng of the bromofluorobenzene (BFB) standard into the GC/MS system. The mass spectra of BFB can be obtained using an average of up to three scans and using a background subtraction from no more than 20 scans before the peak starts. However, the analyst may use other documented approaches by the instrument manufacturer.

15.2 Initial Calibration. An unpreserved calibration curve may be used for high level methanol extracts, waters and low level soils. Standards at various concentrations are analyzed and the instrument responses they generate are entered into the analytical method. Traceability of calibration and calibration verification standards is documented per GL-LB-E-007. Individual identification numbers are assigned to each source standard. The calibration curve must be a contiguous subset of the original set.

NOTE: Prior to tuning or running a multi-point calibration, precautions are taken to ensure that the instrument is clean and functioning properly. Standards should be set up from low concentration to high concentration in deionized water (Refer to Appendix 1). Once the instrument methods have been established the mass range and scan time should not be readjusted.

15.2.1 Establish the GC/MS operating conditions using the following guidelines:

15.2.1.1 Mass Range: 35-300

15.2.1.2 Scan time: 0.6-2 sec/scan

15.2.2 Calibration standards are purchased at multiple concentration levels and packaged separately in sealed ampules. Upon cracking the ampule for each standard, transfer each solution into a micro reaction vessel with a mininert cap. Indicate on the vial label the unique standard identification number, date opened, and the expiration date plus the analyst's initials preparing/opening the standards.

15.2.3 Load a 10 mL gas tight syringe with 5mL of organic-free water. Transfer 5 µL of calibration standard into the syringe and then transfer to a 40 mL vial. Repeat this step for each concentration level of standard. The Calibration Long List is separated into gases and non-gas compounds. The analyst must add each set of concentration levels to a syringe in order to analyze for all the compounds in this list. Similarly, the Calibration Short List is prepared by adding 5 µL of the Short List standard plus 5 µL of the

Acrolein/Cyclohexanone standard into a syringe containing 5 mL of deionized water.

15.2.4 Set up the autosampler to analyze each standard from low to high concentration.

15.2.5 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 its internal standard. 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. The RF is calculated as follows:

$$RF = (AxCis) / (AisCx)$$

Where:

Ax = Area of the characteristic ion of the compound being measured.

Ais = Area of the characteristic ion of the specific internal standard.

Cis = Concentration of the specific internal standard.

Cx = Concentration of the compound being measured.

15.2.6 For 8260B the average RF must be calculated for each compound. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for minimum average response factors. These compounds are: Chloromethane, 1,1-Dichloroethane, Bromoform, 1,1,2,2-Tetrachloroethane, and Chlorobenzene. The minimum acceptable average RF for these compounds is: 0.1 for Chloromethane, 1,1-Dichloroethane, and Bromoform, 0.3 for Chlorobenzene and 1,1,2,2-Tetrachloroethane. These compounds typically have RFs of 0.4 to 0.6 and are used to check compound instability and degradation caused by contaminated lines or active sites in the system. Failure to meet the response factor criteria may be attributed to one or more of the following examples:

- Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.
- Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve Bromoform response.
- 1,1,2,2-Tetrachloroethane and 1,1-Dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

  NOTE: Non-SPCC compounds should have a minimum response factor of 0.01, with the exception of poor purging compounds such as those listed in Appendix 6. Unless otherwise required by client

contract, these compounds may have response factors as low as 0.001. For the analysis of ketones and carbon disulfide at a PQL less than 5 ppb, the relative response factor for these analytes must be equal to or greater than 0.05. Method 8260C has additional requirements for response factors. Refer to Appendix 5. Method 8260D also has additional guidance for response factors however, it is not required.

15.2.7 Calibration curves must be verified using an initial calibration verification standard (ICV). This should be a second source standard from the initial calibration. The laboratory control spike solution can be used for this standard. The response factor or true value (percent difference or drift) is evaluated based on individual client requirements. At minimum the SPCC and CCC's criteria for response and percent drift or difference must be met. For samples from within the state of South Carolina the percent drift or difference should not exceed +/- 30% for requested analytes and +/- 40% for poor purgers (See Appendix 6). The percent drift or difference for non-CCC compounds may be as high as 60% for some clients. For DoD clients the percent drift or percent difference should not exceed ± 20% for requested analytes. If the ICV does not meet the criterion, corrective action should be taken (i.e., inject a different second source, open a new standard mix, perform instrument maintenance and/or reanalyze the initial calibration). If individual client requirements are not met and holding times are expiring, the group leader is notified. Clients will be notified of the nonconformance and analysis of the samples may proceed. Note any nonconformance in the case narrative. See Appendix 4 for 8260C specific criteria. See Appendix 9 for 8260D criteria.

15.2.8 All newly generated calibration curves shall have a secondary review by a Group Leader or Data Validator before being used.

15.2.9 The internal standard responses and retention times in the calibration standards must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds during the calibration, the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the Extracted Ion Current profile (EICP) area for any of the internal standards changes by a factor of two (-50% to +100%) during the calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made reanalysis of the calibration check standard is necessary.

15.2.10 Using the $\overline{RF}$ s from the initial calibration, calculate the percent relative standard deviation (%RSD) for Calibration Check Compounds (CCCs) and all target analytes:

$$\%RSD = \frac{SD}{\bar{x}} \quad 100$$

Where:

RSD = Relative Standard Deviation

$\bar{x}$ = Mean of initial RFs for a compound

SD = Standard deviation of average RFs for a compound

$$SD = \sqrt{\sum_{i=1}^{n} \frac{\left(x_i - \bar{x}\right)^2}{n-1}}$$

15.2.11 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range and may be used for quantitation. If the RSD of any target analyte is greater than 15%, then use one of the options in section 15.2.13. A minimum of five calibration standards must be used. The laboratory may use more than five concentration levels. The maximum % RSD for NNSA client is 60% Refer to Appendix 4 for 8260C and Appendix 10 for 8260D

15.2.12 The % RSD for each individual CCC must be less than or equal to 30 percent difference. This criterion must be met in order for the individual calibration to be valid. The CCCs are:

- 1,1-Dichlorethane
- Chloroform
- 1,2-Dichloropropane
- Toluene
- Ethylbenzene
- Vinyl Chloride

15.2.13 Given the potentially large numbers of analytes that may be analyzed by this method, it is likely that some analytes may exceed that 15% acceptance limits for RSD. In those instances, the following steps may be used:
NOTE: Refer to Appendix 4 and 10 for 8260C criteria.

15.2.13.1 Check the instrument operating conditions. Follow the suggested maintenance procedure in this method to make minor adjustments to the system.

15.2.13.2 Review the results of each standard (area counts, calibration or response factors and RSD) to ensure that the problem is not associated with one of the five initial calibration standards. If the problem appears to be associated with a single standard, then the entire calibration must be reanalyzed.

15.2.13.3 High-end standards may be removed on a compound by compound basis thus narrowing the calibration range of the instrument if there are enough remaining calibration points to meet method requirements. The top of the calibration curve may

not be the mid-point spiking concentration. At least one point must be in the calibration curve above this concentration.

15.2.13.4 The analyst may also choose to construct calibration curves of area ratios versus concentration using first order regression fit of the five calibration points. The regression calculation will generate a coefficient of determination (r2) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r2 must be ≥ 0.990. The minimum acceptable correlation coefficient (r) for any compound using linear regression shall be 0.995. The analyst will select only linear regression or average response factor. Higher order curves such as a quadratic curve must never be used. Correlation coefficients may not be rounded up to meet these requirements.

15.2.13.5 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response

a = slope of the line (also called the "coefficient of x")

x = concentration of the calibration standard

b = the intercept

15.2.13.6 If the analyst chooses to use linear regression, he/she must not force the calibration line through the origin but have the intercept calculated from the data points. In addition, do not include the origin (0,0) as a sixth calibration point.

15.2.13.7 The calculated intercept value needs to be evaluated before reporting sample results. A positive value for the intercept indicates that there is some threshold instrument response that is the limiting factor in establishing linearity. A negative intercept value can be transformed into an x-intercept value that represents a threshold concentration that is the limitation. If the intercept is positive, then as a general rule, results where the instrument response is less than three (3x) the intercept value may be unreliable. This will afford some protection against false positive results. If the intercept is negative, results below the concentration of the lowest concentration calibration standard may be unreliable. The value of the y intercept multiplied by the internal standard concentration must be less than 3 times the

value of the MDL for each matrix for analysis of NNSA client samples. A weighted linear calibration curve may be generated and the intercept re-evaluated for NNSA requirements.

15.2.13.8 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x):

y = ax + b: linear equation

x = (y-b)/a

15.2.14 Exclusion of initial calibration points without technical justification is not allowed. Occasionally, it may be obvious that a condition such as a bad injection or purge had rendered an initial calibration standard unusable.

15.2.14.1 If it is necessary to replace a calibration level in a curve, the entire level must be replaced and not individual analytes.

15.2.14.2 The questionable level may be reanalyzed as long as the reanalysis is performed within the 12 hour window. The second injection must be used in the calibration curve.

15.2.14.2.1 Should the second injection fail, the entire calibration curve must be reanalyzed.

15.2.14.2.2 If the second injection passes, reanalyze the initial calibration verification sample.

15.2.15 Method 8000D outlines two procedures that may be used to determine calibration function acceptability for linear and non-linear curves. These include refitting the calibration data back to the model. % Error and Relative Standard Error (RSE) evaluate the difference between the measured amount and the true amount (or concentration).

15.2.16 % Error is determined as follows:

$$\%Error = \frac{x_i - x_i'}{x_i} \times 100$$

Where:

x′i= Measured amount of analyte at calibration level i, in mass or concentration units

xi= True amount of analyte at calibration level i, in mass or concentration units.

15.2.17 Percent error between the calculated and expected amounts of an analyte should be ≤ 30% for all standards. For some data uses, ≤ 50% may be acceptable for the lowest concentration point.

15.2.18 Relative Standard Error is calculated as follows:

$$RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x_i' - x_i}{x_i} \right]^2 \Big/ (n-p)}$$

Where:

xi= True amount of analyte in calibration level i, in mass or concentration units

x′i= Measured amount of analyte in calibration level i, in mass or concentration units

p= Number of terms in the fitting equation (average =1, linear =2, quadratic =3, cubic =4)

n= Number of calibration points

15.2.19 The RSE acceptance limit criterion for the calibration model is the same as the RSD limit in the determinative method. If the RSD limit is not defined in the determinative method, the limit should be set at ≤ 20% for good performing compounds and ≤ 30% for poor responding compounds.

15.3 Continuing Calibration Verification

15.3.1 Prior to the analysis of calibration verification standards, inject or introduce 5 to 50 ng of the Bromofluorobenzene standard into the GC/MS system. The resulting mass spectra of the BFB must meet all of the criteria given in Appendix 2 before sample analysis begins. The mass spectrum of BFB can be obtained using an average of up to three scans and using a background subtraction of a single scan no more than 20 scans before the peak starts. However, the analyst may use other documented approaches suggested by the instrument manufacturer.

15.3.2 The initial calibration curve for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the mid-point concentration for the working range of the GC/MS by checking SPCCs and CCCs. This will determine the validity of the initial calibration on a daily basis. The continuing calibration check standard may be a second source standard. For SC samples the CCV must come from the same source standard that is used to prepare the initial calibration curve. Refer to Appendix 4 for 8260C and Appendix 8 for Standard Method 6200 specific criteria and Appendix 10 for 8260D for specific criteria.

15.3.3 System Performance Check Compounds (SPCCs): A calibration verification check must be made every 12 hours. If the SPCC criteria are met a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. The minimum response factors for volatile SPCCs are listed in section 15.2.6 of this SOP. Some possible problems that may prevent one from meeting the criteria are outlined in that section.

15.3.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\%\text{Difference} = \frac{\left|\overline{RF_I} - RF_c\right|}{\overline{RF_I}} \times 100$$

Where:

$\overline{RF_I}$ = Average response factor from initial calibration

RFC = Response factor from current verification check standard

15.3.5 If the percent difference for all CCCs is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% difference), corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new calibration will be analyzed.

15.3.5.1 Passing CCC and SPCC criteria should not be the only factors in evaluating a successful calibration verification. All the analytes in the standard should be evaluated before analysis continues. The percent drift or difference for non-CCC compounds may be as high as 60% for some clients. For DOD-QSM clients the percent drift or percent difference should not exceed 20% for requested analytes. For samples from within the state of South Carolina the percent drift or difference should not exceed ± 30% for requested analytes and ± 40% for poor purging compounds (See Appendix 6). If an analyte is flagged as an outlier on the report the analyst should at least evaluate the significance of the flag. The reason for the outlier may be as simple as the computer missing a quant ion, a poor performance compound, or loss of moisture control. Whatever the reason for the flag, all outliers should be evaluated on how the data will be affected by the analyte list. The 20% criteria for CCCs may be waived if all the required target analytes are less than 20% difference/drift. In addition, if the CCC and SPCC criteria are met despite these compounds not being required, the required target analytes may have differences/drifts greater than 20%. Again, every standard should be evaluated carefully in order to obtain quality data. If individual client requirements are not met and holding times are expiring, the group leader is notified. Clients will be notified of the nonconformance and analysis of the samples may proceed. Note any nonconformance in the case narrative. Refer to Appendix 4 for 8260C and Appendix 8 for Standard Method 6200 specific criteria and Appendix 10 for 8260D specific criteria.

15.3.5.2 Internal Standard Response: Internal standard areas in the daily continuing calibration verification standard (CCV) must be within +100 to -50% and retention times for each internal

standard must be within ±30 seconds of the initial calibration midpoint internal standard. If internal standards do not meet these criteria, reanalyze the CCV to verify the problem was not random. If the areas fail again, corrective action must be taken. Several actions may correct the problem, i.e., refreshing the internal standard solution on the autosampler, using a newly opened solution, checking that instrument conditions have not changed, etc. Document the actions taken to correct the problem in the instrument maintenance log. Refer to Appendix 4 for 8260C specific criteria.

15.3.5.3 If the continuing calibration does not meet the aforementioned criteria, the analyst must determine why and take appropriate corrective action. Samples may not be analyzed until the validity of the calibration has been verified.

16.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

16.1 All calibration and verification standards, blanks, quality control samples, and client samples are analyzed using a heated purge. Ultra Pure helium is bubbled through the sample that is contained in a purging chamber at 40° C. The purgables are efficiently transferred from the aqueous phase to the vapor phase that is swept through a sorbent where purgeables are trapped. After purging is complete, the trap is heated and backflushed with the inert gas to desorb the analytes onto a gas chromatograph that is temperature programmed to separate the analytes that are then detected with a mass spectrometer.

16.2 Daily GC/MS Analysis Procedure:

At the beginning of each day or 12-hour tune window, the GC/MS system is checked to see if acceptable performance criteria are achieved. A 5 to 50 ng BFB standard is analyzed and must pass acceptance criteria before any further analyses are performed.

16.3 If the tune passes, a continuing calibration verification sample is analyzed. At a minimum the SPCC and CCC criteria for response factor and percent drift must be met. Additionally for samples within the state of South Carolina, the percent drift or difference should not exceed +/- 30% for the requested target analytes and +/- 40% for poor purgers (See Appendix 6). If the client requested target list does not include SPCC or CCC compounds, all compounds must have a percent difference or drift of less than 20%. For client samples outside of the state of South Carolina, the CCV should be evaluated against client specific requirements if available. The percent drift or difference for non-CCC compounds may be as high as 60%. If individual client requirements are not met and holding times are expiring, the group leader is notified. Clients will be notified of the nonconformance and analysis of the samples may proceed. Note any nonconformance in the case narrative. Refer to Appendices 4 and 5 for 8260C and Appendix 8 for Standard Method 6200 specific criteria and Appendix 10 for 8260D specific criteria.

16.4 Upon passing the calibration verification, a laboratory control sample (LCS) is analyzed. The LCS must pass either the laboratory SPC limits or client specific limits before

continuing analysis. The CCV and LCS may be combined into one analysis as long as the standard is a second source to the initial calibration standards. The standard must pass both sets of criteria for the CCV and LCS to be acceptable. For SC samples the CCV must come from the same source standard that is used to prepare the initial calibration curve and the LCS must come from a second source standard. Some clients may require that the laboratory analyze a CCV and LCS as two separate injections, specific client requirements are indicated on the batch pull sheet. If individual client requirements are not met and holding times are expiring, the group leader is notified. Clients will be notified of the nonconformance and analysis of the samples may proceed. Note any nonconformance in the case narrative.

16.5 Upon analysis of an acceptable LCS(s), the analyst must analyze an acceptable method blank prior to beginning client samples.

16.6 Upon the analysis of an acceptable method blank, client sample analysis may begin. Analysts are encouraged to begin the sequence with the analysis of samples that should be clear of contamination such as trip blanks, field blanks, and methanol blanks.

16.7 If a sample contains target and/or non-target analyte concentrations that exceed the calibration range, the analyst must review subsequent sample analyses for possible carryover contamination of those analytes. Samples containing suspected carryover contamination are reanalyzed. The system is decontaminated either by the analysis of subsequent blanks or subsequent clean samples.

16.8 Sample analysis may continue up to 12 hours from the injection time of the BFB. Any sample analyzed after the 12 hour window will require reanalysis in a valid 12 hour sequence.

16.9 Each instrument has a run log in which each 12 hour sequence is documented. The analyst must document standards used in the analysis, in addition to data files, dates, injection times, sample weights, volumes, pH, residual chlorine, and additional comments.

17.0 QUALITY CONTROL REQUIREMENTS

17.1 Frequency of Quality Control Activities

17.1.1 Instrument Check

Before any initial calibration or continuing calibration checks are performed, the analyst must analyze an acceptable Bromofluorobenzene (BFB) solution (5 to 50ng). Refer to Appendix 2 or 9 for criteria.

17.1.2 Initial and Continuing Calibration

Before the analysis of any blanks, spikes or samples, the instrument must be calibrated. This multilevel calibration is used to establish the linearity of the instrument for the analytes of interest. Once this calibration is in place, the frequency thereafter is determined from the analysis of continuing calibration standards.

17.1.3 The continuing calibration standard is used to verify instrument calibration compared to the last multilevel calibration check and must be performed every 12 hours.

17.1.4 Blank Analysis

17.1.4.1 Method Blanks are used to determine background (laboratory) concentrations of target analytes that have the potential of interfering with sample analysis. A blank is analyzed in each 12-hour analytical sequence.

17.1.4.2 Other types of blanks can be used to determine possible contamination from various points in the process. Trip Blanks can be used for evaluating the bottles in which the samples are collected. Field Blanks are used to discover potential interferences that may originate from the collection process. The frequency at which such blanks are analyzed are determined by the client (internal or external). Refrigerator or Storage Blanks are analyzed on at least a biweekly basis to determine the cleanliness of the storage area.

17.1.5 Spike and Duplicate Analysis

17.1.5.1 Accuracy is monitored through the analysis of sample spikes. Matrix spikes are performed for each batch up to maximum of 20 samples of similar matrix.

17.1.5.2 Precision is monitored through the analysis of duplicates. For method 8260B/C, the matrix spike or sample is duplicated. This ensures the availability of two sets of results for comparison.

17.1.5.3 Laboratory Control Samples (LCS) are used to determine if the process is in control. If a matrix spike fails due to matrix related interference, then the analysis of the LCS demonstrates that the instrument is in control. For non-SC samples, the continuing calibration check may be used as an LCS if it is a second source standard. Analyze the LCS in each 12-hour sequence. The LCS may be analyzed before the method blank as the CCV. For SC samples the LCS must come from a second source standard.

17.1.6 Surrogate Spikes must be added to all standards, blanks, quality control, and client samples.

17.1.7 Internal standards must be added to all standards, blanks, quality control, and client samples.

17.1.8 Samples must be diluted whenever a target analyte concentration exceeds the highest concentration (for that analyte) in the calibration curve. Samples should be diluted in order to put the analyte concentrations near or above the midpoint of the calibration curve. Multiple dilutions may be necessary if multiple analytes at various concentrations require dilutions. Also, if a sample is initially diluted and there are no target or non-target interferences present, the analyst may be required to reanalyze a more concentrated sample. Some factors for consideration when choosing a dilution factor are

pH, nature of the matrix and non-target interferences. Analysts should be aware that diluting samples increases the detection and reporting limits.

17.2 Acceptance Limits for Quality Control Activities

17.2.1 Initial Calibration

17.2.1.1 The initial calibration %RSD and RRF calculated for each compound must meet the criteria in section 15 of this SOP. Refer to Appendix 4 and Appendix 5 for 8260C specific criteria.

17.2.1.2 The internal standard areas and retention times in each calibration standard analysis must meet the criteria in section 15 of this SOP. Refer to Appendix 4 for 8260C and Appendix 10 for 8260D criteria Appendix 8 for 8260D for Standard Method 6200.

17.2.1.3 The initial calibration must be verified by the analysis of an acceptable ICV before client samples can be analyzed. Refer to Appendix 4 for 8260C and Appendix 10 for 8260D criteria.

17.2.2 Continuing Calibration

17.2.2.1 The instrument calibration must be verified every 12 hours by analyzing an acceptable continuing calibration verification standard (CCV). The CCV must meet the criteria indicated in section 15. Refer to Appendix 4 and Appendix 5 for 8260C, and Appendix 8 for Standard Method 6200 specific criteria and Appendix 10 for 8260D criteria.

17.2.3 Method blank criteria require that concentrations of all analytes of interest must be below the client reporting limit or laboratory practical quantitation limit. Ideally, all target analyte concentrations should be below the laboratory method detection limit, however, concentrations below reporting limits are acceptable. Specific client criteria may require that target analyte concentrations in the method blank not exceed one half the reporting limit. The analyst should take corrective action to ensure that target analytes do not exceed the reporting limits. Corrective action may include the analysis of clean up blanks or perhaps, more intense system decontamination. In some cases, concentrations for the common laboratory contaminants (methylene chloride, acetone, 2-butanone, ethyl ether, carbon disulfide) may be present in the method blank above the reporting limit, but the concentration(s) must be less than five times the reporting limit. In this situation if the compounds are detected in the associated samples, the data are flagged and notation is made in the case narrative that detection and quantitation of these analytes in samples would be biased. If the compounds are not detected in the associated samples, no action is required.

17.2.4 Matrix Spikes/Duplicates

17.2.4.1 SW-846 8260C/B/D criteria for both matrix spikes and matrix spike duplicates will be statistically determined after at least 20 to 30 matrix pairs. If data are not available for specific compounds,

a guidance of 70% to 130% recovery for spikes may be used. Some clients may have contract required limits that the laboratory should use.

17.2.4.2 Target analyte concentrations in the parent sample that exceed five times the spike level may cause biased recovery results in the matrix spike samples. Unacceptable recoveries due to high concentrations in the parent sample should be noted in the case narrative.

17.2.4.3 The criteria for sample duplication when analyzing samples using method 8260C/B/D are that any target present over five (5) times the detection limit must be within ± 20% of each other. As a statistical database is built, statistical process control (SPC) limits are generated.

17.2.4.4 Laboratory control sample recoveries must be within the established SPC limits to be considered acceptable. Statistical control limits for each compound should be derived after the analysis of up to 20 to 30 LCSs (per matrix). The SPC limits for most volatile analytes should fall between 70% to 130% recovery; however, due to poor purging efficiencies, water solubilities, and poor chromatography, some analytes may not meet the method recommendation.

17.2.4.5 Surrogates in all quality control and client samples must meet the established SPC limit or client specified limits. Surrogate limits are determined statistically at least semi-annually utilizing a minimum of 20 data points. Samples must be reanalyzed if surrogate recoveries are outside the required limits. If the surrogate recoveries are unacceptable in the reanalysis, the failure is attributed to matrix. One or both analyses may be reported depending on client specifications.

17.2.4.6 Internal standard responses must be within the required criteria in the initial calibration and calibration verification standard (Section 15). In addition to the internal standard area/RT check from the calibration verification standard to the midpoint of the current initial calibration, the laboratory also compares the internal areas and retention times of samples and QC to the associated daily calibration verification standard. If area counts exceed –50% to +100% or retention times are greater than ± 30 seconds, the sample or QC sample must be reanalyzed. If the analyst suspects matrix interference the sample may be diluted to aid in the internal standard recovery. If the response for the internal standards is unacceptable in the reanalysis, the failure is attributed to matrix. One or both analyses may be reported depending on client specifications.

18.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

18.1 New analysts must complete an Initial Demonstration of Proficiency prior to analyzing client samples. The analyst must be able to demonstrate proficiency by analyzing a passing tune, calibration verification, laboratory control samples, and method blank. The initial demonstration is documented using four acceptable LCS analyses in an analytical sequence.

18.2 Continuing Demonstration of Proficiency results are generated by collecting the data from four LCS analyses per method per analyst. The QA/QC group generates the certificates annually. Refer to GL-QS-E-011 Method Validation and Initial and Continuing Demonstration of Capability.

18.3 Method Detection Limits (MDL) are analyzed annually and verified quarterly. Refer to GL-LB-E-001 for The Determination of Method Detection Limits for additional information.

19.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

19.1 Routine Preventative and Special Operational (Failure)

19.1.1 Preventative maintenance on a GC/MS system involves four basic areas:

19.1.1.1 Vacuum pumps for the analyzer should have an oil change when the system demonstrates that it is needed. This includes the mechanical, turbomolecular, and/or diffusion pumps. Generally, this occurs at least once a year.

19.1.1.2 GC maintenance consists mainly of column and injection port maintenance. These procedures are performed when system sensitivity drops, or air (m/z = 28) is noted present in the system.

19.1.1.3 Analyzer maintenance is most often usage dependent. The type and quantity of samples that have been injected, determine the frequency of ion source and electron multiplier cleaning and/or replacement.

19.1.1.4 Autosampler maintenance is very sample dependent. In general, maintenance consists of changing the trap and line cleaning. Line cleaning is accomplished by back flushing the system with methanol.

19.1.2 Non-routine Maintenance Procedures (Special, Operational or Failure Mode Maintenance)

19.1.2.1 Troubleshooting the autosampler and instrument is a function of analyst experience. In-House service is obtained from GEL's Service Technician. If vendor assistance is needed, then the appropriate vendor is contacted.

19.1.2.2 Electronic maintenance logbooks are kept for each instrument and include entries for both routine as well as non-routine maintenance procedures.

20.0 DATA RECORDING, CALCULATIONS AND REDUCTION METHODS

20.1 Qualitative Analysis:

20.1.1 Samples, standards, and quality control samples are processed using HP Chemstation software. The software performs identification and quantitation based off method information applied to the raw data areas or responses. The program generates electronic reports for review and validation. Raw data are stored electronically on servers and transferred to compact disc media.

20.1.2 Compound Identification

20.1.2.1 A comparison of the sample mass spectrum with the mass spectrum of a standard reference may identify the suspected compound. Mass spectrum for standard reference must be obtained from the NIST library.

20.1.2.2 Elution of sample component at the same GC relative retention time (RRT) as those of the standard component may help identify a compound.

20.1.2.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%).

20.1.2.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between the two peaks is less than 25% of the sum of the heights. Otherwise, structural isomers are identified as isomeric pairs.

20.1.2.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample, appropriate selection of analyte spectra and background spectra is important.

20.1.2.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in the qualitative identification of compounds. When analytes coelute, the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

20.1.2.7 Occasionally manual integrations may be required if the sample matrices affect the software's ability to draw appropriate baselines. Manual integrations on calibration levels are permitted although discouraged. In the event that a manual integration is

performed, the software generates a printout of the integration event before the manual integration and after the manual integration. The analyst electronically reviews and initials the data file and includes the reasoning behind the manual integration.

20.1.3 The relative retention time (RRT) of the sample component must be within ± 0.06 RRT units of the RRT of the standard component, analyzed in the same 12 hour period. If coelution of another compound prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the components of interest. Analysts should pay close attention to the following compounds for possible coelution and identification 1,1,1-Trichloroethane, and Carbon tetrachloride; m,p-Xylenes and Ethylbenzene; the three Dichlorobenzene isomers; Chloromethane and Dichlorodifluoromethane, cis-1,2-Dichloroethylene and trans-1,2-Dichloroethylene; cis-1,3-Dichloropropylene and trans-1,3-Dichloropropylene; 2-Chlorotoluene and 4-Chlorotoluene; the two Trimethylbenzenes; the three Butylbenzenes; and the two Trichlorobenzenes.

20.1.4 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analysis being conducted. Refer to Appendix 7 for COA and Form 1 TIC reporting.

20.2 Quantitative Analysis:

20.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of a given analyte. The concentration of each identified analyte in the sample is calculated as follows:

20.2.2 Water and Water- Miscible Waste using Average RRF:

$$\text{Concentration } (\mu g/L) = [(Ax)(Cis)(Vo)] / [(Ais)(RRF)(Vi)]$$

Where :

Ax =	Area of characteristic ion of compound being measured
Cis =	Concentration of internal standard purged in µg/L
Ais =	Area of Characteristic ion for internal standard

RRF= Relative response factor for compound being measured (see above)

Vo = Total purge volume (mL)

Vi = Volume of sample purged (mL)

20.2.3 Water and Water-Miscible using Linear Regression:

$$\text{Conc. } \mu g/L = \frac{\left[\frac{\left(\frac{Ax}{Ais}\right)}{a} + b\right] * Cis * Vo}{Vi}$$

Where:

Ax = Area of characteristic ion of compound being measured

Cis = Concentration of internal standard purged in µg/L

Ais = Area of characteristic ion for the internal standard

RRF = Relative response factor for compound being measured (see above)

Vo = Total purge volume (mL)

Vi = Volume of sample purged (mL)

a = slope

b = y intercept

20.3 Sediment, Soil, Sludge, and Waste

20.3.1 High level using Average RRF:

Concentration (µg/kg) = [(Ax)(Cis)(Vt)(Vo)] /[(Ais)(RRF)(Ws)(Vi)]

20.3.2 Low Level using Average RRF:

Concentration (µg/kg) = [(Ax)(Cis)(Vt)(Vo)] /[(Ais)(RRF)(Ws)(Vi)]

Where :

Ax, Cis, Ais, RRF = Same as for water

Vt = Volume of total extract (use 10,000 µL or factor of this when dilutions are made.)

Vi = Volume of extract added (µL) for purging

Ws = Weight of sample extracted or purged (g). The wet or dry weight may be used, depending upon the specific application of the data

Vo = Total purge Volume (mL)

20.3.3 Low Level using Linear Regression:

$$\text{Conc. } \mu g/kg = \quad \text{Conc. } \mu g/kg = \frac{\left[\frac{\frac{Ax}{Ais}}{a} + b\right] * Cis * Vo}{W_S}$$

20.3.4 High Level using Linear Regression:

$$\text{Conc. } \mu g/kg = \text{Conc. } \mu g/kg = \frac{\left[\frac{\frac{Ax}{Ais}}{a} + b\right] * Cis * Vo * Vt}{Ws * Vi}$$

20.4 Where applicable, an estimate of concentration for non-calibrated components in the sample is made. The formulas given above shall be used with the following modifications: The areas Ax and Ais shall be from the total ion chromatograms, and the RF for the compound shall be assumed to be 1.

20.4.1 The concentration obtained is an indication that the value is an estimate, and identifies which internal standard was used to determine concentrations. Use the nearest internal standard free of interferences.

20.5 SPC limits are determined by criteria set forth in EPA Method 8000D. For a given matrix, calculate the upper and lower control limit for method performance for each standard of interest as follows:

Upper control limit (UCL) = p + 3 s

Lower control limit (LCL) = p - 3 s

Where:

p = Average percent recovery

s = Standard deviation of percent recovery

20.6 Data are reported in units of ug/L or ppb for waters, and ug/kg or mg/kg for soils and sludges unless otherwise specified by the client.

21.0 POLLUTION/CONTAMINATION CONTROL

21.1 The volatile organics laboratory is physically separated from the other areas of the laboratory. Only authorized personnel have access to this area.

21.2 A separate air handling system and frequent filter changes help keep this area free of common contaminants. The laboratory includes a positive pressure air system.

21.3 Volatile samples are stored separately from other samples. Oil or waste samples for volatile organic analysis are generally not stored in the volatile refrigerator. Samples that may cause contamination in the refrigerator are stored in the main walk-in cooler.

Storage blanks are analyzed at least biweekly from each refrigerator and cooler that stores samples for volatile analysis.

21.4 Soils and waste samples are weighed on a balance within a fume hood in the volatile organics laboratory.

21.5 Radioactive and non-radioactive samples are separated in different refrigerators.

21.6 Organic free water obtained by passing laboratory tap water through a series of carbon filters. This system is located in the volatile organics laboratory.

22.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

22.1 After analysis, each analyst is responsible for reviewing their analytical data for completeness and quality control information.

22.2 The analyst electronically dates and initials the front page of the quantitation report generated by the Chemstation software.

22.3 Occasionally, manual integrations may be required if the sample matrices affected the software's ability to draw appropriate baselines. Manual integrations on calibration levels are permitted although discouraged. In the event that a manual integration is performed, the software generates a printout of the integration event before the manual integration and after the manual integration. The analyst electronically initials and dates the printout and includes the reasoning behind the manual integration.

22.4 After the analyst has completed and reviewed the batch raw data, a second review by a peer or validator is performed before data are given a done status. Data deliverables are client specific, however if a fractional case narrative of CLP-like data package is needed, an additional review of the fractional data package is performed by a validator prior to sending to the client.

22.5 The levels of review responsibility are:

22.5.1 First level review: The analyst must ensure the overall quality of the data. Included in this review are: the BFB tune criteria, samples within tune time, calibration verification standard check, method blank, matrix spikes, laboratory control sample, surrogate recovery, internal standard response, over range concentrations include a dilution, reanalysis as required, manual integrations are appropriate and correct.

22.5.2 Second level review: A peer must review all of the data before it can be released from the lab. The peer performs all the checks that the first analyst did and compares the data with the runlog. Particular attention must be paid to the 12-hour tune window, the check standard, and internal standard area counts. All hits must also be reviewed very carefully. When the second level review is complete, the peer reviewer initials and dates the quantitation report.

22.5.3 A flow chart showing the process by which papers and documents undergo review can be viewed in Figure 2.

22.5.4 Data packages are generated electronically in Portable Document Format or PDF. Data packages are sent directly to the client as a PDF and/or hard copies are generated for submittal.

22.5.5 Data packages are stored on compact disc (CD) by the laboratory computer services group.

23.0 NONCONFORMANCE AND CORRECTIVE ACTION FOR UNACCEPTABLE DATA

23.1 When analyzing a multi-point calibration for many analytes at once, the chances are high that a few may not meet the criteria. Additional standards may be reanalyzed. If they still do not meet the requirements, the instrument may need maintenance before continuing or new standards may be needed.

23.2 If the continuing calibration fails any of the criteria in section 15, the analyst must take action to correct the situation. This may be retuning, reanalyzing the standard, adjusting the purge flow, or any number of maintenance practices in order to meet the daily calibration. If all attempts fail, the analyst must analyze a new series of multi-point calibration standards. If individual client requirements are not met and holding times are expiring, the group leader is notified. Clients will be notified of the nonconformance and analysis of the samples may proceed. Note any nonconformance in the case narrative.

23.3 When the method blank fails the criteria defined in section 17.2.3, the analyst must find and eliminate the source of contamination before proceeding with analyses. Another blank must be analyzed before sample analysis begins. Note any nonconformance in the case narrative.

23.4 If any surrogate recovery is outside the acceptance criteria, the sample must be reanalyzed. If the surrogate recoveries fail a second time, in the same manner, and the blank and LCS recoveries do not indicate a system problem, the failure is attributed to matrix effects. Note any nonconformance in the case narrative.

23.5 All analyte recoveries in the LCS should meet either the SPC limits or client required limits. If the LCS recoveries are outside the acceptance criteria, the analysis should stop and corrective actions should be attempted before continuing with the analysis. Corrective action may be repeating the analysis, opening a new spike mix and reanalyzing, or more complex actions may be attempted. If re-tuning the instrument, the analyst must analyze a tune check (BFB) and calibration verification standard before reanalyzing the LCS. If individual client requirements are not met and holding times are expiring, the group leader is notified. Clients will be notified of the nonconformance and analysis of the samples may proceed. Note any nonconformance in the case narrative.

23.6 The manner in which data will be accepted or rejected is described in the flowchart in figure 1.

24.0 RECORDS MANAGEMENT

24.1 Data generated as a result of this procedure are stored in the laboratory for approximately 1 month.

24.2 After approximately 1 month these records are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

25.0 LABORATORY WASTE HANDLING AND DISPOSAL

25.1 All organic waste solvents, extracts and reagents are stored in a certified hazardous waste can. When the can is full, the GEL hazardous waste disposal specialist is called. Refer to the Laboratory Waste Management Plan (GL-LB-G-001).

26.0 REFERENCES

26.1. Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1(Part 2) Section B. SW-846, Third Edition. Method 8260B, "Volatile Organic Compounds by Gas Chromatograph/Mass Spectrometer (GC/MS): Capillary Column Technique," Revision 1, September 1994. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

26.2. Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1(Part 2) Section B. Sw-846, Third Edition. Method 8000D, "Determinative Chromatographic Separations, "Revision 4, July 2014. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

26.3. Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1(Part 2) Section B. SW-846, 3rd Edition. Method 5030B, "Purge-and-Trap for Aqueous Samples," Revision 2, December 1996. USEPA Office Of Solid Waste and Emergency Response, Washington, DC 20460.

26.4. Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1(Part 2) Section B. SW-846, Third Edition. Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," Revision 0, December 1996. USEPA Office Of Solid Waste and Emergency Response, Washington, DC 20460.

26.5. Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.3, July 2019.

27.0 HISTORY

Revision 24: Added LOQ and LLOQ definitions. Removed reference to 8000C 5030C. Updated the data reviewed electronically. Updated Equipment section with specific vials used. Updated calibration short and long list tables.

Revision 25: Added clarification on the frequency at which LLOQs are verified and that the LLOQ is verified on every instrument where data is reported.

Revision 26: Updated 26.2 to reference current revision number and revision month.

Revision 27: Updated to include 8260D. Updated reference section for current DoD QSM Version 5.2, December 2018

Revision 28: Updated the preservation requirement for Acrolein and Acrylonitrile to a 4-5 pH and analyzed within 7 days of sampling. Add the requirements for TCLP and tumble blanks. Updated reference for DOD QSM Version 5.3 July 2019.

FIGURE 1: DECISION FLOWCHART

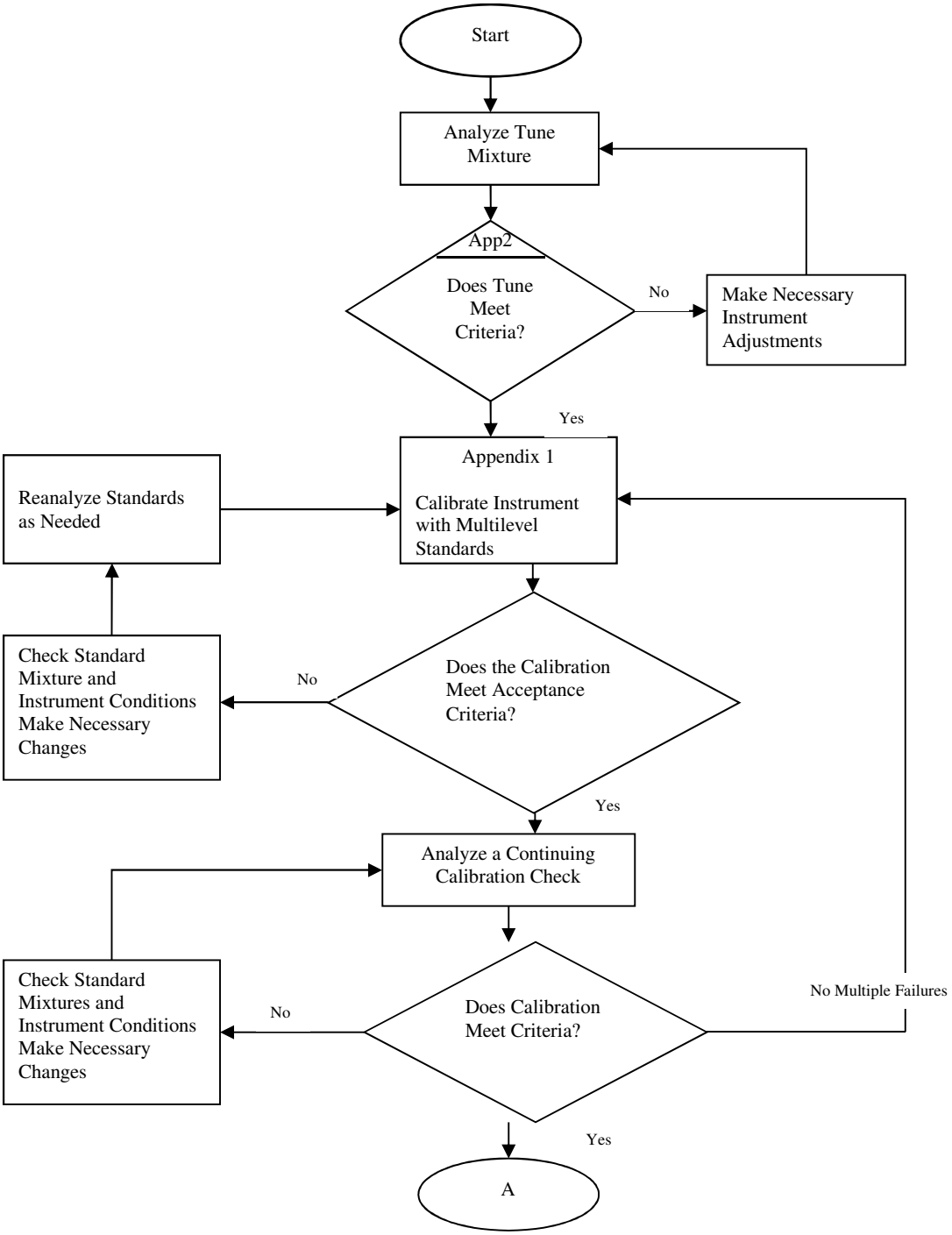


FIGURE 1: DECISION FLOWCHART continued

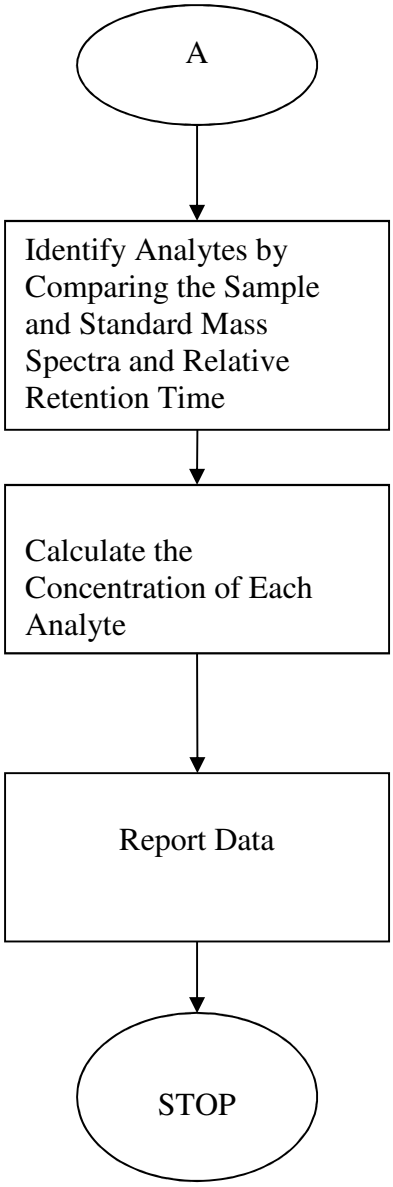
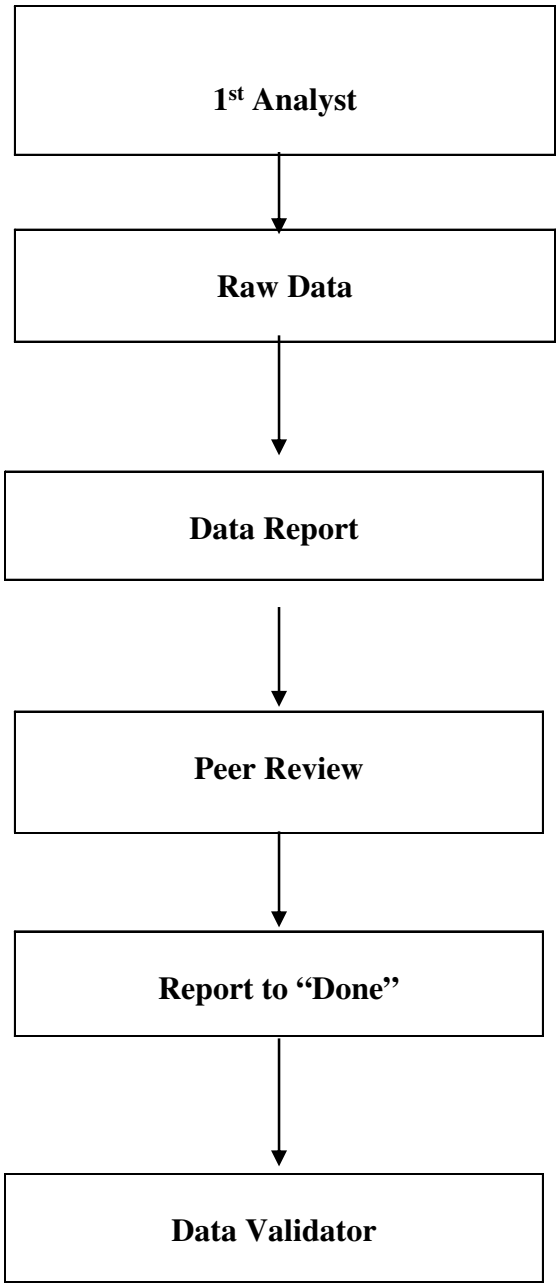


FIGURE 2: LEVELS OF REVIEW



APPENDIX 1: CALIBRATION MIXES

(FOR ILLUSTRATIVE PURPOSES ONLY)

Initial Stock Concentrations

	Stock A/B:	0.5ppm	1.0ppm	2.0ppm	5.0ppm	10ppm	20ppm	50ppm	100ppm
Final Conc.									
0.2ppb		2uL							
0.5ppb		5uL							
1.0ppb			5uL						
2.0ppb				5uL					
5.0ppb					5uL				
10ppb						5uL			
20ppb							5uL		
50ppb								5uL	
80ppb									4uL
100ppb									5uL

Initial Stock Concentrations

	Stock C:	5ppm	10ppm	25ppm	50ppm	100ppm	250ppm	500ppm
	Stock D:	1ppm	2ppm	5ppm	10ppm	20ppm	50ppm	100ppm
Final Conc.								
5.0ppb/1ppb		5uL ea.						
10ppb/2ppb			5uL ea.					
25ppb/5ppb				5uL ea.				
50ppb/10ppb					5uL ea.			
100ppb/20ppb						5uL ea.		
250ppb/50ppb							5uL ea.	
300ppb/ 60ppb								3uL
500ppb/100ppb								5uL ea.

APPENDIX 2: BFB MASS INTENSITY SPECIFICATIONS

Mass	Intensity Required (relative abundance)
50	15-40% of mass 95
75	30-60% of mass 95
95	base peak, 100% relative abundance
96	5-9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5-9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5-9% of mass 176

APPENDIX 3: VOLATILE ORGANIC COMPOUNDS CALIBRATION RANGES

Low level SW846 8260B and Regular level 8260B and EPA 624.1
Calibration Standard Concentration Levels

	Level 1	Level 1a	Level 2	Level 3	Level 4	Level 5	Level 6 #	Level 7 !	Level 7a
Fluorobenzene (IS)	20	20/50	20/50	20/50	20/50	20/50	20/50	20/50	20/50
1,2-Dichloroethane-d4(surr)		20/50	20/50	20/50	20/50	20/50	20/50	20/50	20/50
Dichlorodifluoromethane		0.5	1	2	5	10	20	50	100
Chloromethane		0.5	1	2	5	10	20	50	100
Vinyl chloride		0.5	1	2	5	10	20	50	100
Bromomethane		0.5	1	2	5	10	20	50	100
Chloroethane		0.5	1	2	5	10	20	50	100
Trichlorofluoromethane		0.5	1	2	5	10	20	50	100
1,1-Dichloroethene		0.5	1	2	5	10	20	50	100
Acetone	1	2.5	5	10	25	50	100	250	500
Iodomethane	1	2.5	5	10	25	50	100	250	500
Carbon disulfide	1	2.5	5	10	25	50	100	250	500
Methylene chloride		0.5	1	2	5	10	20	50	100
trans-1,2-Dichloroethene		0.5	1	2	5	10	20	50	100
1,1-Dichloroethane		0.5	1	2	5	10	20	50	100
Ethyl ether		0.5	1	2	5	10	20	50	100
Vinyl acetate	1	2.5	5	10	25	50	100	250	500
cis-1,2-Dichloroethene		0.5	1	2	5	10	20	50	100
1,2-Dichloroethene (total)		1	2	4	10	20	40	100	200
Cyclohexene		0.5	1	2	5	10	20	50	100
2-Chloroethylvinyl ether			5	10	25	50	100	250	500
2,2-Dichloropropane		0.5	1	2	5	10	20	50	100
2-Butanone	1	2.5	5	10	25	50	100	250	500
Bromochloromethane		0.5	1	2	5	10	20	50	100
Chloroform		0.5	1	2	5	10	20	50	100
1,1,1-Trichloroethane		0.5	1	2	5	10	20	50	100
1,1-Dichloropropene		0.5	1	2	5	10	20	50	100
Carbon tetrachloride		0.5	1	2	5	10	20	50	100
Benzene		0.5	1	2	5	10	20	50	100
1,2-Dichloroethane		0.5	1	2	5	10	20	50	100
Trichloroethene		0.5	1	2	5	10	20	50	100
1,2-Dichloropropane		0.5	1	2	5	10	20	50	100
Dibromomethane		0.5	1	2	5	10	20	50	100
Bromodichloromethane		0.5	1	2	5	10	20	50	100
cis-1,3-Dichloropropene		0.5	1	2	5	10	20	50	100
tert-Butylmethylether		0.5	1	2	5	10	20	50	100
Ethyl Ether			1	2	5	10	20	50	100
Acetonitrile			25	50	125	250	500	1250	2500
Methyl acetate			5	10	25	50	100	250	500
Cyclohexane			1	2	5	10	20	50	100
Methylcyclohexane			1	2	5	10	20	50	100
n-Butyl alcohol		50	100	200	500	1000	2000	5000	10000
2-Nitropropane			5	10	25	50	100	250	500
Ethyl acetate			5	10	25	50	100	250	500
Acrolein			5	10	25	50	100	250	500
Trichlorotrifluoroethane			5	10	25	50	100	250	500

APPENDIX 3: VOLATILE ORGANIC COMPOUNDS CALIBRATION RANGES cont'd

Allyl chloride			5	10	25	50	100	250	500
Acrylonitrile			5	10	25	50	100	250	500
1,4-Dioxane			50	100	250	500	1000	2500	5000
Isobutyl alcohol			50	100	250	500	1000	2500	5000
Methacrylonitrile			5	10	25	50	100	250	500
Propionitrile			5	10	25	50	100	250	500
Methyl methacrylate			5	10	25	50	100	250	500
Chlorotrifluoroethylene			5	10	25	50	100	150	200
2-Chloro-1,1,1-trifluoroethane			5	10	25	50	100	150	200
Tetrahydrofuran			5	10	25	50	100	250	500
tert-Butyl alcohol			50	100	250	500	1000	2500	5000
Isopropyl ether			1	2	5	10	20	50	100
Ethyl tert-butyl ether			1	2	5	10	20	50	100
Isopropyl alcohol			50	100	250	500	1000	2500	5000
Methyl tert-amyl ether			1	2	5	10	20	50	100
1-Chlorohexane			1	2	5	10	20	50	100
2-Chloro-1,3-butadiene(chloroprene)			1	2	5	10	20	50	100
Chlorobenzene-d5 (IS)	20	20	20/50	20/50	20/50	20/50	20/50	20/50	20/50
Toluene-d8 (surr)		20	20/50	20/50	20/50	20/50	20/50	20/50	20/50
4-Methyl-2-pentanone	1	2.5	5	10	25	50	100	250	500
Toluene		0.5	1	2	5	10	20	50	100
trans-1,3-Dichloropropene		0.5	1	2	5	10	20	50	100
1,1,2-Trichloroethane		0.5	1	2	5	10	20	50	100
Tetrachloroethene		0.5	1	2	5	10	20	50	100
1,3-Dichloropropane		0.5	1	2	5	10	20	50	100
2-Hexanone	1	2.5	5	10	25	50	20	250	500
Dibromochloromethane		0.5	1	2	5	10	20	50	100
1,2-Dibromoethane		0.5	1	2	5	10	20	50	100
Chlorobenzene		0.5	1	2	5	10	20	50	100
1,1,1,2-Tetrachloroethane		0.5	1	2	5	10	20	50	100
Ethylbenzene		0.5	1	2	5	10	20	50	100
m,p-Xylene		1	2	4	10	20	20	100	200
o-Xylene		0.5	1	2	5	10	20	50	100
Xylenes (total)		1.5	3	6	15	30	60	150	300
Stryene		0.5	1	2	5	10	20	50	100
Ethyl methacrylate			5	10	25	50	100	250	500
1,4-Dichlorobenzene-d4 (IS)	20	20	20/50	20/50	20/50	20/50	20/50	20/50	20/50
Bromofluorobenzene (surr)		20	20/50	20/50	20/50	20/50	20/50	20/50	20/50
Bromoform		0.5	1	2	5	10	20	50	100
Isopropylbenzene		0.5	1	2	5	10	20	50	100
1,1,2,2-Tetrachloroethane		0.5	1	2	5	10	20	50	100
Bromobenzene		0.5	1	2	5	10	20	50	100
1,2,3-Trichloropropane		0.5	1	2	5	10	20	50	100
n-Propylbenzene		0.5	1	2	5	10	20	50	100
2-Chlorotoluene		0.5	1	2	5	10	20	50	100
1,3,5-Trimethylbenzene		0.5	1	2	5	10	20	50	100
4-Chlorotoluene		0.5	1	2	5	10	20	50	100

APPENDIX 3: VOLATILE ORGANIC COMPOUNDS CALIBRATION RANGES CONT'D

1,2,4-Trimethylbenzene		0.5	1	2	5	10	20	50	100
sec-Butylbenzene		0.5	1	2	5	10	20	50	100
1,3-Dichlorobenzene		0.5	1	2	5	10	20	50	100
tert-Butylbenzene		0.5	1	2	5	10	20	50	100
Isopropyltoluene		0.5	1	2	5	10	20	50	100
1,4-Dichlorobenzene		0.5	1	2	5	10	20	50	100
n-Butylbenzene		0.5	1	2	5	10	20	50	100
1,2-Dichlorobenzene		0.5	1	2	5	10	20	50	100
1,2-Dibromo-3-chloropropane		0.5	1	2	5	10	20	50	100
1,2,4-Trichlorobenzene		0.5	1	2	5	10	20	50	100
Hexachlorobutadiene		0.5	1	2	5	10	20	50	100
Naphthalene		0.5	1	2	5	10	20	50	100
1,2,3-Trichlorobenzene		0.5	1	2	5	10	20	50	100
cis-1,4-Dichloro-2-butene			5	10	25	50	100	250	500
trans-1,4-Dichloro-2-butene			5	10	25	50	100	250	500
Pentachloroethane			5	10	25	50	100	250	500
Benzyl chloride			5	10	25	50	100	250	500
Cyclohexanone			25	50	125	250	500	1250	2500
bis(2-Chloro-isopropyl)ether			5	10	25	50	100	250	500

Method	PQL	Concentration range		
SW 846 8260B low level	Level 1&1a	Levels 1-> 7a	IS/SS @ 20 ppb	
SW846 8260B/624.1	Level 2	Levels 1a-> 7a	IS/SS @ 50 ppb	n-butyl alcohol only in 1a

#: Indicates calibration verification concentration level used for low level analysis

!: Indicates calibration verification concentration level used for regular level analysis

APPENDIX 4: Method 8260C Criteria

In addition to the general criteria outlined in the body of this SOP, the following requirements must be met prior to analysis of samples requesting 8260C.

1.0 Initial Calibration

1.1 The calibration curve must be prepared from a minimum of five calibration points. The RSD for all compounds must be less than 20%. If the RSD of any target analyte exceeds 20%, then use one of the options in section 15.2.13.

1.2 If more than 10% of the compounds included in the initial calibration exceed the 20% RSD and do not meet the minimum correlation coefficient of 0.990 for linear regression, system maintenance should be performed and a new calibration curve must be analyzed.

1.3 For compounds utilizing the method of linear regression, a minimum quantitation check should be performed on the lowest calibration point. This involves requantitation of the lowest points of the ICAL as samples (not as calibration levels) and evaluating the recalculated concentrations compared to the true concentrations present. The recalculated concentrations of the low calibration standards should be within ± 30% of the standard's true concentration. It should be noted that not all compounds are present in the calibration levels at the same concentrations. Documentation is made on the ICAL Validation Check Sheet employed by the data validators.

1.4 It is also recommended that a minimum response factor for the most common target analytes be demonstrated for each individual calibration level. See Appendix 5 for a list of compounds and recommended responses. Due to the large number of compounds analyzed by this method, some compounds may fail to meet the criteria. These compounds may not be critical to the specific project and may be used as qualified data or as estimated values.

1.5 SPCC and CCC compounds are not recognized in method 8260C.

2.0 Initial Calibration Verification

2.1 Calibration curves must be verified using an initial calibration verification standard. This must be a second source standard from the initial calibration. It may be from a different vendor or may be a different lot from the same vendor. The response factor or true value (percent difference or drift) should not exceed ± 30%. Documentation is made on the ICAL Validation Check Sheet employed by the data validators.

2.2 In the event that a compound falls outside of the ± 30% acceptance criteria, possible courses of action include reanalysis of the ICV, analysis of a different ICV standard (lot or vendor), maintenance to the analytical system and/or recalibration. If holding times are expiring, sample analysis may proceed. In this case, the Project Manager is notified, documentation is made in the case narrative and the data are qualified.

APPENDIX 4: METHOD 8260C CRITERIA CONTINUED

3.0 Continuing Calibration Verification Analysis

3.1 Each of the most common target analytes in the calibration verification standard should meet the minimum response factors in Appendix 5. If the minimum response factors are not met, check for standard degradation, injection port contamination, column contamination, active sites, or moisture control loss.

3.2 The percent drift or percent difference for each analyte of interest should be +/-20%. The calibration verification standard may be from the same source as the midpoint of the initial calibration or may be a different source. If more than 20% of the total number of requested compounds exceed +/-20% requirement, corrective action should be taken and no samples analyzed. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when a failed compound is present, the concentrations must be reported as estimated values.

4.0 Internal Standard Retention Time Monitoring

The retention times of the internal standards in the calibration verification standard must be evaluated. If the retention time for any internal standard changes by more than 10 seconds from that in the mid-point standard level of the initial calibration, the system must be investigated for malfunctions and reanalysis of all samples analyzed during this period is required.

5.0 Surrogate Monitoring

The recommended surrogates for this method are Toluene-d8, 4-Bromofluorobenzene, and 1,2-Dichloroethane-d4.

APPENDIX 5: RECOMMENDED RESPONSE FACTORS FOR METHOD 8260C

TABLE 4

RECOMMENDED MINIMUM RELATIVE RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION VERIFICATION

Volatile Compounds	Minimum Response Factor (RF)[a]	Typical Response Factor (RF)[b]
Dichlorodifluoromethane	0.100	0.327
Chloromethane	0.100	0.537
Vinyl chloride	0.100	0.451
Bromomethane	0.100	0.255
Chloroethane	0.100	0.254
Trichlorofluoromethane	0.100	0.426
1,1-Dichloroethene	0.100	0.313
1,1,2-Trichloro-1,2,2-trifluoroethane	0.100	0.302
Acetone	0.100	0.151
Carbon disulfide	0.100	1.163
Methyl Acetate	0.100	0.302
Methylene chloride	0.100	0.380
trans-1,2-Dichloroethene	0.100	0.351
cis-1,2-Dichloroethene	0.100	0.376
Methyl tert-Butyl Ether	0.100	0.847
1,1-Dichloroethane	0.200	0.655
2-Butanone	0.100	0.216
Chloroform	0.200	0.557
1,1,1-Trichloroethane	0.100	0.442
Cyclohexane	0.100	0.579
Carbon tetrachloride	0.100	0.353
Benzene	0.500	1.368
1,2-Dichloroethane	0.100	0.443
Trichloroethene	0.200	0.338
Methylcyclohexane	0.100	0.501
1,2-Dichloropropane	0.100	0.382

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APPENDIX 5: RECOMMENDED RESPONSE FACTORS FOR 8260C CONT'D

Volatile Compounds	Minimum Response Factor (RF)[a]	Typical Response Factor (RF)[b]
Bromodichloromethane	0.200	0.424
cis-1,3-Dichloropropene	0.200	0.537
trans-1,3-Dichloropropene	0.100	0.515
4-Methyl-2-pentanone	0.100	0.363
Toluene	0.400	1.577
1,1,2-Trichloroethane	0.100	0.518
Tetrachloroethene	0.200	0.606
2-Hexanone	0.100	0.536
Dibromochloromethane	0.100	0.652
1,2-Dibromoethane	0.100	0.634
Chlorobenzene	0.500	1.733
Ethylbenzene	0.100	2.827
meta-/para-Xylene	0.100	1.080
ortho-Xylene	0.300	1.073
Styrene	0.300	1.916
Bromoform	0.100	0.413
Isopropylbenzene	0.100	2.271
1,1,2,2-Tetrachloroethane	0.300	0.782
1,3-Dichlorobenzene	0.600	1.408
1,4-Dichlorobenzene	0.500	1.427
1,2-Dichlorobenzene	0.400	1.332
1,2-Dibromo-3-chloropropane	0.050	0.129
1,2,4-Trichlorobenzene	0.200	0.806

[a] The project-specific response factors obtained may be affected by the quantitation ion selected and when using possible alternate ions the actual response factors may be lower than those listed. In addition, lower than the recommended minimum response factors may be acceptable for those compounds that are not considered critical target analytes and the associated data may be used for screening purposes.
[b] Data provided by EPA Region III laboratory.

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APPENDIX 6: POOR PURGING COMPOUNDS

Dichlorodifluoromethane
Trichlorofluoromethane
Trichlorotrifluoroethane
Acetone
2-Butanone
2-Hexanone
4-Methyl-2-pentanone
Cyclohexanone
Carbon disulfide
n-Butyl alcohol
tert-Butyl alcohol
Isobutyl alcohol
Isopropyl alcohol
Vinyl acetate
Methyl acetate
Ethyl acetate
1,4-Dioxane
Methyl methacrylate
Ethyl methacrylate
Propionitrile
Methacrylonitrile
1,2-Dibromo-3-chloropropane

APPENDIX 7: TENTATIVE IDENTIFICATION PROCEDURES

1. Relative intensities of major ions (> 10%) in the reference spectrum should be present in sample spectrum. This equates to detects of TICs ≥ 5 ppb concentration (10% of 50 ppb internal standard concentration).

2. Relative intensities of the major ions should agree within ± 30% (i.e., for an ion with an abundance of 50% of the standard spectra, the corresponding sample ion abundance must be between 20 and 80 percent.)

3. Molecular ion present in reference spectrum should be present in sample spectrum.

4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

5. If no valid identification can be made, the compound should be reported as "unknown." If an additional classification can be given to the unknown (unknown hydrocarbon, aromatic, chlorinated, etc.) it should be listed as such.

6. Peaks that are detected in the sample and analytical blank should be flagged as such on the report.

7. TIC detects with “fit” value < 85 will be identified with J qualifier. Detects with “fit” value > 85 will be identified with NJ qualifier and parameter name.

8. The CAS for calibrated compounds not included on the client requested list of parameters will be the true CASRN, while the CASRN for non-calibrated compounds will be reported with leading zeros (000) in front of the probable CASRN.

9. GEL’s policy for reporting calibrated compounds when requested by the client as TICs only is to follow TIC reporting from National Functional Guidelines and report only ≥ 5ppb for VOA with J or NJ qualification.

APPENDIX 8: STANDARD METHOD 6200

1. Perform continuing calibration with one or more of the concentrations of analytical standards in the initial calibration. Vary actual concentration of continuing calibration standard over calibration range, with a minimum concentration greater than 2 times the reporting limit, the acceptance criteria is 70%- 130%. For gases, the acceptance criteria is 60%-140%. If criteria is not met then re-analyze continuing calibration standard or re-analyze initial calibration.

2. The Continuing Calibration Standard must be the same source (lot number) as the Initial Calibration Standard.

3. Internal Standard responses should be in the range ± 30% compared to the mean calibration curve area response.

4. The LCS/LFB/MS/MSD/LFS are from a different primary mix than that used to develop the initial calibration.

5. A closing continuing calibration standard (same lot number) must be analyzed. The acceptance criteria is 70%-130%. For Gases the acceptance criteria is 60%-140%. The concentration of this standard is varied and not the same as the continuing calibration standard.

APPENDIX 9: 4-BROMOFLUOROBENZENE (BFB) SUGGESTED CRITERIA FOR 8260D

m/z	Intensity (relative abundance)
95	50-200% of mass 174
96	5 to 9% of m/z 95 (5 to 15% when using H_2 carrier)
173	<2% of *m/z* 174
174	50-200% of mass 95
175	5 to 9% of *m/z* 174
176	95 to 105% of *m/z* 174
177	5 to 10% of *m/z* 176

*Criteria based on EPA Method 524.4 (Reference 17), with modified m/z and m/z 174 abundance criteria.

APPENDIX 10: SUMMARY OF QC CRITERIA FOR USE WITH 8260D

SUMMARY OF QC CRITERIA FOR USE WITH 8260D[a]

Quality Control Type	Minimum frequency	Specification	Suggested Acceptance Criteria
Instrument performance check (Secs. 9.3.1, 11.3.1)	Prior to initial calibration	Must be verified prior to initial calibration	Meet ion ratio criteria for reference compound: 4-Bromofluorobenzene Appendix 9, or alternative documented criteria
Initial Calibration (ICAL) (Secs. 9.3.2, 11.3.2-11.3.5)	Prior to analyzing samples, and as needed if continuing performance criteria cannot be met	5 points minimum for RF and linear regressions, 6 points minimum for quadratic regressions; >90% of reported target analytes meet initial calibration criteria	For average response factor (RF) calibration model: ≤20% RSD of RFs; For linear or quadratic regression model: R≥0.995, R^2≥0.99; Independent of calibration model: LLOQ standard recalculation (refit) is within ±50% of true value if it is the low calibration point; All other standards within ±30% of true value; Or, relative standard error (RSE) ≤20% (Refer to Method 8000 and Reference 16 for calculation) See Method 8000 for additional criteria.
ICAL Verification (ICV) (Secs. 9.3.2, 11.3.6)	After each initial calibration, and prior to analyzing samples	Prepared from different source of target analytes than initial calibration standards	Calculated concentrations of target analytes are within ±30% of true value
Continuing Calibration Verification (CCV) (Secs. 9.3.3, 11.4)	Once every 12 hours	>80% of target analytes meet CCV criteria	Targets are ≤20% difference or drift; IS responses are within 50% to 200% of mid-point of ICAL or average of ICAL ISs; and RTs for ISs have not shifted >30 seconds relative to ICAL
Blanks (Secs. 9.5, 9.6.1)	One method blank per preparation batch of 20 or fewer samples; other blanks as needed	NA	Target analyte concentrations in blanks are <1/2 LLOQ, or ≤ 10% of concentration in field samples
Laboratory Control Sample (LCS) (Sec 9.6.2)	One per preparation batch of 20 or fewer samples	NA	Meets recovery criteria (CCV criteria may be used if LCS and CCV are identical)

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APPENDIX 10: SUMMARY OF QC CRITERIA FOR THE USE WITH 8260D (CONTINUED)

Quality Control Type	Minimum frequency	Specification	Suggested Acceptance Criteria
Duplicates and Matrix Spikes (Secs. 9.6.3)	A duplicate and matrix spike, or matrix spike/matrix spike duplicate per preparation batch of 20 or fewer samples, provided adequate material is made available to the laboratory	NA	Meets performance-based or project-defined recovery criteria for matrix spikes; Meets relative % difference between measured concentrations in sample and laboratory duplicate or in matrix spike/matrix spike duplicate;
Surrogates (Secs. 9.7)	Added to each sample	NA	Meets performance-based recovery criteria established by the laboratory or criteria chosen for the project
Internal Standards (Secs. 9.8, 11.5.6)	Added to each sample	NA	IS response is within 50 - 200% of the response of the same IS in the midpoint ICAL standard (or average of ICAL) or most recent CCV
Qualitative Analyte Identification (Sec. 11.6.1)	Each target analyte	NA	RT in sample is within ±10 sec of RT in midpoint ICAL or CCV standard or within ±10 seconds relative to the shift of the associated IS (delta RT of the IS ± 10 seconds) Characteristic ion(s) are within ±30% of expected ion ratio in reference spectrum; or, match to reference library spectra ≥0.8 (only for full mass range acquisition modes)

[a] Default acceptance criteria; alternative criteria may be specified for a given application. Refer to Sec. 9 for more information.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

THE ANALYSIS OF POLYCHLORINATED BIPHENYLS BY GC/ECD

(GL-OA-E-040 REVISION 25)

APPLICABLE TO METHODS:
EPA SW-846 Methods 8082, 8082A, 8000D
EPA 608.3

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1.0 STANDARD OPERATING PROCEDURE FOR POLYCHLORINATED BIPHENYLS

2.0 METHOD CODES

2.1 EPA SW-846 Methods 8000D, 8082, and 8082A and EPA Method 608.3

3.0 METHOD OBJECTIVE AND PURPOSE

This is a gas chromatographic procedure for quantitatively determining certain polychlorinated biphenyls (PCBs) as Aroclors or as individual PCB congeners and certain polychlorinated terphenyls (PCTs). Analysis is performed using dual capillary columns and a dual detector GC-ECD. The analytical guidance for the detection and quantitation of the applicable polychlorinated biphenyls has been taken from Methods 8082, 8082A, and 8000D.

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 The following analytes can be quantitatively determined by this procedure:

Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 5432
Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 5442
Aroclor 1260	Aroclor 1262	Aroclor 1268	Aroclor 5460

PCB Congeners (Refer to Appendix 1)

4.2 This method applies to the following matrices:

4.2.1 Groundwater

4.2.2 Wastewater

4.2.3 Soil

4.2.4 Sludge

4.2.5 Miscellaneous matrices

4.2.6 Oil

4.2.7 Filters/Swipes

4.3 This method summarizes the procedures necessary to analyze a sample extract for polychlorinated biphenyls by gas chromatography.

5.0 METHOD SCOPE AND PERFORMANCE CHARACTERISTICS

5.1 The calibration ranges for Aroclors and congeners are compound specific. The lowest concentration calibration standard is used as the quantitation limit.

5.2 The test concentration ranges are:

5.2.1 The tested concentration ranges for liquid matrices are listed below. Please note that these may change and are listed here for guidance only. These limits include an ideal prep factor and are based on a typical calibration.

Compound	Concentration Range
4-CMX (tetrachlorometaxylene)	0.01 µg/L to 0.4 µg/L
DCB (decachlorobiphenyl)	0.01 µg/L to 0.4 µg/L

Aroclor 1016	0.1 µg/L to 4 µg/L
Aroclor 1221	0.1 µg/L to 4 µg/L
Aroclor 1232	0.1 µg/L to 4 µg/L
Aroclor 1242	0.1 µg/L to 4 µg/L
Aroclor 1248	0.1 µg/L to 4 µg/L
Aroclor 1254	0.1 µg/L to 4 µg/L
Aroclor 1260	0.1 µg/L to 4 µg/L
Aroclor 1262	0.1 µg/L to 4 µg/L
Aroclor 1268	0.1 µg/L to 4 µg/L
Aroclor 5432	0.5 µg/L to 20 µg/L
Aroclor 5442	0.5 µg/L to 20 µg/L
Aroclor 5460	0.5 µg/L to 20 µg/L
Congeners (Refer to Appendix 1)	0.02 µg/L to 0.5 µg/L

5.2.2 The tested concentration ranges for solid matrices are as follows:

Compound	Concentration Range
4-CMX (tetrachlorometaxylene)	0.33 µg/kg to 13.3 µg/kg
DCB (decachlorobiphenyl)	0.33 µg/kg to 13.3 µg/kg
Aroclor 1016	3.3 µg/kg to 133 µg/kg
Aroclor 1221	3.3 µg/kg to 133 µg/kg
Aroclor 1232	3.3 µg/kg to 133 µg/kg
Aroclor 1242	3.3 µg/kg to 133 µg/kg
Aroclor 1248	3.3 µg/kg to 133 µg/kg
Aroclor 1254	3.3 µg/kg to 133 µg/kg
Aroclor 1260	3.3 µg/kg to 133 µg/kg
Aroclor 1262	3.3 µg/kg to 133 µg/kg
Aroclor 1268	3.3 µg/kg to 133 µg/kg
Aroclor 5432	16.7 µg/kg to 667µg/kg
Aroclor 5442	16.7 µg/kg to 667µg/kg
Aroclor 5460	16.7 µg/kg to 667µg/kg
Congeners (Refer to Appendix 1)	0.67 µg/kg to 16.7 µg/kg

5.3 Method Detection Limit (MDL) studies for polychlorinated biphenyls, PCTS and congeners are performed annually.

5.4 Precision is determined by the Relative Percent Difference (RPD) between the Laboratory Control Sample (LCS) and the Laboratory Control Sample Duplicate (LCSD), when required, or the Matrix Spike (MS) and the Matrix Spike Duplicate

(MSD). The RPD is determined through Statistical Process Controls (SPC), which are updated on a semiannual basis.

5.5 Accuracy is determined by the percent recovery on LCSs and MSs and the control ranges are determined through SPC limits that are updated semiannually.

6.0 DEFINITIONS

6.1 Definitions specific to this SOP include:

6.2 Limit of Detection (LOD): The lowest concentration level that can be determined by a single analysis and with a defined level of confidence to be statistically different from a blank. The LOD verification is typically spiked at two times the MDL.

6.3 Limit of Quantitation (LOQ): The lowest level in the calibration curve. With the prep factor applied, the LOQ is referred to as the effective LOQ. The LOQ is equivalent to the PQL and LLOQ.

6.4 Lower Limit of Quantitation (LLOQ): The lowest concentration at which a target analyte can be reliably measured and reported. The LLOQ is the lowest point in the calibration curve and represents a concentration at which both quantitative and qualitative requirements can be consistently demonstrated. The LLOQ is verified quarterly as the LOQ verification. The performed by extracting and analyzing an LCS spiked at the LOQ. The LLOQ verification is carried through the same preparation and analytical procedures as environmental samples and QC. The LLOQ is analyzed on every instrument where data are reported and this is the laboratories normal protocol. Recovery of target analytes in the LLOQ are compared to in-house statistically-derived limits.

6.5 Practical Quantitation Limit (PQL): The lowest level in the calibration curve. With the prep factor applied, the PQL is referred to as the effective PQL. The PQL is equivalent to the LOQ and the LLOQ.

6.6 Relative Standard Error (RSE): Standard Error indicates the extent to which a survey estimate is likely to deviate from the true population and is expressed as a number. The Relative Standard Error (RSE) is the standard error expressed as a fraction of the estimate and is usually displayed as a percentage. The RSE acceptance limit criterion is the same as the RSD limit for average CF or RF in the determinative method.

6.7 Lab-wide used definitions can be found in the GL-QS-B-001 the Quality Assurance Plan.

7.0 REFERENCES

7.1 EPA 608.3 and Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1 (Part 2 and Part 3) Section B. SW-846, Third Edition. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460, December 2014.

7.1.1 Method 8082, "Polychlorinated Biphenyls (PCBs) by Gas Chromatography," Revision 0, December 1996.
Method 8082A, "Polychlorinated Biphenyls (PCBs) by Gas Chromatography," Revision 1, February 2007.

7.1.2 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1B, SW846 Update V, Revision 4, Method 8000D, July 2014.

7.3 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.0, July 2013 and Version 5.1, January 2017; DOE QSAS 3.0, July 2013 and Version 3.1 January 2017.

8.0 INTERFERENCES TO THE METHOD

8.1 Interference by phthalates can pose a major problem in PCB determinations and quantitation. These compounds generally appear in the chromatogram as large late-eluting peaks. Common flexible plastics contain varying amounts of phthalates that are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

8.2 Interference for phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

8.3 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting peaks. Sulfur contamination should be expected with sediment samples. Method 3660B is used for sulfur removal. Activated copper powder is used to remove sulfur from sample extracts. Refer to GL-OA-E-045 for Sulfur Cleanup.

8.4 If sample extracts are oily, alumina may be used to remove the oil matrix. A glass wool plug is placed in the bottom of a fused silica pipette and activated alumina is placed on top of the glass wool plug. The sample extract is then introduced into the pipette and allowed to flow through the alumina. A pipette bulb may be used to help gently push the sample through the column. The associated batch QCs are cleaned in the same manner as the sample. The following process is used to prepare alumina for use in this procedure. 400 grams of neutral aluminum oxide are muffled at 550° C for two hours. This process activates the alumina to Brockman Grade I. A minimum of 56 mL of distilled water is added to and evenly mixed with the Grade I alumina to achieve deactivation. A 1660 check standard is passed through the alumina. The recovery is compared to the recovery of a 1660 standard not passed through the alumina. Additional water may be added if the alumina is deemed to be overactive, based on the recovery.

8.5 Single-component pesticides, such as DDT and its analogs, may co-elute with the aroclor peaks. Method 8082A recommends that a DDT standard should be analyzed with each analytical sequence to determine which aroclor peaks may co-elute with the pesticides.

9.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

9.1 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and client sample MSDS forms are maintained in the laboratory.

9.2 Personal protective equipment

9.1.1 Gloves are required when handling the chemicals in this procedure. Nitrile gloves are approved for this procedure.

9.1.2 Laboratory coats and safety glasses should also be worn.

9.3 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling.

9.4 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

9.5 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

9.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the GEL Safety Officer.

9.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located throughout the lab. Training is available on the proper operation of this equipment.

10.0 CAUTION WARNINGS

The helium, nitrogen and hydrogen tanks should be replaced when pressure drops to approximately 250 psi. It is recommended that the injection port septum be changed daily.

11.0 APPARATUS AND MATERIALS, REAGENTS, EQUIPMENT AND INSTRUMENTS

11.1 Apparatus and equipment may include:

11.2.1 Volumetric flasks

11.2.2 Pasteur pipettes

11.2.3 Microliter syringes (10, 25, 50, 100, 250, 500, and 1000 µL)

11.2.4 Capillary cleaving tool

11.2.5 2 mL amber and clear autosampler screw-capped vials with Teflon-lined septa or 2 mL amber and clear autosampler crimp top vials with 500 µL inserts.

11.2.6 Supeltex 0.5 and 0.8 mm ferrules (or equivalent)

11.2.7 Glass Y-splitter or stainless steel column connector

11.2 Reagent, chemicals and standards

11.2.1 Solvents:

11.2.1.1 Acetone

11.2.1.2 Hexane

11.2.1.3 Isooctane

11.2.1.4 Toluene (pesticide grade or equivalent)

11.2.2 For chemical standards, refer to Section 15.0

11.3 Instrumentation

11.3.1 GC: Agilent 6890 or Agilent 7890 GC with electronic pressure control and Agilent 7683 or 7693 autosampler

11.3.2 Columns:

Restek Rtx-CLPesticides1

Restek Rtx-CLPesticides2

30 m x 0.32 mm x 0.5 µm

NOTE: The instrumentation and columns listed above are merely the recommended instrumentation and columns for use with the method.

12.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

12.1 Samples must be collected in an amber glass bottle with a Teflon-lined cap. The collection containers are bought precleaned from a certified vendor.

12.2 Method 8082 and 8082A recommend holding times of up to a year for the extraction of PCBs. Analysis should be completed within 40 days of extraction. Samples are protected from light and stored at 0° ≤ 6° C after collection. Once extracted, the extract must be analyzed within forty days. However, during this period of time, the extracts are refrigerated at 0° ≤ 6° C in amber vials with Teflon sealed screw caps. When holding dates are missed, the data are qualified accordingly and the client notified.

13.0 SAMPLE PREPARATION TECHNIQUES

Liquid samples are extracted using method 3535A (solid phase extraction). Solid samples are extracted using method 3541 (automated soxhlet extractions). Oil samples are prepared using method 3580 (waste dilution).

NOTE: It is assumed that material within the sample container is considered "the sample." Removal of any extraneous material (twigs, leaves, large rocks, etc.) must be documented in the case narrative and sample extraction logbook.

14.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

14.1 In order to maintain the gas chromatograph's columns and detectors, the gases should be changed when the tank pressure is below 500 psi. The gas chromatograph's septum in the injection port should be changed daily or as needed. Column maintenance is performed when baseline rise is present or when the column becomes contaminated.

14.2 Routine Maintenance

COMPONENT	DAILY	WEEKLY	MONTHLY	AS NEEDED	ANNUAL
Injector Septum	as needed				
Gases				X	
Column Maintenance				X	
Detector Wipe Test					X
Detector Cleaning				X	

14.3 Non-routine Maintenance

14.3.1 When a check standard fails, the standard is examined for signs of evaporation or degradation. If nothing is found, column maintenance should be performed. Approximately one loop of each column, or two loops of guard column should be cleaved. The instrument is then baked out until an acceptable baseline is obtained. If an acceptable baseline is not obtained, the column is leaking and column maintenance must be performed again.

14.3.2 When contamination occurs, first replace or clean the autosampler syringe. If contamination is still present, column maintenance should be performed. If contamination is still present after column maintenance has been performed and the system has been cleaned thoroughly, replace the column. The column must then be leak checked and baked. The instrument must then be checked to determine if the problem is solved and if the instrument is stable. If not, the in-house service technician is called.

14.4 When maintenance is done on the instrument, it must be recorded in the maintenance logbook. It must be initialed and dated.

15.0 PREPARATION OF STANDARD SOLUTION AND QUALITY CONTROL SAMPLES

15.1 Source Standard Solutions

15.1.1 Source standard solutions are purchased from Restek, o2si, AccuStandard, and other certified vendors. These standards are traceable to National Institution of Standards and Technology (NIST) standards.

The standard is given a unique identifying number for that day and is recorded in AlphaLIMS. This standard expires after one year, or on the vendor expiration date, whichever comes first. Unopened ampoules containing solutions of organic compounds expire according to the vendor's expiration date.

15.2 For guidance on standard documentation, refer to GL-LB-E-007 for Laboratory Standards Documentation.

15.3 All working standard solutions expire six months from date prepared/opened if no expiration date is provided by the vendor. All other standard solutions must be replaced after six months.

16.0 INSTRUMENT CALIBRATION

16.1 The instrument should be checked for cleanliness and stability prior to analyzing calibration standards. The standards are loaded onto the autosampler with the lowest standard being analyzed first to prevent carryover.

16.2 An external standard technique is used to calibrate the instrument. Both columns are calibrated. Calibration is obtained by analyzing the standards using the same method used for samples. Each standard must contain the same analytes, but at different concentration levels. The area counts of each peak along with the concentration of that particular analyte can then be used to plot a calibration curve. For multi-component peaks such as PCBs, major peaks are chosen to represent the pattern. PCBs require a minimum of five peaks except Aroclor 1221 that requires a minimum of three peaks for quantitation. The area counts of these peaks are then used to obtain a curve. Note that the same peaks are to be used for each concentration level and that a curve is obtained for each peak. The same peaks used in the calibration of the multi-component compounds must be used in any quantitation associated with that calibration curve. The chosen peaks must be at least 25% of the height of the largest Aroclor peak. The typical calibration range is from 100 ug/L to 4,000 ug/L. See section 5.2.2 for calibration ranges with the typical prep factor applied. The lowest calibration level corresponds to the LLOQ (PQL). The MDL, LOD, and LLOQ (LOQ) are verified quarterly. The MDL verification is spiked at the MDL concentration (approximately one third of the LLOQ). The LOD is spiked at two times the MDL. And the LLOQ is spiked at the lowest calibration level (the PQL). Verification samples are extracted using the same methods and processes used for samples and analyzed on each instrument used for that analysis. Statistical Process Limits (SPC) are calculated for the LLOQ using historical data from the lab and are used to evaluate the LLOQ recoveries.

16.3 The initial calibration consists of two parts.

16.3.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 (sometimes referred to as 1660) will include many of the peaks represented in the other Aroclor mixtures. This standard is used to

demonstrate linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. It can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in the sample. Therefore, an initial five-point calibration is performed using this mixture.

16.3.2 Standards of the other Aroclors are necessary for pattern recognition. These standards are also used to determine a single point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 has been used for detector response. The standards for these Aroclors should be analyzed before the analysis of any samples and may be analyzed before or after the analysis of the five 1016/1260 standards.

16.3.3 If Aroclors other than 1016/1260 are detected in samples, the instrument must be calibrated for those Aroclors and the samples reanalyzed.

16.3.4 Similarly, when PCTs are calibrated, Aroclor 5460 is calibrated first. The other PCT standards are analyzed for pattern recognition. If the other PCTs are not detected, then calibration is not required. If they are detected, they must be calibrated and samples re-analyzed.

16.4 Calculate the mean calibration factor and the relative standard deviation for each analyte at each standard concentration using the formula below. Both columns must meet all acceptance criteria for each analyte of interest before running samples.

16.4.1 Calculate the calibration factor for each analyte at each concentration as:

$$CF = \frac{\text{Peak Area of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

16.4.2 Calculate the mean calibration factor for each analyte as:

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where n is the number of standards analyzed.

16.4.3 Calculate the standard deviation and the RSD of the calibration factor for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} \; X\,100$$

If the percent relative standard deviation (%RSD) of the calibration factor is ≤ 20% over the working range, linearity through the origin can be assumed, and the mean calibration factor can be used to quantitate sample

results. When this is not the case, linearity cannot be assumed and the analyst must use a calibration curve.

16.5 If the analyst chooses to use linear regression, he/she must not force the calibration line through the origin.

16.5.1 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response

a = slope of line (also called the "coefficient of x")

x = concentration of the calibration standard

b = the intercept

16.5.2 The analyst should not force the line through the origin, but have the intercept calculated from the five data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0, 0) as a sixth calibration point.

16.5.3 The regression calculation will generate a correlation coefficient (R) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, R must be > 0.99. The calculated intercept value needs to be evaluated before reporting sample results. If the system you are using calculates the coefficient of determination (R^2), the value must be $\geq$ 0.99.

16.5.4 A positive value for the intercept indicates that there is some threshold instrument response that is the limiting factor in establishing linearity. A negative intercept value can be transformed into an x-intercept value that represents a threshold concentration, which is the limitation. If the intercept is positive, then, as a general rule, results where the instrument response is less than three times (3x) the intercept value may be unreliable. This will afford some protection against false positive results. If the intercept is negative, results below the concentration of the lowest concentration calibration standard may be unreliable.

16.5.5 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y - b)}{a}$$

16.6 A minimum number of five calibration standards is required by the method, except for Aroclor 1221, which may use three.

16.7 Method 8000D outlines two procedure that may be used to determine calibration function acceptability for linear and non-linear curves. The calibration data are refitted back to the calibration model. % Error and Relative Standard Error (RSE) evaluate the difference between the measured amount and the true amount (or concentration). % Error is determined as follows:

$$\%Error = \frac{x_i - x_i'}{x_i} \times 100$$

Where:

x'_i = Measured amount of analyte at calibration level I, in mass or concentration units

x_i = True amount of analyte at calibration level I, in mass or concentration units.

16.8 Percent error between the calculated and expected amounts of an analyte should be ≤30% for all standards and ≤50% for the lowest calibration level.

16.9 Relative Standard Error is calculated as follows:

$$RSE = 100 \times \sqrt{\sum_{i-1}^{n} \left[\frac{x_i' - x_i}{x_i} \right]^2} \Big/ (n - p)$$

Where:

x_i = True amount of analyte in calibration level *i*, in mass or concentration units.

x'_i = Measured amount of analyte in calibration level *i*, in mass or concentration units

p = Number of terms in the fitting equation

(average = 1, linear = 2, quadratic =3, cubic = 4)

n = Number of calibration points

16.10 The RSE acceptance limit criterion is the same as the RSD limit for $\overline{CF}$ or $\overline{RF}$ in the determinative method. If the RSD limit is not defined in the determinative method, the limit should be set at ≤20% for well performing compounds.

16.11 Continuing Calibration

16.11.1 The initial calibration curve must be checked and verified prior to conducting any sample analysis. This is accomplished by analyzing a calibration standard of Aroclor 1016/1260 that is at a concentration near the midpoint concentration for the working range of the GC. The standard

must also be injected at intervals no less than once every twenty samples (after 10 is recommended to minimize the number of samples requiring re-injection when the QC limits are exceeded) and at the end of the analysis sequence. The initial calibration check standard must be a second source standard. It must be obtained from a second supplier. This will determine the validity of the initial calibration on a daily basis. Daily calibration check standards may be from a second source or from the same source as the calibration standards.

16.11.2 Calibration verification for linear calibrations involves calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equation below to calculate % Drift or % Difference.

$$\% \text{ Drift} = \frac{\text{Calculated Concentration - Theoretical Concentration}}{\text{Theoretical concentration}} \times 100$$

Where the calculated concentration is determined using the calibration factor or response factor from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

Where:

CF_V = response factor from current verification check standard.

If this criterion is exceeded, inspect the gas chromatographic system to determine the cause, and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis. If the source of the problem can not be determined after corrective action has been taken, a new five-point calibration will be generated.

16.11.3 Each sample must be bracketed with an acceptable continuing calibration standard. The continuing calibration check standard must pass ± 15% of the true value for methods 8082 and ± 20% for method 8082A and 608.3. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last acceptable standard may be re-injected. The South Carolina Department of Health and Environmental Control (DHEC) requires that each peak in a multi-component standard be evaluated individually. Each peak should be evaluated to ensure that the response meets the method required 15% (or 20%) difference for calibration verification. If a bracketing CVS fails with a positive bias and there are no detects in the preceding samples, the data may be reported.

16.11.4 When simultaneous analyses are performed from a single injection, it is not practical to designate one column as the primary and the other as

confirmatory. Since the calibration standards are analyzed on both columns, the results for both columns must meet the calibration acceptance criteria. The laboratory's standard practice is to report the lower column result. In cases where Total Aroclors are reported, one column is selected for reporting.

17.0 INSTRUMENT PERFORMANCE REQUIREMENTS

17.1 Recommended Gas Chromatography Conditions

Detector Temperature: 350° C	Make-up Gas: Nitrogen
Injector Temperature: 250° C	Initial Temperature: 130° C
Column A: Rtx CLPesticides1	Hold = 0 min
Column B: Rtx CLPPesticides2	Ramp = 25° C/min
Column Flow = 5 mL/min	Final Temperature: 320° C
Det. Flow = 30 mL/min	Hold = 0.5 min

NOTE: Slight variations may be needed as column length changes. In addition, please note that other columns and analytical parameters may be used.

17.2 Before samples can be analyzed, the baseline must be stable with little or no background noise. The continuing calibration check standard must pass ± 15% (± 20% for 8082A) of the true value. Please note that SC DHEC requires this criterion be met for each peak in a multi-component analyte.

17.3 After every ten samples, a continuing calibration check standard must be analyzed and be ± 15% (± 20% for 8082A) of the true value. If not, the system must be inspected for malfunctions. All samples must be bracketed by passing check standards. The results from the bracketing standards must meet the calibration criteria as specified above. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be evaluated to prevent mis-quantitations and possible false negative results, and re-injection of the sample extracts may be required. More frequent analysis of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis. However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present. In contrast, if the analyte above the QC criteria was detected in a sample extract, then re-injection is necessary to ensure an accurate quantitation. If an analyte was not detected in a sample and the response is more than 15% (20% for 8082A) below the initial calibration response, then re-injection is necessary to ensure that the detector's response has not deteriorated to the point that the analyte would not have been detected even though it was present (i.e., a false

negative result). If the check standard passes on one column and there are no detects, the data may be reported.

17.4 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative QC criteria are exceeded.

18.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

18.1 To establish that the analyst can perform the procedures in an acceptable manner and that the method generates data of acceptable bias and precision, an Initial Demonstration of Capability (IDOC) is required.

18.1.1 A quality control (QC) check standard must be prepared containing each analyte of interest. It must be prepared from pure standard material or purchased as a certified solution. It must be made from a source independent of that used for calibration.

18.1.2 Four Laboratory Control Samples (LCS) must be prepared and analyzed by the same procedures used to prepare and analyze actual samples.

18.1.3 Calculate the average recovery (X) in µg/L and standard deviation of the recovery (S) in µg/L, for each analyte of interest using the four results.

18.1.4 For each analyte compare S and X with the corresponding acceptance criteria for precision and accuracy, respectively, given in the quality control table at the end of the method. If the S and X for all analytes of interest meet the acceptance criteria, the system's performance is acceptable and analysis of actual samples can begin. If any individual S and X exceeds the precision limits or falls out of the range for accuracy, the system's performance is unacceptable for that analyte and a check standard for that analyte must be prepared and reanalyzed. A copy of these data is kept in a file within the Organics Laboratory area.

18.2 Method detection limits are also determined and documented annually. Precision and accuracy is matrix dependent and are documented by means of a Laboratory Control Sample (LCS) and a Laboratory Control Sample Duplicate (LCS DUP). Refer to Section 5.4 and the GL-LB-E-001 for The Determination of Method Detection Limits.

18.3 Analysts are given Performance Evaluation samples as an ongoing assessment of their ability to perform this procedure.

19.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

19.1 Standards, samples, blanks and quality control samples are introduced into the instrument via direct injection. Retention time windows must be centered daily for each analyte. Refer to GL-OA-E-001 for Establishing Retention Time Windows for GC and HPLC Analysis as to when and how often retention time windows should be established.

19.2 Samples are analyzed in a set referred to as analysis sequence or run sequence. The sequence begins with the initial check standards with the representative multi-component standards for pattern recognition followed by the sample extracts. A mid-level calibration check standard must be analyzed after every 10 extracts and at the end of each run sequence. The sequence ends when all extracts have been injected and analyzed.

19.3 The data are entered into the computer and a data report is generated. The sequence file is created by the analyst on the computer. It lists, in order, every injection made by the instrument for a given date. The raw data along with a copy of the run sequence, batch sheet, case narrative, and a copy of the retention time window are maintained together.

19.4 1.0 µL of the extract is injected into the instrument. Please note that other injection volumes are allowed.

19.5 All gas chromatographs are equipped with autosamplers. The digital integrator converts the analog from the instrument to digital information that is processed into a graphic format showing concentration based on peak area.

19.6 The automated sequence is initiated by starting the "run sequence" made in ChemStation, which, in turn, controls the autosampler.

19.7 Samples containing target analyte concentrations that exceed the linear range of the analyte calibration curve must be diluted. The dilution level should be performed to place the highest analyte concentration between the middle and high points of the calibration curve (on column). If a sample is initially diluted and target analytes are not detected and non-target analytes are not interfering with the analysis, the sample must be reanalyzed at a lower dilution. Analysts should be aware that diluting samples will increase the detection limits for undetected analytes. Random dilutions without due cause are not acceptable. Samples should undergo appropriate clean up methods prior to diluting for observed matrix problems.

19.8 An initial five-point calibration curve is performed using a mixture of Aroclor 1016 and Aroclor 1260 for PCB analysis. This standard will include many of the peaks represented in the other Aroclor mixtures. Therefore, this mixture is used to demonstrate linearity of the detector and that a sample does not contain peaks that represent any one of the other Aroclors. As stated in section 7.4.6.1 of SW-846 8082, at least five peaks must be used for each Aroclor in the Aroclor 1016 and Aroclor 1260 mixture. The standard practice is to use five peaks for calibration and quantitation for each Aroclor except Aroclor 1221. Three peaks are used for this Aroclor. For PCT analysis, Aroclor 546C is analyzed to demonstrate linearity and PCT pattern recognition. PCB congeners are single peaks and a standard containing all of them is injected.

19.9 Once the Aroclor pattern has been identified, compare the responses of the peaks chosen in the calibration standards with those observed in the sample extract. The

amount of the Aroclor is calculated using the individual calibration factors for each peak chosen during the multi-point calibration. A concentration is determined for each peak. The Aroclor concentration is then determined by averaging the concentration of each peak. Co-eluting peaks, whether from another Aroclor or non-target interference, may result in a final concentration that is biased high. Analyst experience and judgment are critical in determining the extent of the interference. Every effort is made to provide the most accurate data to the client. If matrix interference or co-elution results in only a minor inflation of peak concentration, the results will be reported. If the inflation is considered significant, then the results will be reported from the second column and qualified as necessary.

19.10 In cases where compound identification or quantitation is precluded due to matrix interference (e.g., broad, rounded peaks, sulfur, or ill-defined baselines are present) on both columns, additional cleanup of the extract may be needed. Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the Aroclor patterns to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. The analyst must also describe in the case narrative specific problems and actions taken to calculate the sample's concentration.

20.0 CALCULATIONS AND DATA REDUCTION METHODS

20.1 The concentration of each analyte in an extract can be determined by comparing the response obtained from analyzing the extract to the calibration curve. The concentration of a specific analyte is matrix specific and is calculated as follows:

Aqueous Sample

$$Concentration\ (\mu g/L) = \frac{(C)(D)(V_t)}{V_i}$$

Where:

C = Concentration (µg/L) calculated by data system from total area substituted into the linear equation derived from the multilevel calibration

D = Dilution factor, if made prior to analysis. If not, D = 1.

V_t = Total volume of the extract in L

V_i = Initial volume of sample in mL

Nonaqueous Samples

$$Concentration\ (\mu g/kg) = \frac{(C)(D)(V_t)}{W}$$

Where:

C = Concentration (µg/kg) calculated by data system from total area substituted into the linear equation derived from the multilevel calibration

D = Dilution factor, if made prior to analysis. If not, D = 1.

V_t = Total volume of the extract

W = Weight of the sample extracted

21.0 DATA RECORDING

Data are recorded and calculated by Chemstation (or other) data acquisition system. They are stored on a remote server. Data are also entered into AlphaLIMS.

22.0 QUALITY CONTROL REQUIREMENTS

22.1 Before analysis of any quality control samples, the instrument must be calibrated. An outside source initial calibration check standard is analyzed to verify that the curve is linear. This outside source check standard must be analyzed every time a new curve is obtained. This check standard must be within ± 15% (± 20% for 8082A) of the true value. A continuing calibration check standard must be analyzed after every ten to verify that the instrument remained calibrated throughout the run.

22.1.1 A method blank (MB) is used to determine background concentrations of analytes of interest that have the potential to interfere with sample analysis. These blanks are analyzed with every analytical batch that has a maximum number of twenty samples. The criterion for acceptance is that there are no target analytes of interest present above the practical quantitation limit (LLOQ).

22.1.2 If the analyte of interest is present at a concentration between the MDL and LLOQ, all data are qualified with a “B” flag and reported. If the analyte of interest is present at a concentration above the LLOQ and the samples contain the analyte of interest at a concentration of greater than 10 times the concentration found in the blank, the data are qualified with a “B” flag and reported. If the concentration found in the sample is less than 10 times that found in the blank and greater than the LLOQ, the samples must be re-extracted.

22.1.3 A laboratory control sample (LCS) and its duplicate (when requested) are analyzed with every batch. The accuracy and precision of the extraction and analysis are monitored with these samples. LCS and LCSD recovery limits are statistically derived (SPC limits) biannually. For SCDHEC liquid samples, the LCS acceptance criteria of 70 – 130% must be met.

22.1.4 Sample matrix spikes (MS) and sample duplicates (DUP) or sample matrix spike duplicates (MSD) are also used to determine precision and accuracy. As with the LCS, recovery limits are statistically generated biannually.

22.1.5 4-CMX and decachlorobiphenyl surrogates are added to all extracts and standards. Acceptance criteria are based on statistically derived limits and are matrix specific. 4-CMX is added to all congener analyses.

22.1.6 The retention time (RT) window must be established using the continuing calibration check standard over a 72-hour period. Refer to GL-OA-E-001 for Establishing Retention Time Windows for Gas Chromatographic and HPLC Analysis for instructions. In order to report a concentration from the external standard table, the retention time of that particular analyte must be within its established window. If not, the concentration is not reported.

22.2 Nonconformance

22.2.1 When running a calibration curve for more than one analyte at a time, some of the analytes may not meet the acceptance criteria. Additional standards containing the compounds that were not acceptable may be analyzed. If the curve still does not meet the acceptance criteria, maintenance should be performed or a new standard may be needed.

22.2.2 If the percent recovery in the MS or MSD falls outside the established SPC limits for recovery, the analyst should evaluate the LCS recoveries and MB analyses. If the LCS and MB analyses do not indicate a problem with the preparation procedures, the MS recoveries may be attributed to matrix effect. Surrogate recovery data should also be used to evaluate the data. Recoveries of both MS compounds and surrogates that are outside the acceptance limits suggest more pervasive analytical problems than problems with the recoveries of either MS or surrogates alone. Analysts are not required to reanalyze the MS for failing recoveries, however they should seek additional technical support before deciding not to reanalyze MS samples.

22.2.3 If the continuing check standard fails any criteria in section 22.1, the analyst must take action to correct the situation. This may be performing any of the maintenance steps described in Section 14 to get the instrument to meet its daily calibration. If all attempts fail, the analyst must analyze a new series of calibration standards, thus obtaining a new calibration curve.

22.2.4 If a surrogate in a sample falls outside the acceptance limits, the sample should be re-extracted, unless the failure duplicates in an MS, MSD or sample DUP or pesticide fraction extraction and analysis. If the surrogate fails the second time, the failure is attributed to matrix interference and the data from the first extraction are reported. If a surrogate in a sample falls outside the acceptance limit with a negative bias or a surrogate in a sample falls outside the acceptance limit and the sample has a target analytes detected, the sample must be re-extracted, unless the failure duplicates in an MS, MSD or sample DUP. If a surrogate in a sample falls outside the acceptance limit with a positive bias and the sample does not have target analytes detected. The analyst should document it in a

DER and report that data. When a sample or batch is sent back to be re-extracted, and passes, a nonconformance form must be completed. The form describes the reasons for re-extraction. (Refer to GL-QS-E-004 for Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items.)

22.3 Any positive identification and quantitation of an analyte of interest must be confirmed on a separate column. The confirmation column must meet all quality control acceptances described in the method (calibration, retention times, etc.). Calculate the relative percent difference between the two results using the formula:

$$RPD = \frac{|R_1 - R_2|}{\frac{R_1 + R_2}{2}} \times 100$$

22.3.1 Since the same method criteria specified in Sections 22.1, and instrument calibration specified in Sections 16.1 through 16.6 are applied uniformly to both columns, either column can be selected to serve as the primary or confirmatory column.

22.3.2 If one result is significantly higher (> 40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, the lower column result is reported, unless a client specifically requests otherwise.

23.0 DATA REVIEW, VALIDATION AND APPROVAL PROCEDURES

23.1 Upon completion of a batch, the analyst uploads the data. A data report is generated and it is placed in a folder along with the batch and all other raw data (chromatograms). This folder is given to the peer review analyst for reviewing. Data may also be reviewed electronically without printing a hardcopy.

23.2 Levels of review and their responsibilities:

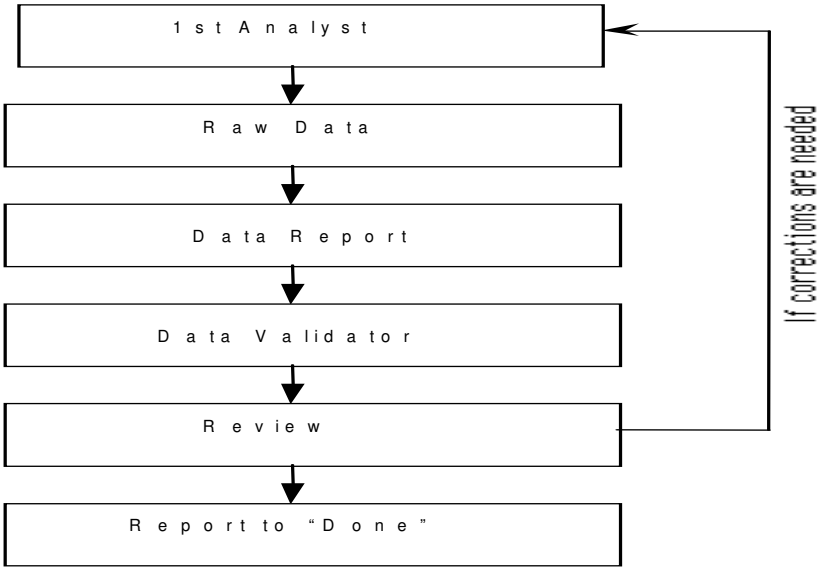
23.2.1 First level review: The analyst must check all chromatograms and will calculate the percent recoveries for the spike, duplicate, and all surrogate recoveries. The analyst must check to see if the check standard passes for the analytes of interest. If a target compound confirms on the conformation column, it must be checked to see if the retention time of the analyte is within the daily retention time window. The peak's shape must also be checked to ensure that it is indeed a peak and not noise. If the hit meets both of these requirements, its concentration should be reported.

23.2.2 Second level review: The data reviewer or other qualified reviewer must ensure that the concentration that appears in the external standards table is indeed what has been entered into the computer. They must check to see if the calibration check standard is acceptable and if the LCS and its

duplicate and the surrogates are all within acceptable ranges. The reviewer must also check the date analyzed, dilution factor, and time of analysis from the raw data against the data report. If everything is acceptable, the reviewer must then initial and date the batch report and the quantitation report, and then complete the checklist to make sure that every item that appears on the review checklist is acceptable. The run log must also be dated and initialed. The data report is then sent to a status of "Done."

23.2.3 To complete a review process, all chromatograms of the calibration check standard, blank, LCS and its duplicate, samples, and the spike and/or duplicates of the sample must be present. The batch sheet, sample tracker log, and the data report should all be present.

23.3 A flow chart of the review process is as follows:



24.0 DATA TRANSMITTAL

After the review process is complete, Data Management receives the data.

25.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with "Quality Records Management and Disposition" (GL-QS-E-008).

26.0 LABORATORY WASTE HANDLING AND DISPOSAL: SAMPLES, EXTRACTS, DIGESTATES AND REAGENTS

Refer to the "Laboratory Waste Management Plan," (GL-LB-G-001) for the proper handling and disposal of sample waste.

27.0 HISTORY

Revision 21: Updated to include 8000D and revised reporting column to the lower column result.
Revision 22: Updated References
Revision 23: Updated for implementation of 8000D. Added LLOQ definitions, % Error and Relative Standard Error (RSE)
Revision 24: Updated for clarification of LLOQ definition. Updated Reference Section for DOD/DOE Version 5.1. Updated sections for reference 608 to 608.3.
Revision 25: Update for new MUR 600 methods.

APPENDIX 1
ANALYSIS OF PCB CONGENERS

PCBs represent a group of 209 individual congeners with varying degrees of toxicity. PCBs are no longer produced in the United States and are no longer used in the manufacture of products. However, small amounts of PCBs may be released into the environment from disposal sites containing transformers, capacitors and other PCB wastes, and from disposing of sediments containing PCBs. This is of particular concern for dredge projects.

While analysis using gas chromatography and high-resolution mass spectroscopy (HR GC/MS) using EPA Method 1668 provides the most definitive identification of all 209 PCB Congeners, Method 8082A (8082B) may also be used for the analysis of various congeners, particularly when cost is a restricting consideration.

The PCB congeners listed below were selected by GEL Laboratories for analysis using Method 8082A (8082B) based on the lists found in the EPA *Evaluation of Dredged Material Proposed for Discharge in Waters of the U.S. – Testing Manual (Inland Testing Manual)* (February 1998) and NOAA guidelines. This list includes those congeners found in the 'summation' and 'highest priority' lists (Table 9-3 of the *Inland Testing Manual*). PCBs have traditionally been quantified with respect to Aroclor mixtures. For dredged material evaluations, the concentration of total PCBs should be determined by summing the concentrations of specific individual PCB congeners. Other congeners may be requested for specific projects and can be added later, provided that all IDOC and quality control criteria are met.

The criteria outlined in this SOP for initial calibrations, initial and continuing calibration verification standards, and quality control samples also apply to congener analyses. Please refer to those sections for acceptance criteria and guidance.

PCB congener samples are extracted and prepped for analysis in the same manner as regular 8082A (8082B) samples using methods 3535A (SPE) and 3541 (automated Soxhlet). Quality control samples include a method blank (MB), laboratory control sample (LCS), laboratory control sample duplicate (LCSD) if appropriate, matrix spike (MS), and matrix spike duplicate (MSD). All samples and QC are spiked with a surrogate standard as well (4-CMX). Note that DCB cannot be used as it is a target analyte.

Congeners 90 and 101 co-elute on the lower column. The concentration of these two analytes is doubled in the calibration table to account for this. For these two congeners, the lab will report results from the front (non-coeluting) column. The lower column result may be reported for the other congeners.

The PCB congener initial calibration is subject to the same acceptance criteria as an 8280A (8082B) calibration (See pertinent sections in this SOP). The typical PCB congener calibration range is from 20 ug/L to 500 ug/L (on-column concentrations). The calibration verification standard (CVS or ICV) is typically made at a concentration of 100 ug/L (on-column concentration). Please note that these ranges reflect conditions at the time of method development and may change over time depending on client and project needs and MDLS and MDLVs would be adjusted accordingly.

APPENDIX 1
ANALYSIS OF PCB CONGENERS (CONT'D)

Analyte	CAS#
BZ# 18 2,2',5-trichlorobiphenyl	37680-65-2
BZ# 8 2,4'-dichlorobiphenyl	34883-43-7
BZ#28 2,4,4'-trichlorobiphenyl	7012-37-5
BZ#170 2,2',3,3',4,4',5-heptachlorobiphenyl	35065-30-6
BZ#180 2,2',3,4,4',5,5'-heptachlorobiphenyl	35065-29-3
BZ#183 2,2',3,4,4',5',6-heptachlorobiphenyl	52663-69-1
BZ#187 2,2',3,4',5,5',6-heptachlorobiphenyl	52663-68-0
BZ#128 2,2',3,3',4,4'-hexachlorobiphenyl	38380-07-3
BZ#138 2,2',3,4,4',5'-hexachlorobiphenyl	35065-28-2
BZ#153 2,2',4,4',5,5'-hexachlorobiphenyl	35065-27-1
BZ#156 2,3,3',4,4',5-hexachlorobiphenyl	38380-08-4
BZ#169 3,3',4,4',5,5'-hexachlorobiphenyl	32774-16-6
BZ#206 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	40186-72-9
BZ#195 2,2',3,3',4,4',5,6-octachlorobiphenyl	52663-78-2
BZ#101 2,2',4,5,5'-pentachlorobiphenyl	37680-73-2
BZ#105 2,3,3',4,4'-pentachlorobiphenyl	32598-14-4
BZ#118 2,3',4,4',5-pentachlorobiphenyl	31508-00-6
BZ#126 3,3',4,4',5-pentachlorobiphenyl	57465-28-8
BZ#87 2,2',3,4,5'-pentachlorobiphenyl	38380-02-8
BZ#44 2,2',3,5'-tetrachlorobiphenyl	41464-39-5
BZ#49 2,2',4,5'-tetrachlorobiphenyl	41464-40-8
BZ#52 2,2',5,5'-tetrachlorobiphenyl	35693-99-3
BZ#66 2,3',4,4'-tetrachlorobiphenyl	32598-10-0
BZ#77 3,3',4,4'-tetrachlorobiphenyl	32598-13-3
BZ#184 2,2',3,4,4',6,6'-heptachlorobiphenyl	74472-48-3
BZ#90 2,2',3,4',5-pentachlorobiphenyl	68194-07-0
BZ#209 decachlorobiphenyl	2051-24-3

APPENDIX 2: PCB SCREENING PROCEDURE

Overview:

The lab may be asked to screen samples for the presence of PCBs. Screening is particularly useful for determining a baseline concentration of contamination or determining appropriate sample extraction and analysis strategies. It may also be helpful in preventing possible carry-over when samples are analyzed by Method 1668.

This screening appendix is applicable to liquid and solid matrices and primarily focuses on the preparation of samples. The same analytical conditions and calibration criteria outlined in this SOP are used for qualitative and quantitative evaluation of samples. MDLs are not required or performed for screening methods. As a point of clarification, it should be noted that this screening procedure is not the same one used internally by analysts to determine dilutions for Method 8082 analyses.

Quality Control:

A method blank (MB) and laboratory control sample (LCS) are prepared and analyzed with each batch of samples to be screened. In addition, every sample and the MB and LCS are fortified with a surrogate standard prior to extraction and analysis. Static limits are used to evaluate surrogate and LCS recoveries. Samples are not typically re-extracted in the event of failures; however, recovery data provide the end user with an understanding of the accuracy of the screening results.

Liquid Samples:

Typically a 20 mL sample aliquot is placed in a 40 mL vial. A clear vial may be used to aid in visibly discerning layers during sample extraction. The customer may send the 20 mL aliquot in a vial, in which case the lab will perform a visual confirmation of the sample volume. If the lab takes the aliquot, then 20 mL are measured using a disposable pipette. 20 mL of clean DI water are used to prepare the MB and LCS.

A surrogate standard containing Tetrachloro-m-xylene (4CMX) and Decachlorobiphenyl (DCB) is prepared in methanol at a concentration of 20 ng/uL. The MB, LCS, and all samples are spiked with 20 uL of the surrogate standard, resulting in a concentration in the 2 mL prepared extract of 200 ug/L (“on-column” result).

A spiking standard containing Aroclors 1016 and 1260 (“1660”) is prepared in methanol at a concentration of 100 ng/uL. The LCS is spiked with 20 uL of the spike standard, resulting in a concentration in the 2 mL prepared extract of 1,000 ug/L (“on-column” result).

Add 2 mL of pesticide grade hexane to each vial. Approximately 7 grams of anhydrous sodium chloride may be added to the vial to aid the extraction efficacy. A color indicator, such as copper sulfate may also be added to aid in discerning the solvent layer from the water. Cap the vials and shake vigorously for at least two minutes, either by hand or on a wrist-action shaker.

APPENDIX 2: PCB SCREENING PROCEDURE (CONTINUED)

Allow the phases to settle. If emulsions develop or the layers do not adequately separate, the vial may be centrifuged for several minutes at 500 G's.

Using a gas tight syringe, transfer the solvent layer to a 2 mL screw cap vial, being careful not to include any water. The sample is now ready to be screened by GC/ECD.

Solid Samples:

For solid samples, typically a 1 gram sample aliquot is taken and placed in a 40 mL vial. A clear vial may be used to aid in visibly discerning layers during sample extraction. The customer may send the 1 gram pre-weighed in a vial. Or, the lab may take an aliquot weighing it on a three place balance. 1 gram of clean Ottawa sand is used to prepare the MB and LCS.

The same surrogate standard used for liquid samples is used with solid samples. The MB, LCS, and all samples are spiked with 50 uL of the surrogate standard, resulting in a concentration in the 2 mL prepared extract of 200 ug/kg ("on-column" result).

The same spiking standard used for liquid samples is used with solid samples. The LCS is spiked with 50 uL of the spike standard, resulting in a concentration in the 2 mL prepared extract of 1,000 ug/kg ("on-column" result).

5 mL of pesticide grade hexane is added to each vial and the same extraction process as above is followed. Note that 2 mL of the extract may be transferred to a 2 mL vial.

Clean-ups:

The analyst may determine that extracts need to be cleaned prior to analysis. Extracts may be cleaned with activated alumina to remove oils and particulates, or copper to remove sulfur.

Screening Limits:

Following the procedures above, the typical reporting limits for screens are 10 ug/L for liquid samples and 500 ug/kg for solid samples. Samples with concentrations of Aroclors below these levels may not be suitable for this screening procedure.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

ORGANOCHLORINE PESTICIDES AND CHLORINATED HYDROCARBONS

(GL-OA-E-041 REVISION 20)

APPLICABLE TO METHODS:

EPA SW-846 Methods 8000D, 8081A, 8081B and EPA 608.3

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1.0 STANDARD OPERATING PROCEDURE FOR ORGANOCHLORINE PESTICIDES AND CHLORINATED HYDROCARBONS

2.0 METHOD CODES

2.1 EPA SW-846 Methods 8000D, 8081A, 8081B and EPA 608.3

3.0 METHOD OBJECTIVE AND PURPOSE

This is a gas chromatographic procedure for quantitatively determining certain organochlorine pesticides. Separation is performed by gas chromatography (GC) and detection is done by electron capture detector (ECD). The analytical guidance for the detection and quantitation of the applicable organochlorine pesticides has been taken from Methods 8081A, 8081B, 8000D and EPA 608.3 of "Test Methods for Evaluating Solid Waste," EPA Manual SW-846.

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 The following analytes can be quantitatively determined by this procedure:

Aldrin	Endosulfan I	Aroclor 1016
Alpha-BHC	Endosulfan II	Aroclor 1260
Beta-BHC	Endosulfan Sulfate	Aroclor 1221
Delta-BHC	Endrin	Aroclor 1232
Chlordane (n.o.s)	Endrin Aldehyde	Aroclor 1242
4,4'-DDD	Endrine Ketone	Aroclor 1248
4,4'-DDE	Heptachlor	Aroclor 1254
4,4'-DDT	Heptachlor Epoxide	Aroclor 1262
Dieldrin	Toxaphene	Aroclor 1268
cis-Chlordane	trans-Chlordane	
Lindane	Methoxychlor	
2,4'-DDD	O-Chlordane	
2,4'-DDE	C-Nonachlor	
2,4'-DDT	T-Nonachlor	
Mirex	Hexachlorobenzene	

NOTE: Method 8081B does not include the analysis of PCBs as Aroclors. The analysis of PCBs should be done by method 8082. PCB (Aroclor) analysis is included in method 608.3 as well as the pesticide analytes listed above.

4.2 This method applies to various matrices, including:

4.2.1 Groundwater

4.2.2 Wastewater

4.2.3 Soil

4.2.4 Sludge

4.2.5 TCLP

4.2.6 Miscellaneous matrices

4.3 This method summarizes the procedures necessary to analyze a sample extract for organochlorine pesticides by gas chromatography/electron capture detector.

5.0 METHOD SCOPE AND PERFORMANCE CHARACTERISTICS

5.1 The calibration ranges for pesticides and chlorinated hydrocarbons are compound specific. The lowest concentration level standard is referred to as the lower limit of quantitation (LLOQ), which is equivalent to the practical quantitation limit (PQL).

5.2 The typical calibration ranges follow. These concentrations represent on-column values and do not include the prep factor.

Compound	Concentration Range
4-CMX	8 µg/L – 400 µg/L
Alpha-BHC	4 µg/L – 200 µg/L
Lindane	4 µg/L – 200 µg/L
Beta-BHC	4 µg/L – 200 µg/L
Heptachlor	4 µg/L – 200 µg/L
Delta-BHC	4 µg/L – 200 µg/L
Aldrin	4 µg/L – 200 µg/L
Heptachlor Epoxide	4 µg/L – 200 µg/L
cis-Chlordane	4 µg/L – 200 µg/L
trans-Chlordane	4 µg/L – 200 µg/L
Endosulfan I	4 µg/L – 200 µg/L
4,4'-DDE	8 µg/L – 400 µg/L
Dieldrin	8 µg/L – 400 µg/L
Endrin	8 µg/L – 400 µg/L
2,4'-DDD	4 µg/L – 400 µg/L
2,4'-DDE	4 µg/L – 400 µg/L
2,4'-DDT	4 µg/L – 400 µg/L
Mirex	4 µg/L – 400 µg/L
O-Chlordane	4 µg/L – 400 µg/L
C-Nonachlor	4 µg/L – 400 µg/L
T-Nonachlor	4 µg/L – 400 µg/L
Hexachlorobenzene	4 µg/L – 400 µg/L
4,4'-DDD	8 µg/L – 400 µg/L
Endosulfan II	8 µg/L – 400 µg/L

4,4'-DDT	8 µg/L – 400 µg/L
Endrin Aldehyde	8 µg/L – 400 µg/L
Endrin Ketone	8 µg/L – 400 µg/L
Endosulfan Sulfate	8 µg/L – 400 µg/L
DCB	8 µg/L – 400 µg/L
Methoxychlor	40 µg/L – 2000 µg/L
Toxaphene	100 µg/L – 3000 µg/L
Chlordane	50 µg/L – 3000 µg/L
Chlordane (n.o.s)	50 µg/L – 3000 µg/L

5.3 Precision is determined by the relative percent difference (RPD) between the laboratory control sample (LCS) and the laboratory control sample duplicate (LCS DUP) or the matrix spike (MS) and the matrix spike duplicate (MSD). The RPD acceptance limits are determined through Statistical Process Controls (SPC), which are updated on a semi-annual basis.

5.4 Accuracy is determined by the percent recovery in LCSs and MSs and the control ranges are determined through Statistical Process Controls (SPC), which are updated at least semi-annually. For South Carolina samples, static limits of 70-130% are used as the LCS acceptance range.

5.5 Method Detection Limit (MDL) studies are performed annually for liquid and solid matrices. MDLs are maintained in AlphaLIMS.

6.0 DEFINITIONS

6.1 Definitions specific to this SOP include:

6.2 Limit of Detection (LOD): The lowest concentration level that can be determined by a single analysis and with a defined lever of confidence to be statistically different from a blank. The LOD verification is typically spiked at two times the MDL.

6.3 Limit of Quantitation (LOQ): The lowest level in the calibration curve. With the prep factor applied, the LOQ is referred to as the effective LOQ. The LOQ is equivalent to the PQL and LLOQ.

6.4 Lower Limit of Quantitation (LLOQ): The lowest concentration at which a target analyte can be reliably measures and reported. The LLOQ is lowest point in the calibration curve and represents a concentration at which both quantitative requirements can be consistently demonstrated. The LLOQ is verified quarterly, as the LOQ verification. The verification is performed by extracting and analyzing an LCS spiked at the LOQ (See table above for calibration concentrations). The LLOQ verification is carried through the same preparation and analytical procedures as environmental samples and QC. The LLOQ is analyzed on every instrument where data are reported and this is the laboratories normal protocol. Recovery of target analytes in the LLOQ are compared to in-house statistically-derived limits.

Concentrations in samples reported below the LLOQ and above the MDL are qualified as estimated.

6.5 Relative Standard Error (RSE): Standard Error indicates the extent to which a survey estimate is likely to deviate from the true population and is expressed as a number. The Relative Standard Error (RSE) is the standard error expressed as a fraction of the estimate and is usually displayed as a percentage. The RSE acceptance limit criterion is the same as the RSD limit for average CF or RF in the determinative method.

6.6 Lab-wide used definitions can be found in GL-QS-B-001 the Quality Assurance Plan.

7.0 REFERENCES

7.1 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1 (Part 2 and Part 3) Section B. SW-846, 3rd Edition.

7.1.1 Method 8000D, "Determinative Chromatographic Separations," Rev. 4, July 2014.

7.1.2 Method 8081A, "Organochlorine Pesticides by Gas Chromatography," Revision 1, December 1996.

7.1.3 Method 8081B, "Organochlorine Pesticides by Gas Chromatography," Revision 2, February 2007.

7.1.4 EPA Method 608.3

7.2 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.2, December, 2018.

8.0 INTERFERENCES TO THE METHOD

8.1 Interference by phthalates can pose a major problem in pesticide determinations. These compounds generally appear in the chromatogram as large late-eluting peaks. Common flexible plastics contain varying amounts of phthalates, which are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

8.2 Interference for phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

8.3 Many of the analytes of interest are susceptible to breakdown from active sites at the front of the column and in the injection port. Care should be taken to ensure that these areas are properly cleaned.

8.4 Additional cleanups are outlined in method 8081B, including silica gel (method 3630), gel permeation chromatography (method 3640), alumina (method 3610), and sulfur clean-up (method 3660).

9.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

9.1 Treat all chemicals and samples as potential health hazards, and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file

of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and client sample MSDS forms are also maintained in the laboratory.

9.2 Personal protective equipment

9.2.1 Gloves are required when handling the samples and chemicals in this procedure.

9.2.2 Safety glasses with side shields and lab coats should also be worn.

9.3 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling.

9.4 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

9.5 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

9.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located throughout the lab. Training is available on the proper operation of this equipment.

9.7 Refer to SOP GL-LB-N-001 Safety, Health and Chemical Hygiene Plan for general safety and health information pertaining to the laboratory.

10.0 CAUTION WARNINGS

The helium, nitrogen and hydrogen tanks should be replaced when pressure drops to approximately 250 psi.

11.0 APPARATUS AND EQUIPMENT, REAGENTS, AND INSTRUMENTS

11.1 Apparatus and Equipment:

11.1.1 Volumetric flasks

11.1.2 Pasteur pipettes

11.1.3 2 mL amber auto sampler screw-capped vials with Teflon-lined septa, or 2 mL amber auto sampler crimp top vials with 500 µL inserts.

11.1.4 Microliter syringes (10, 25, 50, 100, 250, 500, and 1000 µL)

11.1.5 Capillary cleaving tool

11.1.6 Supeltex 0.5 and 0.8 mm ferrules (or equivalent)

11.2 Reagents, Chemicals and Standards

11.2.1 Solvents: Acetone, hexane, isooctane, and toluene (pesticide grade or equivalent)

11.2.2 For chemical standards refer to Section 14.0.

11.3 Instrumentation and Columns

11.3.1 Pesticides

11.3.1.1 GC: Agilent 6890,7890 or equivalent.

11.3.1.2 Agilent GC/SFC Auto Sampler (or equivalent)

11.3.1.3 Restek CLP Pesticides 30m X 0.25mm X 0.2µm Column (used for fast GC)

11.3.1.4 Restek CLP Pesticides II 30m X 0.25mm X 0.25µm Column (used for fast GC)

NOTE: The instrumentation and columns listed above are merely the recommended instrumentation and columns for use with this method.

12.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

12.1 Samples must be collected in an amber glass bottle with a Teflon-lined cap. The collection containers are bought pre-cleaned from a certified vender.

12.2 All liquid samples have a holding date of seven days from the time of collection to be extracted while all solid samples have fourteen days from the collection date to be extracted. Method 608.3 stipulates that unpreserved samples need to be extracted within 72 hours. Preserved samples with a pH of 5 > 9 have a hold time of seven days. Samples are protected from light and stored at 0° ≤ 6° C after collection. Once extracted, the extract must be analyzed within forty days. However, during this period of time, the extracts are refrigerated at 0° ≤ 6° C in amber vials with Teflon- sealed screw caps. When holding dates are missed, the data are automatically flagged.

13.0 SAMPLE PREPARATION TECHNIQUES

13.1 Refer to GL-OA-E-070 for Extraction of Semivolatile and Nonvolatile Organic Compounds from Groundwater, Wastewater and Other Aqueous Samples, and GL-OA-E-066 for Extraction of Semivolatile and Nonvolatile Organic Compounds from Soil, Sludge and Other Miscellaneous Solid Samples.

NOTE: It is assumed that materials within the sample container are considered "the sample." Removal of any extraneous material (twigs, leaves, large rocks, etc.) must be documented in the case narrative and bench logbooks.

14.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

14.1 In order to maintain the gas chromatograph's columns and detectors, the gases should be changed when the tank pressure is below 250 psi. As needed, the septum in the injection port should be changed and the injection port cleaned. Column maintenance is performed when baseline rise is present or when the column becomes contaminated.

14.2 Suggested Routine Maintenance

COMPONENT	DAILY	WKLY	MTHLY	AS NEEDED	ANNUALLY
Injector septum				X	
Gases		X			

Column Maintenance	X	
Detector Wipe Test		X
Detector Cleaning	X	

14.3 Non-routine Maintenance

14.3.1 When a check standard fails, the standard is examined for signs of evaporation or degradation. If nothing is found, column maintenance should be performed. Approximately one loop of each column or two loops of guard column should be cleaved. The instrument is then baked out at 320˚ C until an acceptable baseline is obtained. If an acceptable baseline is not obtained, the column is leaking and column maintenance must be performed again.

14.3.2 When contamination occurs, first replace or clean the auto sampler syringe. If contamination is still present, column maintenance should be performed. If contamination is still present after column maintenance has been performed and the system has been cleaned thoroughly, replace the column. The column must then be leak checked and baked. The instrument must then be checked to determine if the problem is solved and if the instrument is stable. If not, the in-house service technician is called.

14.4 When maintenance is done on the instrument, it must be recorded in the maintenance logbook. It must be initialed and dated.

15.0 PREPARATION OF STANDARD SOLUTION AND QUALITY CONTROL SAMPLES

15.1 Source Standard Solutions

15.1.1 Source standard solutions are purchased from certified vendors. These standards are traceable to National Institution of Standards and Technology (NIST) standards. The source standards are received from the company Purchasing Agent. The standard is given a unique identifying number for that day and is entered and traced in AlphaLIMS using the standards and reagents data base.

15.2 For guidance on standard documentation, refer to GL-LB-E-007 for Laboratory Standards Documentation.

15.3 Source and stock standards expire one year after opening or the manufacturer's expiration, whichever is shorter. Working standards expire after six months or the manufacturer's expiration, whichever is shorter.

16.0 INSTRUMENT CALIBRATION

16.1 The instrument should be checked for cleanliness and stability prior to analyzing calibration standards. The standards are loaded onto the auto sampler with the lowest standard being analyzed first to prevent carryover.

16.2 An external standard technique is used to calibrate the instrument. Internal standard techniques are optional but not used. Calibration is achieved by analyzing multiple

standards (minimum of five for 8000 methods and three for 600 methods) at different concentrations. The laboratory uses a minimum of five concentration levels for each individual and multi-component pesticide compound. All target analytes and surrogates are included in each standard. A calibration curve is plotted for each analyte using the total area under the peak versus the mass (in ng) of the analyte injected. For multi-component compounds such as chlordane and toxaphene, a minimum of five major peaks representing the compound should be chosen for calibration and quantitation purposes. Chlordane (n.o.s) peaks should include cis-chlordane, trans-chlordane and heptachlor. The validator selects the most technically sound result for heptachlor so that the concentration of heptachlor is not reported twice. A response factor is obtained for each representative peak chosen in the multi-component compound. The same peaks in the calibration standards must be used to calculate response factors in continuing calibration checks, spike concentrations, and samples results. Multi-component standards are analyzed separately from the individual pesticide compound mix. Typical calibration levels are listed in the following table. Level 1 corresponds to the LLOQ (PQL).

	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)
Hexachlorobenzene	4	20	100	200	400
alpha-BHC	4	10	50	100	200
gamma-BHC (Lindane)	4	10	50	100	200
Heptachlor	4	10	50	100	200
Aldrin	4	10	50	100	200
beta-BHC	4	10	50	100	200
delta-BHC	4	10	50	100	200
Heptachlor epoxide	4	10	50	100	200
Endosulfan I	4	10	50	100	200
gamma-Chlordane	4	10	50	100	200
alpha-Chlordane	4	10	50	100	200
Mirex	4	10	50	100	200
c-Nonachlor	4	10	50	100	200
o-Chlordane	4	10	50	100	200
t-Nonachlor	4	10	50	100	200
2,4-DDD	4	10	50	100	200
2,4-DDE	4	10	50	100	200
2,4-DDT	4	10	50	100	200
4,4'-DDD	8	20	100	200	400
4,4'-DDE	8	20	100	200	400
4,4'-DDT	8	20	100	200	400
Dieldrin	8	20	100	200	400
Endrin	8	20	100	200	400
Endosulfan II	8	20	100	200	400
Endrin aldehyde	8	20	100	200	400
Endosulfan sulfate	8	20	100	200	400

Endrin ketone	8	20	100	200	400
4-CMX (surr)	8	20	100	200	400
DCB (surr)	8	20	100	200	400
1,2-Dichlorobenzene	20	50	100	150	200
Methoxychlor	40	100	500	1000	2000
Chlordane (nos)	50	100	500	1000	3000
Aroclor 1016	100	250	500	1000	4000
Aroclor 1221	100	250	500	1000	4000
Aroclor 1232	100	250	500	1000	4000
Aroclor 1242	100	250	500	1000	4000
Aroclor 1248	100	250	500	1000	4000
Aroclor 1254	100	250	500	1000	4000
Aroclor 1260	100	250	500	1000	4000
Aroclor 1262	100	250	500	1000	4000
Aroclor 1268	100	250	500	1000	4000
Toxaphene	100	500	1000	2000	3000

16.3 The MDL, LOD, and LLOQ (LOQ) are verified quarterly. The MDL verification is spiked at the MDL concentration (approximately one third of the LLOQ). The LOD is spiked at two times the MDL. And the LLOQ is spiked at the lowest calibration level (the PQL). Verification samples are extracted using the same methods and processes used for samples and analyzed on each instrument used for that analysis. Statistical Process Limits (SPC) are calculated for the LLOQ using historical data from the lab and are used to evaluate the LLOQ recoveries.

16.4 The ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated. Also calculate the mean calibration factor and the relative standard deviation for each analyte at each standard concentration using the formula below.

16.4.1 Calculate the calibration factor for each analyte at each concentration as:

$$CF = \frac{\text{Peak Area of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

The CF can also be calculated using the concentration of the standard rather than the mass in the denominator of the equation above. However, the use of the concentration will require changes to the equations that are used to calculate sample concentration.

16.4.2 Calculate the mean calibration factor for each analyte as:

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where n is the number of standards analyzed.

16.4.3 Calculate the standard deviation and the %RSD of the calibration factors for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} X\ 100$$

If the calculated %RSD for the analyte response factors is ≤ to 20% over the working range, linearity through the origin may be assumed and the mean calibration factor can be used to quantitate sample results. If the %RSD is greater than 20% the only other option the analyst may use to determine linearity is by linear regression using the calibration curve.

16.5 If the analyst chooses to use linear regression, he/she must not force the calibration line through the origin.

16.5.1 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response

a = slope of line (also called the "coefficient of x")

x = concentration of the calibration standard

b = the intercept

16.5.2 The analyst should not force the line through the origin, but have the intercept calculated from the five data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0, 0) as a sixth calibration point.

16.5.3 The regression calculation will generate a correlation coefficient (r) that can be used to calculate a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be ≥ 0.990. The calculated intercept value needs to be evaluated before reporting sample results. If the system you are using calculates the coefficient of determination (r^2), the value must be ≥ 0.990.

16.5.4 A positive value for the intercept indicates that there is some threshold instrument response that is the limiting factor in establishing linearity. A negative intercept value can be transformed into an x-intercept value that represents a threshold concentration, which is the limitation. If the intercept is positive, then, as a general rule, results where the instrument

response is less than three times (3x) the intercept value may be unreliable. This will afford some protection against false positive results. If the intercept is negative, results below the concentration of the lowest concentration calibration standard may be unreliable.

16.5.5 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y - b)}{a}$$

16.6 In some cases, it is likely that certain analytes may not meet the %RSD or linearity criteria. If the calibration curve contains more than the minimum number of concentration levels stated in the method, the analyst may want to narrow the calibration range by eliminating outlying responses. Remember that changing the lowest level in the calibration standard will change the laboratory practical quantitation limit. Consider the project specifications for regulatory limits and action levels to confirm that this option can be used. Individual analyte end points may be eliminated. If the calibration linearity continues to fail despite using the above options, check instrument operating conditions and perform additional maintenance. Changing instrument parameters or columns may be required. Recalibration is required if instrument conditions are changed.

16.7 Method 8000D outlines two procedures that may be used to determine calibration function acceptability for linear and non-linear curves. The calibration data refitted back to the calibration model. % Error and Relative Standard Error (RSE) evaluate the difference between the measured amount and the true amount (or concentration). % Error is determined as follows:

$$\%Error = \frac{x_i - x'_i}{x_i} \times 100$$

Where:

16.8 x_i = True amount of analyte at calibration level i, in mass or concentration units

x'_i = Measured amount of analyte at calibration level i, in mass concentration units

16.9 Percent error between the calculated and expected amount of an analyte should be ≤ 30% for all standards and ≤ 50% for the lowest calibration level.

16.10 Relative Standard Error is calculated as follows:

$$RSE = 100 \times \sqrt{\sum_{i=1}^{n} \left[\frac{x'_i - x_i}{x_i} \right]^2 \Big/ (n - p)}$$

Where:

x_i = True amount of analyte in calibration level I, in mass of concentration units

x'_i = Measured amount of analyte in calibration level I, in mass or concentration units

16.11 p = Number of terms in the fitting equation (average = 1, linear =2, quadratic = 3, cubic = 4)

n = Number of calibration points

16.12 The RSE acceptance limit criterion is the same as the RSD limit for CF or RF in the determinative method. If the RSD limit is not defined in the determinative method, the limit should be set at ≤ 20% for well performing compounds and ≤ 30% for poor responders. Please see the appendix for a list of demonstrated poor responders.

16.13 Continuing Calibration

16.14 The initial calibration curve must be verified for each compound of interest prior to sample analysis. Verification is accomplished by analyzing second source standards at or near the midpoint standards in the calibration curve. It is analyzed after every 10 samples. The laboratory performs the initial calibration verification prior to sample analysis and inject continuing calibration verification standards (minimum Pest A/B mix) after every ten samples. The sequence must be concluded with a final calibration verification standard (Pest A/B mix). The ICV and CCV standards should be followed by an instrument blank (IB) as the next injection in the analytical sequence. A second source standard should be provided by a second vendor whenever available. Otherwise, a second lot will be used. Using a second source verification standard will verify the initial calibration on a daily basis.

16.14.1 The initial calibration is verified if each analyte calibration factor in the calibration verification standard is ≤ 15% difference or drift (≤ 20% for 8081B) of the mean calibration factor in the initial calibration. Use the following equation to calculate the % difference.

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \text{ X } 100$$

Where:

CF_V = response factor from current verification check standard.

If the linearity of the analyte calibration curve uses linear regression, the % drift must not exceed ± 15% (± 20% for 8081B). Calculate the % drift using the calculated value for the analyte and the true value as follows:

$$\% \text{ drift} = \frac{|\text{true value - calculated value}|}{\text{true value}} \text{ X } 100$$

16.14.2 The analyst should evaluate the retention time of each analyte in the initial continuing calibration standards with the absolute retention time windows established over a 72-hour time period. Apply the retention

time window to the absolute retention times of each analyte in the calibration curve midpoint standards and ensure that the initial continuing calibration standard analytes are within the established windows. If retention times have drifted outside the windows, the analyst should stop and investigate the cause for the drift. As the calibration curve ages and column maintenance is performed, retention time shifts should be expected. However, if the calibration verification standards are analyzed after the initial calibration curve, retention time shifts should not occur. If analyte retention times are outside the established windows the system is considered out of control and the analyst must attempt to correct the problem before continuing the analysis.

16.14.3 Update the retention time windows for each analyte on both columns using the initial continuing calibration standards absolute retention times prior to sample analysis whenever a new analytical sequence is started. If continuing verification standard analyte retention times are outside the established windows the instrument is considered out of control and the analysis must stop. Samples analyzed before the unacceptable standard must be reanalyzed when the instrument is returned to control. Common problems associated with retention time shifts include inlet leaks, low carrier gal flow, and broken or cracked columns.

17.0 INSTRUMENT PERFORMANCE REQUIREMENTS

17.1 Before samples can be analyzed, the baseline must be stable with little or no back ground noise. If using dual column/detector both sides must be stable. Analysis of an acceptable degradation standard is required prior to analyzing the initial calibration curve and/or initial calibration verification standards and daily every twelve hours. If breakdown for DDT or Endrin exceeds 15% the analyst must stop and perform instrument maintenance before continuing with the analysis. Refer to Section 20 to calculate percent breakdown.

17.2 Each instrument must have a valid initial calibration curve for each analyte of interest on both columns. Hard copies of the continuing calibration standards are kept with the quality control samples and client samples analyzed in the sequence.

17.2.1 Continuing calibration verification standards (CCV) must meet the criteria in Section 16. When a calibration verification standard fails to meet the criteria, all samples that were injected after the last standard that met the criteria must be evaluated to prevent misquantitations and possible false negative results. Reanalysis of sample extracts may be required. More frequent analysis of standards will minimize the number of sample extracts that will have to be reanalyzed if the standard verification criteria are not met.

17.3 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet the quality control criteria in

Section 16. The sequence ends when the set of samples has been injected or when standards exceed the acceptance criteria.

17.3.1 If during the analysis of a sample group from a single client, the bracketing continuing verification standards do not meet the acceptance criteria, reanalysis of this group of samples is required. The reanalyses are required to confirm that the sample extracts (matrices) are causing the instrument response to fluctuate and standards to fail. The reanalysis must begin with an acceptable CCV. If continuing verification standards fail during the analysis sequence, the failure is attributed to matrix. If the standards meet the acceptance criteria, then matrix interference is not confirmed and the acceptable standards and samples in between should be reported.

17.3.2 In addition, if multiple client sample extracts are analyzed in the analytical sequence where continuing verification standard failures occur, each client's samples must be reanalyzed after an acceptable initial calibration, initial continuing calibration or continuing verification standard.

18.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

18.1 To establish that the analyst can perform the procedures in an acceptable manner and that the method generates data of acceptable bias and precision, the following operations are performed.

18.1.1 A quality control (QC) check standard must be prepared containing each analyte of interest. It must be prepared from pure standard material or purchased as a certified solution. It must be made from a source independent of that used for calibration. AB, toxaphene (TOX), and chlordane (CHL) IDOCs must be each prepped separately. An IDOC is required for each matrix as well.

18.1.2 Four samples must be prepared and analyzed by the same procedures used to prepare and analyze actual samples.

18.1.3 Calculate the average recovery (X) in µg/L, and the standard deviation of the recovery (S) in µg/L, for each analyte of interest using the four results.

18.1.4 For each analyte compare S and X with the corresponding acceptance criteria for precision and accuracy, respectively, given in the quality control table at the end of the method. If the S and X for all analytes of interest meet the acceptance criteria, the system's performance is acceptable and analysis of actual samples can begin. If any individual S and X exceeds the precision limits or falls out of the range for accuracy, the system's performance is unacceptable for that analyte and a check standard for that analyte must be prepared and reanalyzed.

18.2 Precision and accuracy are matrix dependent and are documented by means of a laboratory control sample (LCS) and a matrix spike (MS) and matrix spike duplicate

(MSD). (Refer to Section 5.4 and GL-LB-E-001 for the Determination of Method Detection Limits.)

18.3 Details of how Initial (IDOC) and Continuing (CDOC) Demonstrations of Capability are performed are in GL-QS-E-011.

19.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

19.1 Standards, samples, blanks, and quality control sample extracts are introduced into the instrument via direct injection (autosampler). Retention time windows must be updated for each analyte after the initial verification standard analysis. The absolute retention time windows are determined during a 72-hour period when standards are analyzed. The retention time window is equal to three times the standard deviation of the absolute retention times for each analyte (or peak). Refer to GL-OA-E-001 for Establishing Retention Time Windows for GC and HPLC Analysis.

19.2 Samples are analyzed in a set referred to as an analysis sequence or run sequence. Prior to analyzing a pesticide calibration curve (Pest A/B mixes) or initial check standards, inject a degradation check standard (PEM) to evaluate the potential breakdown of Endrin and DDT. Refer to Section 20 to calculate the percent breakdown. Each sequence begins with a solvent blank and the analysis of the PEM, initial calibration curve or the initial calibration verification standards followed by samples. A mid-level calibration check standard must be analyzed after twenty samples (the lab uses ten) and at the end of the analytical sequence. The sequence ends when all the extracts have been injected and analyzed.

19.3 The data are entered into the computer and a data report is generated. The sequence file is created on the computer by the analyst. It lists every injection made by the instrument, in order, for a given date. The raw data, a copy of the run sequence, batch sheet, case narrative, and a copy of the retention time window are filed together.

19.4 Before the instrument is used, a highly concentrated standard may be analyzed to prime the columns.

19.5 0.5 to 2.0 µL of the extract is injected into the instrument.

19.6 All HP6890 Gas Chromatographs are equipped with the HP 7683 autosampler. It has 100 positions and can be programmed to start from any given position. The digital integrator converts the analog from the instrument to digital information that is processed into a graphic format showing concentration based on peak area.

19.7 A run sequence is entered into the sequence table in the ChemStation software. The samples are entered in the order in which they are to be injected. Additional information, such as vial number, method name, injection vial, and injection volume is also entered. The sequence may be automatically started by selecting “run sequence.”

19.8 Samples containing target analyte concentrations that exceed the linear range of the analyte calibration curve must be diluted. The dilution level should be performed to place the highest analyte concentration between the middle and high points of the calibration curve (on column). If a sample is initially diluted and target analytes are

not detected and non-target analytes are not interfering with the analysis, the sample must be reanalyzed at a lower dilution. Analysts should be aware that diluting samples will increase the detection limits for undetected analytes. Random dilutions without due cause are not acceptable. Samples should undergo appropriate clean up methods prior to diluting for observed matrix problems.

19.9 Samples are analyzed using a dual column procedure. The initial calibration and continuing calibration standards must meet the acceptance criteria on both columns before attempting sample analysis. The analyst may choose one or the other column as the primary (for reporting sample results) and the other as the confirmation column. However, it is the lab's standard practice to report the lower result as per method 8000D. If any analyte in the continuing verification standard does not meet the acceptance criteria on the confirmation column and that target analyte is not detected or confirmed above the analytes practical quantitation limit, then the associated samples do not require reanalysis.

20.0 CALCULATIONS AND DATA REDUCTION METHODS

20.1 The concentration of each analyte in an extract can be determined by comparing the response obtained from analyzing the extract to the calibration curve. The concentration of a specific analyte is matrix specific and is calculated as follows:

AQUEOUS SAMPLE

$$\textit{Concentration } (\mu g/L) = \frac{(C)(D)(V_t)}{1000\ V_i}$$

Where:

C = Concentration (µg/L) calculated by data system from total area substituted into the linear equation derived from the multilevel calibration

D = Dilution factor, if made prior to analysis. If not, D = 1.

V_t = Total volume of the extract in mL

V_i = Initial volume of sample in L

NONAQUEOUS SAMPLES

$$\text{Concentration}(\mu g/kg) = \frac{(C)(D)(V_t)}{W}$$

Where:

C = Concentration (µg/L) calculated by data system from total area substituted into the linear equation derived from the multilevel calibration

D = Dilution factor, if made prior to analysis. If not, D = 1.

V_t = Total volume of the extract in mL

W = Weight of the sample extracted in g

DEGRADATION

$$\%\ Breakdown = [(A_1 + A_2)/(A_1 + A_2 + A_3)](100)$$

Where:

A_1 = Total area of 4,4'-DDE or Endrin Aldehyde

A_2 = Total area of 4,4'-DDD or Endrin Ketone

A_3 = Total area of 4,4'-DDT or Endrin

20.2 Results are reported to the nearest one tenth for all matrices.

20.3 The reporting units are micrograms of analyte per liter of sample for aqueous samples, micrograms of analyte per kilogram of sample for soils, and milligrams per liter for TCLPs.

21.0 DATA RECORDING

Data are recorded and calculated by the Chemstation data acquisition system. They are stored on a remote server. Data are also entered into AlphaLIMS.

22.0 QUALITY CONTROL REQUIREMENTS

22.1 Before sample analysis begins the instrument must have acceptable calibration curves on both columns. Each curve is verified by the analysis of second source continuing calibration standards. Each standard must meet the acceptance criteria for percent difference or drift. Continuing calibration verification standards must be analyzed after every twenty samples. The lab's standard practice is to bracket every ten samples.

22.2 A method blank is used to determine background concentrations of analytes of interest that have the potential to interfere with sample analysis. These blanks are analyzed with every analytical batch that has a maximum number of twenty samples. The criterion for acceptance is that there are no target analytes of interest present above the practical quantitation limit. For DoD QSM, no targets may be present at concentrations > ½ reporting limit (RL). For common lab contaminants, no targets may be detected > RL.

22.3 If the analyte of interest is present at a concentration between the MDL and LLOQ, all data are qualified with a "B" flag and reported. If the analyte of interest is present at a concentration above the LLOQ and the samples contain the analyte of interest at a concentration of greater than 10 times the concentration found in the blank, the data are qualified with a "B" flag and reported. If the concentration found in the sample is less than 10 times that found in the blank and greater than the LLOQ, the samples must be re-extracted.

22.4 The laboratory evaluates the effect of matrix on method performance by performing a matrix spike (MS) and matrix spike duplicate (MSD) for each matrix with up to 20 samples in the same batch. For method 608.3, a matrix spike must be performed for

10% of the samples. Matrix spike recovery limits are generated statistically using at least 20 result pairs of the same matrix. In addition, a laboratory control sample (LCS) and its duplicate (when requested) are analyzed with each sample batch (up to 20 samples of the same matrix). The LCS consists of an aliquot of clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentration as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. LCS recoveries are statistically generated using at least 20 results of the same matrix type. SPC limits are updated semi-annually.

NOTE: For SCDHEC clients, liquid LCS limits of 70-130% are used.

22.5 Tetrachloro-m-xylene (4CMX) and Decachlorobiphenyl (DCB) surrogates are added to all samples (prior to extraction) and standards. Surrogate recovery limits are statistically determined using at least 20 sample results of the same matrix. SPC limits are updated semi-annually.

22.6 The retention time (RT) window must be established using the initial calibration check standard. Refer to OA-E-001 for Establishing Retention Time Windows for GC and HPLC Analysis. In order to report a concentration from the external standard table, the retention time of that particular analyte must be within its established window. If not, the concentration is not reported.

22.7 Nonconformance

22.7.1 When running a calibration curve for more than one analyte at a time, some of the analytes may not meet the acceptance criteria. Additional standards containing the compounds that were not acceptable may be analyzed. If the curve still does not meet the acceptance criteria, maintenance should be performed or a new standard may be needed. Refer to Section 16.5 for other options addressing the initial calibration.

22.7.2 If the continuing check standard fails any criteria in Section 22.1, the analyst must take action to correct the situation. This may be performing any of the maintenance steps described in Section 14 to get the instrument to meet its daily calibration. If all attempts fail, the analyst must analyze a new series of calibration standards, thus obtaining a new calibration curve.

22.7.2.1 If the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit (i.e. >15% or > 20%), and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed. If an analyte above the QC limits was detected in a sample extract, reinjection of the extract is necessary.

22.7.3 If the percent recovery in the matrix or matrix spike duplicate falls outside the established SPC limits for recovery, the analyst should evaluate the LCS recoveries and method blank analyses. If the LCS and method blank analyses do not indicate a problem with the preparation procedures, the matrix spike recoveries may be attributed to matrix effect. Surrogate recovery data should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside the acceptance limits suggests more pervasive analytical problems then problems with the recoveries of either matrix spikes or surrogates alone. Analysts are not required to reanalyze the matrix spikes for failing recoveries; however they should seek additional technical support before deciding not to reanalyze matrix spikes samples.

22.7.4 If a surrogate in a sample falls outside the acceptable fixed range, the sample must be re-extracted. If the surrogate fails the second time, the failure is attributed to matrix interference, and the data from the first extraction are reported. If the surrogate failures are not confirmed, a nonconformance report is filed. (Refer to GL-QS-E-004 for Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items.)

22.8 Any positive identification and quantitation of an analyte of interest must be confirmed on a separate column and/or GC/MS. The confirmation column or GC/MS must meet all quality control acceptance described in the method (calibration, retention times, etc.). Calculate the relative percent difference between the two results using the formula:

$$RPD = \frac{|R_1 - R_2|}{\frac{(R_1 + R_2)}{2}} \times 100$$

22.8.1 Since the same method criteria specified in Sections 22.1 through 22.5, and instrument calibration specified in Sections 16.1 through 16.6 are applied uniformly to both columns, either column can be selected to serve as the primary or confirmatory column.

22.8.2 If one result is significantly higher (> 40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result.

22.9 If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the result lower column.

23.0 DATA REVIEW, VALIDATION AND APPROVAL PROCEDURES

Refer to SOP GL-OA-E-044 Organics Data Validation.

24.0 DATA TRANSMITTAL

After the review process is complete, Data Management receives the data.

25.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

26.0 LABORATORY WASTE HANDLING AND DISPOSAL: SAMPLES, EXTRACTS, DIGESTATES AND REAGENTS

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

27.0 HISTORY

Revision 16: Added clarification to LLOQ definition. Added current reference to DOD/DOE QSM version 5.1 and 3.1 January, 2017.

Revision 17: Added current ECD and FID Method Comparison table in Appendix 1. Update to include DOD/DOE 5.1 requirements.

Revision 18; Updated definitions for variables. Updated missing part of equation in RPD.

Revision 19: MUR update to new 600 methods.

Revision 20: Revised to new method updates 608.3 and QSM 5.2.

APPENDIX 1: ECD, DOD QSM COMPARISON TABLE

ECD Method Comparison Table

Last Updated: March 2019

	8082, 8081A, 8151, 8015B	**8082A, 8081B, 8015D**	**DODQSM 5.2 (QSAS)**	**608.3**
IDOC	Analyze four LCS replicates. Evaluate average and standard deviation of replicates with method limits. Generate QC Summary and training certificate.	Analyze four LCS replicates. Evaluate average and standard deviation of replicates with method limits. Generate QC Summary and training certificate.	Analyze four LCS replicates. Evaluate average and standard deviation of replicates with method limits. Generate QC Summary and training certificate.	Analyze four LCS replicates. Evaluate average and standard deviation of replicates with method limits. Generate QC Summary and training certificate.
MDL & LOD/LOQ	Following initial set-up, MDLs are determined annually using points from each quarter. Q1: 1/2x, 1x, LOD, LOQ, MDL. Q2, Q3, Q4: LOD, LOQ, MDL. Analyzed on every instrument. LOD = 2x MDL LOQ = LLOQ=PQL	Following initial set-up, MDLs are determined annually using points from each quarter. Q1: 1/2x, 1x, LOD, LOQ, MDL. Q2, Q3, Q4: LOD, LOQ, MDL. Analyzed on every instrument. LOD = 2x MDL LOQ = LLOQ=PQL	Following initial set-up, MDLs are determined annually using points from each quarter. Q1: 1/2x, 1x, LOD, LOQ, MDL. Q2, Q3, Q4: LOD, LOQ, MDL. Analyzed on every instrument. LOD = 2x MDL LOQ = LLOQ=PQL .	Following initial set-up, MDLs are determined annually using points from each quarter. Q1: 1/2x, 1x, LOD, LOQ, MDL. Q2, Q3, Q4: LOD, LOQ, MDL. Analyzed on every instrument. LOD = 2x MDL LOQ = LLOQ=PQL
RT Windows	RT study performed over 72 hours at time of method set-up and when significant maintenance is done (column change).	RT study performed over 72 hours at time of method set-up and when significant maintenance is done (column change).	RT study performed over 72 hours at time of method set-up and when significant maintenance is done (column change).	RT study performed over 72 hours at time of method set-up and when significant maintenance is done (column change).
ICAL	Minimum of five levels. RSD for each target analyte ≤ 20% or linear regression for each target analyte R^2 ≥ 0.99. %Error: ± 50%	Minimum of five levels. RSD for each target analyte ≤ 20% or linear regression for each target analyte R^2 ≥ 0.99. %Error: ± 50%	Minimum of five levels. RSD ≤ 20% for all targets or linear regression R^2 ≥ 0.99. Analytes that do not meet either option may not be analyzed per	Minimum of three levels. RSD for each target analyte ≤ 20%.

	for low level and ± 30% for all other levels. RSE: criteria same as RSD for the method. If %Error or RSE fail, consult validator or GL. If adequate sensitivity has been established, ICAL may be acceptable for qualitative analysis.	for low level and ± 30% for all other levels. RSE: criteria same as RSD for the method. If %Error or RSE fail, consult validator or GL. If adequate sensitivity has been established, ICAL may be acceptable for qualitative analysis.	QSAS. If criteria are not met, analyze sample(s) and QC on passing instrument for those compound(s).	
ICV	Second source. Same acceptance criteria as CCV.	Second source. All targets should recover within ± 20%.	Second source. All targets should recover within ± 20%. DOD QSM 5.2 does not allow for exceptions for the ICV. Failing compounds should be re-analyzed on a passing instrument. If re-analysis is not possible, then failures must be documented and corresponding data Q qualified and narrated	Second source ± 20%.
CCV	Analyze at beginning of sequence and after every 10 samples. ± 15% If bracketing CVS fails high and no detects, data may be reported. If CVS fails low on one column with no detects, data may be reported. If CVS fails low on both columns and/or there are detects, bracket	Analyze at beginning of sequence and after every 10 samples. ± 20% If bracketing CVS fails high and no detects, data may be reported. If CVS fails low on one column with no detects, data may be reported. If CVS fails low on both columns and/or there are detects, bracket	Analyze at beginning of sequence and after every 10 samples All targets within ± 20%. QSM 5.2 does not provide exception criteria for failures. Re-analyze failing target compound(s) on a passing instrument. If re-analysis is not possible, then	Analyze every 12 hours. All targets within ± 20%.

	must be reanalyzed to confirm	must be reanalyzed to confirm	failures must be documented and the corresponding data Q qualified and narrated.	
DDT and Endrin Breakdown	≤ 15% for Endrin and DDT.	≤ 15% for Endrin and DDT.	≤ 15% for Endrin and DDT.	≤ 20% for Endrin and DDT.
MB	Detects of target analytes in MB acceptable if not detected in samples or if detects in samples are 10x higher than in MB. Apply B qualifier.	Detects of target analytes in MB acceptable if not detected in samples or if detects in samples are 10x higher than in MB. Apply B qualifier.	No target analytes detected >1/2 LOQ or >1/10 the amount measured in any sample or >1/10 the regulatory limit, whichever is greater. Common contaminants must not be detected > LOQ.	Detects of target analytes in MB acceptable if not detected in samples or if detects in samples are 10x higher than in MB. Apply B qualifier.
LCS	Evaluate with SPC limits. Re-extract samples if LCS fails (can fail high if there are no detects of those analytes in samples). Over-range analytes should be diluted to bring them within the calibration range. When samples are out of holding: consult with validator or GL for industrial clients (re-extraction may not be required); for others, re-extract if within 2x holding. Narrate and DER any failures.	Evaluate with SPC limits. Re-extract samples if LCS fails (can fail high if there are no detects of those analytes in samples). Over-range analytes should be diluted to bring them within the calibration range. When samples are out of holding: consult with validator or GL for industrial clients (re-extraction may not be required); for others, re-extract if within 2x holding. Narrate and DER any failures.	Evaluate with QSM 5.2 limits in Appendix C. If analyte is not listed in the table, use SPC limits. If LCS fails, re-extract samples (can fail high if there are no detects of these analytes). Spike with ALL target analytes. If there are failures and samples cannot be re-extracted, narrate and DER. Identify compounds and validator will apply Q flag.	Evaluate with SPC limits or 608.3 limits. Re-extract samples if LCS fails (can fail high if there are no detects of those analytes in samples). Over-range analytes should be diluted to bring them within the calibration range. When samples are out of holding: consult with validator or GL for industrial clients (re-extraction may not be required); for others, re-extract if within 2x holding. Narrate and DER any failures.
MS/MSD	Evaluate with SPC limits for recovery and RPD. Confirmed failures may be attributed to matrix interference.	Evaluate with SPC limits for recovery and RPD. Confirmed failures may be attributed to matrix interference.	Evaluate with QSM 5.2 limits in Appendix C for recovery and RPD (same limits used for LCS). Confirmed failures may be	Evaluate with SPC limits or 608.3 limits for recovery and RPD. Confirmed failures may be attributed to matrix

			attributed to matrix interference.	interference.
Surrogates	Evaluate with SPC limits. If surrogates fail low, re-extract the sample for confirmation. If there is obvious matrix interference, dilution and re-analysis may be appropriate and re-extraction may not be required. If surrogates fail high with no detects, data may be reported.	Evaluate with SPC limits. If surrogates fail low, re-extract the sample for confirmation. If there is obvious matrix interference, dilution and re-analysis may be appropriate and re-extraction may not be required. If surrogates fail high with no detects, data may be reported.	Evaluate with QSM 5.2 limits. If surrogates fail low, re-extract the sample for confirmation. If there is obvious matrix interference, re-extraction may not be required. Failures are Q qualified.	Evaluate with SPC limits. If surrogates fail low, re-extract the sample for confirmation. If there is obvious matrix interference, dilution and re-analysis may be appropriate and re-extraction may not be required. If surrogates fail high with no detects, data may be reported.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

AUTOMATED SOXHLET EXTRACTION

(GL-OA-E-066 REVISON 9)

APPLICABLE TO METHOD:
EPA SW-846 Method 3541

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1.0 STANDARD OPERATING PROCEDURE FOR AUTOMATED SOXHLET EXTRACTION

2.0 METHOD CODE

EPA SW-846 Method 3541

3.0 METHOD OBJECTIVE AND PURPOSE

This procedure describes the extraction of organic analytes from soil, sediment, sludges, and waste solids. In the initial extraction stage, the sample-loaded extraction thimble is immersed in the boiling solvent. This ensures very rapid intimate contact between the sample and solvent and rapid extraction of the organic analytes. In the second stage the thimble is elevated above the solvent, and is rinse-extracted. In the third stage, the solvent is evaporated. The concentrated extract is then ready for cleanup (Method 3600) followed by measurement of the organic analytes.

4.0 SUMMARY OF THE TEST METHOD

1 to 30 grams of moist solid samples (e.g., soil/sediment samples) is chemically dried with anhydrous sodium sulfate. The prepared sample is extracted using 120 mL of solvent in the automated Soxhlet. The extraction is then concentrated, cleaned, if applicable and analyzed.

5.0 METHOD VARIATIONS

The Zymark TurboVap® II and Biotage used in place of the Kuderna-Danish apparatus for the concentration of soil sample extracts.

6.0 INTERFERENCES TO THE METHOD

6.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures.

6.2 Interferences co-extracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

6.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

6.4 Soap residue (e.g., sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, Aldrin, Heptachlor, and most organophosphorous pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be

difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem.

6.5 The extraction thimble and the o-rings used to seal the extraction cup are both sources of interference. Both should be checked by including a method blank and following the extraction, prior to use, may be necessary to eliminate or reduce interferences. Viton seals contributed least to the interference problem; however, even they contributed some interference peaks when the extraction solvent was analyzed by the electron capture detector. Use of butyl or EPDM rings are not recommended since they were found to contribute significant background when the extraction solvent was 1:1 v/v hexane/acetone or 1:1 v/v methylene chloride/acetone.

7.0 DEFINITIONS

7.1 AlphaLIMS: The Laboratory Information Management System is a computerized database system that records and reports information essential to the quality process of sample analysis.

7.2 Duplicate (DUP): Two aliquots of the same sample analyzed using identical procedures. Analysis of duplicates monitors precision associated with laboratory procedures. Duplicates are done upon customer request.

7.3 Extraction Batch: A group of 20 or fewer samples of similar matrix which are extracted together by the same person/group within the same time period using the same reagents. Each extraction batch will be uniquely identified and include appropriate QC.

7.4 Fractionation Surrogates: Compounds that are added (spiked) to the sample extracts immediately prior to the silica gel fractionation. Used to assess the efficiency of the fractionation process by measuring recovery.

7.5 Laboratory Control Sample (LCS): Reagent grade sand is fortified (spiked) with known quantities of target analytes and subjected to the entire analytical process. The LCS is used to assess the accuracy (recovery) of the method as well as the fractionation efficiency.

7.6 Laboratory Control Sample Duplicate (LCSD): A second LCS that is prepared and extracted in the same manner as the LCS (above). The LCSD is used to assess the accuracy (recovery) and precision of the method as well as the fractionation efficiency.

7.7 Lower Limit of Quantitation (LLOQ): The lowest concentration at which a target analyte can be reliably measured and reported. The LLOQ is ≥ the lowest point in the calibration curve and represents a concentration at which both quantitative and qualitative requirements can be consistently demonstrated. The LLOQ is verified quarterly, as the LOQ verification. The verification is performed by extracting and analyzing an LCS spiked at the lowest level of initial calibration curve (see appropriate analytical SOP for calibration concentration). The LLOQ verification

is carried through the same preparation and analytical procedures as environmental samples and QC. The LLOQ is analyzed on every instrument where data are reported and this is the laboratory's normal protocol. Recovery of target analytes in the LLOQ are compared to in-house-statistically-derived limits. Concentrations in samples reported below the LLOQ and above the MDL are qualified as estimated.

7.8 Matrix: The predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, the sample matrix is soil/sediment. Matrix is not synonymous with phase (liquid or solid).

7.9 Matrix Spike (MS): Aliquot of a matrix fortified (spiked) with known quantities of target analytes and subjected to the entire analytical process. The MS is used to assess the performance of the method for a particular matrix by measuring accuracy (recovery).

7.10 Matrix Spike Duplicate (MSD): A second matrix spike (MS) that is prepared and extracted in the same manner as the MS (above). The MSD is used to assess the performance of the method for a particular matrix by measuring accuracy (recovery) and precision.

7.11 Method Blank: Reagent grade sand that is subjected to the entire analytical process. The method blank is used to assess the level of laboratory background and reagent contamination. At least one method blank per extraction batch will be analyzed.

7.12 Surrogates: Compound(s) added to every blank, LCS, LCSD, sample, MS, and MSD that are used to assess analytical efficiency by measuring recovery. Surrogates are compounds that are not expected to be present in environmental media.

7.13 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions,

8.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

WARNING

METHYLENE CHLORIDE IS A POSSIBLE CARCINOGEN.

HEXANE IS FLAMMABLE AND TOXIC.

ACETONE IS HIGHLY FLAMMABLE.

WARNING

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

8.1 Wear eye protection with side shields while working in the laboratory.

8.2 All chemicals and samples should be treated as potential health hazards, and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client sample MSDSs are also maintained.

8.3 Personal protective equipment

8.3.1 Gloves are required when working with solvents, standards and samples. Solvents, along with any solute in them, can absorb easily through the skin.

8.3.2 Work under a hood when using concentrated acids.

8.3.3 To protect clothes and skin from corrosive material, wear a lab coat.

8.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines to follow:

8.4.1 Wear a dosimeter at all times while working in the lab to monitor radioactive exposure.

8.4.2 Wear a plastic apron over lab coat when working with radioactive samples.

8.4.3 Protect counter tops with counter paper or work from radioactive sample handling trays.

8.4.4 Prohibit admittance to immediate work area.

8.4.5 Post signs indicating radioactive samples are in the area.

8.4.6 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

8.4.7 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

8.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

8.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

8.6 In the event of an accident or medical emergency call for help immediately. When time and safety permit, an accident report form should be completed and turned submitted to the safety committee.

8.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

9.0 APPARATUS AND MATERIALS

9.1 Apparatus

9.1.1 Soxtherm Automated Extraction System

9.1.2 Soxtherm Extraction Beakers

9.1.3 Stainless Steel Thimble Rings

9.1.4 Zymark Turbo Vap® II Concentrator

9.1.5 Zymark Tubes

9.2 Materials

9.2.1 Auxiliary Racks

9.2.2 Treated boiling chips: Rinse with methylene chloride three times and place on aluminum foil to dry.

9.2.3 Treated Cellulose Thimble: Heat the thimbles at 135˚ for 2 to 4 hours.

9.2.4 Glass funnels

9.2.5 Filters, ashless circles, 110 mm

9.2.6 Top-Loading Balance, capable of accurately weighing 0.01 grams

9.2.7 2 mL Autosampler vials with Teflon-lined caps

9.2.8 Syringe, 1 to 10mL

9.2.9 Beakers, various sizes as needed.

9.2.10 Vials, glass, various capacities as needed, with Teflon-lined caps.

9.2.11 Disposable pipettes, 1 to 10 mL

9.2.12 Tongue depressors

10.0 REAGENTS AND STANDARDS

10.1 Reagents

10.1.1 Methylene chloride (CH_2Cl_2), pesticide quality or equivalent

10.1.2 Hexane (C_6H_{14}), pesticide quality or equivalent

10.1.3 Acetone (CH_3COCH_3), pesticide quality or equivalent

10.1.4 1:1 Methylene chloride/Acetone: Add 1000 mL methylene chloride to 1000 mL of acetone in 2000 mL flask with tilt.

10.1.5 1:1 Hexane/Acetone: Add 1000 mL of hexane to 1000 mL of acetone in a 2000 mL flask with tilt.

10.1.6 Treated sodium sulfate, granular, anhydrous, ACS grade: Purify by heating at 400° C for 4 hours in a shallow tray, or by pre-cleaning the sodium sulfate with methylene chloride. A method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

10.1.7 Reagent grade sand purity by muffling at 400°C for 4 hours in a shallow tray.

10.1.8 A method blank must be analyzed demonstrating that there is no interference from the reagent grade sand.

10.1.9 Nitrogen gas, UHP grade

10.2 Standards

10.2.1 LLOQ standard solutions are purchased directly from a certified vendor or made by diluting the working standards.

11.0 SAMPLE HANDLING AND PRESERVATION

11.1 Sample containers are glass or Teflon with a Teflon-line screw cap. Plastic containers are not used to prevent phthalate or hydrocarbon contamination.

11.2 Protect sample containers from light. Some analytes are light sensitive.

11.3 Samples will be maintained at 0° $\leq$ 6° C until extraction begins.

11.4 Samples must be extracted within fourteen days from collection.

11.5 If samples are not in appropriate containers or holding time has expired, notify the Group Leader or the PM for further instructions.

12.0 SAMPLE PREPARATION

12.1 All Batches (up to 20 samples) will be extracted with a MB, LCS, MS, MSD. If insufficient sample is provided, the MS/MSD will be substituted with a LCS DUP.

12.2 Rinse all glassware with appropriate solvent. Label glassware with the sample number.

12.3 For sediment/soil samples decant and discard any water layer. Homogenize the sample before a representative aliquot is taken. Discard sticks, leaves, rocks, etc. Removal of any extraneous material must be documented in the case narrative and bench logbook.

12.4 Dried sediment/soil and dry waste samples amenable to grinding. Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extracted through a 1 mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 20g after grinding.

NOTE: Grinding should only be performed when analyzing for non-volatile organics.

12.5 Gummy, fibrous, oily materials not amenable to grinding should be cut, shredded or otherwise broken up to allow mixing and maximum of the sample surfaces for extraction.

12.6 Add 2 to 3 treated boiling chips and thimble ring to the extraction beaker and rinse thoroughly with extraction solvent.

12.7 Insert a treated thimble by placing in the thimble ring. Label glassware with the sample number.

12.8 Weigh 1 to 30 grams of sample inside of thimble. Record the weight in LIMS.

NOTE: Sample size may be adjusted to meet required detection limits. Sample size may also be adjusted in cases of known or suspended high levels of analyte.

12.9 For paint chip analysis for PCBs. Weigh 1.0g of sample. Record to the nearest 0.1g.

12.10 For swipe analysis, calculations are determined per swipe. Extract the entire swipe.

12.11 Add anhydrous sodium sulfate (Na_2SO_4) granular and mix well to obtain free flowing sample.

NOTE: The spiking and surrogate solutions should be added after the sodium sulfate drying agent to prevent significant recovery issues.

12.12 Add 1 mL appropriate surrogate to all samples and 1 mL of spiking solution to quality control samples. Peer witnessing is practiced during this process.

NOTE: This is for a final volume of 1 mL. (If a different concentration of spiking solution is used, the final volume changes, or the true value changes, adjust solution volume accordingly to determine the new amount of spiking solution to use.)

NOTE: Sample must be free flowing, if not add more treated sodium sulfate.

12.13 Add 120 mL of extraction solvent to the extraction beaker. Add the solvent gently; pouring aggressively may displace the sample from the thimble. Refer to section 22.0 to choose the applicable solvent.

13.0 EXTRACTION PROCEDURE

13.1 Soxtherm Extraction of Solid Samples

13.1.1 Samples are extracted using the Automated Soxhlet Extractor (Soxtherm).

13.1.2 Turn the Soxtherm unit on and verify that the air and water valves are on.

13.1.3 Check the sight glass on the front of the unit to see if the solvent collection tank needs to be drained. When solvent level reaches the bottom of the red mark the collection tank is full. It is good practice to drain the tank before it reaches the bottom of the red mark.

NOTE: Drain in the appropriate waste bottle.

13.1.4 Install the extraction beakers onto the Soxtherm by depressing the holding clamp and carefully sliding the beaker onto the bottom of the Teflon fitting.

13.1.5 Start the automated sequence as follows:

13.1.5.1 Start extraction by pressing “Analysis Start” and then Enter.

13.1.5.2 Select the Soxtherm instruments that will be used for the extractions (U1 through U4).

13.1.5.3 Choose the applicable program then press Enter. Display then asks to confirm program by pressing Enter. Record start time.

NOTE: Refer to Table 1-3 in Section 22.0 for parameters of each program.

13.1.5.4 Press Enter when time and date are displayed. The door of the extractor will close and the extraction beaker will be lowered onto the heating mantle.

NOTE: The soxtherm equipment will give an audio alarm (beeping) if any part of the apparatus requires attention.

13.1.5.5 The extraction is complete when the control box reads "PROGRAM COMPLETE" and the extraction beakers rise off the heating mantle. Record end time.

13.1.5.6 When the extraction beaker has cooled to near room temperature, remove extraction beakers from the soxtherm.

13.1.5.7 If the extract appears to contain water (noticeable droplets or layer on top of the solvent), the following procedure must be used to dry the extract: Otherwise, proceed to section 13.1.5.7.6.

13.1.5.7.1 Add treated sodium sulfate directly to the extract in the extraction beaker. Enough sodium sulfate must be added to cover the bottom of the beaker. Swirl the beaker so that the extract has good contact with the sodium sulfate.

NOTE: Sodium sulfate must be free flowing, if not add more treated sodium sulfate.

13.1.5.7.2 Pour the dried extract in a labeled Zymark tube. Rinse the extraction beaker with 10 to 15 mL of the extraction solvent and add this rinsate to the Zymark tube.

13.1.5.7.3 Alternatively, place a piece of fluted filter paper inside a glass funnel.

13.1.5.7.4 Rinse treated sodium sulfate with the extraction solvent.

13.1.5.7.5 Pour the extract through the packed funnel and collect the dried extract in a labeled Zymark tube The packed funnel must then be rinsed with 10 to 15 mL of the extraction solvent and this rinsate must be collected in the Zymark tube. Proceed to section 13.1.5.7.7.

13.1.5.7.6 Pour the extract in a labeled Zymark tube. Rinse the extraction beaker and thimble with 10-15 mL of the extraction solvent and add this rinsate to the Zymark tube.

13.1.5.7.7 Remove thimble ring and thimble containing spent sample to a hood. Allow thimble and spent sample to air dry. After completely dry, discard the thimble and spent sample in the spent solid waste container.

13.1.5.8 Check that the nitrogen supply to the TurboVap® is turned on.

13.1.5.9 Check the reagent water level in the TurboVap®. It must be at least as high as the inside rack, but not higher than the holes above rack.

13.1.5.10 With the cover closed, turn the unit on and select the pressure mode.

13.1.5.11 Open the lid of the TurboVap® and place the Zymarks in the water bath.

13.1.5.12 Close the cover.

NOTE: During this time extracts need to be checked periodically so that extracts do not go dry. In some cases extracts may need to go longer.

13.1.5.13 Press the cell position START/STOP button. The button's corresponding cell light will come on.

13.1.5.14 Check the gas pressure to verify that the conditions have not changed.

13.1.5.15 For PCBs, concentrate to 1 to 2 mL in Turbo Vap tube and proceed to step 13.1.5.16. For Pesticides, concentrate to 5 mL in Turbo Vap tube and proceed to step 13.1.5.16 if required by client. For BNA and DRO concentrate to 1 mL.

NOTE: Do not allow extract to go below 0.5 mL due to the potential for lower recoveries.

13.1.5.16 Proceed with clean up if necessary. Refer to GL-OA-E-037 for Sulfuric Acid/Permanganate Cleanup of PCB solvent Extract. Refer to GL-OA-E-036 for Florisil Cleanup of Organochlorine Pesticide Solvent Extracts.

13.1.5.17 Transfer to 2 or 4 mL amber vial with Teflon-lined screw cap using a 1 mL disposable pipet. Record final volume. Label wit AlphaLIMS-generate label. Mark the meniscus. All extracts with the exception of those to be analyzed using

BNA 8270C and 8270D should be stored at 0 <6 ˚C. The BNA 8270C and 8270D should be stored in a frost-free freezer at less than -10 ˚C.

13.1.5.18 Refer to GL-LB-E-003 for Soxtherm glassware cleanup.

14.0 EQUIPMENT MAINTENANCE

Maintenance to these devices are recorded in LIMS in an electronic logbook .

15.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL SAMPLES

15.1 Source standards are purchased as certified mixtures. Documentation of the standard's quality and traceability should be provided from the vendor. This documentation is submitted to the Quality department. Standards may be purchased from outside vendors, including o2si smart solutions., NSI, Inc., AccuStandard, Restek, and Supelco. Other vendors on GEL's Approved Vendors list may also be used.

15.2 Source standards are assigned a unique code number for the purpose of traceability. The standard, along with its code, is recorded in AlphaLIMS. AlphaLIMS can be used to generate a label which is affixed to the standards container, or a handwritten label may be created.

15.3 Stock, intermediate, and working standards are likewise assigned a unique code number and recorded in AlphaLIMS.

NOTE: For recipes, concentrations, analytes and diluents generally used, refer to the Create/Edit/View Reference Materials section of AlphaLIMS.

16.0 QUALITY CONTROL REQUIREMENTS

Typically, a blank, laboratory control sample (LCS), matrix spike (MS), and matrix spike duplicate (MSD) are extracted and analyzed with each prep batch. However, this may vary depending on such factors as sample availability and client requirements. Other client requirements may include a laboratory control sample duplicate (LCSD). They are carried through all stages of sample preparation and analysis.

17.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

A review process is used to insure the quality of the data. Extraction logs are peer reviewed by a second technician or group leader. When the reviewer is satisfied that the data have been entered correctly, a data report is generated from AlphaLIMS. The report along with the batch sheets are copied and submitted to the appropriate analytical area for analysis.

18.0 RECORDS MANAGEMENT

18.1 Documentation of Training

Extraction technicians must be properly trained to perform the contents of this SOP. Personnel will extract four laboratory control samples for each analytical SOP referenced within this SOP as training commences. The documents are maintained as quality documents in the employee's training file.

18.2 Documentation of Extraction

18.2.1 In AlphaLIMS, complete the Sample Tracker Form. Record initial weight of sample, final volume of extract, amount of surrogate and spikes added, and any comments about the extraction process. Also record all reagent lot numbers and note any deviations from this standard operating procedure.

18.2.2 Print a hard copy to submit with the extracts.

18.2.3 Have batch peer reviewed using data review sheet. Note all discrepancies about sample handling and preservation.

18.2.4 All documents are stored in AlphaLIMS.

18.3 Documentation of Standards

Refer to GL-LB-E-007.

19.0 SAFETY AND POLLUTION PREVENTION

Follow all laboratory safety rules for preparation, analysis and handling of the reagents of interest. Reference method SOPs and the GEL safety plan for guidance.

20.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

21.0 REFERENCES

21.1 "Test Methods for Evaluation of Solid Wastes, Physical/Chemical Methods", SW-846, Third Edition, Method 3500B, Revision 2, 1996.

21.2 "Test Methods for Evaluation of Solid Wastes, Physical/Chemical Methods", SW-846, Third Edition, Method 3541, Revision 0, 1994.

21.3 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.1.1, February 2018.

22.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

22.1 BNA/DRO parameters

Table 1 Soxtherm Program 01 Parameters

Parameter	Value or Instrument Setting
Extraction Solvent	1:1 Methylene Chloride/Acetone (1:1v)
Initial Solvent Volume	120 mL
Extraction Temperature	150° C
Hot Extraction	10 minutes
Reduction Pulse	3 s

Evaporation A	4 x interval
Rinse Time	30 minutes
Evaporation B	1 x interval
Evaporation C	1.0 minutes
Run Time	1 hr 01 min

22.2 DRO parameters

The DRO extraction uses the BNA program with methylene chloride only as the extraction solvent.

22.3 PEST parameters

Table 2 Soxtherm Program 02 Parameters

Parameter	Value or Instrument Setting
Extraction Solvent	Hexane/Acetone (1:1v)
Initial Solvent Volume	120 mL
Extraction Temperature	165° C
Hot Extraction	20 minutes
Reduction Pulse	3 s
Evaporation A	3 x interval
Rinse Time	20 minutes
Evaporation B	1 x interval
Evaporation C	0.0 minutes
Run Time	52 min

22.4 PCB parameters

Table 3 Soxtherm Program 03 Parameters

Parameter	Value or Instrument Setting
Extraction Solvent	Hexane
Initial Solvent Volume	120 mL
Extraction Temperature	160˚ C

Hot Extraction	1 hr
Reduction Pulse	3 s
Evaporation A	3 x interval
Rinse Time	1 hr
Evaporation B	1.0 x interval
Evaporation C	0.0 min
Run Time	2 hr 04 min

23.0 HISTORY

Revision 9: Updated section 11.5 to include clarification if there are issues with holding times or containers. Updated DOD QSM reference to 5.1.1, February, 2018.

Revision 8: Added LLOQ in definitions section. Added reference to new DoD/DoE QSM version 5.1, January 2017. Removed reference to obsolete SOP.

Revision 7: Updated Reagents Section to reflect current practices

Revision 6: Updated Section 3.0 to include current apparatus.

Revision 5: Methylene chloride added to materials section. Recording of start time and end time included for automated sequence on extraction procedure.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR SOLID PHASE – EXTRACTION

(GL-OA-E-070 REVISION 11)

APPLICABLE TO METHODS:
EPA SW-846 3535A, 3535

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1.0 STANDARD OPERATING PROCEDURE FOR SOLID PHASE-EXTRACTION

2.0 METHOD CODE

EPA SW-846 3535A and 3535.

3.0 PURPOSE

To describe the manner in which aqueous matrices that include groundwaters, wastewaters and Toxicity Characteristic Leaching Procedure (TCLP method 1311) are extracted using Solid Phase Extraction (SPE) media for organic analysis methods, 8081, 8081A, 8081B, 8082A, 8015A, 8015B, 8015C and 8015D and 608. Refer to SOP GL-OA-E-033, appendix 2 for SPE preparation for method 8330A. This method may not be appropriate for aqueous samples with high levels of suspended solids greater than 1%.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all glass systems may be necessary.

4.2 The decomposition of some analytes has been demonstrated under basic extraction condition. Organochlorine pesticides may dichlorinate and phthalate esters may hydrolyze. The rate of these reactions increases with increasing pH.

4.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

4.4 Soap residue (e.g., sodium dodecyl sulfate), which results in basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorous pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500 mL Kuderna-Danish flask). These items should be hand rinsed very carefully to avoid this problem.

4.5 Bonded – phase silica (e.g., C18) will hydrolyze on prolonged exposure to aqueous samples with pH levels of less than 2 or greater than 9. Hydrolysis will increase at the extremes of the pH ranger and with longer contact time. Hydrolysis may reduce extraction efficiency or cause baseline irregularities. Styrene divinylbenzene (SDB) extraction disks should be considered when hydrolysis is a problem.

4.6 Sample particulates may clog the solid – phase media and result in extremely slow sample extractions. Aqueous samples with high levels of suspended solids greater

than 1 % as the extraction efficiency may not be sufficient. However, a 5% solution was filtered using this procedure and no problems were encountered.

5.0 METHOD DEVIATION

5.1 Sample pH adjustment to ≤ 2 with 15 mL of 1:1 H_2SO_4.

5.2 No specific wait time for sample/QC after the addition of surrogate/spike but samples are at a stand while analyst is cleaning glassware and conditioning cartridges for the process.

6.0 DEFINITIONS

6.1 Laboratory Duplicate (DUP, LCSD, or MSD): Aliquots of a sample taken from the same container and processed in the same manner under identical laboratory conditions. The aliquot is analyzed independently from the parent sample and the results are compared to measure precision and accuracy.

6.2 Lower Limit of Quantitation (LLOQ): The lowest concentration at which a target analyte can be reliably measured and reported. The LLOQ is the lowest point in the calibration curve and represents a concentration at which both quantitative and qualitative requirements can be consistently demonstrated. The LLOQ is verified quarterly, as the LOQ verification. The verification is performed by extracting and analyzing an LCS spiked at the lowest level of initial calibration curve (see appropriate analytical SOP for calibration concentration). The LLOQ verification is carried through the same preparation and analytical procedures as environmental samples and QC. The LLOQ is analyzed on every instrument where data are reported and this is the laboratory's normal protocol. Recovery of target analytes in the LLOQ are compared to in-house-statistically-derived limits. Concentrations in samples reported below the LLOQ and above the MDL are qualified as estimated.

6.3 Surrogates: Compounds added to every blank, LCS, LCSD, sample and MS and MSD that are used to assess analytical efficiency by measuring recovery. Surrogates are compounds that are not expected to be present in environmental media.

6.4 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

7.0 APPARATUS AND MATERIALS

7.1 Manifold system

7.2 Collection tube (40 mL vial) - This tube should have an appropriate length so that the drip tip of the standard apparatus can be positioned well into the neck of the tube to prevent splattering.

7.3 Muffle furnace, capable of maintaining 400° C

7.4 Bottle adapter

7.5 Enviro-clean Universal C18 cartridge (#ECUNIC18) and (#ECUNIPAH)

7.6 Cartridge holder

7.7 Kuderna – Danish (KD) apparatus

7.8 Three – Ball macro – synder column

7.9 Two – Ball micro synder column (optional)

7.10 Boiling chips (solvent extracted approximately 10/40 mesh silicon carbide or equivalent.

7.11 Water bath (heated, capable of temperature control to within +/- 5°C. The bath should be in a hood.

7.12 Nitrogen Evaporator apparatus (N – EVAP) Organaomation model 112 or equivalent.

7.13 Glass vials (size 2mL or 10 mL) equipped with polytetrafluoroethylene (PTFE) lined caps for storage.

7.14 Vacuum system

7.15 Graduated cylinders

7.16 Concentrators tubes (10 mL)

7.17 Disposable pipets (1mL)

7.18 Disposable cartridge filter

7.19 Wide range pH indicator paper

7.20 Turbovap II Biotage

7.21 Zymark or Turbovap tubes

7.22 Erlenmeyer flask

7.23 Glass Rods

8.0 REAGENTS AND STANDARDS

8.1 Reagents: Reagents must meet ACS analytical criteria. Reagents will not be stored in plastic containers.

8.1.1 Eluting solvents will be screened prior to use.

8.1.2 Dichloromethane (CH_2CL_2), pesticide quality or equivalent.

8.1.3 Acetone (CH_3COCH_3), pesticide quality or equivalent

8.1.4 Organic – Free reagent water

8.1.5 Sodium Sulfate (granular, anhydrous) NA_2SO4 purify by heating at 400 °C for 4 hours in a shallow tray.

8.1.6 Sulfuric Acid solution (1:1 v/v) - Slowly add 50 mL of concentrated H2SO4 to 50 mL of organic-free reagent water.

8.1.7 Sodium hydroxide solution (10N), NaOH - Dissolve 40 g of NaOH inorganic-free reagent water and dilute to 100 mL.

8.1.8 Methanol (CH_3OH)

8.1.9 Hexane (C_6H_{14})

8.1.10 LLOQ standard solutions are purchased directly from a certified vendor or made by diluting the working standards.

9.0 EQUIPMENT MAINTENANCE

To assure that the manifold is not getting clogged or affected by the acid after samples have completed the extraction process 25 mL of deionized water is flushed through the manifold. Maintenance to these devices are recorded in LIMS in an electronic logbook.

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Sample containers are glass or Teflon with Teflon-lined screw cap.

10.2 Protect sample containers from light. Some analytes are light sensitive.

10.3 Sample will be maintained at 0º ≤ 6º C until extraction begins.

10.4 Samples for semivolatile organic analysis have a 7 day holding time from the collection date. PCB samples must be extracted within 1 year from collection.

10.5 If samples are not in appropriate containers or holding time has expired, initiate a Data Exception Report (DER). For instructions, refer to GL-QS-E-004.

11.0 SAMPLE PREPARATION

11.1 All batches (up to 20 samples) will be extracted with a blank, LCS, MS, and MSD. If insufficient sample is provided, the MS/MSD will be submitted with a LCS/LCS DUP.

NOTE: It is inappropriate to extract only a portion of a sample from a sample container when using SPE. If < 3 L is received for the QC sample, an LCSD Duplicate will be extracted with the batch also. A matrix spike only will be included if volume is available. The client will also be notified. If this approach is not acceptable to the client, per section 11.1 of the method, an aliquot may be transferred to a graduated cylinder and spiked. However, in such instances, the analyst must take great care to mix the sample well, by shaking, to ensure a homogeneous distribution of the particulate matter and must record the fact that the container was not rinsed.

11.2 Cartridge set-up and conditioning

NOTE: The sample will be inspected visually prior to extraction. If the sample contains > 1 inches of sediment in the bottom, this procedure should not be used. Approximately 1 inch of glass wool is added to each filter to aid in filtration process. If samples contain >5% TSS (>1 inches of sediment in bottom of bottle), the liquid fraction will be decanted and prepped by SPE and the solids will be filtered off and prepped by soxtherm and then physically combined into one extract for analysis.

11.2.1 Arrange the cartridges on the manifold in the closed valve position.

11.2.2 Turn on the vacuum pump and set the vacuum to 10 inches (254 mm) of Hg. Do not exceed the manufacturer's recommendation for manifold

vacuum. Flow rates may be controlled by opening and closing cartridge valves.

11.2.3 Condition the cartridges by adding 10 mL of Dichloromethane to each cartridge and allow soaking on the cartridge for approximately 1.5 min.

11.2.4 Open the valve and pull the Dichloromethane through the cartridge to waste leaving a layer just covering the frit with the valve now close.

NOTE: Cartridge conditioning for Diesel Range Organics (DRO) does not include the use of solvent acetone. Proceed to step 11.2.6.

11.2.5 Add 10 mL of Acetone to the cartridge and let the acetone soak for approximately 1.5 minutes. Open the valve and pull the acetone to the waste and air dry the cartridge with full vacuum for a few seconds and close valve.

11.2.6 Add approximately 10 mL of Methanol to the cartridge and allow soaking for approximately 1.5 minutes. From this point until sample addition the cartridge must not go dry. Open valve and pull some of the methanol through the cartridge leaving a layer just covering the frit and close valve.

11.2.7 Add approximately 20 mL of deionized water to the cartridge and open the valve to pull most of the water through the cartridge to waste but do not allow the sorbent to dry.

12.0 EXTRACTION PROCEDURE

12.1 Sample Preparation

12.1.1 Equilibrate the batch of samples to room temperature.

12.1.2 Sample volume of 1000 mL is used for the extraction or the entire bottle. Mark the level of the sample on the outside of the sample container for later determination of the sample volume used. Check the initial pH of each sample and document. Sample final volume can be determined by using the computer calculation of weight to volume. This information is recorded and generated in AlphaLIMS.

12.1.2.1 If sample bottle(s) is full to the rim, transfer sample to precleaned graduated cylinder.

NOTE: All pH measurements require the use of a disposable pipet to deliver small aliquot of sample to a wide-range pH indicator strip.

12.1.3 Transfer any surrogate and matrix spiking compounds (if applicable) to the samples in the original container or graduated cylinder. A peer must witness and document that the spiking process was correctly performed and the correct spike solutions added.

12.1.4 The pH of the sample needs to be adjusted to a designated value of less the 2 with 15 mL of 1:1 sulfuric acid solution. This pH adjustment should be performed after the addition of the surrogates and spikes. The samples that

are in the graduated cylinder are transferred back to its original container, then recapped and shaken thoroughly for a good mixture.

NOTE: Since C18 cartridges are being used for this method, pH must be < 2; Decachlorobiphenyl surrogate has a partial charge which prevents proper bonding to a C18 functional group. Protonating the DCB has been shown to neutralize the charge allowing for a better bond. This allows acceptable recoveries of the DCB surrogate.

12.1.5 Check the pH to make sure that it is within the required range and record.

12.1.6 Shake the container with the cap tightly sealed, to ensure that any particulate matter is evenly distributed throughout the sample.

12.1.7 Turn on the vacuum. Place the sample containers on the manifold apparatus with a quick flipping of the wrist on the bottle adaptor.

12.1.8 Open the valves of each setup to allow the sample to filter through. The sample should pass through the cartridge in approximately 15 – 20 minutes.

NOTE: The excess sample remaining inside the graduated cylinder after the transfer is to be placed in the original container that has been completely filtered and reapplied back on the manifold for complete filtration of the entire bottle.

12.1.9 Allow the cartridge to dry under full vacuum for 10 minutes and close the valves. The sample waste is collected into a waste carboy that is connected to the apparatus.

12.2 Sample Elution

12.2.1 Place a 40 mL receiving vial under each cartridge.

NOTE: The elution for DRO (Diesel Range Organic) is performed with Dichloromethane only.

12.2.2 Rinse the sample bottle that held the sample with 5 mL of acetone and transfer to the cartridge. Allow the solvent to soak for 1 minute and open the valves to vacuum pulling the acetone into the receiving vial then close valve.

12.2.2.1 First, rinse the graduated cylinder containing the sample(s) with 5 mL of acetone. Transfer the rinse to the sample bottle then transfer onto the cartridge. Allow the solvent to soak for 1 minute and open the valves to vacuum, pulling the acetone into the receiving vial, then close valve. Proceed as instructed in section 12.2.3.

12.2.3 Repeat step 12.2.2 three more times using 10 mL Dichloromethane each time. Allow the solvent to soak for 1 minute, then pull through by vacuum into the receiving vial. The final volume of the elution should not exceed 40 mL.

12.3 K-D Concentrated Technique

12.3.1 Where necessary to meet the sensitivity requirements of the particular

application, sample extract may be concentrated to the final volume necessary for the determinative method and specific application using the K –D technique and nitrogen evaporation or TurboVap evaporator.

12.3.2 Assemble a pre-solvent rinsed Kuderna –Danish (K-D) and 10 mL concentrator tube.

12.3.3 Dry the extract in the collection tube by shaking to mix very well then pour on the thistle funnel containing anhydrous Sodium Sulfate. Collect the dried extract in the K-D concentrator setup. Note: Water is in the extract so while pouring on the sodium sulfate use a glass pipet to mix and break up the clumps of sodium sulfate. Otherwise this will result low recoveries.

12.3.4 Rinse the collection tube and drying column in to the K-D apparatus with an additional 20 mL portion of dichloromethane in order to achieve a quantitative transfer.

12.3.5 Add clean boiling chips to K-D apparatus and attach a pre-wet three ball snyder column. Note: At the proper rate of distillation the balls of the snyder column will actively chatter, but the chambers will not flood.

12.3.6 When the apparent volume of the liquid reaches 2 mL, remove the K-D apparatus from the water bath and allow to drain and cool for 10 minutes.

12.3.7 If a solvent exchange is needed add 10 mL of exchange solvent through the snyder column and mix with a swirling motion. Refer to Appendix 1 for extraction conditions.

12.3.8 Concentrate the extract by placing on the water bath which is at the temperature to maintain proper distillation rate. Allow the sample to remain on the water bath until for an approximate 5 mL final volume or for no more than 30 minutes.

12.3.9 Proceed with clean-up if necessary. Refer to Appendix 1 for appropriate clean-up.

12.3.10 Remove K-D apparatus from the water bath allowing to cool and drain for 10 minutes. Label all concentrator tubes before disassembling the apparatus. If further concentration is needed place extract on a nitrogen evaporator (N-EVAP) at 35°C to reach final volume.

12.3.11 Quantitatively transfer the extract to a 2 ml amber vial with Teflon lined cap.

12.4 Turbovap Concentration Technique

12.4.1 Sample extract may be concentrated to the final volume necessary for the determinative method and specific application using the Turbovap technique.

12.4.2 Solvent rinse Turbovap and anhydrous sodium sulfate prior to use.

12.4.3 Transfer the lower layer methylene chloride (top layer is water residue)

from the collection tube to the labeled turbovap tube. Add anhydrous sodium sulfate to the collection tube that contains the water layer. Use a glass rod to break up clumps of sodium sulfate. Not breaking up the clumps may result in lower recoveries. Rinse the collection tube several times with the extraction solvent and add to the turbovap tube.

12.4.4 Check the reagent water level in the turbovap. Make sure to have adequate water covering the bottom rack and not to exceed the level of the top rack.

12.4.5 Open the lid of the Turbovap and gently place the turbovap tube in the water bath rack. Close the cover.

NOTE: During this time, extracts should be monitored periodically, so that extracts do not evaporate completely. Not all extracts evaporate at the same rate.

12.4.6 When the apparent volume of liquid reaches 2-5 mL and if a solvent exchange is needed, add approximately 10-15 mL of the exchange solvent to the turbovap tube. Gently swirl the tube to mix and rinse side of the tube. Return to the water bath for further concentration. Refer to Appendix 1 for extraction conditions.

12.4.7 If clean-up is needed, refer to Appendix 1 for appropriate clean-up.

12.4.8 Quantitatively transfer the final extract to a 2 mL vial with Teflon lined cap.

13.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL SAMPLES

13.1 Source standards are purchased as certified mixtures. Documentation of the standard's quality traceability should be provided from the vendor. This documentation is submitted to the Quality Department. Standards may be purchased from outside vendors, including o2si smart solutions, AccuStandard, Inc., Restek, NSI Solutions, Inc., and Supleco. Other vendors on GEL's vendor list may also be used.

13.2 Source standards are assigned a unique code number for the purpose of traceability. The standard, along with its code, is recorded in AlphaLIMS. AlphaLIMS can be used to generate a label that is affixed to the standards container, or a handwritten label may be created.

13.3 Stock, intermediate, and working standards are likewise assigned a unique code number and recorded in AlphaLIMS.

14.0 SAFETY AND POLLUTION PREVENTION

Follow all laboratory safety rules for preparation, analysis, and handling of the reagents of interest. Refer to method SOPs and the GEL safety plan for guidance.

15.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

WARNING

METHYLENE CHLORIDE IS A POSSIBLE CARCINOGEN.

HEXANE IS FLAMMABLE AND TOXIC.

ACETONE IS HIGHLY FLAMMABLE AND TOXIC

SULFURIC ACID IS CORROSIVE, CAUSES SERIOUS BURS AND MAY BE FATAL IF SWALLOWED.

15.1 PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

15.2 WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

15.3 Wear eye protection with side shields while working in the laboratory.

15.4 All chemicals and samples should be treated as potential health hazards, and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents are maintained in the laboratory. Individual sample MSDS forms provided by the clients are kept in Login.

15.5 Personal protective equipment:

15.5.1 Gloves are required when working with solvents, standards, and samples. Solvents, along with any solute in them, can absorb easily through the skin.

15.5.2 Work under a hood when using concentrated acids and solvents.

15.5.3 To protect clothes and skin from exposure to corrosive material, wear a lab coat.

15.6 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

15.6.1 Wear a dosimeter at all times to monitor radioactive exposure while working in the lab.

15.6.2 Wear a plastic apron over lab coat when working with radioactive samples.

15.6.3 Protect counter tops with counter paper or work from radioactive sample handling trays.

15.6.4 Prohibit admittance to immediate work area.

15.6.5 Post signs indicating radioactive samples are in the area.

15.6.6 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

15.6.7 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

15.7 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

15.7.1 Segregate solid wastes from liquid wastes in the satellite area containers.

15.7.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

15.8 Snyder columns may shoot off due to pressure inside the K-D.

15.9 In the event of an accident or medical emergency call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

15.10 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

16.0 QUALITY CONTROL

The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples. A recovery check must be performed using standards of the target analytes at known concentrations. Therefore, the LCS, extraction blank and all other quality control samples must be processed with the same procedure as client samples.

17.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

A review process is used to insure the quality of the data. Extraction logs are peer reviewed by a second technician or group leader. When the reviewer is satisfied that the data have been entered correctly, a data report is generated from AlphaLIMS. The report along with the batch sheets are copied and submitted to the appropriate analytical area for analysis.

18.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

19.0 RECORDS MANAGEMENT

19.1 Documentation of Training

19.1.1 Analysts and technicians must be properly trained to perform the contents of this SOP. Personnel will extract 4 laboratory control samples for each analytical SOP referenced within this SOP as training commences. Training records are maintained as quality records. LCS/LCS DUP will demonstrate on a continuing basis that personnel are properly trained.

19.2 Documentation of Extraction

19.2.1 Complete sample tracker form as described in the appropriate extraction

procedure. Record the initial and final volumes of the extract, and any comments about the cleanup process. Also record all reagent lot numbers. Note any deviations from this SOP in the comment section.

19.2.2 Have batch peer reviewed using data review sheet. Note all discrepancies. These documents are stored in AlphaLIMS.

19.3 Documentation of Standards

Refer to GL-LB-E-007 for Laboratory Standards Documentation.

20.0 LABORATORY WASTE HANDLING AND DISPOSAL: SAMPLES, EXTRACTS, DIGESTATES, AND REAGENTS

For the proper handling and disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

21.0 REFERENCES

21.1 Single Laboratory Evaluation of Method 8060-Phthalate Esters EPA/600/4-89/039, V. Lopez-Avila, W .Beckert , et.al.,

21.2 Determination of Eight Organochlorine Pesticides at low Nanogram/Liter Concentration in Groundwater Using Filter Disk Extraction and Gas Chromatography, JAOAC International, 75(6),pp. 1091-1099,1992 3M Data Submission to EPA, C. Markell

21.3 Test Methods for Evaluating Solid Waste EPA manual SW846, 3rd Edition, June 1997, Method 3535A "Solid – Phase Extraction".

21.4 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.3, July 2019.

22.0 HISTORY

Revision 7: Removed HR-E-003 for training reference.

Revision 8: Updated Appendix

Revision 9: Added LLOQ in definitions section. Added reference to new DoD/DoE QSM version 5.1, January 2017.

Revision 10: Updated to include turbovap equipment and process of usage.

Revision 11: Revised to reflect current practices. Updated the DOD QSM Version 5.3, July 2019

APPENDIX 1: EXTRACTION CONDITIONS

Extraction Conditions for Various Water Analyses

Prep	Analysis	Surrogate/Spike[a]	Extraction pH	Solvent Exchange	Clean up Required
Pesticide/ PCB[c]	8081B	Pesticide Surrogate/[d] Pesticide Spike	<2	Hexane	Florisil
PCB	8081B 8082A	Pesticide Surrogate/[e] PCB H_2O Spike	<2	Hexane	$KMnO_4$/ H_2SO_4
TPH/DRO	8015C 8015D	TPH Surrogate/ TPH Spike	<2	None	
Pesticide/ PCB	608	Pesticide Surrogate[d]/ 608 Spike	<2	Hexane	Florisil
PCB	608	Pesticide Surrogate /[e] PCB H_2O Spike	<2	Hexane	$KMnO_4$/ H_2SO_4
Pesticide[b]	TCLP	Pesticide Surrogate / [e] TCLP Pesticide Spike/ Toxaphene/ Chlordane	<2	Hexane	
PCB	TCLP	Pesticide Surrogate/ [e] PCB Spike	<2	Hexane	$KMnO_4$/ H_2SO_4

a: Other spiking compounds may be used if client requests non-regulated compounds.

b: GEL has defined Method 8081/8081A into two classes of compounds: Pesticides and Pesticides/PCBs. When a batch consists of samples requesting Pesticides and/or Pesticides/PCBs, use Pesticide Surrogate and Pesticide Spike.

c: Pesticide surrogate 1000 ug/L

d: Pesticide surrogate 200 ug/L

NOTE: For recipes, concentrations, analytes and diluents generally used, refer to the Create/Edit/View Reference Materials section of AlphaLIMS.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

GEL LABORATORIES, LLC

QUALITY ASSURANCE PLAN

(GL-QS-B-001 REVISION 33)

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SECTION 1
INTRODUCTION

Section 1 - Introduction

GEL Laboratories, LLC (GEL) is a privately owned environmental laboratory dedicated to providing personalized client services of the highest quality. Our mission is to be the "Analytical Firm of First Choice."

GEL was established as an analytical testing laboratory in 1981. Now a full service lab, our analytical divisions use state of the art equipment and methods to provide a comprehensive array of organic, inorganic, radiochemical, and bioassay analyses and related support services to meet the needs of our clients.

This Quality Assurance Plan provides an overview of our quality assurance program for analytical services. Outlined in this plan are the responsibilities, policies, and processes essential to maintaining client satisfaction and our high quality of performance. The Director of Quality Systems is responsible for revising, controlling, and distributing the QAP. It is updated/reviewed at least annually.

Everyone on our staff is expected to understand the policies, objectives, and procedures that are described in this plan and to fully appreciate our commitment to quality and their respective roles and responsibilities with regard to quality. We also expect any analytical subcontractors we employ to perform in accordance with the quality assurance requirements delineated in this plan. All GEL employees are required to participate in Annual Quality Systems training.

This Quality Assurance Plan (QAP) has been prepared according to the standards and requirements of the US Environmental Protection Agency (EPA), ANSI/ISO/IEC 17025-2017, and the National Environmental Laboratory Accreditation Conference (NELAC) Quality Systems Standards June 2003 effective July 2005, and the TNI (The NELAP Institute) Standards adopted in August, 2009.

1.1 Quality Policy

GEL's policy is "to provide high quality, personalized analytical services that enable our clients to meet their environmental needs cost effectively."

We define quality as "consistently meeting the needs and exceeding the expectations of our clients." As such, we consistently strive to:

- meet or exceed client and regulatory requirements
- be technically correct and accurate
- be defensible within contract specifications
- provide services in a cost-effective, timely and efficient manner

At GEL, quality is emphasized at every level—from the Chairman and CEO to the newest of employees. Management's ongoing commitment to good professional practice and to the quality of our testing services to our customers is demonstrated by their dedication of personnel and resources to develop, implement, assess, and improve our technical and management operations.

The purpose of GEL's quality assurance program is to establish policies, procedures, and processes to meet or exceed the expectations of our clients. To achieve this, all personnel that support these services to our clients are introduced to the program and policies during their initial orientation, and annually thereafter during company-wide training sessions.

GEL's management is committed to compliance with and continual improvement of our quality assurance program. The program is designed to comply with the guidelines and specifications outlined in the following:

- TNI 2016
- ASME/NQA-1
- ISO/IEC 17025-2017
- QAPPs, U.S. EPA QA/R5
- Department of Energy Order 414.1B, 414.1C and 414.D

- ANSI N42.23-1996 Measurement and Associated Instrument Quality Assurance for Radioassay Laboratories
- DOE STD 1112-98
- Performance Criteria for Radiobioassay- ANSI N13.30-1996.
- Energy Reorganization Act, 1974, Section 206, 10 CFR, Part 21
- MARLAP
- U.S. Department of Defense (DoD), Department of Energy (DOE) Consolidated Quality System Manual (QSM) for Environmental Laboratories, Revision 5.2, December 2018
- 10 CFR Part 21- Reporting of Defects and Noncompliance
- 10 CFR Part 50 Appendix B -Quality Assurance Criteria for Nuclear Power Plants and Fuel Reprocessing Plants
- 10 CFR Part 61- Licensing Requirements for Land Disposal of Radioactive Waste
- NRC REG Guide 4.8
- NRC REG Guide 4.15

1.2 Quality Goals

GEL's primary goals are to:

- Ensure that all measurement data generated are scientifically and legally defensible, of known and acceptable quality per the data quality objectives (DQOs), and thoroughly documented to provide sound support for environmental decisions.
- Ensure compliance with all contractual requirements, environmental standards, and regulations established by local, state and federal authorities.

Additional goals include:

- A comprehensive quality assurance program to ensure the timely and effective completion of each measurement effort.
- A commitment to excellence and improvement at all levels of the organization.
- Early detection of deficiencies that might adversely affect data quality.
- Adequate document control.
- Effective quality assurance objectives for measurement systems and for quality data in terms of accuracy, precision, completeness, and comparability through the use of proven methods.
- The establishment of procedures that demonstrate that the analytical systems are in a state of statistical control.
- The implementation of corrective actions and improvements to ensure the integrity of data.
- Reduction of data entry errors through comprehensive automated data handling procedures.
- The development and implementation of good laboratory and standard operating procedures (SOPs).
- Ability to customize quality assurance procedures to meet a client's specific requirements for data quality.
- Good control of instruments, services, and chemical procurement.
- A continuously capable laboratory information management system (AlphaLIMS).
- Validated and documented computer hardware and software.
- All employees who have access to the AlphaLIMS system are required to participate in computer security awareness training annually.

1.3 Key Quality Elements

A sound quality assurance program is essential to our ability to provide data and services that consistently meet our high standards of integrity. The key features of our program are:

- An independent quality assurance (QA) validation and Quality Systems Department.
- A formal quality policy and QAP.
- Management review.
- Stated data quality objectives.
- A comprehensive employee training program.
- Ethics policy and education program.
- Internal audits and self-evaluations.
- A closed-loop corrective action program.
- State-of-the-art facilities and instruments.

- Adherence to standard operating procedures.
- EPA/NIST traceable reference materials.
- Electronically based document control.
- Chain of custody and electronic sample tracking.
- Inter-laboratory comparison programs.
- Formal laboratory accreditations.
- The evaluation of subcontractor laboratories.
- Statistical controls for analytical precision and accuracy.
- Replicate, method blank, matrix spike, tracer yield, internal standards, and surrogate measurements.
- The preventive maintenance of instrumentation and equipment.
- Independently prepared blind standard reference materials.
- Multi-level review processes.
- Focus on client satisfaction.
- Electronic tracking of client commitments, nonconformances and corrective actions.
- Trend analysis of nonconforming items.

1.4 Management Reviews

The effectiveness of the Quality System is reviewed at least annually by Senior Management. These reviews address issues that impact quality, and the results of the reviews are used to develop and implement improvements to the system. Records of the review meetings are maintained as quality documents.

1.5 Disposition of Client Records

In the event that the laboratory should change ownership, the responsibility for the maintenance and disposition of client records shall transfer to the new owners. In the unlikely event that the laboratory ceases to conduct business, clients shall be notified and asked to provide instructions as to how their records should be returned or disposed. If a client does not provide instructions, those records will be maintained and disposed in a manner consistent with regulations and good laboratory practices for quality records.

1.6 Supporting Documents

Our laboratory operations and the quality of our analytical data comply with the specifications described in the documents listed in Appendix A.

1.7 Definitions

Applicable definitions are listed in Appendix B.

SECTION 2
ORGANIZATION, MANAGEMENT, AND PERSONNEL

Section 2 - Organization, Management, and Personnel

The chart found in Appendix C depicts our corporate organization, chain of command and flow of responsibility. The illustration in this appendix is designed to ensure the overall quality and cost efficiency of our company's analytical products and services.

Our structure is based on customer-focused divisions that follow a project from the point of initial contact to the final invoicing of work. These divisions include expertise in project management, sample receipt and custody, sample preparation and analysis, data review, and data packaging. An independent Quality Systems Management Department monitors the adherence of these divisions to the Quality Assurance Program.

The general responsibilities associated with the following position levels are discussed in this section:

- Chairman and Chief Executive Officer (CEO)
- President
- Chief Operating Officer (COO)
- Chief Financial Officer (CFO)
- Quality Systems Director
- Laboratory Directors
- Project Managers
- Group Leaders
- Laboratory and Technical Staff
- Information Systems Manager
- Environmental Manager
- Radiation Safety Officer
- Director of Human Resources

An overview of GEL's employee training protocol is also provided at Section 2.12.

2.1 Chairman and CEO, President, Chief Financial Officer and Chief Operating Officer

Operational responsibility rests with GEL's owners, CFO and COO. James M. Stelling and Joseph M. Hodgson Jr. are owners and serve respectively as Chairman and CEO, and President. Carey J. Bocklet occupies the position of COO. Laurie Herrington occupies the position of CFO. As the highest level executives, their philosophical approach to quality, technology and customer service keeps GEL unique. They are also part of a Leadership Team that works to create a workplace envirionment that attracts and retains highly qualified professionals.

As Chairman and CEO, Mr. Stelling oversees the Executive Committee and leads management in implementing total quality initiatives that ensure quality services that meet stringent criteria of excellence. He holds a Bachelor of Science in Commerce from the Universtiy of Virginia.

Joseph M. Hodgson Jr. is GEL's President. He has overall operational responsibility and operates the laboratory according to corporate policies, applicable licenses and regulations. He is also responsible for Strategic Planning, Marketing and Business Development. In addition, he has primary responsibility for the development and administration of our analytical testing and environmental consulting services. Mr. Hodgson Jr.holds a Bachelor of Science in Business from Wake Forest University.

The Chief Operating Officer is Carey J. Bocklet. Ms. Bocklet is responsible for the daily operations of the laboratories and client services. Ms. Bocklet holds a Bachelor of Science in Chemical Engineering, and a Master of Science in Business Administration, both from Clemson University.

Laurie Herrington is GEL's Chief Financial Officer and oversees GEL's financial management. She is responsible for contracts administration, invoicing, purchasing, payroll, accounts payable, and receivable, inentroy control, property control and financial forcasting. Ms. Herrington holds a Bachelor of Science in Accounting and Business Adminstration from the College of Charleston. Ms. Herrington also has her licenses as a Certified Public Accountant and a Certiifed Fraud Examiner.

Together, the Chairman and CEO, President, COO and CFO form GEL's Executive Committee. Their responsibilities include the following:

- Ensuring that the individuals who staff our technical and quality positions have the necessary education, training, and experience to competently perform their jobs.
- Ensuring that all staff members receive ancillary training, as needed, to enhance performance in assigned positions.
- Budgeting, staffing, managing, and equipping the laboratory to meet current and future analytical program requirements.
- Overseeing the implementation and overall effectiveness of our Quality Assurance Plan, health and safety initiatives, and environmental programs.
- Managing production and cost control activities.
- Ensuring development of capabilities in response to new or revised regulations, instrumentation and procedures, and quality assurance initiatives.

2.2 Technical Laboratory Co-Directors

To enhance our responsiveness to clients through dedicated expertise and teamwork, our laboratory is divided into two major divisions, Chemistry and Radiochemistry, each with its own Technical Laboratory Director.

The Technical Directors report to the Executive Committee and are ultimately responsible for the technical content and quality of work performed within each division. They are also responsible for strategic planning, profitability and growth, personnel management and business development. Other responsibilities include:

- Monitoring and meeting profitability and growth objectives of the division.
- Establishing and implementing short and long range objectives and policies that support GEL's goals.
- Defining the minimum level of qualification, experience, and skills necessary for positions in their divisions.
- Establishing and implementing policies and procedures that support our quality standards.
- Ensuring that technical laboratory staff demonstrates initial and continuing proficiency in the activities for which they are responsible.
- Documenting all analytical and operational activities of the laboratory.
- Supervising all personnel employed in the division.
- Ensuring that all sample acceptance criteria are verified and that samples are logged into the sample tracking system, properly labeled, and stored.
- Documenting the quality of all data reported by the division.
- Developing internal mechanisms and measurements to improve efficiency.
- Overseeing activities designed to ensure compliance with laboratory health and safety requirements.
- Allocating the resources necessary to support an effective and ongoing quality assurance program.
- Representing the company to the public and to clients.
- Ensuring the appropriate delegation of authorities during periods of absence.
- Ensuring compliance to the ISO 17025:2017 Standard.

2.3 Quality Systems Director

Our Quality Systems Director (QSD) reports directly to the CEO. The QSD manages the design, implementation and maintenance of our quality systems in a timely, accurate, and consistent manner.

In addition to having responsibility for the initiation and recommendation of corrective and preventive actions, the QSD is responsible for:

- Establishing, documenting, and maintaining comprehensive and effective quality systems.
- Developing and evaluating quality assurance policies and procedures pertinent to our laboratory functions, and communicating these with the division directors and managers.

- Ensuring that the operations of the lab are in conformance with the Quality Assurance Plan and meet the quality requirements specific to each analytical method.
- Ensuring that laboratory activities are in compliance with local, state, and federal environmental laws and regulations.
- Reviewing project-specific quality assurance plans.
- Ensuring that quality control limits are established and followed for critical points in all measurement processes.
- Initiating internal performance evaluation studies using commercially purchased certified, high-purity standard reference materials.
- Performing independent quality reviews of randomly selected data reports.
- Conducting periodic audits to ensure method compliance.
- Conducting or arranging periodic technical system evaluations of facilities, instruments and operations.
- Overseeing and monitoring the progress of nonconformance's and corrective actions.
- Communicating system deficiencies, recommending corrective action to improve the system, and defining the validity of data generated during out of control situations.
- Preparing and updating quality assurance documents and reports to management.
- Coordinating inter-laboratory reviews and comparison studies.
- Overseeing Stop Work Orders in out-of-control situations.
- Administering accreditation and licensing.
- Administering our document control system.
- Providing guidance and training to laboratory staff as requested.
- Evaluating subcontractors and vendors that provide analytical and calibration services.
- Designating quality systems authorities in times of absence to one or more appropriately knowledgeable individuals.
- Overseeing notification if required for compliance with Energy Reorganization Act, 1974, 10 CFR, Part 21, should data recall be necessary.
- Ensuring that the laboratory has policies to avoid involvement in activities or relationships which might negatively affect confidence in the laboratory's competence, impartiality, judgement or operational integrity.
- Ensuring that management and personnel are free from undue internal and external pressures and influences that may adversely affect their impartiality, affecting the quality of their work, by mitigating pressures.
- Ensuring that employee competence measurements are established and monitored.

2.4 Quality Systems Review

The effectiveness of the Quality System is reviewed on a regular basis during meetings of the Leadership Team, which may be as often as weekly, but not less than quarterly. These meetings address issues that impact quality, and the subsequent discussions are used to design and implement improvements to the system. At least annually, a management assessment of GEL's Quality System is conducted and reported. The QSD maintains records of these assessments.

2.5 Manager of Client and Support Services

Project Managers (PMs) serve as primary liaisons to our clients. PMs, under the guidance of the Manager of Client and Support Services, manage the company's interaction with clients. They are the client's first point of contact and have responsibility for client satisfaction and for communicating project specifications and changes to the appropriate laboratory areas.

Additional responsibilities include:

- Retaining clients and soliciting new work.
- Managing multiple sample delivery orders and preparing quotes.
- Working with clients to define analytical methodologies, quality assurance requirements, reports, deliverables, and pricing.

- Overseeing sample management and informing laboratory staff of the anticipated arrival of samples for analysis.
- Conducting a review of client documents (i.e. quotes, invoices, routine and specialized reports).
- Working with the accounting team on invoicing and collection issues.
- Working with the Laboratory Directors, Production Manager, and Group Leaders to project workloads and determine schedules.

2.6 Group Leaders

Group Leaders are a critical link between project management, lab personnel, and support staff. They report to the Technical Directors and have the following responsibilities:

- Planning and coordinating the operations of their groups to meet client expectations.
- Scheduling sample preparation and analyses according to holding times, quality criteria, and client due dates.
- Ensuring a multi-level review of 100% of data generated by their groups.
- Coordinating nonconformances and corrective actions in conjunction with the Quality Systems Management team.
- Serving as technical resources to their groups, including data review.
- Managing special projects, reviewing new work proposals, and overseeing the successful implementation of new methods.
- Monitoring and controlling expenses incurred within their groups such as overtime and consumables.
- Providing performance and career development feedback to their group members.

2.7 Laboratory and Technical Staff - General Requirements

At GEL, every effort is made to ensure that the laboratory is sufficiently staffed with personnel who have the training, education, and skills to perform their assigned jobs competently.

Depending upon the specific position, laboratory personnel are responsible for:

- Complying with quality assurance and quality control requirements that pertain to their group and/or technical function.
- Demonstrating a specific knowledge of their particular function and a general knowledge of laboratory operations.
- Understanding analytical test methods and standard operating procedures that are applicable to their job function.
- Documenting their activities and sample interactions in accordance with analytical methods and standard operating procedures.
- Implementing the quality assurance program as it pertains to their respective job functions.
- Identifying potential sources of error and reporting any observed substandard conditions or practices.
- Identifying and correcting any problems affecting the quality of analytical data.
- Identifying and performing all client specific requirements outlined in the special requirements on the pull sheet of every batch.

2.8 Information Systems Manager

The Information Systems Manager reports directly to the COO. The responsibilities of this position include management of the Computer Services Team and AlphaLIMS, our laboratory information management system.

The combined responsibilities of the Information Systems Team, performing under the leadership of the Information Systems Manager, include the:

- Development and maintenance of all software and hardware.
- Translation and interpretation of routines for special projects.
- Interpretation of general data and quality control routines.
- Optimization of processes through better software and hardware utilization.

- Customization, testing and modification of data base applications.
- Maintenance and modification of our computer modeling, bar coding, CAD, statistical process control, project management, and data packaging systems.
- Development and maintenance of client and internal electronic data deliverables.
- Validation and documentation of software used in processing analytical data.

2.9 Environmental Manager

The Environmental Manager oversees our physical facility, laboratory and radiation safety programs, and instrumentation. This position reports to the COO, and manages and supervises the functions and staff assigned to these areas.

Responsibilities of the Environmental Manager include:

- Planning, evaluating, and making recommendations for facility maintenance, additions and renovations.
- Overseeing building renovations and new construction activities.
- Implementation of the Chemical Hygiene and Radiation Safety programs.
- Installing, maintaining, repairing, and modifying analytical instrumentation.
- Providing technical expertise and training in instrumentation operation, calibration, and maintenance.
- Monitoring and ensuring regulatory compliance for waste management operations and off-site disposal.

2.10 Radiation Safety Officer

The Radiation Safety Officer (RSO) reports to the COO. The RSO is responsible for the administration and execution of GEL's Radiation Protection Program. This person provides technical guidance and leadership for all issues concerning radiation health and safety as well as direct operations to ensure compliance with South Carolina Department of Health and Environmental Control (SCDHEC) regulations for radioactive materials.

Responsibilities of the RSO include:

- Establishing and enforcing policies consistent with the principles and practices designated to maintain all exposure to ionizing radiation "As Low As Reasonably Achievable" (ALARA).
- Supervising Radiation Protection Specialists in the execution of radiological surveys and maintenance of the Radioactive Material License inventory.
- Executing the Personal Dosimetry, Air Effluent Monitoring, and Sealed Radioactive Source Leak Test Programs.
- Developing procedures and protocols to establish and maintain compliance.
- Providing training for staff in proper radiation protection practices.

2.11 Director of Human Resources

The Director of Human Resources reports directly to the CEO. The DHR manages the design, implementation, and ongoing development of our Human Resources. Responsibilities of the DHR include:

- Administration, orientation, and indoctrination of all new employees.
- Administration and compliance with Federal, State, and Local employment regulations.
- Sourcing candidates for all functional positions to maintain and strengthen the technical services provided by GEL.
- Management of occupational health and safety as it relates to Federal, State, and OSHA regulations.

2.12 Employee Training

To ensure that our clients receive the highest quality services possible, we train our employees in the general policies and practices of the company, as well as the specific operating procedures relative to their positions. We conduct and document this training

according to GL-HR-E-002 for Employee Training and GL-QS-E-017 for Maintaining Technical Training Records.

New employees participate in a company orientation shortly after they are hired. During orientation they receive information on quality systems, ethics/data integrity, laboratory safety, and employment practices. Each new employee is also provided a manual that reiterates our policies on equal opportunity, benefits, leave, conflicts of interest, employee performance, and disciplinary action. Employees can access standard operating procedures, the Quality Assurance Plan, Safety, Health, and Chemical Hygiene Plan, and the Laboratory Waste Management Plan on GEL's Intranet.

Other training provided on an ongoing basis may include:

- Demonstration of initial proficiency in analytical methods and training to SOPs conducted by a trainer who has been documented as qualified and proficient in the process for which training is being provided.
- Demonstration of continued analyst proficiency is updated continuously, using the most recent data available in AlphaLIMS. Proficiency is demonstrated using the same processes as those used for initial Demonstration of Capability. (Refer to Section 8.3.1.)
- Company-wide, onsite training.
- Courses or workshops on specific equipment and analytical techniques.
- University courses.
- Professional and trade association conferences, seminars, and courses.

Documentation of employee training is the joint responsibility of the employee and the applicable Group Leader. If an SOP is revised during the course of the year, training to the revised SOP must be documented.

2.13 Ethics and Data Integrity

As our corporate vision statement explains, "We are a company that values: Excellence as a way of life, Quality Service, a Can-Do attitude, and a fundamental commitment to Ethical Standards." Employees attend ethics education programs that focus on the high standards of data integrity and ethical behavior mandated by our company and expected by our clients.

The annual ethics training includes:

- Specific examples of unethical behaviors for the industry and for the laboratory.
- Explanation of Internal Auditing for unethical behaviors and practices.
- GEL use of electronic audit functions using instrument and AlphaLIMS software.
- Explanation of GEL's Ombudsman policy for reporting inappropriate activities.
- Examples of consequences of inappropriate or unethical behaviors/practices.
- Examples of impartiality from commercial, financial or other pressures, both external and internal.

All employees sign an Ethics and Data Integrity Agreement that reflects their commitment to always perform their duties with these high standards. (Refer to Appendix F.) During the initial and continuing Ethics and Data Integrity training, GEL's policy on confidential reporting of potential integrity issues is thoroughly discussed. Potential business or data integrity issues are handled and reviewed in a confidential manner until such time as a follow-up evaluation, full investigation, or other appropriate actions have been completed and issues clarified. All investigations are confidentially processed by GEL's QSD, or other members of GEL's Laboratory Management staff under the direction of the QSD. All investigations that result in finding of inappropriate activity are properly documented and include any disciplinary actions involved, corrective actions taken, and all appropriate notifications of clients. The QSD is responsible for updating GEL's Executive Committee on the progress of integrity investigations during regularly scheduled meetings.

2.14 Confidentiality

The laboratory maintains the confidentiality and proprietary rights of information including the type of work performed and results of analysis. Laboratory personnel and staff are informed of this policy and sign a confidentiality agreement.

A confidentiality statement accompanies the electronic transfer of data from GEL via telefacsimile (fax) or electronic mail systems (email). Government affiliated auditing agencies have access to pertinent laboratory records. However, contract, third party, and client auditors have access only to those records that may be applicable to their inspection and shall not be granted access to client records that may be considered in conflict with their interests, unless prior authorization has been given by the submitting client. Confidential information may be purged of references to client identity, project and/or sample identity by the laboratory so that records may be provided to other entities (e.g. auditors) for review.

2.15 Impartiality

The laboratory is committed to Impartiality in producing valid results derived under its range of activities or scope of work. Results are provided accurately, objectively, clearly and in a report format which includes all the information necessary for the interpretation of the results. All information required by the method used and agreed with the customer is reported. The laboratory strives to maintain impartiality from commercial, financial or other pressures which might compromise impartiality. In addition to internal management structure mitigating undue pressures on employees, the laboratory reviews requests and tenders for possible risks to impartiality prior to bidding on work.

Our Core Values, along with procedures, plans, and policies outlined in this Quality Assurance Plan, scheduled management meetings, and monitoring of key performance indicators help in the management of risks on an on-going basis.

SECTION 3
QUALITY SYSTEMS

Section 3 - Quality Systems

Our Quality Systems include all quality assurance (QA) policies and quality control (QC) procedures necessary to plan, implement, and assess the work we perform. GEL's QA Program establishes a quality management system (QMS) that governs all of the activities of our organization.

GEL's quality management system is designed to conform to the requirements specified in the standards referenced in Appendix A. Essential elements of our quality management system are described in this section and Appendix E.

3.1 Quality Systems Team

The Quality Systems Team monitors risks to impartiality, confidentiality and other undue influences which could adversely affect confidence in the laboratory's competence, judgement or operational integrity. This team monitors conformity to the range of activity under which it performs. Risks which may affect the validity of results are identified, monitored and assessed as to the potential impact on the validity of the results. This group is responsible for recording and managing customer complaints through the laboratory non-conformance reporting system. .

Following is a summary of the responsibilities of each position, in addition to the duties discussed in section 2.3

3.1.1 Quality Systems Director

- Reports to the CEO
- Demonstrates strict adherence to and support of the company ethics policy
- Serves as management's representative for quality
- Responsible for the implementation and maintenance of the QMS
- Supervises the Quality Systems Team and their functions
- Initiates and recommends preventive action and solutions to quality problems
- Implements appropriate action to control quality problems until solutions are implemented and verified to be effective
- Verifies that effective solutions are implemented
- Demonstrates knowledge of the Quality System as defined by NELAC, TNI, NUPIC, ISO/IEC 17025, DOECAP DoD ELAP, and DOELAP.

3.1.2 Quality Systems Lead Auditor

- Reports to the Quality Systems Director
- Demonstrates strict adherence to and support of the company ethics policy.
- Demonstrates knowledge of the Quality System defined under NELAC, TNI, DOECAP,DoD ELAP, DOELAP, NUPIC and other quality standards such as ISO/IEC 17025-2017.
- Plans, schedules and participates in GEL's client audits, internal audits, and subcontractor audits
- Conducts conformance audits as necessary to verify implementation and closure of audit action items
- Serves as liaison to client and third party auditors
- Coordinates laboratory responses to audit reports and prepares final response
- Monitors progress of corrective actions
- Prepares and monitors progress of internal and subcontractor audit reports

3.1.3 Quality Assurance Officers

- Report to the Quality Systems Director
- Demonstrate strict adherence to and support of the company ethics policy.
- Demonstrate the ability to evaluate data objectively without outside influence
- Have documented training and/or experience in QA/QC procedures and knowledge of the Quality system as defined under NELAC, TNI and ISO 17025
- Have knowledge of analytical methods

- Assist in the conduct of internal and supplier audits and requests for pricing reviews
- Administer corrective actions and nonconformances
- Monitor and respond to client -identified nonconformances and technical inquiries
- Implement and maintain statistical process control (SPC) system
- Ensure the monitoring of balances and weights, and temperature regulation of ovens, water baths, and refrigerators
- Coordinate the monitoring of DI water system and volatile organics storage coolers
- Maintain Method Detection Limit studies
- Write or review quality documents and standard operating procedures under the direction of the QS Director
- Provide training in quality systems and good laboratory practices.
- Manage laboratory certification processes
- Coordinate the receipt and disposition of external and internal performance evaluation samples.

NOTE: Once PE samples have been prepared in accordance with the instructions provided by the PE vendor, they are managed and analyzed in the same manner as environmental samples from clients. The analytical and reporting processes for PE samples are not specially handled.

3.1.4 Quality Systems Specialists/Document Control Officer

- Reports to the Quality Systems Director
- Demonstrates strict adherence to and support of the company ethics policy.
- Assist the team as directed with respect to Records Management, Document Control, Laboratory Certification, temperature and weight calibrations, logbook review, training documentation, and nonconformances, etc.

3.2 Quality Documents

Our Quality Systems policies and procedures are documented in this and other supporting documents. GEL's management approves all company quality documents. Pre-approval is secured for any departures from such documents that may affect quality.

In addition, to the QA Plan, Quality Systems allows for QA Project Plans (QAPjP) and includes standard operating procedures and any other quality assurance program requirements defined by individual contracts. The QA Plan describes the quality standards that we apply to our laboratory operations. We use Quality Assurance Project Plans to specify individual project requirements. The QA Plan and supporting documents are verified to be understood and are implemented throughout the laboratory fractions to which they apply.

Finally, our Standard Operating Procedures (SOPs) are used to describe in detail those activities that affect quality. SOPs are prepared, authorized, changed, revised released, and retired in accordance with GL-ADM-E-001. SOPs are accessible electronically via GEL's Intranet.

3.3 Document Control

The control of quality documents is critical to the effective implementation of our Quality Program. We define and control this process in accordance with GL-DC-E-001 for Document Control. Responsibilities for document control are divided between the Group Leaders and the Document Control Officer (DCO).

Group Leaders are responsible for:

- Supporting the development and maintenance of controlled documents that apply to their respective departments.
- Reviewing all quality documents annually for continued validity.
- Ensuring documentation that the affected employees are aware of revisions to documents or manuals.

The Computer Services Team is responsible for:

- Electronic maintenance of all records required for control, re-creation, and maintenance of analytical documentation.
- Maintenance of electronic copies of archived data and the electronic log of how they were determined.

The DCO is responsible for:

- Demonstrating strict adherence to and support of the company ethics policy.
- Managing the system for the preparation, authorization, change, revision, release, and retirement of the Quality Manual, QAP, project plans, and standard operating procedures.

- Ensuring that current controlled documents are accessible via GEL's Intranet.
- Managing a system to document current revision numbers and revision dates for all distributed documents and manuals.
- Managing a system to identify the nature of document revisions.
- Maintaining hard or electronic copies of obsolete documents.
- Maintaining electronic or hard copy originals of all controlled documents.

Revisions to controlled quality documents are made by replacing individual sections or the entire document, as determined by the DCO.

3.4 Controlled Document Review

Internally generated controlled documents undergo a multi-level review and approval process before they are issued. These levels include a procedural review, technical and/or quality review and final authorization of the appropriate manager or director if necessary. To ensure that new or revised standard operating procedures are not implemented prematurely, SOPs are effective upon the date of the final approval signature.

3.5 Quality Records

Quality records provide evidence that specified quality requirements have been met and documented. We generate them in accordance with applicable procedures, programs, and contracts. Quality records include but are not limited to:

- Observations
- Calculations
- Calibration data
- Certificates of analysis
- Certification records
- Chains of custody
- Audit records
- Run logs, instrument data, and analytical logbooks
- Instrument, equipment, and building maintenance logs
- Material requisition forms
- Monitoring logs
- Nonconformance reports and corrective actions
- Method development and start-up procedures including method detection limit studies
- Technical training records
- Waste management records
- Standard logs
- Software validation documentation
- Standard Operating Procedures (SOPs)
- Sample collection and field data

Our quality records are:

- Documented in a legible manner.
- Indexed and filed in a manner conducive to ready retrieval.
- Stored in a manner that protects them from loss, damage, and unauthorized alterations.
- Accessible to the client for whom the record was generated.
- Retained and disposed in the identified time period.

The generation, validation, indexing, storage, retrieval, and disposition of our quality records are detailed in GL-QS-E-008 for Quality Records Management and Disposition. The quality records of subcontracted services are also required to meet the conditions established in this SOP.

3.6 Internal and Supplier Quality Audits

We conduct internal audits annually to verify that our operations comply with the requirements of our QA program and those of our clients. We perform supplier audits as necessary to ensure that they too meet the requirements of these programs. Both internal and supplier audits are conducted in accordance with GL-QS-E-001 for the Conduct of Quality Audits.

3.6.1 Audit Frequency

Internal audits are conducted at least annually in accordance with a schedule approved by the Quality Systems Director. Supplier audits are contingent upon the categorization of the supplier, and may or may not be conducted prior to the use of a supplier or subcontractor (Refer to GL-QS-E-001.) Type I suppliers and subcontractors, regardless of how they were initially qualified, are re-evaluated at least once every three years.

Additional internal and supplier audits may be scheduled if deemed necessary.

3.6.2 Audit Team Responsibilities

Internal and supplier audits are conducted by qualified staff under the direction of the Lead Auditor or Quality Systems Director. A qualified audit team member shall have the technical expertise to examine the assigned activities.

We do not allow staff to audit activities for which they are responsible or in which they are directly involved. It is the responsibility of the Lead Auditor to ensure that such conflicts of interest are avoided when the audit team is assembled.

The Leadership Team has a significant role in the internal audit process, including:

- Provision of audit personnel
- Empowerment of the audit team with authority to make the audit effective
- Development and implementation of timely corrective action plans

3.6.3 Identification and verification of OFIs

Opportunities for Improvement are identified conditions that have potential to improve the quality of products or services. Several examples of objective evidence are used to support an OFI, which might be classified as an , observation, and/or recommendation.

The Lead Auditor may initiate an OFI and may reference a Nonconformance Report (NCR) or Corrective Action Request and Report (CARR) The OFI, is then entered into the NCR system per GL-QS-E-012 for NCR Database Operation.

Implementation of any changes or action is verified as effective prior to implementation. The OFI may be verified for continued effective implementation during the next scheduled audit.

3.7 Managerial and Audit Review

Our Leadership Team reviews the audit process at least annually. This ensures the effectiveness of the corrective action plan and provides the opportunity to introduce changes and improvements.

We document all review findings and corrective actions. Implementation plans and schedules are monitored by the Quality Systems Team.

3.8 Nonconformances

Processes, materials, and services that do not meet specifications or requirements are defined as nonconforming. Such nonconformances can include items developed in-house or purchased from vendors, samples received from clients, work in progress, and client reports.

At GEL, we have a nonconformance reporting system (NCR) that helps us prevent the entry of defective goods and services into our processes and the release of nonconforming goods and services to our clients. Our NCR system provides a means for documenting the disposition of nonconforming items and for communicating these to the persons involved in the process affected by the adverse condition(s).

Nonconformances are documented according to GL-QS-E-004 for the Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items. We regularly review SOPs, client complaints, and quality records, including completed NCRs, to promptly identify conditions that might result in situations or services that do not conform to specified quality requirements.

Our Quality Group processes, categorizes and trends nonconformances. Trending information may be provided to the Leadership Team and Group Leaders of the affected areas.

3.9 Corrective Action

There are two categories of corrective action at GEL. One is corrective action implemented at the analytical and data review level in accordance with the analytical SOP. The other is formal corrective action documented by the Quality Systems Team in accordance with GL-QS-E-002. Formal corrective action is initiated when a nonconformance reoccurs or is so significant that permanent elimination or prevention of the problem is required.

We include quality requirements in most analytical SOPs to ensure that data are reported only if the quality control criteria are met or the quality control measures that did not meet the acceptance criteria are documented.

Formal corrective action is implemented according to GL-QS-E-002 for Conducting Corrective/Preventive Action and Identifying Opportunities for Improvement

and documented according to GL-QS-E-012 for NCR Database Operation.

Any employee at GEL can identify and report a nonconformance and request that corrective action be taken. Any GEL employee can participate on a corrective action team as requested by the QS team or Group Leaders. The steps for conducting corrective action are detailed in GL-QS-E-002.

In the event that correctness or validity of the laboratory's test results is doubted, the laboratory will take corrective action. If investigations show that the results have been impacted, affected clients will be informed of the issue in writing within 5 calendar days of the discovery.

GEL will notify all affected customers of any data quality issues resulting from nonconforming work within 15 business days of discovery. GEL will provide and submit records of the corrective actions to resolve the nonconformance(s) to the customer(s) with 30 business days. This procedure will also be followed to notify GEL's accrediting body if the laboratory experiences any instances of inappropriate and prohibited laboratory practices. GEL will perform these procedures in accordance with SOP GL-QS-E-002 Conducting Corrective/Preventative Action and Identifying Opportunities for Improvement.

3.10 Performance Audits

In addition to internal and client audits, our laboratory participates in annual performance evaluation studies conducted by independent providers. We routinely participate in the following types of performance audits:

- Proficiency testing and other inter-laboratory comparisons.
- Performance requirements necessary to retain certification (Appendix D).
- Evaluation of recoveries of certified reference and in-house secondary reference materials using statistical process control data.
- Evaluation of relative percent difference between measurements through SPC data.

We also participate in a number of proficiency testing programs for federal and state agencies and as required by contracts. It is our policy that no proficiency evaluation samples be analyzed in any special manner.

Our annual performance evaluation participation generally includes a combination of studies that support the following:

- US Environmental Protection Agency Discharge Monitoring Report, Quality Assurance Program (DMR-QA). Annual national program sponsored by EPA for laboratories engaged in the analysis of samples associated with the NPDES monitoring program. Participation is mandatory for all holders of NPDES permits. The permit holder must analyze for all of the parameters listed on the discharge permit. Parameters include general chemistry, metals, BOD/COD, oil and grease, ammonia, nitrates, etc.
- Department of Energy Mixed Analyte Performance Evaluation Program (MAPEP). A semiannual program developed by DOE in support of DOE contractors performing waste analyses.
- ERA's MRAD-Multimedia Radiochemistry Proficiency test program. This program is for labs seeking certification for radionuclides in wastewater and solid waste. The program is conducted in strict compliance with USEPA National Standards for Water Proficiency study.
- ERA's InterLaB RadCheM Proficiency Testing Program for radiological analyses. This program completes the process of replacing the USEPA EMSL-LV Nuclear Radiation Assessment Division program discontinued in 1998. Laboratories seeking certification for radionuclide analysis in drinking water also use the study. This program is conducted in strict compliance with the USEPA National Standards for Water Proficiency Testing Studies.
- Water Pollution (WP). Biannual program for waste methodologies. Parameters include both organic and inorganic analytes.
- Water Supply (WS): Biannual program for drinking water methodologies. Both organic and inorganic parameters are included.

At GEL, we also evaluate our analytical performance on a regular basis through statistical process control acceptance criteria. Where feasible, this criterion is applied to both measures of precision and accuracy and is specific to sample matrix.

We establish environmental process control limits at least annually. In Radiochemistry, quality control

evaluation is based on static limits rather than those that are statistically derived, unless specified by regulatory programs such as Drinking Water. Our current process control limits are maintained in AlphaLIMS. GEL maintains client-specific and program-specific control limits and reporting requirements in the LIMS. Examples of client or program specific limits may be found in documents such as the DoD QSM tables in Appendices B and C of DOD-DOE QSM version 5.2, and in the HASQARD Standard which are available as Quality Systems documents.

We also measure precision through the use of matrix duplicates and/or matrix spike duplicates. The upper and lower control limits (UCL and LCL respectively) for precision are plus or minus three times the standard deviation from the mean of a series of relative percent differences. The static precision criteria for radiochemical analyses are 0 – 20% for activity levels exceeding the contract required detection limit (CRDL).

Accuracy is measured through laboratory control samples and/or matrix spikes, as well as surrogates and internal standards. The UCLs and LCLs for accuracy are plus or minus three times the standard deviation from the mean of a series of recoveries. The static limit for radiochemical analyses is 75 – 125%, except as specified by the Drinking Water regulations. Specific Instructions for out-of-control situations are provided in the applicable analytical SOP.

3.11 Control Charts

Per the U.S. Department of Energy, Quality Systems for Analytical Services (DOE QSAS): Control charts are a graphical representation of data taken from a repetitive measurement or process. Control charts may be developed for various characteristics, (e.g. mean, standard deviation, range, etc.) of the data. Per MARLAP "A control chart has two basic uses:

- As a tool to judge if a process was in control.
- As an aid in achieving and maintaining statistical control.

For applications related to radiation detection instrumentation or radiochemical processes, the mean (center line) value of a historical characteristic (e.g. mean detector response), subsequent data values and control limits placed symmetrically above and below the center line are displayed on a control chart."

For GEL's Chemistry, Radiochemistry, and Bioassay laboratories, the Computer Services Team (CST) developed a program where Group Leaders are sent email notifications that provide LCS failures by compound/analyte name. This assists the Group Leader with monitoring out of control situations due to laboratory contamination or analyst error. This program sends notifications once a week.

Each Group Leader may utilize programs in LIMS where they can review trending data as control charts by work order or by the SPC program.

GEL's QA Officer or designee shall review control charts during the period when the LIMS SPC program queries data points for analyses that require dynamic SPC limits for quality control parameters. This is performed on a biannual basis. At this time, any out of control conditions will be identified and a corrective action initiated. The QA Officer shall be able to stop unsatisfactory work or prevent the reporting of results generated from this program.

Dynamic SPC limits for control parameters are generally developed when more than 20 data points are available for review. Data points may be determined as outliers based on the process knowledge of the procedure being evaluated and the professional opinion of the data reviewer.

During their annual system review, management will evaluate the need to consolidate any redundant procedures and/or policies to help eliminate any confusion for work processes.

3.12 Essential Quality Control Measures

Some quality control measures are method-specific. There are, however, general quality control measures that are essential to our quality system. These quality measures include:

- Monitoring of negative and positive controls
- Defining variability and reproducibility through duplicates
- Ensuring the accuracy of test data including calibration and/or continuing calibrations, use of certified reference materials, proficiency test samples, etc.
- Evaluating test performance using method detection limits and quantitation limits or range of applicability such as linearity
- Selecting the appropriate method of data reduction

- A copy of GEL's Ethics and Integrity Agreement is provided in Appendix F.

SECTION 4
FACILITIES

Section 4 – Facilities

Our laboratory is designed with a full-service approach to handling environmental needs. The layout provides dedicated space for radiochemical analyses, bioassay analysis, organic extractions, semi-volatile organic analyses, volatile organic analyses, metals analyses, general chemistry analyses, and air analyses.

The laboratory and support offices occupy approximately 85,000 square feet engineered to meet the stringent quality control and utility requirements of the modern environmental laboratory. Records are temporarily stored on-site then warehoused in a climate-controlled building off-site. The diagram in Appendix H depicts the layout of the laboratories.

Discussed in this section are:

- Facility security
- Utility services and deionized water
- Prevention of contamination
- Assessment of contamination

4.1 Facility Security

Our facility features secured laboratory and storage areas. Restricted entry assures sample integrity and client confidentiality, which satisfies clients and potential national security interests.

Visitors cannot gain entry without being escorted through the laboratory by authorized personnel. A designated sample custodian and a bar-coded chain-of-custody provide a second level of security.

4.2 Utility Services

Each defined laboratory area is equipped with the following utilities:

- Cold water
- Hot water
- Deionized water
- Compressed air
- Natural gas
- Vacuum
- 110 Volt AC
- 208 Volt AC (at selected stations)
- Specialty gases (as required)

4.2.1 Deionized Water

We have two independent deionized water (DI) systems. One serves radiochemistry while the other serves the remaining laboratories. DI water is made from city water flowing through a reverse osmosis system and a deionization system capable of producing 5 gallons per minute of Type I laboratory water.

We monitor compliance according to GL-LB-E-016 for The Collection and Monitoring of the DI Water Systems. Our monitoring activities and frequencies can be found in Table 1 of the SOP.

4.2.2 Specialty Gasses

The specialty compressed gasses may be required by specific analytical systems. Each specialty compressed gas system is monitored for background contamination that would negatively impact the efficiency of the operating system. Monitoring is generally conducted through use of routine instrument control samples which are introduced to the operating system prior to instrument calibrations and throughout the analytical process. Requirements for the purity of the gasses are identified in the instrument operating manuals and standard operating procedures.

4.3 Prevention of Contamination

Work areas that are free of sample contaminants, constituents and measurement interferences are important to the generation of quality data. With this in mind, we designed our laboratories to prevent contamination and reinforce this design with good laboratory practices.

In addition to keeping our work areas free of dust and dirt accumulations, policies and features that prevent or minimize contamination include:

- An air conditioning system that controls the environment of individual laboratories for optimum performance of sensitive instruments and to eliminate potential cross contamination.
- Segregation of volatile and semi-volatile laboratories to minimize potential contamination associated with the use of commonly required solvents.

- Negative and positive pressure air locks to isolate selected laboratories to prevent the entry of airborne contaminants.
- Fume hoods to remove fumes and reduce the risk of aerosol and airborne contaminants and personal safety hazards are monitored in accordance with GL-FC-E-003 for Local Exhaust Ventilation Systems.
- Restricted access to the volatiles laboratory (authorized personnel only).
- Designated area for glassware preparation wherein all glassware used in sample prep and analysis is cleaned according to GL-LB-E-003 for Glassware Preparation.
- Segregated storage areas for volatiles and radioactive samples.
- Production, use, and monitoring of Type I DI water.
- Tracking and trending of any significant sample and/or reagent spills using the AlphaLIMS NCR system, allowing efficient analysis of any potential contamination.

4.4 Assessment of Contamination Levels

We evaluate contamination resulting from the following sources on the basis of quality assurance and quality control data derived from the analytical method and method blanks.

- Sample containers
- Reagent water
- Reagents and solvents
- Sample storage
- Chemical and physical interference
- Constituent carryover during analysis

Contamination in each of the volatile storage coolers is monitored by the weekly analysis of water blanks. Two DI water blanks are placed in each monitored cooler at the beginning of each month with one being analyzed each week. If the concentration of any target analyte exceeds the PQL, this is verified (with the second blank for that week) and corrective action is implemented to eliminate the source of contamination, evaluate the effect of samples stored in the cooler, and to notify clients. SOP GL-OA-E-058 discusses these practices in detail.

SECTION 5
EQUIPMENT AND REFERENCE MATERIALS

Section 5 – Equipment and Reference Materials

GEL's ability to efficiently generate data that are reproducible, accurate, and legally defensible is attributable to our use of high-quality instruments, equipment, and reference materials.

Provided in this section are:

- GEL's policies governing instruments, equipment, and reference materials
- Identification of instrumentation and support equipment
- Procurement protocol

5.1 General Policies

It is our policy to purchase instrumentation, equipment and high-quality reference materials that meet or exceed the method and regulatory requirements for the analyses for which we are accredited. If we need to use instruments or equipment not under our permanent control, we ensure that it also meets these standards.

Instrumentation and equipment are placed into service on the basis of ability to meet method or regulatory specified operating conditions such as range and accuracy. All laboratory instrumentation and testing equipment is maintained in accordance with standard operating procedures (SOPs).

Instrumentation and equipment is used in a manner that assures, where possible, that measurement uncertainty is known and consistent with specified quality requirements. Instruments and equipment are taken out of service and segregated or labeled as such under the following conditions:

- Mishandling and/or overloading
- Results produced are suspect
- Demonstrated defect or malfunction

Tagged or segregated instruments and equipment remain out of service until repaired and shown by test, calibration, or verification to perform satisfactorily. Instruments that are in service and normally calibrated prior to and during use are not tagged.

Each item of equipment, including reference materials is, if appropriate, labeled, marked or otherwise identified to indicate its calibration status. We maintain records for each major item of equipment, instrumentation, and all reference materials significant to quality performance. These records are often in the form of maintenance logs, which are kept in accordance with GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms, and Other Recordkeeping Devices.

Documentation included in these records may include but is not limited to:

- Equipment name
- Manufacturer's name
- Type identification
- Serial number or other unique identification
- Date received and date placed in service (if pertinent)
- Current location
- Condition when received (if known)
- Manufacturer's instruction, where available
- Dates and results of calibrations and or verifications
- Date of next calibration and/or verification, where written procedures do not specify frequency
- Details of maintenance carried out to date and planned for the future
- History of any damage, malfunction, modification or repair

5.2 Instrumentation and Support Equipment

Appendix G lists the instruments we use for the analysis of environmental, radiochemical and bioassay samples. Where feasible, our instruments are equipped with autosamplers that improve efficiency and facilitate consistent sample introduction to the sample detector. They are also connected to an area network to facilitate data transfer.

Devices that may not be the actual test instrument but are necessary to support laboratory operations are referred to as support equipment. We also maintain this equipment in proper working order. Support equipment utilized at GEL includes:

- balances
- ovens
- refrigerators
- freezers
- incubators
- water baths
- temperature measuring devices
- volumetric dispensing devices
- muffle furnaces
- distillation apparatus
- grinders and homogenizers
- hot plates and heating mantles
- ultraviolet sterilizers.

Guidelines for the required calibration and evaluation of this equipment are discussed in Section 7.

We perform radiochemical and bioassay analytical services in accordance with the instrumentation and reference methods approved by the Department of Energy (DOE), the Environmental Measurements Lab (EML), the Environmental Protection Agency (EPA), ASTM, and Los Alamos Health and Environmental Chemistry (LAHEC). Modifications to these methods may be appropriate as a result of Performance Based Measurement Systems (PBMS).

SOPs are used to describe our procedures for all routine analyses performed by our labs. These procedures include step-by-step instructions for sample collection, storage, preparation, analysis, instrument calibration, quality control, disposal, and data reporting.

5.3 Procurement and Control of Purchased Items

Materials, equipment, and services that affect the quality of our products are designated as Quality Materials, Equipment, and Services and are only purchased from approved suppliers. We approve and document suppliers according to GL-QS-E-001 for the Conduct of Quality Audits.

At GEL, we maintain documentation of specific quality requirements for Quality Materials and Services. Records that document the quality of a product or service may include:

- certificates of analysis and traceability
- verifications of chemical quality
- inspections of equipment or materials
- verifications or inspections of vendor product specifications

Our procedure for requisitioning supplies, instruments, equipment and other common use material is described in GL-RC-E-002 for Material Requisition. These requests typically include:

- The date and name of person(s) requesting materials
- Account, department, project number to which the material is to be billed
- Recommended supplier or vendor
- Additional information necessary to expedite the purchase request
- Specifications that could affect the quality of products and services
- Vendor's material part number
- Amount of material needed
- Description of material
- Cost per unit
- Person(s) authorizing the purchase
- Time frame in which the material is needed

The equipment, instruments, and reference materials we purchase are inspected upon receipt in accordance with GL-RC-E-001 for the Receipt and Inspection of Material and Services. This inspection is to verify that procured items meet the acceptance criteria defined in the procurement documentation. Staff performing initial inspection routinely:

- Open and inspect all items for damage
- Compare the items with the issued purchase order or contract for catalog or part number, description or procurement specification, quality requirement, and acceptance criteria
- Label items with a limited shelf life with the date received
- Determine if the items conform to the specifications agreed to by the vendor.

The individual responsible for the technical acceptance of the item provides procurement and receiving staff with the proper acceptance documentation. Items found not to conform to quality standards are returned to the supplier, identified as nonconforming or disposed according to the established procedures in GL-

QS-E-004 for AlphaLIMS Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items. These nonconforming items may also include those identified as suspect/counterfeit items as identified in DOE guide DOE G 414.-3 for use with DOE 414.1B, C and D.

SECTION 6
HEALTH AND SAFETY

Section 6 – Health and Safety

GEL maintains a safe work environment and promotes healthy work practices. Our corporate Safety, Health, and Chemical Hygiene Plan was developed by a resident certified industrial hygienist. Procedures outlined in the plan are consistent with Occupational Safety and Health Administration, CERCLA, the Environmental Protection Agency, and SCDHEC.

All employees are trained in the safety practices applicable to their job functions. This training is conducted in accordance with GL-HR-E-002 for Employee Training.

Discussed in the section are:

- Fire safety and safety equipment
- Safety equipment and procedures related to handling radioactive samples

6.1 Fire Safety

Our facility is equipped with a fire alarm system designed to detect smoke in all areas of the facility. Certain high-risk areas, such as, the cold and ambient storage areas, organic sample preparation lab, hazardous waste lab, and solvent storage are additionally equipped with automatic halon systems. Fire blankets and dry chemical extinguishers are located at strategic points throughout the lab. We routinely inspect these extinguishers in accordance with GL-FC-E-004. Lab personnel are trained in the proper use and selection of fire extinguishers.

In order to decrease the risk of fire, bulk solvents are stored in a halon-protected storage room.

6.2 Evacuation

In the unlikely event of a fire (or other emergency), we have defined evacuation routes depicted in Appendix H. This diagram is posted in pertinent areas of the facility and designated staff members serve as evacuation leaders for the work groups.

6.3 Safety Equipment

Safety equipment, including safety glasses, lab coats, safety goggles, protective gloves, hard hats, and coveralls, is available to all employees as needed. We also provide respirators when needed to those who have completed training in the use of this specialized equipment.

Eyewashes and overhead showers are located throughout the laboratory. We routinely inspect these as directed in GL-FC-E-002 for Testing Emergency Eyewash and Shower Equipment.

6.4 Radiation Safety

Since GEL specializes in the handling of radioactive material, we have health physics procedures to ensure its safe handling. While lab personnel do not encounter significant levels of radiation requiring personal monitoring, a Dosimetry Program is in effect utilizing personal dosimeters for designated personnel. These dosimeters are exchanged quarterly and records of exposure are maintained. Instructions for the proper use of dosimeters are addressed in GL-RAD-S-009 for Personnel Dosimetry.

We take special precautions to ensure that samples are safely processed. Upon receipt, trained personnel use a survey meter to screen all samples for the presence of radioactivity. Protocols for the receipt of radioactive samples and for surveying suspected or known radioactive samples are detailed in GL-RAD-S-007 for Receiving Radioactive Packages and GL-RAD-S-001 for Radiological Surveys. This process is described in Section 9.

Upon leaving a radiologically controlled area, personnel check their hands and feet for potential contamination. This is done utilizing detection instrumentation that employs Geiger-Mueller or scintillation technologies. In addition, stations with portable detection instruments are set up for personnel frisking and in-process contamination surveys.

Key areas throughout the facility are surveyed:

- Laboratory analytical areas (Monthly smears)

- Radioactive Sample Storage Areas (Monthly smears and exposure rate)
- Sample Receipt and Waste Handling Areas (Monthly smears and exposure rate)
- Unrestricted and Radioactive Material Prohibited Areas (Quarterly smears)

SECTION 7
MEASUREMENT, TRACEABILITY, AND CALIBRATION

Section 7 – Traceability and Calibration

Traceability of measurements and the calibration of testing equipment are imperative to our ability to produce accurate and legally defensible data. As such, we have implemented procedures to ensure that equipment calibration and measurement verification are traceable to nationally recognized standards obtained from the National Institute of Standards and Technology (NIST) or accredited reference material producer (RMP) with traceability to NIST. Reference materials purchased outside the United States must be traceable back to each country's national standards laboratory or another national or international reference organization such as ILAC, APLAC and/or IAAC. The RMP may also have established acceptability by its approval as an ISO Guide 34 RMP. Commercial suppliers of radiochemistry reference standards/sources must conform to ANSI N42.22 and must be accompanied by a certificate of calibration consistent with ANSI N42.22-1995, section 8.

Where possible, calibration certificates provide traceability to national and/or international standards of measurement.

Calibration certificates provide measurement results and any associated uncertainty of measurement, and/or a statement of compliance with the identified specification. Calibration certifications are maintained as quality records.

When traceability to a national standard is not applicable, verification of measurement is achieved through inter-laboratory comparisons, proficiency tests, or independent analyses.

The following measurement and traceability practices are described in this section:

- Calibration criteria for support equipment
- General requirements
- Balances
- Temperature-sensitive devices and temperature monitoring
- Air displacement pipets
- Calibration criteria for instruments
- Calibration verification
- Initial calibration verification
- Continuing calibration verification

7.1 Calibration Criteria for Support Equipment

This section addresses calibration protocols for support equipment, including balances, temperature – sensitive equipment, and air displacement pipets. The general criteria applicable to the calibration of support equipment are as follows:

- Equipment is maintained in proper working order. Records of all maintenance activities including service calls are kept.
- Calibrations or re-verifications over the entire range of use, using NIST-traceable references when available, are conducted either quarterly, annually or biennially.
- The laboratory is allowed to re-verify some standards, sources and reagents to extend their expiration dates. However these reverifications must meet method acceptance criteria for their specific method and intended use. This has been GEL's process for numerous years and the laboratory has established a track record for both the reference materials and the producers. The reference materials verified/re-verified by the process have been subjected to numerous interlaboratory comparisons and cross-checked by use of different methods over a period of many years.
- If results of calibration and verification are not within the specifications for the equipment's application, then:
  1. The equipment is removed from service until repaired
  2. Under certain conditions, a deviation curve may be prepared. All measurements are corrected for the deviation, recorded and maintained.

- Prior to use each day, balances, ovens, freezers, refrigerators, incubators, and water baths are checked with NIST-traceable references (where possible) in the expected range of use.
- If prescribed by the test method, additional monitoring is performed for a device used in a critical test (such as an incubator or water bath).
- Support equipment is used only if the reference standard specifications (provided by the supplier or described in the analytical method) are met.
- Reference standards of measurement such as Class S or equivalent weights or traceable thermometers may be used for calibration when demonstrated that their performance as reference standards will not be invalidated.
- Reference standards of measurement are calibrated by a body that can provide, where possible, traceability to a national standard.
- Reference standards and measuring and testing equipment are, subject to in-service checks between calibrations and verifications, in accordance with ANSI/ISO/IEC 17025-2017.
- Reference materials, where possible, are traceable to national or international standards of measurement, or to national or international standard reference materials.
- Mechanical volumetric dispensing devices, except Class A glassware, are checked monthly for accuracy.

7.1.1 Balances

Our balances are under a service contract for annual calibration, maintenance, and cleaning. Each balance is labeled with a serial number, service date, date of next service, and signature or initials of the service technician.

Balances are set up, calibrated, and operated in the range required by the analytical method in accordance with GL-LB-E-002 for Balances. Prior to using a balance, the analyst is responsible for checking its calibration.

Calibration and calibration verification are performed using weights that are or have been calibrated against Class S or equivalent weights. These weights are traceable to NIST and calibrated biennially by a calibration service provider that meets the requirements of the ANSI/ISO/IEC 17025-2017 standard.

Calibration and calibration verification are recorded in the electronic balance calibration logbook. If the calibration or calibration verification does not meet the specified acceptance criteria, the balance is recalibrated. If the calibration criteria are still not met, the balance is removed from service and tagged as such.

7.1.2 Refrigerators, Freezers, Incubators, Ovens, Water Baths, and Similar Devices

Careful control of temperature is often central to the production of acceptable data. Temperature excursions beyond the established limits may invalidate a procedure and the associated data. Constant monitoring in accordance with GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators, and Other Similar Devices assures us that regulatory and/or method temperature requirements are being met.

We measure temperatures with thermometers that are verified either quarterly or annually against a NIST-traceable thermometer. The NIST traceable thermometers are independently verified at least annually by a verification service that meets the requirements of the ANSI/ISO/IEC 17025-2017 standard. The protocol for thermometer verification is described in GL-QS-E-007. We monitor the temperature of the following equipment according to GL-LB-E-004:

- Refrigerators and freezers used to store samples, standards, and other temperature-sensitive materials
- Incubators
- Ovens
- Water baths

We monitor the temperatures of refrigerators and freezers prior to use on each working day. The temperatures of ovens, water baths, and other devices used as part of an analytical process must be

monitored prior to, during, and immediately after use. Incubators and other devices used for other specialized analytical methods may require more frequent monitoring as specified in the corresponding SOP.

Temperature measurements are documented on logs specific to each piece of equipment. These logs may be paper or recorded electronically in LIMS. The logs may be posted on or near each refrigerator, freezer, water bath, oven, or other temperature control device. Electonic monitoring logbooks for refrigerators, freezers, and coolers with temperature probes are found in AlphaLIMS. Each log includes the following information:

- Date and time of each measurement
- Acceptance limits for device being monitored
- Whether device conforms with specifications at time of measurement
- Name, location, and number of device being monitored
- Notation of any out-of-control condition
- Any corrective action

When the process to maintain and document temperatures within acceptance limits does not conform to specificationsappropriate action is then taken to document the nonconformance. According to GL-QS-E-004 for AlphaLIMS Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items. Any corrective action taken to bring the equipment back into acceptable use is discussed.

Examples of nonconformances are:

- Failure to maintain process temperature within acceptance limits
- Failure of device to achieve calibration
- Total failure of temperature control device
- Failure to monitor the temperature as required

7.1.3 Air Displacement Pipets

We calibrate air displacement pipets in accordance with GL-LB-E-010 for Maintenance and Use of Air Displacement Pipets. As specified in the SOP, the calibration of an air displacement pipet is verified daily prior to use, based on a single point measurement.

The acceptance criteria for each measurement are based on the standard deviation of the calibration measurements. Tolerance limits for commonly used verification volumes and accuracy and precision checks are included in the pipet calibration logbook. Calibrations and daily calibration verifications are traceable to each pipet using the unique identification found on its label.

If a pipet does not meet the calibration tolerance limits, it is removed from service until it again demonstrates compliance after being cleaned and/or repaired. Analysts whose jobs may require the use of air displacement pipets are trained in their proper use and calibration.

7.2 Instrument Calibrations

To ensure that the data generated by an instrument are accurate, we calibrate the instrument using standards containing known concentrations of target analytes. We verify the accuracy of calibration standards by analyzing an additional standard containing the target analytes. This initial calibration verification standard (ICV) originates from a second source. Verification that the instrument response is reliable and has not changed significantly from the current calibration curve is accomplished by the analysis of a continuing calibration verification (CCV) standard. Some analytical methods employ the use of CCVs at varying concentrations.

Traceability of calibration, calibration verification, and other quality control standards to the recognized standard is documented per GL-LB-E-007 for Laboratory Standards Documentation. Preparation and Verification of Radioactive Standards is described in GL-RAD-M-001. Individual identification numbers are assigned to each source standard and each subsequent intermediate and working standard prepared.

The identification number makes it possible to trace a standard to a parent standard and ultimately to the source standard. The date each standard is prepared, the protocol used in the preparation, the person preparing the standard, and the standard's expiration date are documented in the appropriate standards log, usually maintained in AlphaLIMS. The information is accessible via the standard ID number.

We record standard and reagent ID numbers on instrument run logs, analytical logbooks, sample preparation logs, and instrument raw data. Calibration standards that are used in the analysis of a particular sample or group of samples can be traced to NIST, US EPA, or other nationally recognized standards.

Calibration procedures for specific instruments, and the frequencies of performance for defined methods, are described in the applicable operating or analytical SOP. Calibration is discussed in general terms in GL-QS-E-014 and includes standard laboratory practices and formulas used for determinations made by these practices. General guidelines include:

- Verification of initial calibrations with a standard obtained from a second source (unless one is not available).
- Analysis of verification standards (ICV and CCV) with each initial calibration within 15% of the true value unless historical data have demonstrated that wider limits are applicable.
- Preparation of calibration curves as specified in the reference method.

  If a test method does not specify the number of calibration standards, the minimum number is two, not including blanks, with one at the lowest quantitation limit. The reference SOP must establish the initial calibration requirements.

7.3 Calibration Verification

Unless otherwise specified by the method, regulatory program or demonstrated through historical data, the recovery of target analyte(s) in calibration verification standards shall be between 85 – 115%. We discuss additional requirements below.

7.3.1 Initial Calibration Verification (ICV)

- If an initial calibration curve is not established on the day of analysis, the integrity of the curve should be verified each day of use or every 24-hour period. Verification requires the initial analysis of a blank and standard from a second source. The standard concentration should be at the method-defined level. If not specified, a standard at a mid-level concentration may be used.
- If the initial calibration verification does not meet acceptance criteria, the analytical procedure is stopped and evaluated, and appropriate corrective measures are taken. Initial calibration verification must be acceptable before any samples are analyzed.

7.3.2 Continuing Calibration Verification (CCV)

Additional standards called CCVs are analyzed after the initial calibration curve or the integrity of the initial calibration curve is accepted. CCVs are analyzed at a frequency of 5% or every 12 hours, whichever is more frequent. If an instrument consistently drifts outside the acceptance criteria before the next calibration, the frequency is increased.

CCVs may be from the same source as the calibration standards or from a second source. The concentration is determined by the anticipated or known concentration of the samples and/or method-specified levels. At least one CCV shall be at a low-level concentration.

To the extent possible, we bracket the samples in each interval (every 20 samples or every 12 hours) with CCV concentrations closely representing the lower and middle range of reported sample concentrations. If this is not possible, the standard calibration checks should vary in concentration throughout the range of the data being acquired.

If the recovery of a CCV does not meet the acceptance criteria and routine corrective actions fail to produce a second consecutive check within acceptance criteria, a new initial calibration curve should be constructed. Analytes of interest found in corresponding environmental samples may be reported, however, only if all of these criteria are met:

1. CCV recovery for target analyte exceeds the acceptance criteria (biased high)
2. Target analyte in the environmental sample is not detected at a concentration exceeding the level required by client contract (i.e., MDL, PQL).

   Non-detects that meet these criteria are also referred to as “passable non-detects.”

If samples are found to contain target analytes that exceed the associated quantitation limits, and the CCV recovery does not meet the acceptance criteria, the

affected samples are re-analyzed. This occurs only after a new calibration curve has been established, evaluated, and accepted.

7.4 Bioassay Instrument Calibration and Frequency

Our Bioassay instruments are calibrated at the frequency of the instrument's use, stability, and method requirements. The calibration procedure for each instrument is described in the corresponding analytical SOP and is performed by those individuals proficient in the analyses described in the SOP.

SECTION 8
ANALYTICAL METHODS AND STANDARD OPERATING PROCEDURES

Section 8 – Analytical Methods and Standard Operating Procedures (SOPs)

We provide a wide array of parameters including volatile organics, extractable organics, metals, general inorganic/wet chemistry, radiochemistry, and radiobioassay. The procedures we use to determine these parameters are consistently executed due to our extensive system of SOPs and our training requirements for analytical staff.

A list of our SOPs and the analytical methods they represent (if applicable) is provided in Appendix I. Discussed here are:

- Selection of analytical methods
- Standard operating procedures
- Method validation and initial demonstration of capability
- Sample aliquots
- Data verifications
- Standard and reagent documentation and labeling (Refer to Section 10.1)
- Computers and data requirements

8.1 Selection of Analytical Method

Project Managers are ultimately responsible for selecting the test codes and methods assigned to a client based on client requirements and sample collection techniques. In selecting methods, our goal is to meet the specific needs and requirements of the client while providing data that are scientifically valid.

When the use of a specific test method is mandated, only that method is used. If the analysis cannot be performed by the client-requested method, we notify the client. We do not perform method substitutions without the client's consent. We recommend that clients who submit data to regulatory agencies also obtain the agency's approval of method modifications.

When clients have specific process or reporting deviations from GEL's standard practices, the laboratory may document the deviations in contracts, case narratives and/or with specific work instructions from the Project Management Team to the laboratory. Approval of the deviations is made after consideration of all safety and quality concerns have been resolved by GEL's management.

A Project Management AlphaLIMS Manual (GL-CS-M-001) is available to assist PMs and PMAs in selecting test codes and methods and communicating the client's analytical and data reporting specifications.

8.2 Standard Operating Procedures (SOPs)

We determine each parameter by the protocol detailed in the corresponding SOP. The defined protocol originates from the analytical method or methods referenced in the SOP and may incorporate regulatory and client requirements. Descriptions of the methods we employ can be found in:

- EPA SW-846
- EPA/600/479/020
- Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC)
- American Society for Testing and Materials (ASTM)
- Standard Methods for the Examination of Water and Wastewater (SM)
- South Carolina Department of Health and Environmental Control (SCDHEC)
- Code of Federal Regulations (CFR) Titles 40 and 49
- Department of Energy Environmental Measurements Laboratory (EML)
- Los Alamos Health and Environmental Chemistry (LAHEC)
- DOE
- DoD
- HASL

In addition to these references, a number of our radiochemistry procedures were developed in conjunction with Florida State University (FSU) under the guidance of Dr. Bill Burnett.

Laboratory sections have access to GEL's SOPs to ensure that each operational system and analytical procedure is performed in a uniform manner. SOPs are controlled according to GL-DC-E-001 for Document Control and are posted on the Intranet by the Document Control Officer.

We write and issue SOPs in accordance with GL-ADM-E-001 for the Preparation, Authorization, Change, Revision, and Release of Standard Operating Procedures. A technical and/or quality review is made of each new or revised SOP prior to its implementation.

Technical reviews ensure that procedures are technically sound and method-compliant, and are conducted by a senior analyst, group leader, or data reviewer. The quality review is an independent review by a member of the Quality Systems team and ensures that the quality requirements of the method, regulatory agencies, and GEL are adequately and accurately identified.

SOPs are modified when:

- Instruments or equipment change
- An error is identified
- Improvements in technology and/or reagents need to be incorporated
- Reference methods are revised or discontinued

Proposed revisions are submitted for review on Documentation Initiation and Revision Request (DIRR) forms. Changes are not implemented without a technical and quality review.

We review our technical SOPs annually and revise them as necessary. Analytical SOPs either contain or reference other SOPs that contain:

- reference method
- applicable matrix or matrices
- method detection limit
- scope and application including parameters to be analyzed
- method summary
- definitions
- interferences and limitations
- specific safety requirements
- required equipment and supplies
- reagents and standards
- sample collection, preservation, shipment, and storage
- quality control
- calibration and standardization
- procedure
- calculations
- method performance
- pollution prevention
- data assessment and acceptance criteria for quality control measures
- corrective actions for out of control or unacceptable data
- waste management
- references
- tables, diagrams, flowcharts, validation data
- identification of any modifications we have made to the published procedure

8.3 Method Validation and Initial Demonstration of Capability

Method validation requirements for Radiochemistry are documented and maintained in accordance with GL-RAD-D-002, Analytical Methods Validation for Radiochemistry.

An initial demonstration of method performance is required before a new analytical method is implemented and any time that there is a significant change in instrumentation or methodology. Exempted from this requirement are any tests for which spiking solutions are not available. Analyses that are exempt include those for determining:

- total dissolved, total suspended, total volatile, and total solids
- pH
- color
- free liquids
- temperature
- dissolved oxygen
- turbidity

We conduct the initial demonstration as described in Section 8.3.1. Records of initial demonstration are maintained in accordance with GL-QS-E-008 for Quality Records Management and Disposition. These records are available upon request.

After we demonstrate our ability to perform a specific analysis, we continue to demonstrate method performance through the analysis of laboratory control samples and performance evaluation samples.

If spiking solutions or quality control samples are not available, an analyst is trained by a qualified trainer to conduct the analysis. Analyst capability and proficiency is evaluated by the appropriate Group Leader before the

analyst is qualified to perform the analysis on client samples. The evaluation is documented and maintained according to GL-QS-E-017 for Maintaining Technical Training Records.

Method Validation must also occur when substantive modifications are made to stoichiometry, technology, mass tuning acceptance criteria, quantiation ions, compressing digestion or extraction timeframes, reducing reagent or solvent volumes, changing solvents or compressing instrument.

8.3.1 Procedure for Initial and Continuing Demonstrations of Capability (IDOC and CDOC)

We conduct initial demonstrations of capability for mandated analytical or EPA reference test methods following the procedure outlined below. This procedure is adapted from the EPA test method published in 40 CFR part 136, Appendix A and the 2003 NELAC and 2009 TNI Standards. IDOCs are completed whenever there is a change in instrument type, method or personnel. CDOCs are updated constantly in the laboratory AlphaLIMS.

Step 1: A quality control sample is obtained from an outside source (if possible). If one is not available, the sample may be prepared internally using stock standards that are prepared independently from those used in instrument calibration. The concentration is not known to the analyst.

Step 2: The QC sample is diluted in a volume of clean matrix. Sufficient volume of the diluted QC sample is prepared so that at least four aliquots of the required method are analyzed. Alternatively, four matrix spike samples may be evaluated for levels of precision and accuracy.

Step 3: Four aliquots of the diluted quality control sample are prepared and analyzed according to the analytical test method. This may occur concurrently or over a period of days.

Step 4: With the results obtained from the analysis of the diluted QC sample, the average recovery (x) in the appropriate reporting units (such as µg/L) and the standard deviation of the population sample (n-1) (in the same units) are calculated for each parameter of interest.

Step 5: For each parameter, the standard deviation (s) and the average recovery (x) are compared to the corresponding acceptance criteria for precision and accuracy in the test method (if applicable) or in laboratory-generated acceptance criteria. If "s" and "x" for all parameters meet the acceptance criteria, analysis of samples may begin. If any one parameter exceeds the acceptance range, the performance is unacceptable for that parameter.

Step 6: When one or more tested parameters fail one or more of the acceptance criteria, we locate and correct the source of the problem and repeat the test for every parameter of interest.

Other options for successful IDOCs are the following:

- PT Study- successful analysis of a PT Sample. If 4 LCSs cannot be performed, successful analysis of a PT sample may be used to demonstrate capability to perfrom a test. The PT sample may be single-blind to the analyst or double blind to the laboratory.
- Supervised Analysis- where other options are not practical, supervised analysis of a procedure may be used to demonstrate capability.
- Analysis of authentic sample with results statistically matching those obtained by another trained analyst.
- Other – this option may be used for certain personnel having sufficient analytical skills to develop a new procedure, as deemed appropriate by the supervisor or Quality Assurance personnel.

8.4 Sample Aliquots

When obtaining aliquots from a sample, it is imperative that the subsamples be representative of the parent sample. This ensures that the results obtained from the analysis of the aliquots are representative of the entire parent sample, not just the subsample. We employ different techniques to obtain subsamples. GEL's SOP for subsampling is GL-LB-E-029.

We can obtain representative aliquots of soil samples for the determination of metals through quartering. This involves the repeated quartering of the sample until the resulting quarter is equivalent to the amount of sample needed for analysis. Quartering may not be appropriate for obtaining subsamples for volatiles or other analyses where potential contamination or loss of target analytes is a concern.

Water samples are inverted several times prior to the collection of a subsample. This ensures a thorough mix and is absolutely required for the accurate

determination of analytes like total and total suspended solids.

The appropriate techniques for obtaining sample aliquots for designated analyses are discussed in the applicable SOPs.

8.5 Data Verification

All of the data we include in final reports to our clients undergoes extensive data verification. At GEL, we have a multi-level review process that takes place in all areas of the laboratory beginning with sample login. This process and the responsibilities of each level of review are delineated in a number of procedures, including GL-GC-E-092 for General Chemistry Data Review and Packaging, GL-MA-E-017 for Metals Data Validation, and GL-RAD-D-003 for Data Review, Validation, and Data Package Assembly.

8.5.1 Sample Login:

Samples are analyzed by the methods and for the target analytes identified when samples are logged into our database. If there is an error in this entry that is not promptly identified, the incorrect analytical method may be used or certain analytes may not be determined.

To prevent this, the person who enters the information into the database is generally the client's assigned Project Manager or PM Assistant. This entered information is reviewed against the client confirmation letter and/or chain of custody. If errors are identified, they are immediately corrected.

8.5.2 Data Validation in the Laboratory

The multi-level review process in our laboratory includes initial review by the analyst, a second review by a peer, and a final review by a group leader or data reviewer. Where appropriate based on personnel and client needs, the industrial division institutes two levels of review.

Our analytical data reviews ensure that:

- The analytical procedures comply with current SOPs.
- Quality control samples are analyzed at the frequency specified in the SOP or client specifications.
- The acceptance criteria for quality control samples are met, including recoveries of matrix spikes and laboratory control samples, the relative percent difference for matrix duplicates, matrix spike duplicates, laboratory control sample duplicates, and concentrations of target analytes in the method blank.
- Instrument data, run logs, and logbooks are reviewed to ensure that all method quality control criteria were met (e.g., calibration, initial calibration verifications, and continuing calibration verifications).
- Documentation is sufficient to reconstruct the analytical procedure.
- Data are maintained according to GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms, and Other Recordkeeping Devices.
- Raw data are in agreement with the computer generated batch sheets and data reports.
- The calculations, dilution factors, concentration reported, and nominal concentrations are verified.
- Comments, qualifiers, or nonconformances for noncompliant or questionable data are documented.
- Data generated when the analytical process appears to be out of statistical control are not reported.

8.5.3 Validation of Data Reports and Packages

Before we report data to the client, we review the requested data report for package accuracy, completeness, and client-specifications. Responsibilities for review are dependent upon the type of report or package being generated. (Refer to Section 11 for Laboratory Report Formats.)

When a client is receiving a certificate of analysis or certificate of analysis and Quality Control Summary Report, the Project Manager (PM) or Project Manager Assistant (PMA) reviews the information for accuracy, completeness and the addition of pertinent comments made by the laboratory about the analysis or sample. The PM or PMA also reviews data for consistency as described in the Project Management AlphaLIMS Manual, GL-CS-M-001. For Bioassay results, the package is then reviewed for completeness by validator, team or group leader as described in GL-RAD-B-026.

If a client requests a case narrative, our data validators review the analyst-prepared case narrative for

accuracy and to assure its consistency with the information included on the certificate of analysis and Quality Control Summary Report. If a client requests a more detailed level of data package up to and including a CLP-like package, every laboratory fraction of data is reviewed by that fraction's data validator. The data are then compiled into a final data package. The Quality manager or designee will review a minimum of 10% of all data packages for technical completeness and accuracy on a quarterly basis and if data quality issues are discovered during the review, the client will be notified with fifteen (15) business days of the discovery of the issue.

8.6 Standard and Reagent Documentation and Labeling

The documentation and labeling of standards and reagents is addressed in GL-LB-E-007 and GL-RAD-M-001 for Laboratory Standards Documentation, and in Section 10.1 of the QAP, Recordkeeping System and Design.

8.7 Computer and Electronic Data Related Requirements

Our Information Management System (IT) SOPs describe the way in which we manage our software programs and hardware systems. Control of software development and modification activities is described in GL-IT-E-003 for Requirements, Design, Operation, Validation, and Removal of Hardware and Software Systems Used by the GEL Group, Inc. All development and revision activities are validated, and revision activities are validated, verified, and controlled with revision software or other procedures prior to production use.

Analytical software that is purchased from a vendor is validated and verified in accordance with GL-IT-E-005 for Requirements, Design, Operation, Validation, and Removal of Applications Used by The GEL Group, Inc. Documentation requirements are also described in this SOP.

Electronic signature requirements for confidentiality of records are described in GL-IT-E-001 for Instrument Technology Program for Good Laboratory and Good Manufacturing Practices.

SECTION 9

SAMPLE HANDLING, ACCEPTANCE, RECEIPT, AND INTERNAL CHAIN OF CUSTODY

Section 9 – Sample Handling, Acceptance, Receipt, And Internal Chain of Custody

The way we receive and handle samples is critical to providing our clients with data that are of the highest quality and are legally defensible. We have strict policies that govern the acceptance and receipt of a sample, sample handling and integrity, maintenance of the internal chain of custody, and storage of the sample upon completion of the required analytical processes. This section describes the policies and practices that we employ, including the following:

- Agreements to perform analysis
- Proper labeling of submitted samples
- Chains of custody
- Sample receipt procedures
- Sample receipt procedures for radioactive samples
- Sample tracking
- Sample storage
- Sample disposal

9.1 Agreement to Perform Analysis

Before we accept samples, we should have an agreement with the client that specifies the analytical methods, the number of samples to be analyzed, the price for the analysis, the date by which the client must receive results, and the reporting format. Any special requirements the client may have, such as non-routine methods and reporting limits, should be part of that agreement.

An agreement to perform analysis should be in one of three forms, further detailed in our Analytical Services Reference Manual and the SOPs for Delegated Authority to Commit the Company and Request for Proposal (RFP) and Contract Review (GL-CO-E-002 and GL-CO-E-003):

- Client confirmation letter (CCL) between the client and project manager for a specific group of samples. This letter includes the cost, turn-around time, requested analysis, sample matrix, number of samples, and type of client report.
- Sample acceptance by the Project Manager from an established client based on previously agreed conditions and confirmed by the client's submission of the sample(s).
- Contractual agreement for analytical services over a designated time period or project that delineates the specifications agreed upon.
- When the laboratory agrees to perform analyses with exceptional departures from normal processes, these exceptions are clearly defined in the client-laboratory agreement.

9.2 Sample Labels and Chain of Custody Forms

Once an agreement is established, we assume joint responsibility with the client to ensure that the samples submitted are properly labeled and accompanied by full and complete documentation that includes chain of custody and, where possible, material safety data sheets. Samples that are submitted without proper documentation may be refused.

Sample labels should include the:

- client's sample identification
- location, date, and time of collection
- collector's name
- chemical preservatives used
- constituents of interest (if space permits)

When requested, we ship labeled sample containers with appropriate preservatives and a chain of custody to the client for use during sample collection. There are several advantages to using these containers, including:

- Dedication of appropriate type sample container for the intended analyte or analytical method.
- Proper sample preservation for analytical test
- Traceability of bottle lot number to the manufacturer's certification that the containers are clean and show no signs of contamination.
- If a manufacturer cannot provide a certificate of cleaniness for radiochemistry parameters, a gross alpha-beta screen can be performed on the lot of containers being used. This is mandatory for containers used in support for SDWA programs.

Chain of custody forms include the following information and are initiated at the time of sample collection:

- name and address of client
- client sample identification
- date and time of sample collection
- sample matrix
- description of sampling site location
- number of containers
- methods, chemical and physical constituents for which the analyses are to be conducted
- preservatives
- date and signature of person who collected the sample
- date of transfer and signature of person relinquishing sample to the laboratory.

When our Field Services personnel collect samples, our standard chain of custody form and certified containers are automatically used. Our standard chain of custody forms are also available to our clients and are included with each shipment of pre-labeled and preserved containers. GEL chain of custody forms should always be used unless otherwise agreed to by contract.

9.3 Sample Conditions

In addition to properly documenting sample container labels and the chain of custody form, we need to make sure that samples meet the established requirements for analytical testing. This is particularly critical for samples that are being analyzed to meet regulatory requirements.

Samples should be collected in the appropriate type of container, preserved as directed, and stored in the conditions specified in the analytical method or established regulatory guidelines. In addition, samples should be submitted with sufficient time to conduct the specified analysis within the regulatory or method holding time. Aliquots should be of sufficient volume to perform the requested analyses. A summary of these conditions and holding times for routine analyses can be found in Appendix J.

9.4 Sample Receipt

Samples submitted to us are received in a central sample receiving area by our sample custodian or login clerk. Every sample is subject to the protocols established in GL-SR-E-001 for Sample Receipt, Login and Storage.

Our sample custodian acknowledges receipt of a sample by signing the chain of custody and recording the date and time custody was transferred from the client to the laboratory. The date, time, and person receiving the sample are also recorded on a standard or client-specific Sample Receipt Review (SRR) form.

The sample custodian is also responsible for noting the condition of a sample upon its arrival. This information may be recorded on both the sample chain of custody and the Sample Review Receipt form. As detailed in GL-SR-E-001, the sample custodian should:

- Inspect all sample containers for integrity.
- Document any unusual physical damage or signs of tampering with custody seals.
- Place any samples that appear to be leaking or have unusual odor under the fume hood while notifying the responsible project manager.
- Review the chain of custody submitted by the client for completeness.
- Compare descriptions and other information on the sample container labels to that listed on the chain of custody.
- Verify the sample is within the regulatory holding time for the analyses.
- Measure and record the temperature of sample aliquots that are to be used for analyses requiring thermal preservation.
- Measure and record the pH of all sample aliquots submitted for analyses that require chemical preservation to a specific pH.
- Verify that there are adequate sample aliquots for the requested analyses.
- Verify that appropriate sample containers were used for requested analyses.

If the sample custodian discovers any abnormalities or departures from standard conditions, the PM is

informed immediately. The PM will then notify the client as quickly as possible so that a decision can be made to proceed with the analysis or submit another sample or additional sample aliquots.

Common abnormalities or departures from standard conditions include:

- Sample containers with signs of damage, leaking, or tampering.
- Incomplete/missing chain of custody.

NOTE: If a nonradioactive sample has no chain of custody, the sample custodian should initiate one. "INITIATED ON RECEIPT" should be documented on the chain of custody.

- Discrepancies between the information on the chain of custody and the sample container labels.
- Method or regulatory holding time is exceeded.
- Sample is not preserved to the method or regulatory-required pH.
- The sample container does not meet method or regulatory criteria.
- The sample temperature exceeds or falls below the thermal preservation regulation or method requirement of 0° ≤ 6° C.

NOTE: If a sample is hand delivered to the laboratory immediately after collection with evidence that the chilling process has begun (arrival on ice), the sample shall be deemed acceptable.

- Radioactivity that exceeds that allowed by our radioactive license. (The handling of radioactive samples is discussed in 9.5.)

Samples that are not appropriate for the requested analyses or have no full test specifications require:

- Retention of all correspondence and records of conversations concerning the final disposition of the sample.
- Full documentation on the chain of custody and Sample Receipt Review form of the nonconforming condition and a decision to proceed with analysis.
- Documentation that the analysis is qualified appropriately on the final report.

9.5 Receipt of Radioactive Samples

The radioactive samples we receive are subject to the same monitoring identified in 9.4 when radioactivity levels do not exceed the level permitted by our license. Special procedures governing the receipt of radioactive samples are described in the GL-RAD-S-007 for the Receiving Radioactive Packages. These procedures prevent the inadvertent spread of radioactive contamination.

Because we cannot exceed the limits of our radioactive license, it is imperative that our clients notify us of impending shipments of radioactive samples. We reserve the right to refuse and return any radioactive sample where the radioactivity:

- Exceeds our permitted level by itself or in combination with other samples already on site; or
- Exceeds our administrative level of 25 mrem/hr.

The following special requirements for receiving radioactive samples are applicable:

- Only designated staff trained in the proper handling of radioactive materials handle radioactive samples.
- If a sample is labeled as radioactive, the custodian will immediately inform the Radiation Safety Officer (RSO) before opening the sample.
- The radioactivity of the sample will be measured by scanning the exterior surface of the cooler using a survey meter calibrated in Mr/hr. Refer to GL-RAD-S-001 for our Radiological Survey Procedures.
- If the radioactive level of the exterior of the cooler exceeds 0.5 Mr/hr, the RSO will be notified before the cooler is opened.
- If the radioactivity level of a sample or group of samples is found to exceed 25 mrem/hr, the RSO will be notified immediately. The client will be contacted and arrangements will be made to return the sample(s) or reduce the per sample exposure.
- If a chain of custody is not submitted with a sample, it will be placed on hold until a chain of custody is submitted.
- The inside of the cooler will be surveyed to ensure that no leakage or contamination has occurred.

- Each sample container will be surveyed and the highest reading will be documented on the Radioactive Shipment Inventory.

9.6 Sample Tracking

We track the samples we receive by a unique laboratory identification number that is automatically assigned when information pertaining to the sample is first entered into our database. Pursuant to GL-SR-E-001, the following information is entered for each sample received:

- client and/or project code
- client sample ID
- sample matrix
- equivalent laboratory sample matrix
- type of report format specified by client
- date and time of collection
- date received
- initials of person making entries
- number of containers submitted for the sample
- requested analyses
- pertinent observations or comments affecting the sample analysis or rejection

As soon as this information is entered, AlphaLIMS automatically assigns a unique number to the sample and its containers. We use the number to track the location of a sample container and to link to any subsamples and subsequent digestates and extracts.

The unique laboratory identification number is printed on a durable barcode label that contains the client identification, sample date and time. Once labeled, the sample container's identification number is uploaded into the database by scanning the barcode. Information included in the database at the time of sample scanning is the container's storage location, bottle type and volume, physical characteristics of the bottle, preservative, and the initials of the person entering this information. Entering of this information into the database is an important part of initiating our electronic internal chain of custody.

9.7 Internal Chain of Custody

Chain of custody procedures ensure traceability and sample integrity. Our legal and evidentiary chain of custody protocol establishes a continuous record of the physical possession, storage, and disposal of sample containers, collected samples and aliquots, and sample digestates or extracts.

The internal chain of custody starts with the scanning of a container's barcode label into an electronic database while identifying the location of the sample and the person having custody, or placing the sample in a secured storage area. If we supply the containers, the chain of custody may begin when the containers are provided to the client.

With regard to the internal chain of custody, a sample is defined as being in someone's custody if:

- It is in one's actual physical possession
- It is in one's view after being in one's physical possession
- It is in one's possession and then is locked up so that no tampering may occur
- It is kept in a secured area restricted to authorized personnel only

The protocol for ensuring sample integrity using the internal chain of custody is detailed in GL-LB-E-012 for Verifying the Maintenance of Sample Integrity. The electronic internal chain of custody works in conjunction with the chain of custody submitted by the client with a sample to:

- Account for all time associated with a sample, its subsamples, and extracts or digestates from the time the sample is received at GEL to its disposal
- Identify all individuals who physically handled the sample
- Provide evidence that the sample was stored in accordance with method and regulatory protocols

The electronic internal chain of custody is stored in AlphaLIMS so that information demonstrating the proper maintenance of custody can be provided to the client on the data reports or electronic data deliverables.

9.8 Sample Storage

In order to ensure the maintenance of sample integrity, all aliquots are stored in secured areas designated for sample storage. The storage location of

each sample aliquot can be tracked using the internal chain of custody. Areas designated for sample storage include:

- Main cooler where most samples requiring maintenance at a temperature range of 0° ≤ 6° C are stored.
- Volatile coolers for samples to be analyzed for volatile contaminants.
- Radioactive cooler for segregation of radioactive sample aliquots requiring refrigeration.
- Ambient storage for non-radioactive samples not requiring refrigeration.
- Ambient storage for radioactive samples.

The temperature of each refrigerated storage unit is monitored daily and documented per GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators Freezers, Ovens Incubators, and Other Similar Devices. In addition, the main and radioactive coolers are monitored twenty-four hours a day by temperature sensors that are connected to our main security system. If the temperatures exceed the required range, the security system notifies the facilities manager or his designee immediately. This allows corrective actions to be initiated promptly.

Prior to and immediately after analysis, samples and their digestates and extracts are stored in compliance with the requirements of the requested analytical methods and GL-SR-E-001 for Sample Receipt, Login, and Storage. If a single aliquot is supplied for analyses by several methods, the most stringent analytical storage requirements are applied to the sample.

If samples are to be analyzed for volatile organic compounds, they are stored in designated volatile coolers that are maintained at a temperature range of 0° ≤ 6° C. No sample aliquots are stored in these refrigerators unless they are to be analyzed for volatiles. These storage units are monitored on a weekly basis for contamination by the analysis of volatile cooler storage blanks.

At the beginning of each month, two 40 mL vials are filled with treated deionized water, which is used for volatile method blanks and placed in each monitored cooler. Each week, two vials may be analyzed by EPA 8260B and the data are reported to the Quality Department. If the analysis reveals evidence of potential contamination, appropriate corrective actions are immediately implemented. SOP GL-OA-E-058 discusses the laboratory practices pertaining to monitoring and testing for VOA contamination.

Sample aliquots for non-volatile analysis, which also should be maintained at 0° ≤ 6° C, are stored in the main cooler unless they are radioactive. In order to reduce the chance of contamination, radioactive samples are stored in a designated cooler.

Sample aliquots to be analyzed for biochemical oxygen demand (BOD) are also delivered to the bacteriology laboratory and stored in the designated BOD cooler. This cooler is also maintained at 0° ≤ 6° C. After initiation of this analysis, the sample aliquots are returned to the main cooler.

After all analyses are complete and results are submitted to the client, sample aliquots are transferred to the sample archive area. They are stored in this area until they are disposed.

Radioactive and non-radioactive samples remain segregated in archive to reduce the risk of contamination.

9.9 Sample Disposal

Our policies concerning sample disposal are described in the Laboratory Waste Management Plan, GL-LB-G-001 and can be divided into two categories: those governing the disposal of sample laboratory waste, and those governing the disposal of residual client sample after the completion of all analyses.

9.9.1 Sample Laboratory Waste

Unless otherwise requested by contract, laboratory waste is collected in designated satellite containers found in sample collection and accumulation areas. These areas are monitored by both the waste department and analysts trained in waste collection. Wastes are segregated based on the type of hazard they present. I.e. radioactive, acid, base solvent, etc. when containers are full, the waste department is notified and the containers are removed from the laboratory for disposal. Direction for disposal activities, such as

packaging, shipping, and disposal site selection are provided in the Laboratory Waste Management Plan (GL-LB-G-001).

9.9.2 Residual Client Sample

Unused client sample material that is not consumed during the sample preparation or analytical procedures is either disposed of in accordance with the Laboratory Waste Management Plan (GL-LB-G-001) or at the client's request, returned in accordance with GEL's SOP GL-SR-E-002 for Transportation and Shipping of Samples and Pre-preserved Sample Containers.

It is our policy to hold samples for a minimum of sixty days after invoicing and before disposal, unless otherwise specified by contract or if the sample is part of litigation. If the sample is part of litigation, disposal of the physical sample shall occur only with concurrence of the affected legal authority, sample data user, and/or client.

When sample analyses are complete and regulatory and/or contractual holding times have expired, samples are moved from their storage locations to the radioactive or non-radioactive archives. Samples that are to be returned to the client or held for an extended time period are segregated from the other samples. Radioactive and non-radioactive samples remain segregated.

When internal or client-specified storage time expires, samples with like matrices are composited into appropriate containers. The composites are then subject to the same treatment and disposal protocol. Samples that are approved for disposal are scanned into our LIMS and assigned the status of "Disposed."

SECTION 10
RECORDS

Section 10 – Records

Our quality records provide the documentation we need to support analytical results and conclusions. Documented evidence that quality assurance and quality control requirements have been met is critical to providing data that fulfill the specifications of applicable procedures, programs, and contracts.

As described in Section 3 of this Quality Assurance Plan (QAP), quality records include but are not limited to:

- Observations
- Calculations
- Calibration data
- Certificates of analysis
- Certification records
- Chains of custody
- External, supplier, and internal audits
- Run logs
- Instrument data and analytical logbooks
- Instrument, equipment and building maintenance logs
- Material requisition forms
- Monitoring logs
- Nonconformance reports
- Corrective actions
- Method development and start-up procedures including MDL studies
- Training records
- Waste management records
- Standard logs
- Software validation
- Standard operating procedures (SOPs)
- Sample collection and field data

Our procedures provide a legal and evidentiary chain of custody and are described in Section 9 of this QAP. Described in this section are:

- Record keeping system and design
- Records management and storage
- Sample handling records
- Records of support activities
- Analytical records
- Administrative records

10.1 Recordkeeping System and Design

We manage, maintain and store our quality records according to GL-QS-E-008 for Quality Records Management and Disposition. The protocols established in this document work in conjunction with those for specific types of records addressed in other SOPs to govern our record keeping system. Our record keeping system allows the historical reconstruction of all laboratory activities that produced analytical data.

We facilitate historical reconstruction by maintaining the following records and information, from the time a sample is received until it is disposed.

- A master list of all employee signatures and initials is maintained in Human Resources. This allows the identification of any GEL personnel who accept, handle, analyze, prepare, review, store, or dispose of a sample, its subsamples, associated data and reports, and other related documentation.
- If we provide bottles and containers to a client or sampling personnel, these records are kept in accordance with GL-SR-E-002 Transportation and Shipping of Sample and Pre-preserved Sample Containers. These electronic and paper records include:
    - Supplier and lot numbers of containers and/or bottles provided
    - Certifications that the containers are free of contaminates that may bias the analyses
    - Addition of preservatives and identity of person responsible for this preservation.
    - Barcode of containers supplied to a particular client or for a specific field-sampling event.

The person or agency responsible for collecting a sample is documented on the chain of custody and entered into AlphaLIMS. Other records supporting the acceptance of a sample include:

- Date and time of sample receipt

- Person accepting sample
- Condition of sample upon receipt
- Client-confirmation letter and/or sample quote
- Client chain of custody
- Electronically generated sample ID numbers specific to each sample aliquot and linked to the client's sample description, sample collection and receipt information, and analyses to be performed.
- Identification of each person who has custody of a sample, its subsamples, extracts, or digestates. (This is provided through the internal chain of custody procedures described in Section 9.)

Documentation that materials purchased for use in the analysis or preparation of samples meet specifications is maintained in accordance with GL-RC-E-001 for Receipt and Inspection of Material and Services.

Records of equipment calibrations are maintained and traceable by date and ID number to a specific analysis. These records include certifications of calibration and service that have been initialed or signed.

Our thermometers are verified against a NIST traceable thermometer and records of this verification are maintained as described in GL-QS-E-007 for Thermometer Verification. Records of the daily and monthly calibration verifications of our analytical balances are kept in accordance with GL-LB-E-002 for Balances. The calibration records for our air-displacement pipets are maintained in pipet calibration logs specific to each pipet according to GL-LB-E-010 for Maintenance and Use of Air Displacement Pipets.

When methods and/or regulations specify that samples, subsamples, extracts, and/or digestates be stored at designated temperatures, or when the method, itself, has temperature sensitive steps, we document those temperatures on monitoring logs at the frequency defined in the corresponding SOPs. We can trace the specific storage location of a sample through the internal chain of custody.

We require that the initials of all personnel responsible for monitoring temperatures be recorded in the temperature monitoring logs pursuant to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators and Other Similar Devices. The logs are reviewed for completeness in accordance with GL-QS-E-005 for Review of Monitoring Device Logs.

Documentation on the instruments and equipment used for the analysis of samples is recorded in run logs, laboratory logbooks, instrument data and/or sample preparation logs. Routine or corrective maintenance that is performed on equipment or instruments is recorded in the maintenance log specific to the instrument. We document these records in accordance with GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms and Other Recordkeeping Devices.

The standards containing known quantities of target analytes that we use in instrument calibration, calibration verification, and as quality control samples, such as matrix spikes and laboratory control samples, are documented according to GL-LB-E-007 and GL-RAD-M-001 for Laboratory Standards Documentation. These records contain the following information.

- Protocol by which each standard was prepared
- Traceability of each child standard to its parent
- Date each standard was prepared
- Initials of person preparing the standard
- Expiration dates
- Concentration of each standard

This information allows us to document that the standards used were prepared in accordance with the established protocol, produced using source standards that meet the method and regulatory criteria, and used prior to their expiration date.

If required, reagents used in the preparation, dilution, and analysis of samples are verified to be free of interferences or target analytes. We record these verifications in the Reference Material in LIMS in accordance with GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms and Other Recordkeeping Devices.

Analytical and sample preparation methods applied to each sample aliquot are documented via the internal chain of custody, method information, and information recorded in lab notebooks, sample preparation logs, run logs, and instrument data. The laboratory protocol we employ during analysis is dictated by the SOP in effect at the time the sample was analyzed or prepared by a specific method.

Run logs, laboratory notebooks, instrument data and sample preparation logs are used to document the preparation and analysis of samples and the associated instrument calibrations. These logs and notebooks are governed by GL-LB-E-009 for Run Logs and GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms, and Other Recordkeeping Devices. As stated in these SOPs, sample preparation and analytical records that are not electronically generated should be:

- Legible
- Recorded in permanent ink
- Corrected using one line marked through the error, initialed and dated
- Initialed by the responsible party

We maintain electronic records for each analytical batch. These records include the ID numbers of each client and quality control sample prepared and/or analyzed together, the method of preparation and analysis, and the matrix of the samples included in the batch.

Through our electronic statistical process control system (SPC), the acceptance criteria applied for all quality control (QC) samples are stored and maintained. The acceptance limits for target analytes are method, matrix, and time-period specific, which allow us to regenerate the criteria applied to QC samples associated with identified client samples.

Our Quality Systems Team maintains the records of nonconformances and corrective actions associated with specific samples, batches, and processes. We maintain these records according to GL-QS-E-004 for the Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items; and GL-QS-E-002 for Conducting Corrective/Preventative Action and Identifying Opportunities for Improvement.

Electronic data records are maintained in a secured database designed to protect the integrity of the data. Data that are uploaded directly from instruments and that are manually entered are backed up by a second system.

Permanent records of electronic data deliverables are maintained along with the corresponding sample preparation and analytical data review records. This documentation includes the initials of the reviewer and date of the review.

Records of the data we report to our clients are maintained in a manner that protects client confidentiality, as well as any potential national security concerns. These records include copies of certificates of analysis, quality control summary reports, case narratives, CLP forms, and other information we provided to the client. The copies may be paper or electronic. The majority of the data packages submitted to Federal clients are stored electronically prior to being submitted to the client.

Records of samples being disposed or returned to the client are documented in accordance with GL-SR-E-002 for Transportation and Shipping of Samples and Pre-Preserved Sample Containers. Such records include the date samples are returned or disposed, the destination of the samples, and name of the person transferring the samples.

10.2 Record Storage

We store quality records in compliance with GL-QS-E-008 for Quality Records Management and Disposition. The records are:

- Stored in a secured area to maintain data integrity and protect client confidentiality, including any national security concerns.
- Kept in areas where they are protected from fire loss, environmental deterioration, and, in the case of electronic records, electronic or magnetic sources.
- Indexed and filed in a manner allowing for ready retrieval.

- Accessible to the client for whom the record was generated.
- Retained for an identified period of time that equals or exceeds ten years as determined by applicable law and client contract requirements.

Electronic data records are stored on compact disks.

All of the hardware and software we need to reconstruct data is maintained according to GL-IT-E-003 for Requirements, Design, Operation, Validation and Removal of Hardware and Software Systems Used by the GEL Group, Inc. Records that are stored or generated by network or personal computers have either hard copy or write-protected backup.

10.3 Sample Handling Policy

Records of all procedures applicable to samples are maintained in our possession. These records include documents that pertain to:

- Preservation, including sample container and holding time
- Sample identification, receipt, acceptance or rejection, and login
- Sample storage and tracking including shipping receipts, transmittal forms, routing and assignment records
- Sample preparation (ID codes, cleanup and separation protocols, volumes, weights, instrument printouts, meter readings, calculations, reagents)
- Sample analysis
- Standard and reagent origin, receipt, preparation, and use
- Equipment receipt, use, specification, operating conditions and preventative maintenance
- Instrument calibration frequency and acceptance criteria
- Data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions
- Method performance criteria including expected quality control requirements
- Quality control protocols
- Electronic data security, software documentation and verification, software and hardware audits, backups and records of any changes to automated data entries
- Automated sample handling systems
- Disposal of hazardous samples

10.4 Records of Laboratory Support Activities

In addition to sample handling records, we maintain the following:

- Original raw data for calibrations, samples and quality control measures, including worksheets and data output records (chromatograms, strip charts, and other instrument readout records)
- A written description of or reference to the specific method used, including the computational steps used to translate parameter observations into a reportable analytical value
- Copies of final reports
- Archived standard operating procedures
- Correspondence relating to project-specific laboratory activities
- Corrective action reports, audits and audit responses
- Proficiency test results

10.5 Analytical Records

We document and maintain analytical records, such as strip charts, tabular printouts, computer data files, analytical notebooks, and run logs according to GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms, and Other Recordkeeping Devices, and GL-LB-E-009 for Run Logs.

The information that is documented in analytical records includes:

- Laboratory sample ID code
- Date and time of analysis
- Instrument ID and operating conditions/parameter (or reference to such data)

- Method of analysis
- All calculations
- Dilutions
- Initials of analyst or operator
- Units of measurement

Our policy is to produce and maintain analytical records that are:

- Accurate
- Reviewed and verified
- Legible and understandable
- Traceable and authentic to their source
- Grouped in a contemporary manner with data entered and information recorded as it is obtained

10.6 Administrative Records

A number of pertinent records are maintained by Human Resources or Quality Systems, including:

- Staff qualifications and experience.
- Training records, including initial demonstrations of proficiency. (Refer to procedure GL-HR-E-002 for Employee Training.)
- A log of names, initials and signatures for individuals having responsibility for initialing laboratory records.

We monitor continuing demonstrations of proficiency through AlphaLIMS per GL-HR-E-002 for Employee Training.

SECTION 11
LABORATORY REPORT FORMAT AND CONTENTS

Section 11 – Laboratory Report Format and Contents

Accurate data are of little benefit to a client unless they are reported in a format that is easy to interpret and provides all pertinent information relating to the analysis of a sample. At GEL, we have developed certificate of analysis report formats that meet the different needs of our clients, yet provide all of the information necessary to satisfy regulatory requirements while allowing for the interpretation of the data. Each format provides accurate, clear, unambiguous and objective data.

In addition to a certificate of analysis, a client can request and receive an extended data package. This package may include any of the following: certificates of analysis; summaries of quality control; case narratives; instrument data; sample preparation data; measurement traceability and calibration information; and electronic data deliverables. If clients require the reporting of data following the established contract laboratory protocol (CLP), we can provide a CLP-like data package that will meet their needs.

It is important that the certificate of analysis format and data package requirements be discussed with the client prior to our acceptance of the samples. Project Managers and contract staff are responsible for establishing an agreement with the client concerning data reporting and the potential cost to the client for data packages and/or specialized reporting. Our analytical data are reported to three significant figures unless otherwise required by client contract.

Laboratory reports and data packages are stored and transmitted in a manner that protects client confidentiality and potential matters of national security. No reports or data packages are released to persons or organizations outside GEL without the expressed consent of the client. If directed by a regulatory agency or subpoenaed to submit documents to a court of law, we will notify the client of the demand and the records being released.

The following elements of report formats and data packages are described in this section:

- Certificates of analysis (C of A)
- Quality control summary reports (QCSR)
- Analytical case narratives
- Electronic data deliverables (EDDs)
- Types of data packages and reporting formats
- Review of data packages and reports

11.1 Certificates of Analysis

We have two primary C of A report formats, Level 1 and Level 2. Both contain the following information when applicable:

- Title
- GEL address and phone number
- Name of PM or person serving as the primary client contact
- Barcode identification of the C of A
- Number of page and total number of pages
- Name and address of client, where appropriate
- Project name or code if applicable
- Client-provided sample description
- Unique laboratory ID number for the sample
- Sample matrix
- Characterization and condition of the sample where relevant
- Date of receipt of sample
- Date and time of sample collection, if provided
- Date and time of sample analysis, reanalysis, and/or sample preparation
- Initials of analyst and person responsible for sample prep
- Analytical batch number
- Sample analysis and preparation methods (or unambiguous description of any non-standard method used)
- Reference to sampling procedure
- Additions to or deviations or exclusions from the test method, and other information relevant to a specific test, such as environmental conditions and the use and meaning of data qualifiers
- Nonconformances that affect the data
- Whether data are calculated on a dry weight or wet weight basis

- Identification of the reporting units, such as µg/L or mg/kg
- Statement of the estimated uncertainty of the test result, if applicable
- Signature and title of the person(s) accepting responsibility for the content of the C of A
- Date C of A was issued
- Clear identification of data provided by outside sources, such as air temperature or ambient water temperature
- Identification of the reporting detection limit (RDL) or practical quantitation limit (PQL) for each analyte, if applicable.

If a portion of the sample analysis is subcontracted, the C of A will identify the subcontractor or applicable accreditation number, and the data that was determined by the subcontracting laboratory

Level 2 Certificates of analysis contain the following additional information:

- Dilution factors
- Method detection limits
- Surrogate recoveries and the acceptance criteria for all organic analyses
- Estimated concentrations determined for nondetects and appropriate "U" and "J" qualifiers for nondetects and concentrations that fall between the MDL and PQL respectively.

Once issued, a C of A is not altered unless a subsequent C of A is identified as a revised report.

11.2 Quality Control Summary Report (QCSR)

We prepare and analyze samples in groups of twenty or less. The quality control data that demonstrate the sample preparation and/or analytical efficiency of the batch are summarized on a QCSR. The data reported on the QCSR may be limited to a sample delivery group contained in the batch or may include all quality control for the batch. Information reported on QCSR includes:

- Quality control sample ID number
- Type of quality control sample
- Concentrations determined, where applicable, for method blanks, matrix spikes, matrix spike duplicates, matrix duplicates, laboratory control samples, serial dilutions, and laboratory control sample duplicates
- Acceptance criteria for matrix spikes, matrix spike duplicates, matrix duplicates, laboratory control samples, and laboratory control sample duplicates
- Nominal concentrations of matrix spikes, matrix spike duplicates, LCSs, and LCS duplicates
- Concentration of parent sample for the matrix spikes, matrix spike duplicates, or sample duplicates
- Percent recoveries for LCS and matrix spikes
- Relative percent differences for the matrix spike duplicates, matrix duplicates, and LCS duplicates
- Analytical batch number with which the quality control data is associated
- Parent sample numbers for matrix spikes, matrix duplicates, and matrix spike duplicates
- Sample or sample delivery group ID
- Project code
- Date issued, page numbers/total number of pages
- Identification of recoveries or relative percent differences that do not meet the acceptance criteria

11.3 Analytical Case Narratives

Analytical case narratives are written by an analyst or data validator to describe the overall conditions affecting the analysis of a batch or a specific sample in the batch. Case narratives usually include:

- Sample delivery group ID number
- Analytical batch number
- Methods of preparation and analysis
- Sample matrix
- Initial of person preparing and/or reviewing the narrative
- Specific sample ID numbers
- Identification and description of batch quality control samples including parent sample identification
- Affirmation that all sample preparation conditions specified by the method or regulatory agencies were met or identification of specific deviations
- Affirmation that all analysis criteria specified by the method or regulatory agencies were met or identification of specific deviations

- Instrumentation employed if applicable and verification of its calibration
- Summary of batch quality control as compared to acceptance criteria
- Identification of nonconformances
- Pertinent comments and observations of factors that affect sample data quality

11.4 Electronic Data Deliverables (EDDs)

Electronic data deliverables are generated according to client specifications. EDDs use programs supplied by the client or created internally by our EDD team. Internally generated EDDs are usually written in Perl and/or PL/SQL.

11.5 Types of Data Packages and Reports

We offer three levels of data reports and the ability to design packages to meet the needs of our clients. The levels of data reports are summarized in Table 1.

Table 1: Data Report Formats

Level	Contents
1	Level 1 C of A
2	Level 2 C of A plus QCSR
3	Level 2 plus Case Narrative

If a client so requests, the above reports can be accompanied by EDDs, case narratives, copies of associated nonconformance reports, and other support documentation. The client's specific requirements are communicated to the laboratory and data reviewers through AlphaLIMS.

GEL's SOP GL-CS-E-002 for The Internal Review of Contractually Required Quality Criteria for Client Package Delivery defines preparation and review of the package.

If a client requests a CLP-like data package, and we agree to provide one, it is compiled in accordance with GL-LB-E-013 for CLP-Like/DOE Data Package Assembly and Revision. If a client does not request a full CLP-like data package but asks for data to be provided on CLP forms generated from software, we follow the applicable procedures in GL-LB-E-013.

11.6 Review of Data Reports, EDDs, and Data Packages

Level 1 and Level 2 data reports are reviewed for accuracy and completeness by the PM or PMA. Level 3 and CLP-like data packages are reviewed in the laboratory by a data reviewer, who is responsible for reviewing specific fractions of the data package for accuracy, consistency, and completeness in accordance with the SOP for that lab area.

No data package fraction is to be provided to the data packaging team without the approval of the appropriate data reviewer.

CLP-like data packages are reviewed in compliance with the basic protocol. Specific requirements are described in GL-LB-E-013 for the CLP-Like/DOE Data Package Assembly and Revision.

11.7 State Specific Reporting Criteria

Some state agencies require laboratories who perform drinking water analyses in support of Clean Water Act programs to communicate specific results to clients and/or agencies in some circumstances. If samples are found to contain concentrations of target analytes above those required by Federal or State regulations, the state must be informed. Please see Appendix K for state specific reporting criteria for drinking water programs.

SECTION 12
SUBCONTRACTING ANALYTICAL SAMPLES AND OUTSIDE SUPPORT SERVICES

Section 12 – Subcontracting Analytical Samples and Outside Support Services

We provide a full array of organic, inorganic, and radiochemical analyses. The subcontracting of samples to other facilities, while infrequent, may occur when:

- The client has requested analytical services for which we are not certified or do not offer as a routine product.
- The regulatory or method holding times and/or client due dates are in danger of not being met as the result of instrument malfunction or the unexpected influx of a large group of samples.

No samples are subcontracted without the client's consent. The laboratories selected to receive subcontracted samples are expected to meet the following criteria:

- Demonstrated technical capability to provide data that meet and conform to our quality standards.
- Established certification, if available, for the requested analyses.
- Successful proficiency evaluation results, if available.
- Commitment to meet time requirements for delivery of results to the client.
- Agreement to provide all documentation requested in conjunction with the analysis.
- NELAP, or ISO/IEC 17025 accreditation for the analysis if required by the client.

We audit potential subcontractors for technical and administrative compliance as directed in GL-QS-E-001 for Conduct of Quality Audits. An audit may be in the form of a book audit or an on-site review.

If there is evidence of a technical, administrative, or quality deterioration, the laboratory is removed from our list of approved subcontractor laboratories pending further evaluation, which may include an on-site audit. Once the laboratory again demonstrates compliance with GEL's standards, it can be reclassified as an approved subcontractor laboratory.

At GEL, we have a multi-faceted and trained staff. There are occasions, however, when it may be necessary to obtain the services of professionals outside of GEL. This may be due to such things as sample workload, introduction of a new instrument or method requiring special knowledge, or employee leaves of absence.

Any outside support services or service personnel are subject to the same scrutiny as a subcontract laboratory. If a service fails to meet our standards for excellence, the appropriate parties are promptly notified. If immediate corrections are not implemented and services are not of adequate quality to maintain confidence, the contract is canceled.

SECTION 13
CLIENT SATISFACTION

Section 13 – Client Satisfaction

Meeting the needs and expectations of our clients is essential to meeting our commitment to be the environmental laboratory of first choice. An important part of meeting this commitment involves receiving and resolving client concerns and complaints.

Client complaints that question the quality of laboratory data or data deliverables are directed to Quality Systems. These concerns are responded to with input from the laboratory, EDD team or data packaging group as may be needed.

The types of complaints, area(s) affected, and any impacts on quality are trended on a quarterly basis. This information is available to members of the Leadership Team and other managers and group leaders.

We use AlphaLIMS to monitor client complaints, nonconformances and corrective actions. Every complaint is entered into the system upon receipt and assigned an internal and external due date. The external due date is often established by client contract. The internal due date allows time for the Quality Systems Team to review the response and transmit it to the client on or before the due date.

If we notice a trend that significantly affects the quality of our data, a corrective action is initiated following GL-QS-E-002 for Conducting Corrective/Preventive Action and Identifying Opportunities for Improvement. The implementation and verification of the corrective action affirms an effective and permanent solution.

The Quality Systems Team promptly audits those areas of activity or responsibility for which a complaint or concern has been stated.

APPENDIX A: REFERENCES

- The NELAC Institute, TNI Standard, 2016.
- 10 CFR 50, Appendix B, US Code of Federal Regulations.
- 40 CFR Part 136, August 19, 2014 Guidelines Establishing Test Procedures for the Analyses of Pollutants.
- 40 CFR Part 141- National Primary Drinking Water Regulations, July 1, 2009, Subpart C-Monitoring and Analytical Requirements
- DOE Orders 414.1B 414.1C, and 414.D Quality Assurance, U.S. Department of Energy.
- EPA Requirements for Quality Assurance Project Plans (QAPPs), US EPA QA/R5.
- EPA 815-R-05-004 EPA Manual for the Certification of Laboratories Analyzing Drinking Water.
- Model Statement of Work for Analytical Laboratories, Prepared for Department of Energy NNSA Service Center by Analytical Quality Associates, Rev 7, November 2006.
- Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs, American National Standard ANSI/ASQC E4-2004.
- Measurement Associated Instrument Quality Assurance for Radiobioassay Laboratories ANSI N42.23-1995.
- US Department of Defense (DoD) Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories, DoD/DOE QSM Version, 5.2, December 2018.
- MARLAP- Multi-Agency Radiological Laboratory Analytical Protocols
- 10 CFR Part 21- Reporting of Defects and Noncompliance
- 10 CFR Part 50 Appendix B –Quality Assurance Criteria for Nuclear Power Plants and Fuel Reprocessing Plants
- 10 CFR Part 61- Licensing Requirements for Land Disposal and Radioactive Waste
- NRC REG Guide 4.15 and NRC REG Guide 4.8
- ISO/IEC 17025-2017
- DOE G 414/1-3, 11-3-04, Suspect/ Counterfeit Items Guide for use with 10 CFR 830 Subpart A. Quality Assurance Requirements, and DOE O 414.B, Quality Assurance.

APPENDIX B: DEFINITIONS

The following definitions are used throughout the text of our Quality Systems Plan. These definitions were reprinted from "Definitions for Quality Systems," NELAC, July 1, 1999. For most entries, the original source of each definition is provided.

AlphaLIMS: GEL's Laboratory Information Management System.

Acceptance Criteria: Specified limits placed on characteristics of an item, process, or service defined in the requirement documents. (ASQC)

Accreditation: The process by which an agency or organization evaluates and recognizes a program of study or an institution as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory. In the context of the National Environmental Laboratory Accreditation Program (NELAP), this process is a voluntary one. (NELAC)

Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (Glossary of Quality Assurance Terms, QAMS, 8/31/92)

Aliquot: A discrete, measured, representative portion of sample taken for analysis. (DoD, EPA QAD Glossary)

Analyst: The designated individual who performs the "hands-on" analytical methods and associated techniques and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality. (NELAC)

Analyte: The specific chemicals or components for which a sample is analyzed; may be a group of chemicals that belong to the same chemical family, and are analyzed together. (EPA Risk Assessment Guide for Superfund, OSHA Glossary)

Analytical Detection Limit: The smallest amount of an analyte that can be distinguished in a sample by a given measurement procedure throughout a given confidence interval. (NELAC Quality Systems Committee)

Analytical Reagent (AR) Grade: Designation for the high purity of certain chemical reagents and solvents given by the American Chemical Society. (NELAC Quality Systems Committee)

Analytical Sample: Any solution of media introduced into an instrument on which an analysis is performed excluding instrument calibration, initial calibration verification (ICV), intitial calibration blank (ICB), continuing calibration verification (CCV), and continuing calibration blank (CCB)

ANSI: American National Standards Institute–this consensus standards body approves standards as a guide to aid the manufacturer, the consumer and the general public who may be concerned with its scope and provisions.

Audit: A systematic evaluation to determine the conformance to quantitative and qualitative specifications of some operational function or activity. (EPA-QAD)

Batch: Environmental samples prepared and/or analyzed together with the same process and personnel using the same lot(s) of reagents. A **preparation batch** is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) that are analyzed together as a group using the same calibration curve or factor. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples. (NELAC Quality Systems Committee)

Blank: A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subject to the usual analytical and measurement process to

establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. (ASQC)

Blind Sample: A subsample for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample but not its composition. It is used to test the analyst's or laboratory's proficiency in the execution of the measurement process. (NELAC)

Calibrate: To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device, or the correct value for each setting of a control knob. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC)

Calibration: The set of operations that establish, under specified conditions, the relationship between values indicated by a measuring device, or the correct value of each setting of a control knob. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC)

Calibration Curve: The graphical relationship between the known values, such as concentrations, of a series of calibration standards and their analytical response. (NELAC)

Calibration Standard: A substance or reference material used to calibrate an instrument. (QAMS)

Certified Reference Material (CRM): A reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation that is issued by a certifying body. (ISO Guide 30 – 2.2)

Chain of Custody: A record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number of and types of containers; the mode of collection; collector; time of collection; preservation; and requested analyses. (NELAC Quality Systems Committee)

Commercial Grade Items: When applied to analytical services provided to nuclear power plants licensed pursuant to 10 CFR Part 50, commercial grade item means a structure, system, or component, or part there of that affects its safety function, that was not designed and manufactured as a basic component. In the laboratory operations, commercial grade items may include calibration standards, quality control standards, reagents, instrument software conducting calculations, calibration services for support instrumentation, and other process controls, verifying their acceptability by inspections, tests, validation, or analyses by the purchaser or third-party dedicating entity (such as NIST, A2LA, NPL and TNI). This activity assures that a critical characteristic is acceptable. Commercial grade items do not include items where the design and manufacturing process require in-process inspections and verifications to ensure that defects or failures to comply are identified and corrected. These types of items are considered Consumables.

When applied to facilities and activities licensed pursuant to 10 CFR Parts 50, commercial grade item means an item that is:

(245) Not subject to design or specification requirements that are unique to those facilities or activities;

(ii) Used in applications other than those facilities or activities; and

(iii) To be ordered from the manufacturer/supplier on the basis of specifications set forth in the manufacturer's published product description (for example, a catalog).

It is the responsibility of the purchaser to identify the vendor type, grade, and use of the purchased item

Confirmation: Verification of the presence of a component through the use of an analytical technique that differs from the original test method. These may include: (NELAC)

Second column confirmation
Alternate wavelength
Derivatization
Mass spectral interpretation
Alternative detectors or
Additional cleanup procedures

Continuing Calibration Blank (CCB): Aliquot of reagent water or other blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

Continuing Calibration Verification Standard (CCV): An aliquot of reagent water or to the blank matrix to which known quantities of the method analytes are added in the laboratory. The CCV is analyzed exactly like a sample periodically thoughout the sequence. Its purpose is to determine whether the analytical sequence is in control during the sample analysis. It may be prepared from the same source as the calibration standards and is usually of varied concentrations.

Control Limits: A range within which specified measurement results must fall to be compliant.

Corrective Action: Action taken to eliminate the causes of an existing nonconformity, defect, or other undesirable situation in order to prevent recurrence. (ISO 8402)

Data Audit: A qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data are of acceptable quality (i.e., that they meet specified acceptance criteria). (NELAC)

Data Exception Report (DER): An indication or judgement that a product or service has not met the requirements or the relevant specifications, contract or regulations: also a state of failing to meet the requirements.

Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useful form. (EPA-QAD)

Detection Limit: The lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated degree of confidence. Refer to Method Detection Limit. (NELAC)

Document Control: The act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly, and controlled to ensure use of the correct version at the location where the prescribed activity is performed. (ASQC)

Duplicate Analyses: The analyses or measurements of the variable of interest performed identically on two subsamples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory. (EPA-QAD)

Holding Times (Maximum Allowable Holding Times): The maximum times that samples may be held prior to analysis and still be considered valid. (40 CFR Part 136)

Initial and Continuing Demonstrations of Capability: Procedures to establish the ability of the laboratory to generate acceptable accuracy and precision which is included in many of the EPA's analytical test methods. In general, the procedure includes the addition of a specified concentration of each analyte in each of four separate aliquots of laboratory pure water or authentic samples. These are carried through the analytical procedure and the percentage recovery and the standard deviation are compared to specified limits. (40 CFR Part 136, 2003 NELAC)

Internal Standard: A known amount of standard added to a test portion of a sample and carried through the entire measurement process as a reference for evaluating and controlling the precision and bias of the applied analytical test method. (NELAC)

Initial Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination after injection of the mid-level ICV.

Initial Calibration Verification (ICV): A solution of method analytes of known concentrations that is used to fortify an aliquot of blank or sample matrix. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

Instrument Performance Check Solution (IPC): A solution of one or more method analytes, surrogates, internal standards, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

Internal Standard (ISTD): A known amount of standard added to a portion of the sample extract as a reference for evaluating and controlling the precision and bias of the applied analytical method.

Interferents: Substances that affect the analysis for the element of interest.

ISO/IEC 17025: The International Organization for Standardization and International E

lectrotechnical Commission form this specialized system for worldwide standardization. Members of ISO or IEC participate in the development of International Standards through technical committees established by their organization to deal with particular fields of activity. Other international organizations, government and non-government, also take part in development of these standards. The ANSI/ISO/IEC 17025-2017 is approved as an American National Standard and covers general requirements for the competence of testing and calibration laboratories.

Laboratory: A body that calibrates and/or tests.

1. In cases where a laboratory forms part of an organization that carries out other activities besides calibration and testing, the term "laboratory" refers only to those parts of that organization that are involved in the calibration and testing process.
2. As used herein, the term "laboratory" refers to a body that carries out calibration or testing at or from a permanent location, from a temporary facility, or a mobile facility. (ISO 25)

Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst specific precision and bias to assess the performance of all or a portion of the measurement system. (NELAC)

Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently. (NELAC Quality Systems)

Limit of Detection (LOD): The lowest concentration level that can be determined by a single analysis and with a defined level of confidence to be statistically different from a blank. See also Method Detection Limit. (Analytical Chemistry, 55, p.2217, Dec. 1983, modified)

Limit of Quantitation (LOQ): The lowest concentration level of the initial calibration curve used to quantitate an analyte. (DoD clarification) The LOQ must be ≥ 3X the LOD, and is usually not more than 10X the LOD.

Lower Limit of Quanitiation (LLOQ): The lowest concentration at which a target analyte can be reliably measured and reported. The LLOQ is ≥ the lowest point in the calibration curve and represents a concentration at which both quantitative and qualitative requirements can be consistently demonstrated. The LLOQ is verified at least annually, by typically quarterly, as the LOQ verification. The verifications are performed by extracting and analyzing an LCS spiked at 0.5 to 2 times the LOQ. The LLOQ verification is carried through the same preparation and analytical procedures as envrionmentat samples and QC.

Linear Calibration Range: The concentration range over which the instrument response is linear.

Matrix: The component or substrate that contains the analyte of interest. For purposes of batch determination, the following matrix types shall be used:

- ◊ Aqueous: Any aqueous sample excluded from the definition of a drinking water matrix or saline/estuarine source. Includes surface water, groundwater, and effluents.
- ◊ Drinking Water: Any aqueous sample that has been designated a potable or potential potable water source.
- ◊ Saline/Estuarine: Any aqueous sample from an ocean or estuary, or other salt-water source.
- ◊ Non-aqueous liquid: Any organic liquid with <15% settleable solids.
- ◊ Biological Tissue: Any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.
- ◊ Solids: Includes soils, sediments, sludges and other matrices with >15% settleable solids.
- ◊ Chemical Waste: A product or by-product of an industrial process.
- ◊ Air Samples: Media used to retain the analyte of interest from an air sample such as sorbent tubes or summa canisters. Each medium shall be considered as a distinct matrix. (Quality Systems)

Matrix Spike (MS): Prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency. (Glossary of Quality Assurance Terms, QAMS, 8/31/92)

Matrix Spike Duplicate (spiked sample/fortified sample duplicate): A second replicate matrix spike is prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte. (Glossary of Quality Assurance Terms, QAMS, 8/31/92)

May: Denotes permitted action, but not required action. (NELAC)

Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses. (NELAC)

Method Detection Limit (MDL): The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater that zero and is determined from analysis of a sample in a given matrix containing the analyte. (40 CFR Part 136 Appendix B)

Must: Denotes a requirement that is required to be met. (Random House College Dictionary)

Negative Control: Measures taken to ensure that a test, its components, or the environment does not cause undesired effects, or produce incorrect test results. (NELAC)

NELAC: National Environmental Laboratory Accreditation Conference. A voluntary organization of state and federal environmental officials and interest groups purposed primarily to establish mutually acceptable standards for accrediting environmental laboratories. A subset of National Environmental Laboratory Accreditation Program (NELAP).

Performance Audit: the routine comparison of independently obtained quantitative measurement system data with routinely obtained data in order to evaluate the proficiency of an analyst or laboratory. (NELAC)

Performance Based Measurement System (PBMS): A set of processes wherein the data quality needs, mandates, or limitations of a program or project are specified and serve as criteria for selecting appropriate test methods to meet those needs in a cost-effective manner. (NELAC)

Positive Control: Measures taken to ensure that a test and/or its components are working properly and producing correct or expected results from positive test subjects. (NELAC)

Practical Quantiation Limit (PQL): The lowest level in the calibration curve. With the prep factor applied, the PQL is referred to as the effective PQL.

Precision: The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms. (NELAC)

Preservation: Refrigeration and or reagents added at the time of sample collection to maintain the chemical and or biological integrity of the sample. (NELAC)

Proficiency Test Sample (PT): A sample, the composition of which is unknown to the analyst and is provided to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria. (Glossary of Quality Assurance Terms, QAMS, 8/31/92)

Proficiency Testing: A means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source. (NELAC, Section 2.1)

Proficiency Testing Program: The aggregate of providing rigorously controlled and standardized environmental samples to a laboratory for analysis, reporting of results, statistical evaluation of the results in comparison to peer laboratories and the collective demographics and results summary of all participating laboratories. (NELAC)

Protocol: A detailed written procedure for field and/or laboratory operation (e.g., sampling, analysis) that must be strictly followed. (EPA-QAD)

Pure Reagent Water: Shall be water in which no target analytes or interferences are present at a concentration that would impact the results when using a particular analytical test method. (NELAC)

Quality Assurance: An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality within a stated level of confidence. (Glossary of Quality Assurance Terms, QAMS, 8/31/92)

Quality Control: The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the need of users. (Glossary of Quality Assurance Terms, QAMS, 8/31/92)

Quality Manual: A document stating the quality policy, quality system and quality practices of an organization. This may also be called a Quality Assurance Plan or a Quality Plan. **NOTE:** The quality manual may call up other documentation relating to the laboratory's quality arrangements. (Quality Systems Committee)

Quality System: A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC. (ANSI/ASQC E-41994)

Quantitation Limits: The value at which an instrument can accurately measure an analyte at a specific concentration that includes the maximum or minimum levels, concentrations, or quantities of a target that can be quantified with the accuracy required by the data user. These values establish the upper and lower limits of the calibration range. (NELAC with DoD clarification)

Range: The difference between the minimum and the maximum set of values. (EPA_QAD)

Raw Data: Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies,

computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes that have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted. (EPA-QAD)

Reagent Blank (method reagent blank): A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps. (Glossary of Quality Assurance Terms, QAMS, 8/31/92)

Reference Material: A material or substance one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. (ISO Guide 30 -2.1)

Reference Standard: A standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived. (VIM – 6.08)

Relative Percent Difference (RPD): The difference between two duplicate samples, such as a MS/MSD/, LCS/LCSD, or sample/sample DUP. It is determined by taking the difference between the two results and dividing by the average.

Reporting Limit (RL): The level at which a target analyte would meet the data quality objectives of the laboratory and/or a project, which may include establishing compliance with a regulatory and/or action limit. The RL may be equal to the laboratory practical quantitation limit (PQL)

Requirement: Denotes mandatory specification; often designated by the term "shall." (NELAC)

Sample: Portion of material collected for chemical analysis, identified by a single, unique term. A sample may consist of portions in multiple containers, if a single sample is submitted for multiple or repetitive analysis. (DoD)

Safety Related Procured Items: As specified in 10 CFR Part 50 and other Nuclear Power related activities, a basic component includes safety-related analytical services that are associated with the component information in support of an early site permit application or other safety related services identified by the client, whether the services are performed by the laboratory or others. GEL has identified the primary safety related basic component item for these services as:

- ◊ Calibration Standards for Radiochemical Analyses used in the direct issuance of analytical data reported to a Nuclear Facility. These standards are the primary sources (critical characteristic) of calibration for instruments that will provide the analytical results to our client. All Safety Related Procured Items are considered Type I procurement and must meet all specifications as identified in SOP GL-RC-E-002.

Standard Operating Procedure (SOP): A written document that details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and is accepted as the method for performing certain routine or repetitive tasks. (Glossary of Quality Assurance Terms, QAMS, 8/31/92)

Standard Reference Material (SRM): A certified reference material produced by the U.S. National Institute of Standards and Technology and characterized for absolute content, independent of analytical test method. (NELAC)

Statistical Process Control (SPC): Statisitically derived limits that establish acceptable reanges for recoveries fo analytes of interest, including LCS, MS, MSD, PS, PSD and internal standards.

Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

Selectivity: The capability of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances. (NELAC Quality Systems)

Sensitivity: The capability of a test method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. (NELAC Quality Systems)

Serial Dilution: The dilution fo a sample by a known factor. When corrected by the dilution factor, the diluted sample should agree with the original undiluted sample within the specified limits. Serial dilution may reflect the influence of interferents.

Shall: Denotes a requirement that is mandatory whenever the criterion for conformance with the specification requires that there will be no deviation. This does not prohibit the use of alternative approaches or methods for implementing the specification so long as the requirement is fulfilled. (ANSI)

Should: Denotes a guideline or recommendation whenever noncompliance with the specification is permissible. (ANSI)

Spike: A known mass of target analyte added to a blank sample or subsample; used to determine recovery efficiency or for other quality control purposes.

Subsample: A portion of the entire sample randomly collected and composited to create weight used for the solvent extraction process. The saubsample should be representative of the entire sample.

Surrogate: A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes. (Glossary of Quality Assurance Terms, QAMS, 8/31/92)

Test: A technical operation that consists of the determination of one or more characteristics or performance of a given product, material equipment, organism, physical phenomenon, process or service according to a specified procedure. The result of a test is normally recorded in a document sometimes called a test report or a test certificate. (ISO/IEC Guide 2 – 12.4)

Test Method: An adoption of a scientific technique for a specific measurement problem, as documented in a laboratory SOP. (NELAC)

Tolerance Chart: A chart in which the plotted quality control data is assessed via a tolerance level (e.g. ± 10% of a mean) based on the precision level judged acceptable to meet overall quality/data use requirements instead of a statistical acceptance criteria (e.g. ± 3 sigma). (ANSI N42.23-1995, Measurement and Associated Instrument Quality Assurance for Radiochemistry Laboratories)

Traceability: The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons. (VIM-6.12)

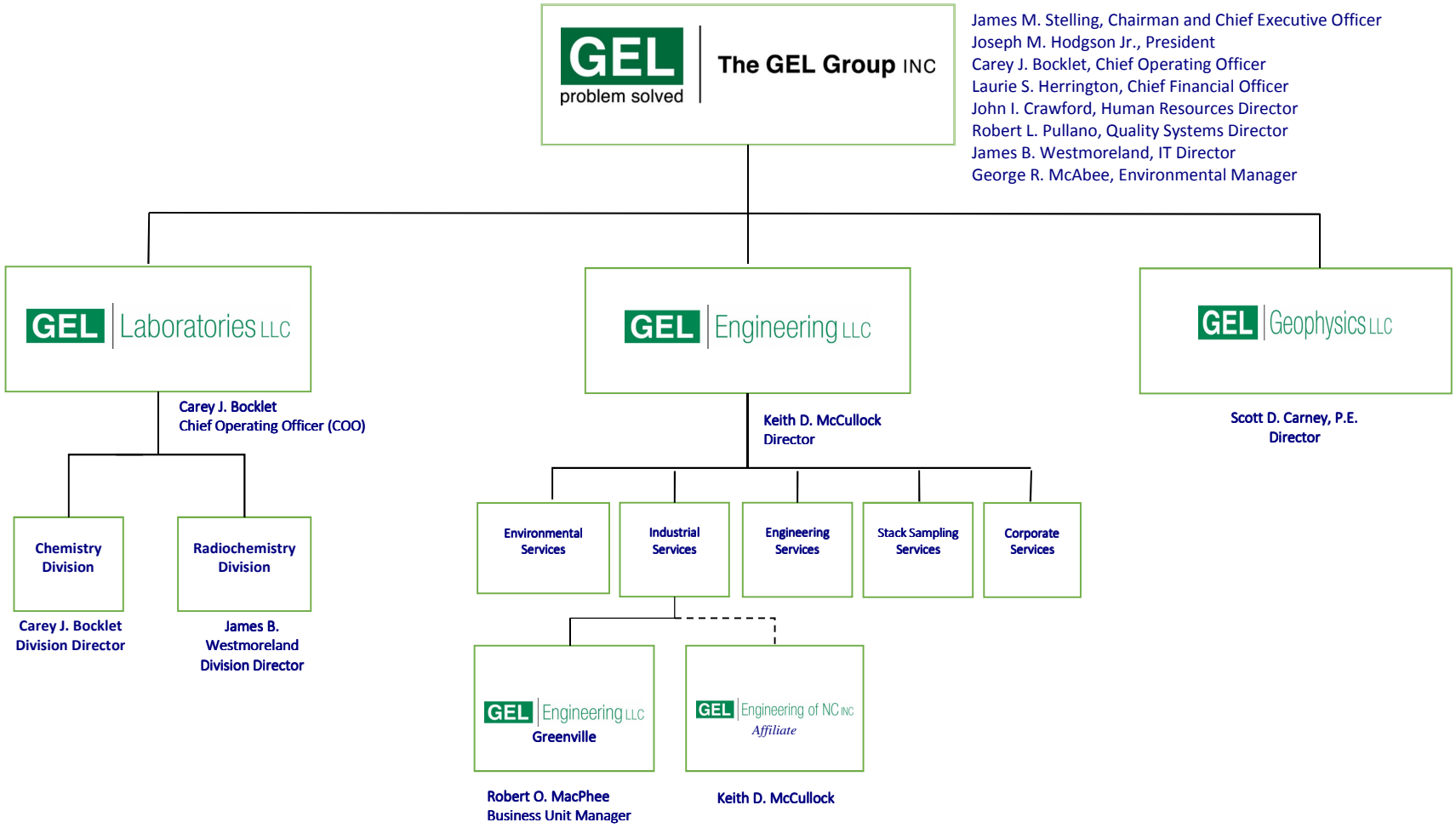
Validation: The process of substantiating specified performance criteria.

Verification: confirmation by examination and provision of evidence that specified requirements have been met. (NELAC)

NOTE: Verification provides a means for checking that the deviations between values indicated by a measuring instrument and corresponding known values of a measured quantity are consistently smaller than the maximum allowable error defined in a standard, regulation, or specification peculiar to the management of the measuring equipment.

The result of verification leads to a decision either to restore in service, to perform adjustments, or to repair, or to downgrade, or to declare obsolete. In all cases it is required that a written trace of the verification performed shall be kept on the measuring instrument's individual record.

APPENDIX C: CORPORATE ORGANIZATION CHART



APPENDIX D: CERTIFICATIONS

GEL Laboratories, LLC maintains environmental laboratory certification in many states, including primary NELAP in Utah and secondary in Florida, Illinois, Kansas, Louisiana, New Hampshire, New Jersey, New York, Pennsylvania, Texas and Virginia. We expand our list of certifications as needed.

Original Scope of Accreditation/Range of Activities are maintained in the Quality Assurance work area. Electronic copies are available in .pdf form on the GEL intranet. *Please call to confirm the status of any certification of interest.*

- **Department of Defense (DoD) Department of Energy (DOE**) Consolidated Quality Systems Manual Version 5.2, December 2018 through American Association for Environmental Laboratory Accrediation (A2LA) (A2LA 2567.01)
- **U.S. Department of Agriculture –** Foreign soil importation permit # P330-18-00302, P330-18-00203
- **National Environmental Laboratory Accreditation Program (NELAP) –** Primary issued through the State of Utah, Department of Health; Secondary issued through the States of Florida, Illinois, Kansas, Louisiana, New Hampshire, New Jersey, New York, Pennsylvania, Texas and Virginia
- **Clinical Laboratory Improvement Amendments (CLIA) –** U.S. Department of Health and Human Services, Certificate of Compliance for Acceptance of Human Specimens (GEL ID: 42D0904046)
- **Alaska Department of Environmental Conservation Contaminated Sites** Laboratory Approval 17-018
- **Arkansas** Department of Environmental Quality Laboratory Certification Program for Wastewater, Groundwater, Solid Waste Reciprocal Certification to SC DHEC (88-0651)
- **California** Environmental Laboratory Accreditation Program Certification, ELAP (GEL ID: 2940)
- **Colorado** Department of Public Health and Environment, Reciprocal Certification to SC DHEC Environmental Laboratory Certification Program for Safe Drinking Water Chemistry and Radiochemistry (SC00012)
- **Connecticut** Department of Public Health – Potable Water, Waste Water and/or Trade Waste, Sewage and/or Effluent, Soil and Radiochemistry Reciprocal Certification (GEL ID: PH-0169)
- **Florida** Department of Health, Bureau of Laboratories, Secondary NELAP (GEL ID E87156)
- **Georgia** Department of Natural Resources, Reciprocal Certification to SC DHEC Environmental Laboratory Certification Program for Safe Drinking Water (GEL ID: 967)
- **Hawaii** Department of Health, Safe Drinking Water, reciprocal to Utah NELAP, SC00012
- **Idaho** Department of Health and Welfare, SC00012
- **Illinois** EPA Environmental Laboratory Accreditation for Drinking Water, Wastewater, and Hazardous and Solid Waste, Secondary NELAP (GEL ID: 200029)

- **Indiana** State Department of Health (C-SC-01)
- **Kansas** Department of Health and Environmental Laboratory, Non-potable Water and Solid and Hazardous Waste, Secondary NELAP (GEL ID: E-10332)
- **Kentucky** Department of Environmental Protection for Drinking Water and Waste Water (GEL ID: 90129)
- State of **Louisiana** Department of Health and Hospitals (LA 180011), Safe Drinking Water, Secondary NELAP
- State of **Louisiana** Department of Environmental Quality, (03046, AI 33904), Non-drinking water, Secondary NELAP
- **Maryland** Department of Health and Mental Hygiene, Laboratories Administration, Reciprocal Certification to SC DHEC Environmental Laboratory Certification Program for Safe Drinking Water –Radiochemistry (GEL ID: 270)
- **Massachusetts** Department of Environmental Protection, Division of Environmental Analysis – Potable Water, Radiochemistry (GEL ID: M-SC012)
- **Michigan** Department of Environmental Quality – Potable Water, Radiochemistry (GEL ID: 9976)
- **Mississippi** State Department of Health NELAP reciprocity
- **Nebraska**, Department of Health and Human Services (GEL ID: NE-QS-26-13)
- **Nevada** Department of Human Resources, Health Division, Bureau of Licensure and Certification, Radiologicals and Non-Radiologicals (GEL ID: SC000122019-1), Nevada Mining
- State of **New Hampshire** Environmental Laboratory Accreditation Program, Secondary NELAP (205)
- **New Jersey** Department of Environmental Protection, Safe Drinking Water, Solid and Hazardous Waste, and Water Pollution Certification, Secondary NELAP (GEL ID: SC002)
- State of **New Mexico** Environment Department, Drinking Water Bureau, reciprocal to NELAP SC00012
- **New York** Department of Health, Environmental Laboratory Approval Program Certification, Potable Water, Non-potable Waters and Solids/Hazardous Wastes, Secondary NELAP (GEL ID: 11501)
- **North Carolina** Division of Water Quality Lab Certification Program, Waste Waters/Ground Waters. (GEL ID: 233)
- **North Carolina** Department of Health and Human Services, North Carolina State Laboratory Public Health Environmental Sciences, Safe Drinking Water. (GEL ID: 45709)
- **North Dakota** State Department Protection- Bureau fo Laboratories, Secondary NELAP (GEL ID: 68-00485)
- **Oklahoma** Department of Environmental Quality, General Water Quality/Sludge Testing Laboratory Dual Certification (GEL ID: 9904)

- **Pennsylvania** Department of Environmental Protection – Bureau of Laboratories, Secondary NELAP (GEL ID: 68-00485)

- **Puerto Rico** Department of Health Recipricol certification to Manual for the Certification of Laboratories Analyzing Drinking Water. PRDOH (SC00012)

- **South Carolina** Department of Health and Environmental Control – Environmental Laboratory Certification Program, Clean Water, Safe Drinking Water, Radiological, and Solid/Hazardous Wastes (GEL ID: 10120001/10120002)

- **South Carolina** Department of Health and Environmental Control (DHEC) Radioactive Material License (License #362)

- **Tennessee** Department of Health – Division of Laboratory Services, Reciprocal Certification to SC DHEC Environmental Laboratory Certification Program, Safe Drinking Water-Radiochemistry and Non-radiochemistry (GEL ID: 02934)

- **Texas** Commission on Environmental Quality, Secondary NELAP (GEL ID: T104704235-18-13)

- **Utah** Department of Health, Division of Epidemiology and Laboratory Services, Safe Drinking Water, Clean Water and Resource and Conservation and Recovery Act Certifications Primary NELAP (Customer ID: SC000122018-27)

- **Vermont** Department of Environmental Conservation, Water Supply Division, Secondary NELAP (VT87156)

- Commonwealth of **Virginia** Department of General Services – Division of Consolidated Laboratory Services, Safe Drinking Water, Clean Water Act and Resource and Conservation Act Certifications, Secondary NELAP (GEL ID: 460202)

- **Washington** State Department of Ecology, Safe Drinking Water, Clean Water and Resource and Conservation and Recovery Act Certifications (GEL ID: C780)

APPENDIX E: ESSENTIAL QUALITY CONTROL REQUIREMENTS

At GEL, we enforce strict adherence to quality control measures. Quality control measures for each type of analysis are delineated in the associated standard operating procedure and include those specified in the identified analytical method. Client requests for additional quality control agreed to by us will be communicated to the laboratory by the Project Manager and performed accordingly.

All quality control measures are assessed and evaluated on an ongoing basis. We use these measures to establish statistically derived quality control acceptance criteria. The acceptance criteria are used to evaluate whether the analytical process is in control and to assist us in establishing the validity of the data. Our procedures for handling out- of-control situations are written in the analytical standard operating procedure.

Method-specific quality measures are described in the appropriate standard operating procedure. Essential but general quality control requirements are summarized in the sections below for chemical testing, including inorganic and organic analyses, and radiochemical testing.

E1 Chemical Testing

This section includes our quality control requirements for inorganic and organic analyses, and discusses:

- Negative controls
- Positive controls
- Analytical variability and reproducibility
- Method evaluation
- Method detection limits
- Data reduction
- Quality of standards and reagents
- Selectivity
- Constant and consistent test condition

E1.1 Negative controls

We implement a negative control at least once per analytical batch of samples having the same matrix, and where, if applicable, the same extraction or preparation method is employed. The negative control is a method blank that we use to determine the presence of contamination. If discovered, we must investigate the source of contamination and take measures to correct, minimize, or eliminate the source if:

1. The concentration of target analyte exceeds the established practical quantitation limit and exceeds a concentration greater than 1/10 of the measured concentration of any sample in the analytical batch;
2. The concentration of a target analyte in the method blank exceeds that present in the samples and is greater than 1/10 of the specified regulatory limit.

If a method blank is indicative of contamination, we must assess each sample in that batch against the above criteria to determine if the data are acceptable. Any sample associated with a contaminated method blank shall be reprocessed for analysis, as needed, or we will report the results with appropriate data qualifiers.

E1.2 Positive Control – Method Performance

E1.2.1 Laboratory Control Sample (LCS)

Purpose: The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. Results of the LCS are compared to established criteria and, if found to be outside of these criteria, indicates that the analytical system is “out of control.” Any

affected samples associated with an out-of-control LCS shall be reprocessed for re-analysis or the results reported with appropriate data qualifying codes, as necessary.

Frequency: The LCS is analyzed at a minimum of 1 per preparation batch. Exceptions would be for those analytes for which no spiking solutions are available such as total suspended solids, total dissolved solids, total volatile solids, total solids, pH, color, temperature, dissolved oxygen or turbidity. In those instances for which no separate preparation method is used (example: volatiles in water) the batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

Composition: The LCS is a controlled matrix, known to be free of analytes of interest, spiked with known and verified concentrations of analytes. **NOTE:** The matrix spike may be used in place of this control as long as the acceptance criteria are as stringent as for the LCS. Alternatively the LCS may consist of a medium containing known and verified concentrations of analytes or as Certified Reference Material (CRM). All analyte concentrations shall be within the calibration range of the methods. The following shall be used in choosing components for the spike mixtures:

The components to be spiked shall be as specified by the mandated test method or other regulatory requirement or as requested by the client. In the absence of specified spiking components the laboratory shall spike per the following:

For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene, and PCBs, the spike should be chosen that represents the chemistries and elution patterns of the components to be reported.

For those test methods that have extremely long lists of analytes, a representative number may be chosen. The analytes selected should be representative of all analytes reported. The following criteria shall be used for determining the minimum number of analytes to be spiked.

a) For methods that include 1-10 targets, spike all components;
b) For methods that include 11-20 targets, spike at least 10 or 80%, whichever is greater;
c) For methods with more than 20 targets, spike at least 16 components.

NOTE: Unless otherwise noted in project quality assurance plans or if components interfere with an accurate assessment, all Department of Defense projects will have LCS, MS, and MSD that contain all target analytes.

Evaluation Criteria and Corrective Action: The results of the individual batch LCS are calculated in percent recovery. The laboratory shall document the calculation for percent recovery. The individual LCS is compared to the acceptance criteria as published in the mandated test method. Where there are no established criteria, the laboratory determines internal criteria or utilizes client specified assessment criteria.

An LCS that is determined to be within the criteria effectively establishes that the analytical system is in control and validates system performance for the samples in the associated batch. Samples analyzed along with a LCS determined to be “out of control” should be considered suspect and the samples reprocessed and re-analyzed or the data reported with appropriate data qualifying codes as necessary.

E1.2.2 Sample Specific Controls

The laboratory must document procedures for determining the effect of the sample matrix on method performance. These procedures relate to the analyses of matrix specific Quality Control (QC) samples and are designed as data quality indicators for a specific sample using the designated test method. These controls alone are not used to judge

laboratory performance. Examples of matrix specific QC include: Matrix Spike (MS); Matrix Spike Duplicate (MSD); Post Spike (PS) and Post Spike Duplicate (PSD) sample duplicates; and surrogate spikes.

E1.2.3 Matrix Spike ; Matrix Spike Duplicates, Post Spike ; Post Spike Duplicates :

Purpose: Matrix specific QC samples indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. The information from these controls is sample/matrix specific and would not normally be used to determine the validity of the entire batch.

Frequency: The frequency of the analysis of matrix specific samples shall be determined as part of a systematic planning process (e. g. Data Quality Objectives) or as specified by the required mandated test method.

Composition: The components to be spiked shall be as specified by the mandated test method. Any permit specified analytes, as specified by regulation or client requested analytes shall also be included. If there are no specified components, the laboratory shall spike per the following:

For those components that interfere with an accurate assessment such as spiking simultaneously with technical chlordane, toxaphene and PCBs, the spike should be chosen that represents the chemistries and elution patterns of the components to be reported.

For those test methods that have extremely long lists of analytes, a representative number may be chosen using the following criteria for choosing the number of analytes to be spiked. However, the laboratory shall insure that all targeted components are included in the spike mixture over a 2-year period.

a) For methods that include 1-10 targets, spike all components;
b) For methods that include 11-20 targets, spike at least 10 or 80%, whichever is greater;
c) For methods with more than 20 targets, spike at least 16 components.

Evaluation Criteria and Corrective Action: The results from matrix spike/matrix spike duplicate and post spike/post spike duplicate are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD).

Results are compared to the acceptance criteria as published in the mandated test method. Where there are no established criteria, the laboratory should determine internal criteria and document the method used to establish the limits. For matrix spike or post spike results outside established criteria, corrective action shall be documented or the data reported with appropriate data qualifying codes.

E1.2.4 Matrix Duplicates:

Purpose: Matrix duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The results from this analysis indicate the precision of the results for the specific sample using the selected method. The matrix duplicate provides a usable measure of precision only when target analytes are found in the sample chosen for duplication.

Frequency: The frequency of the analysis of matrix duplicates may be determined as part of a systematic planning process (e. g. Data Quality Objectives) or as specified by the mandated test method.

Composition: Matrix duplicates are performed on replicate aliquots of actual samples. The composition is usually not known.

Evaluation Criteria and The results from matrix duplicates are primarily designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD) or another

Corrective Action	statistical treatment (e. g., absolute differences). The laboratory shall document the calculation for relative percent difference or other statistical treatments. Results are compared to the acceptance criteria as published in the mandated test method. Where there are no established criteria, the laboratory shall determine internal criteria and document the method used to establish the limits. For matrix duplicates results outside established criteria corrective action shall be documented or the data reported with appropriate data qualifying codes.

E1.2.5 Surrogate Spikes:

Purpose	Surrogates are used most often in organic chromatography test methods and are chosen to reflect the chemistries of the targeted components of the method. Added prior to sample preparation/extraction, they provide a measure of recovery for every sample matrix.
Frequency	Except where the matrix precludes its use or when not available, or is not a method requirement, surrogate compounds are added to all samples, standards, and blanks for all appropriate test methods.
Composition:	Surrogate compounds are chosen to represent the various chemistries of the target analytes in the method. They are often specified by the mandated method and are deliberately chosen for their being unlikely to occur as an environmental contaminant. Often this is accomplished by using deuterated analogs of select compounds.
Evaluation Criteria and Corrective Action:	The results are compared to the acceptance criteria as published in the mandated test method or determined using statistical process controls (SPC). Where there are no established criteria, the laboratory determines internal criteria and documents the method used to establish the limits. Surrogates outside the acceptance criteria must be evaluated for the effect indicated for the individual sample results. The appropriate corrective action may be guided by the data quality objectives or other site specific requirements. Results reported from analyses with surrogate recoveries outside the acceptance criteria include appropriate data qualifiers.

E1.3 Method Evaluation

The following procedures, as described in the other sections of the QAP, are in place in order to ensure the accuracy of the reported result:

- Procedure for initial demonstration of analytical capability performed initially (prior to the analysis of any samples) and if there is a significant change in instrument type, personnel, matrix or test method. Refer to Section 8.
- Procedures for initial and continuing calibration protocols as specified in Section 7.
- Procedures for utilizing proficiency test samples to evaluate the ability of a procedure and/or analyst laboratory to produce accurate data as specified in Section 3.

E1.4 Method Detection Limits

Method detection limits (MDLs) are determined as described in GL-LB-E-001 for The Determination of Method Detection Limits. This procedure is based on that established in 40 CFR Part 136, Appendix B.

Where possible, MDL studies are conducted for both aqueous and solid matrices and biological tissues using a clean matrix appropriate to the test method (such as laboratory pure reagent water or Ottawa sand). MDL studies for the majority of routine parameters are conducted by:

- analyzing a minimum of seven replicates of the lowest calibration standard
- determining the standard deviation of the seven replicates

- multiplying the standard deviation by 3.143 (based on six degrees of freedom and representing a 99% confidence level) to obtain the calculated MDL.

If the MDL study is being conducted for a new method or target analyte, the following steps are taken:

- the MDL is estimated based on information provided in the method or analytical experience
- a standard with a concentration three to five times the estimated MDL is prepared and analyzed a minimum of seven times
- the MDL is calculated as above based on the standard deviation and degrees of freedom
- the MDL is evaluated for reasonableness by verification through analysis of a prepared standard solution two to three times the calculated MDL.

MDL studies are not performed for any target analyte for which spiking solutions are not available such as total volatile solids, pH, color, , temperature, dissolved oxygen, or turbidity.

Practical quantitation limits (PQLs) are determined by either multiplying the MDL by approximately 2 to 10 or are equal to that of the lowest calibration standard. Concentrations of a target analyte determined to be greater that it's PQL are defined as quantitative results. All quantitative reported results are bracketed by calibration or calibration verification standards.

All MDL studies conducted by the laboratory are submitted to the Quality Group for an independent review. Upon acceptance of the MDL study, the MDLs reported to clients via our computer system are updated unless otherwise specified by contract. PQLs are also updated as directed by the new MDLs or changes to procedures.

All data pertaining to the study and the calculation of MDLs is stored on the production file system for data packages for four years and then archived to DVD.

GEL uses an industry standard approach to establishing radiochemistry and radiobioassay MDA (minimum detectable activity). This approach is based on MARLAP guidance for posteriori determination of MDA. The approach incorporates real time events that affect the observed sensitivity for every measurement performed in the laboratory. GEL recognizes for EPA radiological drinking water samples, that a MDL study is required similar to chemical constituents tested for drinking water.

GEL will follow the source document EPA 815-R-05-004 EPA Manual for the Certification of Laboratories Analyzing Drinking Water. In Chapter VI Critical Elements for Radiochemistry, section 1.5 of this document and alternate procedure is given for radiological constituents.

The analyst should prepare and measure a sample set of at least four reagent blanks and four laboratory fortified blanks that have the radioanalyte of interest added to quantitation levels appropriate for drinking water samples, the activity level added to the laboratory fortified blanks should be between the radioanalyte's MCL and its required detection limit. To be deemed an acceptable demonstration of proficiency, the mean recoveries and the standard deviation of the recoveries of the replicate measurements should be consistent with the requirements for accuracy and precision described in Section 7.7, and reagent blank measurements must have a mean result below the detection limit for each analyte measured with the method.

E1.5 Data Reduction

The procedures for data reduction, such as use of linear regression, are documented in the individual analytical standard operating procedures. GEL's policy governing the manual integration of chromatographic data is detailed in GL-LB-E-017, Procedure and Policy for Manual Integration. Manual integrations of chromatographic peaks can only be performed in accordance with GL-LB-E-017. This ensures that the integrations are done in a consistent and technically justifiable manner while meeting the requirements set forth under the Good Automated Laboratory Practices.

SOP GL-QS-E-014, Quality Assurance Measurement Calculations and Processes, discusses the use of laboratory data in statistical determinations and includes discussion of Estimation of Total Analytical Uncertainty, Statistical Process Control (SPC) Limits, and Calibration of Instrumentation. Understanding of the procedures used for data generation and reduction is an important part of an analyst demonstrating proficiency in an analytical procedure. All analysts and technicians responsible for generating curves and using curve-generated data are trained to this SOP per GEL annual and interim training requirements.

E1.6 Quality of Standards and Reagents

The quality of standards used in instrument calibration or quality control samples and reagents used in sample preparation and/or analysis must meet the criteria described in Section 7. In methods where the purity is not specified, analytical grade reagents are used. Reagents of lesser purity than those specified by the test method are never used. Upon receipt and prior to use, the labels on the container are checked to verify that the purity of the reagents meets the documented requirements of the particular test method.

The quality of water sources is monitored and documented as described in Section 4. The quality of water used in sample preparation or analysis meets the method-specified requirements. The type of water available in the laboratory is described in Section 4.

E1.7 Selectivity

Absolute and relative retention times aid in the identification of components in chromatographic analyses and in evaluation of the effectiveness of a column in separating constituents. The procedures governing retention time widows are documented in the applicable analytical SOP and meet all regulatory and method requirements.

In addition to retention time windows, the acceptance criterion for mass spectral training is also documented in the appropriate analytical SOP. In all cases, the acceptance criteria meet or exceed those specified in the analytical methods.

Unless stipulated in writing by the client, confirmations are performed to verify the compound identification of positive results detected on a sample from a location that has not been previously tested by our laboratory. Such confirmations are performed on a second column for organic tests such as pesticides, herbicides, or acid extractable or when recommended by the analytical test method except when the analysis involves the use of a mass spectrometer. All conformation is documented.

E1.8 Constant and Consistent Test Conditions

GEL's implementation of standard operating procedures that specify quality criteria including initial and continuing calibrations assures that our test instruments consistently operate within the specifications required of the application for which the equipment is used.

In addition to the specifications applied to instrumentation, glassware used for sample preparation or analysis is cleaned in a manner that reduces the potential for positive or negative interferences. Glassware is prepared in accordance with GL-LB-E-003 for Glassware Preparation.

This SOP details the procedures used to clean the following groups of glassware:

- That used for the determination of metals
- Reusable bottles and plasticware
- Bottles sued for the determination of biochemical oxygen demand (BOD)
- Glassware used in the determination of organic compounds
- That used for the determination of methylene blue active substances (MBAS)
- Glassware used in the determination of total organic halides (TOX)
- Glassware used in the analyses of samples for total Kjeldahl nitrogen (TKN) and total phosphorous
- Generic glassware used in all other analyses

If the method specifies that the glassware be stored in a particular manner, this requirement is documented in the appropriate analytical SOP.

Section E2 Radiochemical Analysis

This section describes the general quality control applied to radiochemical analysis. The specific quality control criteria applied to each analysis are delineated in the corresponding SOP. Detector Capabilities, Relative Bias, Relative Precision, and methods of calculating results for periodic Quality Control Determinations are discussed in the appropriate SOPs.

Discussed in this section are:

- Negative controls
- Positive controls
- Test variability/reproducibility
- Tracers and carriers
- Method evaluation
- Radiation measurement system calibration
- Data reduction
- Quality of standards and reagents
- Test conditions

E2.1 Negative Controls

Method blanks serve as the primary negative controls providing a means of assessing the existence and magnitude of contamination introduced via the analytical scheme. A method blank is analyzed at a frequency of one per preparation or analytical batch and is one of the quality control measures used to assess batch acceptance.

The activity level determined for each target in the method blank is assessed against the specific acceptance criteria specified in the applicable SOP. These criteria are based on a designated sample aliquot size and include appropriate calculations to compare the blank to activity levels determined for different sizes of sample aliquots.

The activity level of any target analyte in the method blank should be less than or equal to the contract required detection limit. The method blank may exceed this limit if the activity is less than 5% that of the lowest sample activity in the batch.

If the method blank acceptance criteria are not met, the specified corrective action and contingencies delineated in the SOPs are followed. Any failures of method blanks to meet the acceptance criteria are documented in the laboratory report and through GEL's nonconformance reporting system specified in GL-QS-E-004 for the Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items.

The activity levels determined for method blanks are not subtracted from those obtained for the samples in the associated preparation or analytical batch. Correction factors such as instrument background and analyte presence in the tracer may, however, be applied to all analyzed samples including both client samples and internal quality control samples.

E2.2 Positive Controls

Positive controls routinely employed in radiochemical analyses include both laboratory control samples (LCS) and matrix spikes (MS).

The laboratory standards used to prepare LCS and MS are from a different source than those used in instrument calibration, except when the calibration has been verified with a different source. This requirement may be superseded by client specific contract requirements. The activity levels of target analytes in the LCS and MS exceed ten times the prior detection limit and are less than one hundred times this detection limit. If a radiochemical method,

however, has more than one reportable analyte isotope, the LCS and MS need to only include one of the analyte isotopes.

Gamma spectroscopy is the exception to this guideline requiring the LCS and MS to contain isotopes representing the low, medium, and high-energy range of the analyzed gamma spectra.

E2.2.1 Laboratory Control Sample (LCS)

Laboratory control samples are analyzed at a minimum of once per preparation or analytical batch containing twenty or less samples.

The recovery of target analytes in the LCS is compared to the acceptance criteria specified in the applicable analytical SOP. If the recovery of the LCS does not fall within the acceptance range, the corrective actions and contingency steps specified in the SOP are implemented. These steps include the completion of an internal nonconformance report in accordance with GL-QS-E-004 and noting the failure on the laboratory report.

E2.2.2 Matrix Spike (MS)

Matrix spikes are analyzed at a minimum of once per preparation or analytical batch containing twenty samples or less under the following conditions:

- The analytical method does not utilize an internal standard or carrier
- There is a physical or chemical separation process
- There is sufficient sample volume provided for the analysis.

The target analyte recoveries are one of the quality control measures used to assess batch acceptance. The recovery of target analytes in the MS is compared to the acceptance criteria specified in the applicable analytical SOP. If the recovery of the MS does not fall within the acceptance range, the data associated with that matrix spike are qualified accordingly.

E2.3 Test Variability/Reproducibility

The reproducibility of measurements is evaluated by the use of matrix duplicates. Matrix duplicates are analyzed once per preparation or analytical batch of twenty samples. The relative percent difference (RPD) obtained between the activity levels obtained for the sample and its duplicate is evaluated against the range in the SOP.

E2.4 Tracers and Carriers

Two additional quality control measures specific to radiochemical analysis are tracers and carriers. If the analytical method requires a tracer or carrier, each sample result will be associated with a tracer recovery that is calculated and reported. For radiochemistry procedures requiring gravimetric or radiometric recovery (tracer yields), the acceptable limits are 15% - 125%. These limits may vary for specific clients and/or projects. If the applicable limits are not met, the corrective actions delineated in the SOP are implemented.

E2.5 Method Evaluation

GEL evaluates the radiochemical preparation and analytical methods to ensure the accuracy of the reported result. This evaluation includes initial demonstrations of capability as described in Section 8 and the analysis of proficiency test samples as described in Section 3. The suppliers of proficiency test samples conform to the requirements of ANSI N42.22 and ISO/IEC 17025-2017.

E2.6 Radiation Measurement System Calibration

It is not generally necessary or practical to calibrate radiochemical instrumentation each day of use due to its stability and the time-consuming nature of some of the measurements. There are, therefore, significant differences in the calibration requirements for radiochemical instrumentation from that used for chemical analyses.

Calibration differences include but are not limited to the following:

- The requirement in Section 7 for the determination of the appropriate number of standards for initial calibration is not applicable to radiochemical methods. If the radiochemical method requires multiple standards for initial calibration, the number of standards is included in the applicable SOP.
- If linear regression or non-linear regression is used to fit standard response or calibration standard results to a calibration curve, the correlation coefficient is determined. This differs from Section 7.
- The requirement identified in Section 7 for the bracketing of quantitative results by calibration or calibration verification standards is not applicable to radiochemical analyses due to the non-correlated event nature of decay counting instrumentation.
- As indicated in Section 7, the LCS may fill the requirements for the performance of an initial calibration and continuing calibration verification standard. The calibration verification acceptance criteria are the same as specified for the LCS (75 -125%).
- Background calibration measurements are made on a regular basis and monitored using control charts. These values are subtracted from the total measured activity in the determination of the sample activity. The frequency of these measurements is indicated in the SOP GL-RAD-I-010.
- Instrument calibration shall be performed with reference standards as defined in Section E3.8.
- The frequency of calibration shall be addressed in the governing SOPs.

E2.7 Data Reduction

All sources of method uncertainties and their propagation must be traceable to reported results. This is performed under the guidance of the ISO "Guide to the Expression of Uncertainty in Measurement" and the NIST Technical Note 1297 on "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results." Details of calculations and equations used in reporting Radiochemistry analytical results may be found in GL-RAD-D-003 for Data Review, Validation and Data Package Assembly.

E2.8 Quality of Standards and Reagents

The reference standards we use are obtained from the National Institute of Standards and Technology (NIST), EPA, or suppliers providing NIST standards. Reference standards should be accompanied by a certificate of calibration whose content is described in ANSI N42.22 – 1995, Section 8, Certificates. All reagents used shall be analytical reagent grade or better.

E2.9 Test Conditions

GEL adheres to written procedures that minimize the possibility of cross contamination between samples. This prevents incorrect analysis results from the cross contamination. Procedures are in place, for example, to separate known radioactive and nonradioactive samples from the time of sample receipt to analysis and sample disposal.

Instrument performance checks are performed on a regular basis and monitored with control charts. This ensures that the instrument is operating properly and that the calibration has not changed. The same check source used in the preparation of the control chart at the time of calibration is used in the performance checks of the instrument. The sources must provide adequate counting statistics for a relatively short count time and should be sealed or encapsulated to provide loss of activity and contamination of the instrument and laboratory personnel.

Instrument performance checks include checks on the counting efficiency and the relationship between channel number and alpha or gamma ray energy.

APPENDIX F: ETHICS AND DATA INTEGRITY AGREEMENT

The GEL Group Inc.

ETHICS and DATA INTEGRITY AGREEMENT

I. I, (Name), state that I understand the high standards of integrity required of me with regard to the duties I perform and the data I report in connection with my employment at The GEL Group, Inc.

II. I agree that in the performance of my duties at The GEL Group, Inc.:

A. I shall not intentionally report data values that are not the actual values obtained,

B. I shall not intentionally report data that does not meet method or procedural specifications unless that data is properly qualified through comments or other notations in the analytical report.

C. I shall not intentionally report dates and times of data analyses that are not the actual dates and time of data analyses; and

D. I shall not intentionally represent another individual's work as my own.

III. I agree to inform a Group Leader, Manager, Director, or member of the Executive Committee of The GEL Group, Inc. of any accidental or intentional reporting of non-authentic data by myself or other employees in a timely manner.

IV. I will not knowingly participate in any questionable activities or violations of the Procurement Integrity Act during purchasing or sales activities. I will report any questionable activities to a Group Leader, Manager, Director, or member of the Executive Committee of The GEL Group, Inc. This includes discussions on analytical, consulting, and geophysical services pricing and contracts, vendor pricing, or other essential business information to anyone outside of The GEL Group, Inc. family.

This Ethics and Data Integrity Agreement has been explained to me by the Director of Quality Systems, my Group Leader, or at a training session, at which time I have been provided the opportunity to ask questions on any part of this agreement that I did not understand. It has also been explained to me that any violation of this agreement conducted during work performed under a subcontract or direct contract to a government agency could subject me to potential prosecution.

I understand that violation of this policy subjects me to disciplinary action, up to and including termination of my employment with The GEL Group Inc.

Employee Signature: _____ Date: _____

Trainer Signature: _____ Date: _____

APPENDIX G: EQUIPMENT LIST

List of Equipment and Instrumentation

ORGANICS EXTRACTIONS

#	Equipment	Model #	Purchase Date	ID/Serial #
3	Tekmar Sonic Distribution	600		22461D
1	J2 Scientific GPC	Accup-MP5	Jul-05	05C-1159-4-0
10	Zymark Turbovap	Turbovap II	May-96	TV9612N6726 TV9631N6975 TV9628N6939 TV9809R7994 TV0146N10597 TV0146N10596 TV0146N10598 TV0146N10595 TV1346N20168 TV1246N17453
10	Soxtherms	SOX416/SE416	Jan-05 Nov-16	4041427 4040014 4040019 4040018 SX2033 SX2050 1/846516004 1/8465160005 1/8465160006

				1/8465160007
6	Turbovap II Biotage	Turbovap II	Feb-18	180600348 174600239 180200293 180600353 180600350 180300303
3	N-Evaps Organomation	115 1205	Jun-93 Jun-95	2812 6184 2038 11634
1	Sartorius Toploading Balance	CP 323S	N/A	19350208
1	Sartoris AG Toploading Balance	LP8200P	N/A	14908834

LIQUID CHROMATOGRAPHY/HPLC

#	Equipment	Model #	Purchase Date	ID/Serial #
7	LC/MS/MS	Quattro Ultima	May-02	D99SM9012R (LC) VB150 (MS)
		ABSCiex 4000	Sep-05	DE91608981 (LC) V04290402 (MS)
		ABSciex 4000	Apr-07	DE43619731 (LC) V113820703 (MS)
		ABSciex QTRAP 5500	Dec-14	L20435252316(LC) L20435252317(LC) AU212181403 (MS)
		ABSciex 5500	Nov-16	L20435453570(LC) L20435453571(LC) BB214331608 (MS)

		ABSciex 5500	Apr-17	L20435453807(LC) L20435453808(LC) BB215361701 (MS)
		ABSciex 5500	Nov-17	L20435553978(LC) L20435553979(LC) BB231241708 (MS)

LIQUID CHROMATOGRAPHY/HPLC

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Shimadzu Column Heater	CTO-20AC	Dec-14	L20215251917
1	Shimadzu Degasser	DGU-20A	Dec-14	L20705263668
1	ABSciex PAL Autosampler	MXY013-02A	Dec-14	326966
1	Shimadzu Column Heater	CTO-20AC	Nov-16	L20215452846
1	Shimadzu Degasser	DGU-20A	Nov-16	L20705467839
1	CTC Analytics PAL Autosampler	MXY04-01A	Apr-07	141417
1	Shimadzu Column Heater	CTO-20AC	Apr-17	L20215553065
1	Shimadzu Degasser	DGU-20A	Apr-17	L20705366534
1	ABSciex PAL Autosampler	MXY013-02A	Nov-17	410574
1	Shimadzu Column Heater	CTO-20AC	Nov-17	L20215452696

LIQUID CHROMATOGRAPHY/HPLC

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Shimadzu Degasser	DGU-20A	Nov-17	L20705568380
1	ABSciex PAL Autosampler	MXY013-02A	Nov-17	410574
1	Agilent ALS	1100	Sep-05	DE91604756
1	Agilent Degasser	1100	Sep-05	JP13212623
1	Agilent Column Heater	1100	Sep-05	US82404465
1	Agilent Column Heater	1100	Apr-07	DE11120879
1	Hewlett Packard Quantum Pump	1100	Oct-99	DE23919817
1	Hewlett Packard ALS	1100	Oct-99	DE91607770
1	Hewlett Packard DAD	1100	Oct-99	DE14913984
1	Hewlett Packard Degasser	1100	Oct-99	JP03925183
1	Hewlett Packard Column Heater	1100	Oct-99	US72103603
1	Hewlett Packard Quantum Pump	1100	Nov-99	DE91606066

LIQUID CHROMATOGRAPHY/HPLC

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Hewlett Packard ALS	1100	Nov-99	US80603453
1	Agilent HPLC with DAD and FLD	1100	Nov-99	DE54627302 DE14904242
1	Hewlett Packard Degasser	1100	Nov-99	JP63203519
1	Hewlett Packard Column Heater	1100	Nov-99	DE91609651
1	Aglient Quantum Pump	1100	Jun-05	DE33224733
1	Agilent ALS	1100	Jun-05	DE23909584
1	Agilent HPLC with DAD and FLD	1100	Jun-05	DE91608331 DE92001137
1	Agilent Degasser	1100	Jun-05	JP13211588
1	Agilent Column Heater	1100	Jun-05	DE33235932
1	Aglient Quantum Pump	1100	Jun-07	DE23919852
1	Aglient ALS	1100	Jun-07	US64401050
1	Agilent DAD	1100	Jun-07	DE43603083

1	Agilent Degasser	1100	Jun-07	JP73016466
1	Agilent Column Heater	1100	Jun-07	US82404303
1	OHAUS Analytical Balance	CQ10R11-2E1	N/A	00119266EK
1	Organomation N-EVAP112	9125	Nov-16	61476

VOLATILE ORGANIC ANALYSIS

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Hewlett Packard Gas Chromatograph/Mass Spectrometer Chemstation with OI 4560/Arcon Autosampler (Screening Instrument)	5972	N/A	336A51009 (VOA 0)
1	Hewlett Packard Gas Chromatograph/Mass Spectrometer Chemstation with OI 4560/Arcon Autosampler	5973	Oct-99	K842460828P US91911845(US00030386)VOA1
1	Hewlett Packard Gas Chromatograph/Mass Spectrometer chemstation with 0I Eclipse/Arcon Autosampler	5973	Nov-98	G107466806P US71191097(US00023264)VOA9
1	Aglient Gas Chromatograph/Mass Spectrometer Chemstation with OI 4560/Arcon Autosampler	5973	Apr-09	B237010 US71191093/US00026073 VOA4

VOLATILE ORGANIC ANALYSIS

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Hewlett Packard Gas Chromatograph/Mass Spectrometer Chemstation with OI 4560/Arcon Autosampler	5975	Aug-06	K736460761 US61332879(CN10848050)(VOA5)
1	Hewlett Packard Gas Chromatograph/Mass Spectrometer Chemstation with 0I4560/Arcon Autosampler	5973	Jan-98	K523466628P US71191112(US00010331)VOA8
1	Hewlett Packard Gas Chromatograph/Mass Spectrometer Chemstation with OI Eclipse/Arcon Autosampler	5975C	Apr-09	(E911466523P) VOA2 US83131318/CN10606080
1	Hewlett Packard Gas Chromatograph/Mass Spectrometer Chemstation with OI 4560/Arcon Autosampler	5973	Jul-04	M948460722 US71191113(US00028288)VOA3
1	Agilent Gas Chromatograph/Mass Spectrometer Chemstation	5977A	July-15	H352460344 US51523M408/CN15173066 VOAC
1	Agilent Gas Chromatograph/Mass Spectrometer Chemstation with OI 4560/Arcon Autosampler	5975	Sep-05	N222460467 US52430466(CN10525054)VOA6
1	Agilent Gas Chromatograph/Mass Spectrometer Chemstation with OI Eclipse/Arcon Autosampler	5975	Apr-09	E911466524P CN10848117 (VOAA) US83131219

1	Hewlett Packard Gas Chromatograph/Mass Spectrometer Chemstation with OI Eclipse/Arcon Autosampler PID/FID Detectors	6890	June-11	US0026725 (B431466149P) (VOAB) FID=1471 PID=54500
1	Agilent Flame Ionization Detector /Chemstation with OI 4560	6890N	Aug-08	CN10813002 (VOC4)
1	OHAUS Toploading Balance	AV812N	N/A	323410747
1	Sartorius Toploading Balance	CP622	N/A	19452583

SEMIVOLATILE ORGANIC ANALYSIS

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Agilent 6890N Gas Chromatograph/ 5973 Mass Spectrometer w/ 7683 Autosampler Tower	5973	Sep-05	CN10521005/US52440275 MSD1
1	Agilent 7890A Gas Chromatograph/ 5975C Inert Mass Spectrometer w/ 7683 Autosampler Tower	5975	April-09	CN10848121/US83131300 MSD2
1	Agilent 7890A Gas Chromatograph/ 5975C Inert Mass Spectrometer w/ 7683 Autosampler Tower	5975	April-09	CN10821032/US83131355 MSD3

SEMIVOLATILE ORGANIC ANALYSIS

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Agilent 7890A Gas Chromatograph/ 5975C Inert Mass Spectrometer w/ 7683 Autosampler Tower	5975	Nov-07	CN10727001/US90704000 MSD4
1	Hewlett Packard 6890 Gas Chromatograph/ 5973 Mass Spectrometer w/ 7683 Autosampler Tower	5973	May-97	US00023050/US82311233 MSD5
1	Hewlett Packard 6890 Gas Chromatograph/ 5973 Mass Spectrometer w/ 7683 Autosampler Tower	5973	May-97	US00025502/US82311417 MSD6
1	Agilent 7890 Gas Chromatograph with MMI/ 5977A Mass Spectrometer w/ 7693 Auto injector	5977A	June-15	CN15233175/US1523M414 MSDA
1	Hewlett Packard 6890 Gas Chromatograph/ 5973 Mass Spectrometer w/ 7683 Autosampler Tower	5973	May-97	US00028102/US82311616 MSD8
1	Agilent 6890N Gas Chromatograph-FID w/ 7683B Autosampler	6890	March-08	CN10805005 FID6
1	Agilent 6890N Gas Chromatograph-FID w/ CTCH5500 Headspace Autosampler	6890	July-08	CN10805007 FID8

SEMIVOLATILE ORGANIC ANALYSIS

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Agilent 6890N Gas Chromatograph-FID w/ 7683B Autosampler	6890	June-08	CN10811015 FID7
1	Agilent 6890N Gas Chromatograph-FID w/ 7683B Autosampler	6890	July-07	US10604037 FID5
1	Hewlett Packard 6890 Gas Chromatograph-FID w/ 6890 Autosampler	6890	March-98 (Installed 4/11/2011. Old MSD2 GC)	US0009213 FID9
1	Hewlett Packard 6890 Gas Chromatograph-Dual ECD w/ 7683 Autosampler	6890	March-98	US00023402 ECD1
1	Hewlett Packard 6890 Gas Chromatograph-Dual ECD w/ LEAP PAL RSI Autosampler	6890	March-98	US00028911 ECD2
1	Agilent 7890ª Gas Chromatograph-Dual Micro ECD w/ 7693 Autosampler	7890A	March-10 (Purchased from CFA December-11)	CN10842125 ECD3
1	Hewlett Packard 6890 Gas Chromatograph-Dual ECD w/ 7673 Autosampler	6890	November-97	US00009591 ECD5

SEMIVOLATILE ORGANIC ANALYSIS

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Hewlett Packard 6890 Gas Chromatograph-Dual ECD w/ 7683 Autosampler	6890	Nov-97	US00023343 ECD6
1	Hewlett Packard 6890 Gas Chromatograph-Dual ECD w/ 7673 Autosampler	6890	Nov-97	US00010134 ECD7
1	Agilent 6890 Gas Chromatograph-Dual ECD w/ 7683 Autosampler	6890	July-98	US10133016 ECD8
1	Agilent 7890ª Gas Chromatograph-Dual Micro ECD w/ 7693 Autosampler	7890A	July-10	CN10261088 ECD9

METALS ANALYSIS

#	Equipment	Model #	Purchase Date	ID/Serial #
2	Perkin Elmer Mercury Analyzer	Fims 100 Fims 100	Feb-14 Oct-18	101S14020102 101S18092701

METALS ANALYSIS

#	Equipment	Model #	Purchase Date	ID/Serial #
1	AA WINLAB (Software)	6.5.0.0266	Feb-14	NA
1	Syngistix for AA (software)	Ver 3.1	Oct-18	NA
1	PS Analytical Atomic Fluorescence Mercury Analyzer	10.035	Aug-17	606
4	Perkin Elmer Inductively Coupled Plasma Mass Spectrometer	ELAN 9000 NexION 300 NexION 350 NexION 350X	Apr-10 May-14 Aug-14 Mar-18	AJ13141002 81VN4031301 85VN4061701 85XN7111002
4	Perkin Elmer ICPMS (Software)	2.4 SP3	Apr-10 May-14 Aug-14 Mar-18	NA
4	Perkin Elmer Inductively Coupled Plasma Spectrometer	7300DV 8300DV AVIO500 AVIO500	Mar-10 Apr-14 Feb-18 Oct-18	077C0022701 078S1403012 081S1711281 081S1807072
2	Winlab 32 (software)	Ver 3.1.0	Mar-10 Apr-14	NA

METALS ANALYSIS

#	Equipment	Model #	Purchase Date	ID/Serial #

2	Syngistix (software)	Ver 3.0	Mar-18 Oct-18	NA
1	Thermo Orion 3Star	3Star	Dec-17	9731
1	Thermo Orion pH meter	420	Prior to 2008	065576
1	OHAUS Balance	AV313	Jan-14	B351136893
2	OHAUS Balance	AX423/E	Jan-19	B848841591 B843640835
4	TCLP Tumblers	NA	Prior to 2008	T 101 T 104 T 105 T 106
3	Environmental Express HotBlock	SC100	Prior to 2008	Various units
11	Environmental Express HotBlock	SC154	Prior to 2008	Various units
2	Torrey Pines Scientific Hotplate	HP51	Prior to 2008	08301024 08301025
GENERAL CHEMISTRY				
#	**Equipment**	**Model #**	**Purchase Date**	**ID/Serial #**

1	U.S. Filter Modulab Water System	M00100	Prior to 2008	LW2264
1	Barnstead NANOpure Diamond	D11901	Aug-02	1190030186870
1	Thermo Centrifuge	CL30	Apr-08	307070484
1	OI Analytical, TOC 1030S	OI1030S	Oct-15	A536733677
2	OI Analytical, TOC 1030W	OI1030W	Apr-15 Jan-16	P504730315 P550730559P
2	ATOC (software)		Apr-15	NA
2	Horizon Speed Vap II	9000 9000	Oct-01 Apr-02	01-337 01-340
2	Lachat QuikChem 8000	8000 series	Jul-01 Jul-02	A83000-1910 A83000-2077
1	Lachat QuikChem 8500	8500 series	Jan-06	60900000344
3	Omnion (software)	3.0.218 3.0.218 3.0.219	Jul-01 Jul-02 Jan-06	NA
GENERAL CHEMISTRY				
#	**Equipment**	**Model #**	**Purchase Date**	**ID/Serial #**

2	ThermoSpectronic	20D+	Nov-03 Aug-06	3DUD255001 3DUJ199004
2	Mitsubishi Total Organic Halogen Analyzer	AOX-200	Jul-10 Mar-16	E7B00117 E7BA0376
1	Dionex Ion Chromatograph	DX500	Oct-99	99040041
1	PeakNet (software)	5.21	Oct-99	NA
3	Dionex Ion Chromatograph	ICS-3000	Feb-08 Apr-09 Apr-09	07120836 09030720 09030721
1	Dionex Ion Chromatograph	ICS-5000	Jul-10	10060501
4	Chromeleon (software)	6.80 SP2	Feb-08 Apr-09 Apr-09 Jul-10	NA
1	Dionex Ion Chromatograph	ICS-1600	Jul-14	14060002
1	Chromeleon (software)	7.2.1	Jul-14	NA
1	Turbidimeter	Orion AQ4500	Feb-11	B04279
1	Titroline Karl Fischer Moisture Analyzer	D55122	Feb-07	00635172
GENERAL CHEMISTRY				

#	Equipment	Model #	Purchase Date	ID/Serial #
2	TKN Block Digestor	TKN100	Jul-16 May-17	2016TKNBC115 2017TKNBC133
2	Fried Electronics Stirring Hotplates	MH1-3x2	Jul-17	0568 0569
1	YSI Dissolved Oxygen Meter	5000	Apr-15	15D100827
1	IEC Clinical Centrifuge	Clinical	Prior to 2008	428-17189
1	Rapid Tester Setaflash	RT-00001	May-14	142271
2	Baxter TDS Ovens	DN63	Prior to 2008	DN63
2	VWR Oven	1370FM 13703M	Prior to 2008	101399
1	Vulcan Furnace	3-550PD	Apr-15	DKZ1316115V
2	HACH COD Reactor	95600-00	Jan-94	911005731C 9807000017919
1	Orion Conductivity Meter	A212	Dec-17	X40725
1	Parr 6200 Calorimeter	Parr 6200	Aug-14	M40303

GENERAL CHEMISTRY

#	Equipment	Model #	Purchase Date	ID/Serial #
6	Sartorius Balance	1872 BP2100S BA210S BA221S LC4800-P ED2200S	Prior to 2008	3410156 90710197 40245216 90606741 410010032 25150025
2	OHAUS Balance	PA 114 AX124	Jan-11 Apr-17	8331440032 B649420569
1	Brookfield Viscometer	LVDVE	Apr-05	E6515383
1	PerpHect pH Meter Orion	370	Prior to 2008	19742
1	Beckman Centrifuge	TJ-6	Prior to 2008	4359
1	VWR Centrifuge	Clinical 200	Nov-11	68105001
5	Simple Cn Hotblocks	SC6002	Apr-09 Apr-09 Jan-09 Jan-09 Dec-18	5388DIS1012 5388DIS1016 5873DIS1030 5873DIS1036 2018DISW1225
2	BOD incubator	2020 818	Jan-99 Jan-10	10059509 26AW-9
1	Thermo Orion Star A111	A111	Sep-15	J10067

1	Thermo Orion Star A111	A111	Feb-14	J06078
2	Electronic Digital Caliper	Y305811 030150	Prior to 2008	62379-531 CO0130150
2	MicroBlock R Distillation	EMD 1920-107	Nov-17 Dec-18	2262 2386

RADIOCHEMISTRY/BIOASSAY

#	Equipment	Model #	Purchase Date	ID/Serial #
96	Canberra Alpha Spectrometers for Alpha Spectroscopy System (environmental)	7401	1992 to 1995	Various
168	Canberra Alpha Analyst Spectrometers with PIPS Detectors (environmental)	7200	1988 to 2009	Various
1	Perkin Elmer Automatic Gamma Counter	1480	Jun-05	4800440
1	Gamma Products G5400W Low background Alpha/Beta Counting System with 4 detectors	G5420-400T	Jan-17	121603
4	Compaq/DEC Alpha Work Stations for Alpha/Gamma Data Management System	500AU 500AU 500AU DS-10 DS-10	Nov-98 Nov-98 Jan-04 May-06 Mar-09	N188806229 406DP9Z1060 AY93206555 AY30703843

RADIOCHEMISTRY/BIOASSAY

#	Equipment	Model #	Purchase Date	ID/Serial #
2	Protean Automatic Proportional Counter (Bioassay)	WPC 9550	Oct-2003 Jul-2004	EMC 0329438 924233
11	Protean Multi-Detector (40) Proportional Counter	MDS-16	Apr-02 Jul-2005 Oct-05 Mar-02	10751,10752,10753,10754 0525767,0525768 0531474,0531474 311437,311438, 0021910
4	Protean Multi-Detector (16) Proportional Counter	MDS-16	Feb-09	9115168, 169, 170,171
2	Tennelec LB-4100 Proportional Counter with 32 detectors	LB4100	Jun-93 Dec-98	18483 21938
1	Tennelec LB-4100 Proportional Counter with 16 detectors	LB4100	2010	70562
1	Gas Flow Proportional Counter with 4 detectors	G5420-400T	Jan-17	121603
8	Beckman Liquid Scintillation Counters	LS6000 LS6500 LS6500 LS6000 LS6500 LS6500 LS6000 LS6000	Jun-93 Jun-93 Apr-94 Mar-03 Oct-03 Dec-98 Dec-98 Jan-14	7065155 7067083 7067404 7060655 7070506 7069123 7060656 7069693

RADIOCHEMISTRY/BIOASSAY

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Perkin Elmer Inductively Coupled Plasma Mass Spectrometer	ELAN9000	Jun-10	AJ13351006
2	Perkin Elmer Liquid Scintillation Counter – Wallac Guardian (environmental)	1414	1997 2010	4140127 4140421
2	Protean Automatic Proportional Counter	WPC 4550		2910 1111
1	Perkin Elmer Liquid Scintillation Counter – Wallac Guardian (bioassay)	1414	1998	4140299
2	Perkin Elmer Quantulus	1220	1998 2009	2200082 DG06095168
2	Ortec – Alpha Spectrometers	alpha ensemble-8	2010	10235232 10230971
7	Ortec – Alpha Spectrometers	octete-pc	2010	177, 182, 217, 266, 264, 144, 176
1	Perkin Elmer Liquid Scintillation Counter – Rackbeta	1219	2010	206147
1	Perkin Elmer ICPMS	ELAN 9000	2010	AJ13271005
1	Broad-Energy Germanium Detector(Carbon Comp. Window)	BE3825	2006	3068173
1	High Purity Germanium Coaxial Detector	GEM90210-P	1990	30-TP30546-A
1	High Purity Germanium Coaxial Detector	GEM-35190	2004	CV-P122204CA
1	High Purity Germanium Coaxial Detector	GEM35	2007	CV-PO42407CA

RADIOCHEMISTRY/BIOASSAY

#	Equipment	Model #	Purchase Date	ID/Serial #
1	High Purity Germanium Coaxial Detector	GEM35P4-83	2008	CV-TP011608CA
1	High Purity Germanium Well Detector	GCW3523	1994	3941466
1	Low Energy Germanium Detector (Beryllium Window)	GL1015	1988	488926
1	Low Energy Germanium Detector (Beryllium Window)	GL1010S	1990	10902649
1	Low Energy Germanium Detector (Beryllium Window)	GL2820R	1995	1954119
1	Low Energy Germanium Detector (Beryllium Window)	GL2820R	1998	3984452
1	Low Energy Germanium Detector (Beryllium Window)	GL2020R	2007	9078304
1	Low Energy Germanium Detector (Carbon Comp. Window)	GL2020-S	1992	12922782
1	N-Type High Purity Germanium Coaxial Detector	GMX 45225-P-S	1990	37-TN11260A
1	N-Type High Purity Germanium Coaxial Detector	GMX30200-P	1990	30-TN10348
1	N-Type High Purity Germanium Coaxial Detector	NIG3019	1991	PGT2461

RADIOCHEMISTRY/BIOASSAY

#	Equipment	Model #	Purchase Date	ID/Serial #
1	P-Type High Purity Germanium Coaxial Detector (Bioassay)	IGC3919	1993	2605
1	Reverse-Electrode Coaxial Germanium Detector (Beryllium Window)	GR3019	1986	9861606
1	Reverse-Electrode Coaxial Germanium Detector (Beryllium Window)	GR2020	1991	1912509
1	Reverse-Electrode Coaxial Germanium Detector (Carbon Comp. Window)	GR3520	1993	8932581
1	Reverse Electrode Coaxial Germanium Detector	GR3021	1992	3922553
1	Reverse Electrode Coaxial Germanium Detector (Beryllium Window)	GR4019	1996	1966073
2	Standard Electrode Coaxial Germanium Detector	GC3519	1991	9912854, 11912876
2	Standard Electrode Coaxial Germanium Detector	GC3520	1992 2000	12922955 2007152
4	Standard Electrode Coaxial Germanium Detector	GC2018	1992	9923035 9923043 10923049 10923050

RADIOCHEMISTRY/BIOASSAY

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Standard Electrode Coaxial Germanium Detector	GC3018	1993	5933088
1	Standard Electrode Coaxial Germanium Detector	GC3519	1994	1943234
1	Standard Electrode Coaxial Germanium Detector	GC8021	1994	8943324
1	Standard Electrode Coaxial Germanium Detector (Bioassay)	GC3519	1994	1943199
1	Standard Electrode Coaxial Germanium Detector	GC3519	1992 2005	3922907 7059000
8	Standard Electrode Coaxial Germanium Detector	GC4019	1995 2001 2006 2007	6953489 6953483 6953542 10017452 10017444 9069163 9069175 10079344
3	Standard Electrode Coaxial Germanium Detector	GC4020	2005 2006	10059017 10059015 4069118

RADIOCHEMISTRY/BIOASSAY

#	Equipment	Model #	Purchase Date	ID/Serial #
4	Standard Electrode Coaxial Germanium Detector	GC4520	2009	4099544 4099570 10099624 11099639
1	N-Type High Purity Germanium Coaxial Detector	GMX35195-P-S	1991	34-TN-20891A
8	Ludlum Alpha Scintillation Detector	Ludlum-182	2007 Mar-17 Jul-17 Jan-17	PR086493 PR140731 PR101846 PR078964 PR364855 PR139590 PR286612 PR286613
1	Perkin Elmer Automatic Gamma Counter	Model 2480	Oct-17	DG12095812
1	Sartorius Balance	A200S		38080204
1	Sartorius Balance	CP2201		18150253
2	Sartorius Balance	CP323S		18550299 15750050
1	Sartorius Balance	CP 2202S		17955156
1	Sartorius Balance	HD 2000 D		39020004

RADIOCHEMISTRY/BIOASSAY

#	Equipment	Model #	Purchase Date	ID/Serial #
2	Sartorius Balance	I 12000 S		40109033 39039003
1	Sartorius Balance	L2200S		38110007
1	Sartorius Balance	BP3100S		51204863
1	Sartorius Balance	U5000D		36080009
1	Sartorius Balance	R 300S		38110047
1	Sartoris Balance	LC6200S		30503875
1	Sartoris Balance	LC3201D		60108592
1	Sartoris Balance	TE313S		16107662
1	Sartoris Balance	ENTRIS5201		34104035
3	Sartoris Entirs Balance	ENTRIS5201-1S		33003774 33003775 33005595
1	Sartoris Entris Balance	ENTRIS224-15		33604148
1	Sartoris Entris Balance	ENTRIS52202-1S		33010896

RADIOCHEMISTRY/BIOASSAY

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Mettler Analytical Balance	AE160		C31514
1	Mettler Analytical Balance	AE163		F33394
2	Mettler Analytical Balance	AE200		F30560 1113021018
1	Mettler Analytical Balance	AE240		L28658
1	Mettler Analytical Balance	AE50		1113092273
1	Mettler Analytical Balance	PM16-N		N39169
1	Mettler Analytical Balance	PM 4600		J93763
1	OHAUS Toploader Balance	RD6RM		2525244

HIGH RAD ALIQUOT ROOM

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Adventurer Pro	AV2102	Oct-14	B440101411

LABORATORY INFORMATION MANAGEMENT SYSTEMS

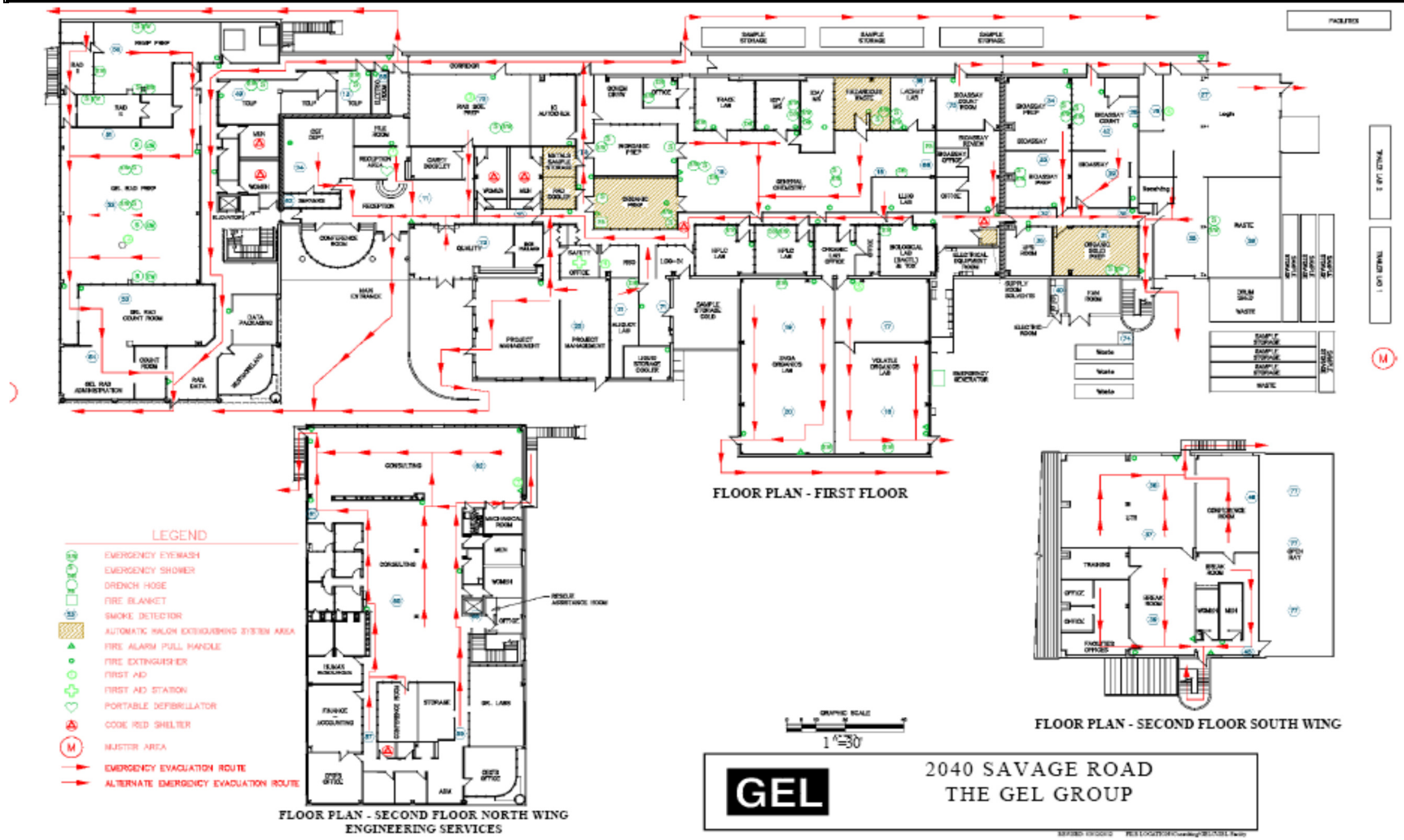
#	Equipment	Model #	Purchase Date	ID/Serial #
1	DELL Poweredge 2950 (mailsvr01) 2 X 3.0Ghz 2GB ram	2950	2007	DG2CNB1
1	HP9000 Dclass, HP-UX 10.20, 2 cpu, 256 MB RAM, (hpclp1) 50GB Disk (mirrored and RAID%), Raid tower, 100 Mbps Eth card, Target Software	N/A	Nov-97	A3480A
1	HP9000 Dclass, HP-UX 10.20, 2 cpu, 256 MB RAM, (104ilroy) 50GB Disk (mirrored and RAID5), Raid tower, 100 Mbps Eth card, Target Software	N/A	Nov-97	A3480A
1	HP9000 Dclass, HP-UX 10.20, 2 cpu, 256 MB RAM, (prdsvr07) 50GB Disk (mirrored and RAID5), Raid tower, Target Software	N/A	Nov-97	A3480A
1	Sun V890 (prodsvr01) 8X1.5Ghz) 128GB ram (mirrored and raid5)	V890	2007	0529AM019F
1	Sun V890(standbysvr01) 4X1.35Ghz 32GB (mirrored and rad5)	V890	2008	0526AM02F
1	HP-Prolient DL380 (vmhost01) 2-10QuadCoreX2.40GHz 25GB	DL360	2009	MXQ904A2SR
1	HP-Prolient DL380 (vmhost02) 2-10QuadCoreX2.40GHz 19GB	DL361	2009	MXQ903A3RA

1	HP-Prolient DL360 (vmhost04) 2-QuadCoreX2.83GHz 16GB	DL362	2009	MXQ903A3KSS
1	HP2012i (san01) DC Modular Smart Array	2012i	2009	3CL904C108
1	EMC Storage Array Network (SAN)	VNX5200	Jan-2015	APM00145036951

UNIVERSAL POWER SUPPLY

#	Equipment	Model #	Purchase Date	ID/Serial #
1	Power ware 9315	9315	Jul-05	ES443ZXX57

APPENDIX H: FACILITIES WITH EVACUATION ROUTES



APPENDIX I: STANDARD OPERATING PROCEDURES AND ANALYTICAL METHODS

Standard Operating Procedures and Analytical Methods		
SOP #	**SOP Title**	**Methods**
GL-ADM-E-001	Preparation, Authorization, Advance Change, Revision, Release, and Retirement of Standard Operating Procedures	N/A
GL-AP-E-001	Invoicing Analytical Lab Numbers	N/A
GL-CO-E-001	Revising GEL Laboratories Catalog of Analytical Services	N/A
GL-CO-E-002	Delegated Authority to Commit the Company	N/A
GL-CO-E-003	Request for Proposal (RFP) and Contract Review	N/A
GL-CS-E-002	Internal Review of Contractually Required Quality Criteria for Client Package Delivery	N/A
GL-CS-E-005	Electronic Data Deliverables	N/A
GL-CS-E-006	Subcontracting Analytical Services	N/A
GL-CS-E-008	Prelogin, Login, and Login Review	N/A
GL-CS-M-001	Project Management AlphaLIMS Manual	N/A
GL-DC-E-001	Document Control	N/A
GL-FC-E-001	Facility Security	N/A
GL-FC-E-002	Testing Emergency Eyewash and Shower Equipment	N/A
GL-FC-E-003	Local Exhaust Ventilation Systems	N/A
GL-FC-E-004	Inspection of Fire Extinguishers	N/A
GL-GC-E-001	Total Dissolved Solids	EPA 160.1, 2540C
GL-GC-E-004	General Chemistry Standards, Definitions, and Preparation	N/A
GL-GC-E-007	Total Organic Halogen (TOX) and Adsorbable Organic Halides on Liquid Samples Using the Mitsubishi AOX-200 Analyzer	1650C, 9020B
GL-GC-E-008	pH	EPA 150.1, 9040, 9041, 9045 4500-H^+-00
GL-GC-E-009	Conductivity and Salinity	EPA 120.1, 9050A, SM 2510B-97, SM 2520B-10
GL-GC-E-010	Paint Filter Test	EPA 9095
GL-GC-E-011	Total Solids	EPA 160.3, 2540B, 2540G-2011
GL-GC-E-012	Total Suspended Solids	EPA 160.2, 2540D
GL-GC-E-028	Carbonaceous Biochemical Oxygen Demand (CBOD)	EPA 405.1, 5210B-01
GL-GC-E-029	Corrosivity Toward Steel	1110(M), 1110A(M)
GL-GC-E-032	Carbon Dioxide (Total and Free) by Calculation	4500-CO_2 D
GL-GC-E-033	Alkalinity: Total, Bicarbonate, Carbonate, Hydroxide, and Phenolphthalein	EPA 310.1(M), 2320B-97
GL-GC-E-035	Volatile Suspended Solids	EPA 160.4, 2540E
GL-GC-E-036	Color by Visual Comparison	EPA 110.2, 2120B
GL-GC-E-037	Turbidity	180.1, 2130-B

Standard Operating Procedures and Analytical Methods		
SOP #	**SOP Title**	**Methods**
GL-GC-E-040	Pretreatment of Cyanide Amenable to Chlorination	EPA 335.1, 9010, 9012 4500-CN^- G-99
GL-GC-E-044	Colorimetric Determination of Hexavalent Chromium	7196A, 3500-Cr B, 3060A
GL-GC-E-045	Biochemical Oxygen Demand (BOD)	EPA 405.1, 5210B
GL-GC-E-047	Methylene Blue Active Substance	EPA 425.1, 5540C
GL-GC-E-048	Heating Value Determination by Bomb Calorimeter	ASTM D 240, 4809-13, E 711(M)
GL-GC-E-052	Sulfide (Methylene Blue Method)	EPA 376.2(M), HACH 8131, 4500 S^{2-} D
GL-GC-E-056	Sulfite	4500-SO_3^{2-} B-2000, EPA 377.1
GL-GC-E-057	Volatile Solids and % Ash Procedure for Water Samples	EPA 160.4, 2540E
GL-GC-E-058	Volatile Solids and % Ash Procedure for Solid and Semisolid Samples	2540G
GL-GC-E-059	Dissolved Oxygen Analysis by Membrane Electrode Method	4500-O^- G, EPA 360.1
GL-GC-E-061	Chemical Oxygen Demand (COD) Digestion Reactor Method	EPA 410.4, 5220-D, HACH 8000
GL-GC-E-062	Total Carbon and Total Organic Carbon Analysis Using the OI Analytical 1030S TOC Solids Module	9060 (M), 5310-B
GL-GC-E-064	Density	ASTM D5057
GL-GC-E-065	Specific Gravity	ASTM D5057
GL-GC-E-066	Flashpoint by Setaflash	1020 ASTM D 3278-78
GL-GC-E-067	Cyanide Sample Distillation	9012, 9010 335.3, 335.4, 335.2-M, 4500-CN^- C
GL-GC-E-068	Viscosity	Manufacturer's Method
GL-GC-E-069	Reactive Cyanide and Sulfide	SW-846 Chap 7.3.3, Chap 7.3.4
GL-GC-E-071	Total Phosphorous and Total Kjeldahl Nitrogen Sample Preparation	EPA 365.4, 351.2, 4500N_{org}-D-2011
GL-GC-E-072	Ammonia-Nitrogen Sample Preparation	EPA 350.1, 4500-NH_3^- B
GL-GC-E-073	Free Cyanide Analysis by Microdiffusion	ASTM D 4282
GL-GC-E-074	Extractable Organic Halides (EOX)	SW-846 9023
GL-GC-E-076	Total Residue Chlorine	4500-Cl G
GL-GC-E-077	Cyanide Weak Acid Dissociable Sample Preparation and Analysis	EPA 335.4, 4500-CN^-I
GL-GC-E-079	Bomb Preparation Method for Solid Waste	5050
GL-GC-E-082	Acid-Soluble Sulfides	9030, 9034
GL-GC-E-086	Ion Chromatography (IC)	EPA 300.0, 9056
GL-GC-E-087	Percent Water by Karl Fischer Titration	ASTM E203-08
GL-GC-E-090	Acidity	2310B

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SOP #	**SOP Title**	**Methods**
GL-GC-E-091	Wavelength Calibration Verification of Thermospectronic Spectrophotometers	N/A
GL-GC-E-092	General Chemistry Data Review and Packaging	N/A
GL-GC-E-093	Total, Total Inorganic and Total Organic Carbon (TOC) using the OI Analytical Model 1010 TOC Analyzer	EPA 415.1, 9060, 5310B-2011
GL-GC-E-094	N-Hexane Extractable Material (HEM; Oil and Grease) and Silica GEL Treated N-Hexane Extractable Material (SGT-HEM Non-Polar Material) in Aqueous Matrices	1664, 1664B
GL-GC-E-095	Cyanide Analysis by Lachat QuikChem 8000 FIA	335.3. 335.4, 9010, 9012, 4500-CN^- C
GL-GC-E-096	Perchlorate by Ion Chromatography (IC)	EPA 314.0
GL-GC-E-100	Total Hardness by Titration	SM 2340C-97
GL-GC-E-102	Total Recoverable Phenol by the Lachat QuikChem FIA+ 8000 Series	EPA 420.4, 9066
GL-GC-E-103	Total Phosphorus by the Lachat Quickchem FIA+ 8000 Series Instrument	EPA 365.4, 4500 P H
GL-GC-E-104	Total Kjeldahl Nitrogen (TKN) Using the Lachat QuikChem FIA+ 8000 Series Instrument	EPA 351.2, 4500 N_{org} D
GL-GC-E-106	Ammonia Determination by the Lachat Quickchem FIA + 8000 Series	EPA 350.1 Rev 2, 4500-NH_3 H
GL-GC-E-107	Inorganic Calculations	N/A
GL-GC-E-123	Column Settling	EM 1110-02-5027
GL-GC-E-127	Modified Elutriate Test	N/A
GL-GC-E-128	Nitrate/Nitrite (NO_3+NO_2) Analysis Using The Lachat QuickChem FIA + 8000 Series Instrument	EPA 353.2, 4500-NO_3^- F-2011
GL-GC-E-130	Percent Ash Determined at 775 C Procedure for Solid and Semisolid Samples	ASTM D 482-03 (M)
GL-GC-E-132	Hexavalent Chromium Analysis Using the Lachat Quikchem FIA +8000 Series Instrument	SM 3500-Cr B, SW-846 7196A
GL-HR-E-002	Employee Training	N/A
GL-IT-E-001	Information Technology Program for Good Laboratory and Good Manufacturing Practices	N/A
GL-IT-E-002	Computer Systems Team Roles and Responsibilities	N/A
GL-IT-E-003	Requirements, Design, Operation, Validation and Removal of Hardware and Software Systems Used by the GEL Group, Inc.	N/A
GL-IT-E-004	Change Control Requirements for Hardware and Software	N/A
GL-IT-E-005	Requirements, Design, Operation, Validation and Removal of Applications Used by The GEL Group, Inc.	N/A
GL-IT-E-006	Change Control Requirements for Applications	N/A
GL-IT-E-007	User Roles and Responsibilities for Personnel Using Computer Services	N/A

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SOP #	**SOP Title**	**Methods**
GL-IT-E-009	Archive and Retrieval of Systems Information	N/A
GL-IT-E-010	Backup of Computer Controlled Instrumentation	N/A
GL-IT-E-011	System Security and Virus Protection	N/A
GL-IT-E-012	Application Tools used by Computer Services Personnel	N/A
GL-IT-E-013	GEL Electronic Processes and LIMS Audit System	N/A
GL-IT-E-014	Disaster Recovery	N/A
GL-IT-E-015	Operation of LIMS Database Primary and Failover Servers	N/A
GL-LB-E-001	The Determination of Method Detection Limits and Method Quantiation Limits	N/A
GL-LB-E-002	Balances	N/A
GL-LB-E-003	Glassware Preparation	N/A
GL-LB-E-004	Temperature Monitoring and Documentation Requirements for Refrigerators, Ovens, Incubators, and Other Similar Devices	N/A
GL-LB-E-005	Data Review and Validation	N/A
GL-LB-E-006	Toxicity Characteristic Leaching Procedure Preparation	SW-846 1311
GL-LB-E-007	Laboratory Standards Documentation	N/A
GL-LB-E-008	Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms and Other Recordkeeping Devices	N/A
GL-LB-E-009	Run Logs	N/A
GL-LB-E-010	Maintenance and Use of Air Displacement Pipets	N/A
GL-LB-E-012	Verifying the Maintenance of Sample Integrity	N/A
GL-LB-E-013	CLP-Like/DOE Data Package Assembly and Revision	N/A
GL-LB-E-016	The Collection and Monitoring of the DI Water Systems	N/A
GL-LB-E-017	Procedure and Policy for Manual Integration	N/A
GL-LB-E-018	Instrument Clock Verification	N/A
GL-LB-E-020	Tuning of High Intensity Ultrasonic Processor	N/A
GL-LB-E-023	Waste Extraction Test (WET)	N/A
GL-LB-E-024	Synthetic Precipitation Leaching Preparation	EPA 1312
GL-LB-E-026	Container Suitability Testing	N/A
GL-LB-E-027	Bioassay Kit Delivery and Retrieval	N/A
GL-LB-E-029	Laboratory Sub-Sampling	N/A
GL-LB-E-030	Silica Gel and Air Filter Removal and Replacement	N/A
GL-LB-E-031	Sample Compositing	N/A
GL-LB-E-032	The Distribution of High Risk and Limited Volume Samples	N/A
GL-LB-E-033	Proper Peak Identification for Organics	N/A
GL-LB-E-034	Laboratory Filtration Samples	N/A
GL-LB-G-001	Laboratory Waste Management Plan	N/A
GL-LB-N-001	Safety, Health and Chemical Hygiene Plan	N/A

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SOP #	**SOP Title**	**Methods**
GL-LB-S-001	Disaster Preparedness and Recovery Plan	N/A
GL-MA-E-006	Acid Digestion of Total Recoverable or Dissolved Metals in Surface and Groundwater Samples for Analysis by ICP or ICP-MS	3005A
GL-MA-E-008	Acid Digestion of Total Metals in Aqueous Samples and Extracts for Analysis by ICP and ICP-MS	3010A
GL-MA-E-009	Acid Digestion of Sediments, Sludges, and Soils	3050B, 6010, 6020
GL-MA-E-010	Mercury Analysis Using the Perkin Elmer Automated Mercury Analyzer	245.1, 245.2, 7470A, 7471A, 7471B
GL-MA-E-013	Determination of Metals by ICP	EPA 200.7, 6010
GL-MA-E-014	Determination of Metals by ICP-MS	6020, EPA 200.8,
GL-MA-E-016	Sample Preparation for Total Recoverable Elements by EPA Method 200.2	EPA 200.2
GL-MA-E-017	Metals Data Validation	N/A
GL-MA-E-018	Mercury Analysis using the PS Analytical Millennium Automated Mercury Analyzer	EPA 1631 Rev E
GL-MA-E-020	Acid Digestion of Personal Cassette Filters for Analysis by ICP	NIOSH 7303
GL-OA-E-001	Establishing Retention Time Windows for GC and HPLC Analysis	SW-846 8000
GL-OA-E-003	Non-Volatile Total Petroleum Hydrocarbons by Flame Ionization Detector	8000, 8015, 3541, 3580
GL-OA-E-004	Volatile Total Petroleum Hydrocarbons by Flame Ionization Detector	5030, 5035, 8000, 8015
GL-OA-E-009	Analysis of Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry	8270, EPA 625.1
GL-OA-E-010	Extraction of Semivolatile and Nonvolatile Organic Compounds from Soil, Sludge, and Other Miscellaneous Solid Samples	3500, 3550, 8270, 8081, 8082, 8015, 8310
GL-OA-E-011	Analysis of Chlorophenoxy Acid Herbicides by ECD	8000, 8151A
GL-OA-E-013	Extraction of Semivolatile and Nonvolatile Organic Compounds from Groundwater, Wastewater, and Other Aqueous Samples	3510, 8270, 8081, 8082, 8015 8310, 608.3, 625.1, AK102, 103,
GL-OA-E-015	The Extraction of Herbicides from Groundwater, Wastewater, and Other Aqueous Samples	8151
GL-OA-E-020	Percent Moisture	ASTM D2216-05
GL-OA-E-022	Volatile Organic Compounds by Gas Chromatograph/Mass Spectrometer Applicable to EPA Method 524.2	EPA 524.2
GL-OA-E-026	Volatile Organic Compounds (VOC) by Gas Chromatograph/Mass Spectrometer	EPA 624.1
GL-OA-E-027	The Extraction of Herbicides from Soil and Sludge Samples	8151
GL-OA-E-030	Polynuclear Aromatic Hydrocarbons	8310

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SOP #	**SOP Title**	**Methods**
GL-OA-E-033	Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)	8000, 8330A,
GL-OA-E-036	Florisil Cleanup of Organochlorine Pesticide Solvent Extracts	3510, 3620, 3550,8081,
GL-OA-E-037	Sulfuric Acid/Permanganate Cleanup of PCB Solvent Extract	3550C, 3665A, 8082,
GL-OA-E-038	Volatile Organic Compounds (VOC) by Gas Chromatograph/Mass Spectrometer	8260, 5030, 5035, 8000, 3585, SM 6200
GL-OA-E-039	Closed-System Purge-and-Trap Collection and Extraction Volatile Organics in Soil and Waste Samples	EPA 5035
GL-OA-E-040	Polychlorinated Biphenyls	8000, 8082, 608.3
GL-OA-E-041	Organochlorine Pesticides and Chlorinated Hydrocarbons	8000, 8081, 608.3
GL-OA-E-044	Organics Validation	N/A
GL-OA-E-045	Sulfur Clean-up	3660B
GL-OA-E-046	Common Industrial Solvents, Glycols, and Various Organic Compounds by Flame Ionization Detector	8000, 8015
GL-OA-E-047	Gel Permeation Cleanup of Solvent Extracts	3640A, 3510C, 3550C, 8270, 8081, 8082
GL-OA-E-049	Silica Gel Cleanup Using Solid Phase Silica Gel Extraction Cartridges	3550C, 3510C, 3630C, 3541
GL-OA-E-050	The Extraction of Semi-Volatile and Nonvolatile Organic Compounds from Oil	3580, 8015, 8081, 8082, 8081, 8270
GL-OA-E-054	The Determination of Gasoline Range Organics Using Flame Ionization Detection Per Alaska Method AK101	AK101
GL-OA-E-055	The Determination of Diesel Range and Residual Range Organics	AK102. AK 103, 3510C, 3550B
GL-OA-E-056	Definitive Low Level Analysis of Nitroaromatic Explosives Utilizing Liquid Chromatography/Mass Spectrometry/Mass Spectrometry (LC/MS/MS) by SW-846 Method 8321 Modified (8321M)	8321A(M), 8000, 8330(M), , 8330B(M)
GL-OA-E-058	Volatile Storage Blanks	N/A
GL-OA-E-059	Analysis of 1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-Chloropropane (DBCP) in Water by GC/ECD Using Methods 504.1 or 8011	EPA 504.1, 8011
GL-OA-E-061	Haloacetic Acids in Water	EPA 552.2
GL-OA-E-063	Massachusetts Method for the Determination fo Extractable Petroleum Hydrocarbons	Massachusetts EPH
GL-OA-E-064	Dissolved Gases in Water by Flame Ionization Detector (FID)	RSK-175
GL-OA-E-065	Reagent/Solvent/Standards Screening for Organic Prep	N/A
GL-OA-E-066	Automated Soxhlet Extraction	EPA 3541, 3600
GL-OA-E-067	Definitive Low Level Perchlorate Analysis Utilizing Liquid Chromatography/Mass Spectrometry/Mass Spectrometry (LC/MS/MS) by EPA Method 6850 Modified (6850M)	6850(M), 8000

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SOP #	**SOP Title**	**Methods**
GL-OA-E-068	The Processing, Extraction, and Analysis of Nitroaromatics, Nitroamines, and Nitrate Esters by SW-846 8330B	8330B, 3535
GL-OA-E-070	Solid-Phase Extraction	EPA 3535
GL-OA-E-071	The Pre-Extraction Processing of Soil Samples Collected Using Multi-Incremental Sampling (MIS) Techniques	EPA 8330B
GL-OA-E-073	Analysis of 1,4-Dioxane in Drinking Water by Solid Phase Extraction (SPE) and Gas Chromatography/Mass Spectrometry	EPA 522
GL-OA-E-074	Massachusetts Volatile Petroleum Hydrocarbons by Photoionization and Flame Ionization Detectors	N/A
GL-OA-E-075	Washington Method for the Determination of Extractable Hydrocarbons	WA EPH
GL-OA-E-076	The Extraction and Analysis of Per and Polyfluroalkyl Substances Using LCMSMS	DOD QSM Table B-15 V., 5.1; ASTM D79698-17A; 537 Version, 1.1
GL-OA-E-077	The Extraction and Analysis of Cannabinoids by QuEChERS and GC/MS SIM	GEL Devoloped Method
GL-OA-E-078	The Extraction and Analysis of Cannabinoids by QuEChERS and High Performance Liquid Chromatography	GEL Developed Method
GL-OA-E-079	The Extraction of Herbicides using Solid Phase Extraction	GEL Developed Method
GL-OA-E-080	The Analysis of Naphthalene Sulfonate Using High Performance Liquid Chromatography	GEL Developed Method
GL-QS-B-001	Quality Assurance Plan	N/A
GL-QS-E-001	Conduct of Quality Audits	N/A
GL-QS-E-002	Conducting Corrective/Preventive Action and Identifying Opportunities for Improvement	N/A
GL-QS-E-003	Training and Qualifying Quality Assurance Audit Personnel	N/A
GL-QS-E-004	AlphaLIMS Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items	N/A
GL-QS-E-005	Review of Monitoring Device Logs	N/A
GL-QS-E-007	Thermometer Verification	N/A
GL-QS-E-008	Quality Records Management and Disposition	N/A
GL-QS-E-011	Method Validation and Initial and Continuing Demonstrations of Capability	N/A
GL-QS-E-012	Client NCR Database Operation	N/A
GL-QS-E-013	Handling of Proficiency Evaluation Samples	N/A
GL-QS-E-014	Quality Assurance Measurement Calculations and Processes	N/A
GL-QS-E-015	Use of Logos and Describing Accredited Status	N/A

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SOP #	**SOP Title**	**Methods**
GL-QS-E-016	Identification and Implementation of New and Revised Methods	N/A
GL-QS-E-017	Maintaining Technical Training Records	N/A
GL-QS-E-018	Communication of Substantial Nonconforming Safety Related Services	N/A
GL-QS-E-019	Trending of Performance Evaluation Data	N/A
GL-RAD-A-001	The Determination of Gross Alpha And Gross Non-Volatile Beta in Water	900.0, 9310
GL-RAD-A-001B	The Determination of Gross Alpha And Gross Non-Volatile Beta in Soil, Filters, Solid Matrices and Direct Count Air Filters	900.0(M), 9310
GL-RAD-A-001C	The Determination of Gross Alpha in Water by Co-precipitation	520/5-84-006 Method 00-02
Gl-RAD-A-001D	The Determination of Gross Alpha Gross Non-Volatile Beta in Drinking Water	600/4-80-032 Method 900.0
GL-RAD-A-002	The Determination of Tritium	600/4-80-032, 906.0(M)
GL-RAD-A-003	The Determination of Carbon-14 in Water, Soil, Vegetation and Other Solid Matrices	N/A
GL-RAD-A-004	The Determination of Strontium 89/90 in Water, Soil, Milk, Filters, Vegetation and Tissues	905.0(M), DOE RP501 Rev1(M), HASL 300(M)
GL-RAD-A-005	The Determination of Technitium-99 Using ICP-MS	HASL 300(M) TC-02-RC, DOE RP550(M), ASTM C 1387-03(M), ASTM 1476-00(M)
GL-RAD-A-006	The Determination of Radiometric Iodine	901.1(M), HASL 300(M) I-01
GL-RAD-A-007	The Determination of Radon-222 in Water	SM 7500 Rn-B
GL-RAD-A-008	The Determination of Radium-226	903.1(M), HASL 300(M) Ra-04-RC
GL-RAD-A-009	The Determination of Radium-228 in Water and Solids	904.0(M)
GL-RAD-A-010	Total Alpha Radium Isotopes in Soil and Water	900.1(M)
GL-RAD-A-011	The Isotopic Determination of Americium, Curium, Plutonium, and Uranium	DOE RP800 1997(M), HASL-300 U-02-RC(M), HASL-300 Am-05-RC(M) HASL-300 Pu-11-RC(M)
GL-RAD-A-013	The Determination of Gamma Isotopes	901.1 (M), HASL-300 (M) Sec. 4.5.2.3, HASL-300 Ga-01-R
GL-RAD-A-015	Digestion for Soil	N/A
GL-RAD-A-016	The Determination of Radiometric Polonium	EPA 600/4-80-032
GL-RAD-A-017	The Determination of Iodine-131 in Drinking Water	902.0, 7500 I^- B
GL-RAD-A-018	The Determination of Lead-210 in Liquid and Solid Matrices	N/A
GL-RAD-A-019	Determination of Phosphorus-32 in Soil and Water	N/A
GL-RAD-A-020	The Determination of Promethium-147 in Soil and Water	N/A
GL-RAD-A-021	Soil Sample Preparation for the Determination of Radionuclides	N/A
GL-RAD-A-021B	Soil Sample Ashing for the Determination of Radionuclides	N/A
GL-RAD-A-022	The Determination of Ni-59 and Ni-63	N/A

Standard Operating Procedures and Analytical Methods		
SOP #	**SOP Title**	**Methods**
GL-RAD-A-026	The Preparation of Special Matrices for the Determination of Radionuclides	N/A
GL-RAD-A-028	Radium-226 in Drinking Water by EPA Method 903.1	EPA 903.1
GL-RAD-A-029	The Determination of Strontium-89/90 in Drinking Water by EPA Method 905.0	EPA 905.0
GL-RAD-A-030	Determination of Radium-228 in Drinking Water	904.0, 9320
GL-RAD-A-031	The Determination of Selenium	N/A
GL-RAD-A-032	The Isotopic Determination of Neptunium/Thorium	N/A
GL-RAD-A-033	Determination of Chlorine-36 in Solid and Liquid Samples	N/A
GL-RAD-A-035	The Isotopic Determination of Plutonium-241	HASL-300 Pu-11-RC(M)
GL-RAD-A-036	The Isotopic Determination of Americium, Curium, and Plutonium in Large Soil Samples	DOE RP800(M) HASL-300 Am-05-RC(M) HASL-300 Pu-11-RC(M) HASL-300 Pu-12-RC(M)
GL-RAD-A-037	Radium-226 and Radium-228 in Drinking Water by Sulfate Precipitation and Gamma-Ray Spectrometry	N/A
GL-RAD-A-038	The Isotopic Determination of Thorium	DOE RP800(M), HASL-300(M) Pu-02-RC, Pu-03-RC
GL-RAD-A-040	The Determination of Fe-55 in Liquid and Solid Matrices by Liquid Scintillation Counter	N/A
GL-RAD-A-041	The Determination of Total Activity in Solids and Liquids	N/A
GL-RAD-A-044	Total Alpha Radium Isotopes In Drinking Water	903.0, 9315, HASL 300(M)
GL-RAD-A-046	The Determination of Radium-224 and Radium-226 by Alpha Spectroscopy	N/A
GL-RAD-A-047	48 Hour Rapid Gross Alpha Test	ECLS-R-G-A, EPA 600/4-80-032, 900.0(M)
GL-RAD-A-048	The Determination of Calcium-45 in Soils and Waters	N/A
GL-RAD-A-049	The Determination of Sulfur-35	NAS-NS-3054
GL-RAD-A-050	The Determination of Tritium in Drinking Water Samples	600/4-80-032, 906.0
GL-RAD-A-051	The Rapid Determination of Strontium 89/90 by Cerenkov Counting	N/A
GL-RAD-A-052	The Determination of Organically Bound Tritium	600\4-80-032, 906.0
GL-RAD-A-053	Isotopic Determination of Plutonium in Large Water Resin Samples	HASL 300 Pu-11-RC
GL-RAD-A-054	The Determination of Strontium-90 in Brine	N/A
GL-RAD-A-055	The Preparation of Environmental Samples for Isotopic Uranium Analysis Via ICP-MS	N/A
GL-RAD-A-056	The Determination of Gross Alpha and Beta by Liquid Scintillation Counter	N/A
GL-RAD-A-058	The Rapid Determination of Strontium 89/90 by Gas Flow Proportional Counting	N/A

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SOP #	**SOP Title**	**Methods**
GL-RAD-A-059	The Determination of Technetium-99 Using Analytical Grade 1X8 Resin	N/A
GL-RAD-A-060	The Preparation of Vegetation and Filter Samples Via Organic Destruction and Strong Acid Leach for Radiochemistry Metals Analysis	N/A
GL-RAD-A-063	The Determination of Radium-228	N/A
GL-RAD-A-065	The Determination of Carbon-14 in Atmospheric Screening Cartridges	N/A
GL-RAD-A-066	The Determination of Radiometric Polonium Using DGA Cartridges	N/A
GL-RAD-A-067	The Determination of Radiometric of Tritium and Carbon 14 in Combustible Materials Using Pyrolysis	N/A
GL-RAD-A-068	The Determination of Americium, Curium, Plutonium, Uranium, and Thorium in Liquid and Solid Matrices Using Eichrom Resin	N/A
GL-RAD-B-001	The Sequential Determination of Isotopic Americium, Curium, Californium, Plutonium, Strontium and Uranium in Urine	N/A
GL-RAD-B-002	The Determination of Polonium-210 or Radium-226 in Bioassay Samples	N/A
GL-RAD-B-005	Management of Blank Populations	N/A
GL-RAD-B-008	The Determination of Gross Alpha Activity in Nasal Swipes	N/A
GL-RAD-B-009	Bioassay Countroom Alpha Spectroscopy Instrument Standardization and Performance	N/A
GL-RAD-B-010	The Determination of Thorium in Fecal Samples	N/A
GL-RAD-B-011	The Determination of Tritium in Urine	EPA 906
GL-RAD-B-012	The Ashing of Fecal, Bone, and Tissue Samples	N/A
GL-RAD-B-013	Sequential Determination of Americium, Plutonium, Strontium, Plutonium-241, and Uranium in Fecal, Bone, and Tissue Samples	N/A
GL-RAD-B-014	The Preparation of Synthetic Urine and Fecal Material	N/A
GL-RAD-B-016	The Determination of Technetium-99 in Urine	N/A
GL-RAD-B-020	The Determination of Ni-59 and Ni-63 in Urine	N/A
GL-RAD-B-022	The Determination of Gross Alpha and Gross Non-volatile Beta in Urine	EPA 900.0, 9310, EERF 00-01, USGS R-1120-76
GL-RAD-B-023	The Determination of Carbon-14 in Urine	EERF C-01(M)
GL-RAD-B-024	Managing Statistical Data in the Bioassay Laboratory	N/A
GL-RAD-B-025	The Combination and Preservation of Urine Samples	N/A
GL-RAD-B-026	Bioassay Data Review, Validation and Data Package Assembly	N/A
GL-RAD-B-027	Specific Gravity in Urine	ASTM D5057
GL-RAD-B-029	The Determination of Radiometric Iodine in Urine	N/A
GL-RAD-B-030	The Preparation and Determination of Gamma Isotopes in Urine and Fecal Samples	600/4-80-032

Standard Operating Procedures and Analytical Methods		
SOP #	**SOP Title**	**Methods**
GL-RAD-B-031	Bioassay Quality Control Package Assembly	N/A
GL-RAD-B-033	Bioassay Count Room Alpha Spectrometry Instrument Calibration	N/A
GL-RAD-B-034	The Determination of Metals by ICP-MS	N/A
GL-RAD-B-035	The Preparation of Urine Samples for Total Uranium Analysis by ICP-MS	N/A
GL-RAD-B-036	Initial Installation and Returning to Service of Repaired Instrumentation	N/A
GL-RAD-B-038	The Determination of Neptunium in Fecal Samples	N/A
GL-RAD-B-039	The Determination of Iron-55 in Urine	N/A
GL-RAD-B-040	The Determination of Radium-224 and Radium-226 by Alpha Spectroscopy in Bioassay Sample	N/A
GL-RAD-B-041	The Isotopic Determination of Thorium and Neptunium in Fecal Samples	N/A
GL-RAD-B-042	The Isotopic Determination of Thorium and Neptunium and Fecal Samples	N/A
GL-RAD-D-002	Analytical Methods Validation for Radiochemistry	N/A
GL-RAD-D-003	Data Review, Validation, and Data Package Assembly	N/A
GL-RAD-D-005	REMP Quality Control Package Assembly	N/A
GL-RAD-D-006	Equations Used in Data Reduction for Environmental Radiochemistry	N/A
GL-RAD-I-001	Gamma Spectroscopy System Operation	N/A
GL-RAD-I-004	Beckman LS-6000/6500	N/A
GL-RAD-I-006	LB4100 Gross Alpha/Beta Counter Operating Instructions	N/A
GL-RAD-I-007	Ludlum Lucas Cell Counter	N/A
GL-RAD-I-008	VAX/VMS Quality Control Software Program	N/A
GL-RAD-I-009	Alpha Spectroscopy System	N/A
GL-RAD-I-010	Counting Room Instrumentation Maintenance	N/A
GL-RAD-I-012	Managing Statistical Data in the Radiochemistry Laboratory	N/A
GL-RAD-I-013	Column Preparation	N/A
GL-RAD-I-014	WALLAC Guardian Model 1414	N/A
GL-RAD-I-015	WPC 9550 Gross Alpha/Beta Counter: Operating Instructions	N/A
GL-RAD-I-016	Multi-Detector Counter: Operating Instructions	N/A
GL-RAD-I-017	Wallac 1220 Quantalus Liquid Scintillation Counter	N/A
GL-RAD-I-018	Operation of Wallac 1480 Gamma Wizard	N/A
GL-RAD-I-019	Management of Blank Populations	N/A
GL-RAD-I-021	G5400W Series Alpha/Beta Counting System Operating Instructions	N/A

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SOP #	**SOP Title**	**Methods**
GL-RAD-M-001	Preparation and Verification of Radioactive Standards	N/A
GL-RAD-M-003	Restoring Data from Magnetic Tape for Bioassay and Alpha Spectroscopy	N/A
GL-RAD-S-000	Radiation Safety Plan for GEL Laboratories, LLC	N/A
GL-RAD-S-001	Radiological Surveys	N/A
GL-RAD-S-002	Radiation Related Emergencies	N/A
GL-RAD-S-003	Administration of the Radioactive Material License Inventory	N/A
GL-RAD-S-004	Radioactive Material Handling	N/A
GL-RAD-S-006	Radiation Worker Training	N/A
GL-RAD-S-007	Receiving Radioactive Packages	N/A
GL-RAD-S-009	Personnel Dosimetry	N/A
GL-RAD-S-010	The Handling of Biological Materials	N/A
GL-RAD-S-013	Air Sampling for Radioactivity	Guide 825
GL-RAD-S-014	Release of Laboratory Coats	N/A
GL-RAD-S-015	The Acceptance and Classification of Radioactive Material	N/A
GL-RAD-S-016	Radiation Work Permits	N/A
GL-RAD-S-018	Laboratory Analysis of High Activity (RAD 3) Samples	N/A
GL-RC-E-001	Receipt and Inspection of Material and Services	N/A
GL-RC-E-002	Material Requisition	N/A
GL-SR-E-001	Sample Receipt, Login, and Storage	N/A
GL-SR-E-002	Transportation and Shipping of Samples and Pre-Preserved Sample Containers	N/A
GL-SR-E-003	The Inspection, Cleaning and Screening of Sample Coolers	N/A
GL-SR-E-004	Control of Foreign Soils	N/A
GL-SR-E-005	Wipe Test	N/A
GL-SVR-D-001	Design Specifications for the Network Infrastructure	N/A
GL-SVR-D-002	Design Specifications for the Mail Server	N/A
GL-SVR-D-005	Design Specifications for Backupsvr01	N/A
GL-SVR-E-001	Network Infrastructure	N/A
GL-SVR-E-002	The Mail Server	N/A
GL-SVR-E-005	Backupsvr01	N/A
GL-SVR-R-001	System Requirements for Network Infrastructure	N/A
GL-SVR-R-002	System Requirements for The Mail Server	N/A
GL-SVR-R-005	System Requirements for Backupsvr01	N/A

APPENDIX J: SAMPLE STORAGE AND PRESERVATION REQUIREMENTS
STORAGE AND PRESERVATION

Parameter	Container [1]	Preservation	Holding Time[2]	Min. Volume[5]
INORGANICS				
Acidity	P,G	0 ≤ 6° C	14 days	25 mL / NA
Adsorbable Organic Halides (AOX)	G, amber	0 ≤ 6° C, HNO_3 to pH < 2, zero headspace	>3 days and < 6 months from collection	50 mL / 1 g
Alkalinity	P,G	0 ≤ 6° C	14 days	50 mL / NA
Biochemical Oxygen Demand (BOD) and Carbonaceous Oxygen Demand (CBOD)	**P,G**	**0 ≤ 6° C**	**48 hours**	**500 mL / NA**
Bromide	P,G	None required	28 days	10 mL / 4 g
Carbon Dioxide	**P,G**	**0 ≤ 6° C**	**Immediate**	**50 mL / NA**
Chemical Oxygen Demand (COD)	P,G	0 ≤ 6° C, H_2SO_4 to pH < 2	28 days	2 mL / NA
Chlorine by Bomb Calorimeter	P,G	0 ≤ 6° C	None	NA / 0.5 g
Chloride	P,G	None required	28 days	10 mL / 4 g
Color	**P,G**	**0 ≤ 6° C**	**48 hours**	**50 mL / NA**
Conductivity	P,G	0 ≤ 6° C	28 days	25 mL / NA
Corrosivity by pH	**P,G**	**None**	**Immediate**	**25 mL / 5 g**
Corrosivity to Steel	P,G	None	None	290 mL / NA
Cyanide amenable to chlorination	P,G	0 ≤ 6° C, NaOH to pH > 12, 0.6 g ascorbic acid [3]	14 days [4]	50 mL / NA
Cyanide, Reactive Releasable	G, amber	Zero headspace	7 days liquids, 28 days solids	10 mL / 10 g
Cyanide, total, available, free or Weak Acid Dissociable	P,G	0 ≤ 6° C, NaOH to pH > 12, 0.6 g ascorbic acid [3]	14 days [4]	50 mL / 1 g
Density	P,G	0 ≤ 6° C	7 days	NA / 10 g
Dissolved Oxygen	**G (bottle and top)**	**None, Zero headspace**	**Immediate**	**300 mL / NA**
Extractable Organic Halides (EOX)	G, amber	Zero headspace, 0 ≤ 6° C	**28 days**	**25 mL**
Flashpoint	Metal, G	None	None	25 mL / 2 g Setaflash
Fluoride	P,G	None Required	28 days	25 mL / 4 g
Fluorine by Bomb	P,G	0 ≤ 6° C	None	NA/ 0.5 g
Hardness (EDTA titration)	P,G	0 ≤ 6° C, HNO_3 to pH < 2	6 months	50 mL / NA
Hardness (calculation)	P,G	HNO_3 to pH < 2	6 months	50 mL / NA
Heating Value	P,G	0 ≤ 6° C	None	1 mL / 0.5 g
Nitrogen-Ammonia	P,G	0 ≤ 6° C, H_2SO_4 to pH< 2	28 days	20 mL / 5 g
Nitrate – Liquids	**P,G**	**0 ≤ 6° C**	**48 hours**	**10 mL**

Nitrate – Solids	P,G	0 ≤ 6° C	28 days for extraction, 48 hrs from extraction to analysis	4 g
Nitrite - Liquids	**P,G**	**0 ≤ 6° C**	**48 hours**	**10 mL**
Nitrite - Solids	P,G	0 ≤ 6° C	28 days for extraction, 48 hrs from extraction to analysis	4 g
Nitrate/Nitrite	P,G	0 ≤ 6° C, H_2SO_4 to pH < 2	28 days	4 mL / 4 g
Nitrogen - Total Kjeldahl and Organic	P,G	0 ≤ 6° C, H_2SO_4 to pH < 2	28 days	20 mL / 5 g
Oil and Grease	G	0 ≤ 6° C, HCl or H_2SO4 to pH < 2	28 days	1000 mL
Orthophosphate -Liquids	**P,G**	**Field filter immediately, 0 ≤ 6° C**	**48 hours**	**10 mL**
Orthophosphate – Solids	P,G	0 ≤ 6° C	28 days for extraction, 48 hrs from extraction to analysis	4 g
Paint Filter Liquids Test	Any	None	None	100 g
Percent (%) Moisture	P,G	0 ≤ 6° C	None	2 mL / 5 g
Perchlorate by Ion Chromatography	P,G	0 ≤ 6° C	28 days	10 mL / 4g
Total Phenols	G,	0 ≤6° C, H_2SO_4 to pH < 2	28 days	50 mL / 1 g
pH	**P,G**	**None if within 15 mins of collection,** 0 ≤ 6° C when shipped to lab	**Immediate**	**25 mL / 5 g**
Total Phosphorus	P,G	0 ≤ 6° C, H_2SO_4 to pH < 2	28 days	20 mL / 1 g
Residual Chlorine	**P,G**	**None Required**	**Immediate**	**25 mL / NA**
Residue, Total	P,G	0 ≤ 6° C	7 days	100 mL / NA
Residue, Filterable (TDS)	P,G	0 ≤ 6° C	7 days	70 mL / NA
Residue, NonFilterable (TSS)	P,G	0 ≤ 6° C	7 days	1000 mL
Residue, Volatile and Fixed (% Ash)	P,G	0 ≤ 6° C	7 days	25 mL / 1 g
Salinity	P,G	0 ≤ 6° C	28 days	25 mL / NA
Specific Gravity	P,G	0 ≤ 6° C	7 days	50 mL / NA
Sulfate	P,G	0 ≤ 6° C	28 days	10 mL / 4 g
Sulfide	P,G	0 ≤ 6° C, add ZnAc and NaOH to pH > 9	7 days	200 mL / 20 g
Sulfide, Reactive Releasable	G, amber	Zero headspace, 0 ≤ 6° C	7 days liquids, 28 days solids	10 mL / 10 g
Sulfide, Acid-Soluble	P,G	Zero headspace, 0 ≤ 6° C Liquids: ZnAc and NaOH to pH > 9. Solids: Fill surface with 2N ZnAc	7 days liquids, 365 days solids	200 mL / 20 g
Sulfite	**P,G**	**EDTA[9]**	**Immediate**	**50 mL / NA**
Sulfur by Bomb	P,G	0 ≤ 6° C	None	NA / 0.5 g
Surfactants	**P,G**	**0 ≤ 6° C**	**48 hours**	**100 mL / NA**

Total Organic Carbon (TOC), also applies Dissolved Organic Carbon (DOC), Total Carbon (TC) and Total Inorganic Carbon (TIC)	G, amber	0 ≤ 6° C, HCl or H_2SO_4 to pH < 2	28 days	50 mL / 5 g
Total Organic Halides (TOX)	G	0 ≤ 6° C, H_2SO_4 to pH < 2, Zero headspace	28 days	50 mL / 1 g
Total Petroleum Hydrocarbons	G	0 ≤ 6° C, H_2SO_4 to pH < 2	28 days	1000 mL / NA
TCLP (Toxicity Characteristic leaching Procedure) and Synthetic Precipitation Leaching Procedure (SPLP)	P,G depending on test	0 ≤6° C, depends on test	14 days, VOA 14 days, SVOA 28 days Mercury 180 days non-Hg metals	105 g or 130 g for full TCLP list
Turbidity	**P,G**	**0 ≤ 6° C**	**48 hours**	**50 mL / NA**
Viscosity	P,G	0 ≤ 6° C	None	7 mL
Metals – Liquids (except chromium VI, Boron, Silica and mercury)	P, (G as long as no B or Si is required)	HNO_3 to pH < 2	6 months	20 mL
Boron-Liquids	P, Teflon or Quartz	HNO_3 to pH <2	6 months	50 mL
Silica- Liquids	P or Quartz	0 ≤ 6° C	28 days	50 mL
Metals – Solids[8] (except chromium VI and mercury)	P, (G as long as no B or Si is required)	None	6 months	2 g
Chromium VI – Liquids	**P,G**	**0 ≤ 6° C**	**24 hours**	**25 mL**
Chromium VI - Liquids	P,G	0 ≤ 6° C, $(NH_4)_2SO_4$, pH = 9.3 to 9.7	28 days	25 mL
Chromium VI - Solids[8]	P,G	0 ≤ 6° C	30 days to digestion, 7 days from digestion to analysis	1 g
Mercury - Liquids	P,G	HNO_3 to pH < 2	28 days	50 mL
Mercury - Solids[8]	P,G	0 ≤ 6° C	28 days	2 g
Mercury – Low Level Liquids	P,G	HCl or BrCl	90 days when preserved w/in 48 hrs or oxidized w/in 28 days	50 mL

ORGANICS				
Method AK101-Solids[7]	Amber G	4 ± 2 °C, zero headspace, methanol	14 days	4 oz[7]
Method AK101-Liquids	Amber G	4 ± 2 °C, HCl < 2	14 days	3x40 mL
Method AK102-Liquids	Amber G	4 ± 2 °C, HCl or H_2SO_4 to pH < 2	14 days	1000 mL
Method AK102/103-Solids	Amber G	4 ± 2 °C	14 days for extraction 40 days after extraction for analysis	4 oz
MADEP EPH - Liquids	Amber G	4 ± 2 °C, HCl < 2	14 days	4 oz
MADEP EPH – Solids	Amber G	4 ± 2 °C	14 days	1000 mL

MADEP VPH – Liquids (ambient purge) Trip Blank Required	G, teflon-lined septum	4 ± 2 °C, HCl < 2	14 days	3x40 mL
MADEP – VPH Liquids (Heated Purge) Trip Blank Required	G, teflon-lined septum	4 ± 2 °C, Add 0.40 – 0.44g trisodium phosphate dodecahydrate to pH>11	14 days	3x40 mL
MADEP VPH – Solids Trip Blank Required	G, Teflon-lined septum	1mL MeOH/g sample at sampling or within 48 hrs, 4 ± 2 °C	28 days	60mL vials add 25g sample, 40 mL vials add 15 g sample
BTEX – Liquids	G, Teflon-lined septum	0 ≤ 6° C, zero headspace, HCl to pH < 2, 0.008% $Na_2S_2O_3$ [3]	14 days [6]	3x40 mL
BTEX - Solids[8]	**G, Teflon-lined septum**	**0 ≤ 6° C**	**48 hours for preservation and 14 days for analysis**	**3x5 g EnCores or 2 low and 1 high level vials**
Volatiles - Drinking Water, Wastewater/groundwater (except 2-CLEVE, acrolein, and acrylonitrile)	G, Teflon-lined cap	0 ≤ 6° C, zero headspace, HCl to pH < 2	14 days	3x40 mL
Volatiles (including 2 CLEVE) - Wastewater	G, Teflon-lined cap	0 ≤ 6° C, zero headspace, unpreserved	7 days [6]	3x40 mL
Volatiles - (acrolein and acrylonitrile)	G, Teflon-lined cap	0 ≤ 6° C, zero headspace, unpreserved	3 days [6] by EPA 624.1 7 days [6] by EPA 8260	3x40 mL
Volatiles - Solids[8]	**EnCore Sampler**	**0 ≤ 6° C**	**48 hours for preservation 14 days for analysis**	**3x5 g EnCores**
Volatiles - Concentrated Waste	G, teflon-lined septum	None	14 days	1x40 mL
Base/Neutral and Acid Extractables and 1,4-Dioxane – Liquids	Amber G, Teflon-lined cap	0 ≤ 6° C, 0.008% $Na_2S_2O_3$ [3]	7 days for extraction 40 days after extraction for analysis	1000 mL / 50 g
Base/Neutral and Acid Extractables and 1,4-Dioxane-Solids[8]	G, Teflon-lined cap	0 ≤ 6° C	14 days for extraction 40 days after extraction for analysis	1000 mL / 50 g
Base/Neutral and Acid Extractables - Concentrated Waste	G, Teflon-lined cap	None	7 days for extraction 40 days after extraction for analysis	1000 mL / 50 g
TPH-GRO	G, Teflon-lined cap	0 ≤ 6° C, HCl to pH < 2, zero headspace	14 days	3x40 mL
TPH-DRO	G, Teflon-lined cap	0 ≤ 6° C, HCl to pH < 2	7 days for extraction (Liquids) 14 days for extraction (Solids) 40 days after extraction to analysis	1000 mL / 50 g
Chlorinated Herbicides - Liquids	Amber G, Teflon-lined cap	0 ≤ 6° C, 0.008% $Na_2S_2O_3$ [3]	7 days for extraction 40 days after extraction for analysis	1000 mL

Chlorinated Herbicides - Solids[8]	G, Teflon-lined cap	0 ≤ 6° C	14 days for extraction 40 days after extraction	50 g
Organochlorine Pesticides by SW-846 EPA 8081 Liquids	Amber G, Teflon-lined cap	0 ≤ 6° C, 0.008% $Na_2S_2O_3$	7 days for extraction 40 days after extraction for analysis	1000 mL
Organochlorine Pesticides by SW-846 EPA 8081 Solids	G, Teflon-lined septum	0 ≤ 6° C	14 days for extraction 40 days after extraction for analysis	50g
Organochlorine Pesticides and PCBS by EPA 608.3 only	Amber G, Teflon-lined cap	0 ≤ 6° C, 0.008% , $Na_2S_2O_3$ [3], NaOH and H_2SO_4preserve to pH 5.0 -9.0 (for prep >72 hrs and < 7 days)	**Unpreserved Prep within 72 hrs** Preserved prep within 7 days 40 days after extraction for analysis	**1000 mL / NA**
PCBs- Liquids	Amber G, Teflon-lined cap	0 ≤ 6° C, 0.008% $Na_2S_2O_3$ [3]	365 days for extraction 40 days after extraction for analysis	1000 mL
PCBs- Solids	Wide-mouth glass	0 ≤ 6° C	365 days for extraction 40 days after extraction for analysis	50g
PCBs in Oil	G, Teflon-lined cap	None	365 days for extraction 40 days after extraction for analysis	1x40 mL
Solvents, Glycols, Alcohols and Acetates -- Liquid	G, Teflon-lined septum	0 ≤ 6° C, zero headspace or 0 ≤ 6° C, zero headspace HCl to pH < 2	7 days unpreserved 14 days preserved	1 x 40mL
Solvents, Glycols, Alcohols and Acetates -- Solids	G, Teflon-lined septum	0 ≤ 6° C	14 days	10g
Industrial Solvents	G, Teflon-lined septum	0 ≤ 6° C	14 days	1x40 mL
1,4-Dioxane in Drinking Water by EPA 522	G, Teflon-lined septum	<10ºC during transport, Sodium sulfite (50mg/L), sodium bisulfate (1g/L)	28 days for extraction at 0 ≤ 6° C (not frozen) and 28 days after extraction for analysis at -5º C, protected from light	100 mL to 500 mL
Dioxin Screen	G, Teflon-lined cap	0 ≤ 6° C	7 days for extraction 40 days after extraction for analysis	1000 mL / 50 g
EDB and DBCP	G, Teflon-lined septum	0 ≤ 6° C, 0.4% $Na_2S_2O_3$	14 days	3x40 mL / NA

Polynuclear Aromatic Hydrocarbons	Amber G, Teflon-lined septum (Liquids), Teflon-lined cap (Solids)	0 ≤ 6° C	7 days for extraction (Liquids) 14 days to extraction (Solids) 40 days to analysis after extraction	1000 mL / 30 g
Nitroaromatics and Nitroamines	Amber G, Teflon-lined septum	0 ≤ 6° C	7 days for extraction 40 days after extraction for analysis	1000 mL / 2 g
Nitroaromatics and Nitroamines by MIS Prep (solid samples)	Protect from light	0 ≤ 6° C until air drying 22 ± 4° C (or cooler) after drying	14 days for extraction, 40 days after extraction for analysis	Entire Sample
RDX Breakdown	Amber G, Teflon-lined septum for liquids and Teflon-lined cap for solids	0 ≤ 6° C	7 days to extraction for liquids 14 days to extraction for solids 40 days to analysis after extraction	1000 mL / 2 g
Low Level Perchlorate	P	0 ≤ 6° C , headspace required	28 days	10 mL / 2 g
Haloacetic Acids	G, amber, Teflon-lined septum	0 ≤ 6° C , zero headspace, ammonium chloride	14 days to extraction, 7 days after extraction for analysis	3x40 mL
Dissolved Gases	G, Teflon-lined septum	0 ≤ 6° C, HCl to pH < 2, zero headspace	7 days if unpreserved, 14 days if preserved	2x40 mL
Perfluorinated Alkyl Acids PFAS	HDPE Bottle - unlined polyethylene screw cap	0 ≤ 10° C for liquids, 0 ≤ 6° C for solids, 1.25g Trizma® (Drinking Water only)	14 days from collection to extraction, 28 days from extraction to analysis (liquids) 28 days from collection to extract and analyze (solids)	250 mL/10 g
RADIOCHEMISTRY				
Americium – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Americium – Solids[8]	P,G	None	6 months	20 g
Calcium-45 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	500 mL
Calcium-45 - Solids[8]	P,G	None	6 months	20 g
Carbon-14 Liquids & Solids[8]	P,G	None	6 months	500 mL / 20 g
Cesium 134 – Drinking Water	P,G	HCl to pH < 2	6 months	2000 mL
Chlorine-36 Liquids & Solids[8]	P,G	None	6 months	500 mL / 20 g
Curium - Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Curium - Solids[8]	P,G	None	6 months	20 g

Gamma Isotopes - Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	2000 mL
Gamma Isotopes - Solids[8]	P,G	None	6 months	200 g
Gross Alpha & Beta – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	500 mL
Gross Alpha & Beta, Rapid - Liquids	**P,G**	**HNO_3 or HCl to pH < 2**	**48 – 72 hrs**	**500 mL**
Gross Alpha & Beta - Solids[8]	P,G	None	6 months	20 g
Iodine-129 - Liquids & Solids[8]	P,G	None	6 months	1000 mL / 50 g
Iodine -131 - Liquids	**P,G**	**None**	**8 days**	**1000 mL**
Iron 55 -Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	500 mL
Iron 55 - Solids[8]	P,G	None	6 months	20 g
Lead-210 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Lead-210 - Solids[8]	P,G	None	6 months	200 g
Neptunium - Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Neptunium - Solids[8]	P,G	None	6 months	20 g
Nickel-59 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Nickel-59 – Solids[8]	P,G	None	6 months	20 g
Nickel-63 - Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Nickel-63 - Solids[8]	P,G	None	6 months	20 g
Phosphorus-32 –Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Phosphorus-32 - Solids[8]	P,G	None	6 months	20 g
Plutonium – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Plutonium - Solids[8]	P,G	None	6 months	20 g
Polonium - Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Polonium - Solids[8]	P,G	None	6 months	20 g
Promethium-147/Samarium-151 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Promethium-147/Samarium-151 - Solids[8]	P,G	None	6 months	20 g
Radium-223 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	2000 mL
Radium-224 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	2000 mL
Radium-226 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Radium-228 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Radon-222 – Liquids	**G**	**None, Zero headspace**	**4 days**	**2x40 mL**
Selenium-79 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	500 mL
Selenium-79 - Solids[8]	P,G	None	6 months	20 g
Strontium-89/90 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Strontium-89/90 - Solids[8]	P,G	None	6 months	20 g
Sulfur-35 - Liquids	P,G	None	6 months	500 mL
Sulfur-35 - Solids[8]	P,G	None	6 months	20 g
Technetium-99 – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Technetium-99 – Solids[8]	P,G	None	6 months	20 g
Thorium – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Thorium - Solids[8]	P,G	None	6 months	20 g
Total Activity Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	100 mL
Total Activity - Solids[8]	P,G	None	6 months	20 g
Total Alpha Radium – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	500 mL
Total Alpha Radium - Solids[8]	P,G	None	6 months	20 g
Total Uranium - Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	100 mL

Total Uranium - Solids[8]	P,G	None	6 months	20 g
Tritium – Drinking Water	G	None	6 months	250 mL
Tritium – Liquids & Solids[8]	P,G	None	6 months	250 mL / 20 g
Uranium – Liquids	P,G	HNO_3 or HCl to pH < 2	6 months	1000 mL
Uranium - Solids[8]	P,G	None	6 months	20 g

[1] P = Polyethylene; G = Glass

[2] Samples should be analyzed as soon as possible after collection. The holding times listed are maximum times that samples may be held before analysis and be considered valid.

[3] Used only in the presence of residual chlorine.

[4] Maximum holding time is 24 hours when sulfide is present. All samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If present, remove by adding cadmium nitrate powder until a negative spot test is obtained. Filter sample and add NaOH to pH 12.

[5] Minimum amount of sample needed to prepare and analyze for the parameter. Some parameters may be combined into one analysis, others may need additional amount if quality control is being requested for site-specific samples. Please check with GELs Project Manager for proper sample amounts based on project specific requirements.

[6] Volatiles Groundwater/Wastewater: If samples are to be analyzed for vinyl chloride, styrene, or 2-chloroethylvinyl ether (2-CLEVE) for soil or water, separate samples must be collected without acid preservation and analyzed within 7 days. For aqueous samples to be analyzed for acrolein and acrylonitrile, by EPA Method 624.1, the samples are not to be acidified and must be analyzed within 3 days of collection.

[7] Solids Method AK101 2-4 oz amber wide-mouth jars tared and labeled, 1-4 oz amber wide-mouth jar labeled (evaporative loss), 2-25 mL 2.5 ppm surrogated P/T methanol tubes.

[8] Solids matrix typically applies to soils, sludges and sediments. Some tests have been developed for filters, miscellaneous solid waste, plant and animal tissue, also referred to as solids. Contact GEL to verify a particular matrix for the test of interest.

[9] 1mL of 2.5% EDTA solution per 100mL sample

APPENDIX K: STATE SPECIFIC REPORTING CRITERIA

Massachusetts: Drinking Water (Only)

Regulations at 310 CMR 42.13 (5) require that a laboratory have current knowledge of all Federal and Massachusetts standards for all categories in which it has been certified. Within 24 hours of obtaining valid data, a certified laboratory must notify its clients for any results exceeding an EPA-or Department-established maximum contaminant level, maximum residual disinfectant level or reportable concentration.

The laboratory must identify, in writing, those samples needing special reports (e.g. MCL exceedance) when the laboratory subcontracts with another laboratory.

Reports for drinking water samples must contain information relating to the maximum contaminant levels for each analyte. 310 CMR 42.13(3) specifies that with exception of reports submitted to the Department in a format approved by the Department, all reports of finished drinking water analyses must indicate the maximum contaminant level for each analyte measured. This can be accomplished in AlphaLIMS through the permit level in client set up. (Project Managers must enter these values). The maximum contaminant levels should be verified prior or sample log-in. **Please check with Quality Assurance Officer to verify that the information is correct.**

The report must identify, analyses for which the laboratory holds Department certification and which it does not. Regulations at 310 CMR 42.13(3) (b-c) require that such a distinction be made and that the laboratory clearly distinguish in the report between those analyses that it conducted in accordance with Department certification standards and those it did not.

Pennsylvania: Drinking Water (Only)

Any individual (laboratory, sample collection/pic-up facility, consultant, PWS, etc.) providing a sample to an accredited laboratory for SDWA compliance testing purposes must ensure that all relevant, and necessary information is provided along with the sample. Since the laboratory that performs the testing is responsible for reporting and making any notifications (such as MCL violations) to the PWS and the Department, the PWS and sample specific information is both relevant and necessary. If a laboratory chooses, or is required, to subcontract testing to another accredited laboratory, § 109.810(b)(1)(ii) requires that the following information MUST be provided to the subcontract laboratory:

- PWSID# and Name of the System
- Sample Location ID#
- Dates and Times of Sample Collection
- Name and Contact Number of the PWS

The testing laboratory may, if it chooses to, relinquish its authority to report the sample results. However, this relinquishment can only be made to another accredited laboratory and must be made in writing as described in § 109.810(c). The other accredited laboratory, to which the reporting and notification responsibilities are delegated, is then responsible for meeting all of the 25 Pa. Code Chapter 109.810 requirements.

Failure of the testing laboratory to provide verbal and written notification to the Public Water Supply ("PWS") or the Department, or both of an MCL violation with the required timeframes:
The Department requires in § 109.810(b)(1) that the testing laboratory **notify the PWS by telephone within 1 hour of the determination** that an MCL violation has occurred for any SDWA compliance testing result that is at or above the listed MCL for that contaminant. Chapter 252, §§ 252.708(a)(2) and (3) outline the allowable time that may elapse between initial acquisition of the sample result and the final "determination" of the sample result. The time of the determination of the final sample result triggers the start of the clock for the allowable timeframes to provide notification to the PWS and the Department. It is of upmost importance that you understand that leaving a message or voicemail is not considered "notification" of an MCL exceedance. Should the testing laboratory be unable to notify the PWS within 1 hour of the determination, the laboratory must **notify the appropriate DEP regional office by telephone within 2 hours of the determination** of the MCL exceedance. Finally, the testing laboratory is responsible for providing written notification to the Department of any MCL exceedance within 24 hours of the determination.

Failure of the testing laboratory to maintain full and complete records documenting the notification made to the PWS or the Department, or both, when an MCL violation occurs:
The accreditation regulations require that an accredited laboratory maintain accurate and complete records that allow historical reconstruction of the activities undertaken in the laboratory. The testing laboratory must maintain documentation outlining the steps taken to meet the requirements of § 109.810(a)(1) and § 252.708(a)(2) and (3), also known as the acquisition of the initial sample results and the final determination of the sample results to determine compliance with the 1-hour or 2-hour notification requirements. Specifically, the testing laboratory must maintain the following:

- Date and Time of the initial acquisition of the sample result
- Date and Time of the determination of the sample result
- Date and Time of the telephone call(s) to the PWS
- Individual at the PWS to whom the notification was made
- Date and Time of the telephone call(s) to the Department, if required
- Individual at the Department to whom the notification was made, if required
- Any other pertinent information that would be necessary to ensure a complete record

If the testing laboratory delegates the reporting and notification responsibility to another accredited laboratory, as allowed by § 109.810(c), both laboratories must maintain the records to document their activities and must ensure that the notifications occur with the required timelines. It is important to note that the **reporting laboratory has 1 hour from the determination of the result made by the testing laboratory** to notify the PWS of the MCL violation. The 1-hour notification cannot be extended due an intermediate notification from a testing laboratory to a reporting laboratory.

Failure of the laboratory to accurately and fully report the subcontracting testing laboratory's results to the PWS:
It is the laboratory's responsibility to report the final test results of any PA-DEP compliance sample accurately, correctly, unambiguously, and with any specific client instructions or regulations. The laboratory is required to ensure that it reports only those test results that are associated with appropriately collected, handled, stored, prepared, and analyzed samples or report the results with appropriate data qualifiers. In some cases, a laboratory that subcontracts the testing to another accredited laboratory may choose to transcribe the accredited

laboratory's results onto its own letterhead/report format. In these cases, the reporting laboratory is responsible for full, accurate, and complete transcription of all sample results; data qualifiers; sample collection, handling, preparation comments; any case narrative or other applicable comment directly to the PWS.

The Department recommends that laboratories provide the testing laboratory's final test report directly to the PWS instead of the transcribing the results. The Department also reminds all laboratories that only results that are associated with acceptable sample collection, storage, handling, preparation, analysis, test conditions, and quality control may be reported to DWELR. A laboratory may request permission to report qualified DW results by using the "Request to Report Qualified DW Results" form and submission instructions. Please note that microbiology test results are handled differently than chemistry results. Once the microbiology samples are accepted and the analysis begins, positive microbiology test results can only be invalidated by the Department regardless of the performance of the QC, instrument test conditions, etc.

Failure to maintain an SOP for reporting PA-DEP SDWA compliance samples that meet the requirements of 25 PA. Code Chapter 109:
The Department requires all laboratories accredited to perform SDWA compliance testing to maintain an SOP that meets the requirements of § 109.810(b)(3)(ii), also known as the "SWDA Reporting SOP." The SWDA Reporting SOP must be established initially upon accreditation and updated annually thereafter. The SOP must include procedures to meet all of the reporting, documentation, notification requirements of § 109.810. At a minimum, the SOP must include:

- The procedure for ensuring that the laboratory obtains and maintains the information regarding the Public Water Supplier, including PWSID#, name of the PWS, contact name and telephone number for the PWS;
- The procedure for ensuring that the laboratory obtains the sample specific information, including sample location, contaminants(s) of interest, date and time of sample collection;
- The procedure for notifications of MCL exceedances, both telephonic and in writing;
- The procedure for documenting the laboratory's activities related to MCL violations and notifications of such violations;
- The procedure for reporting results to DWELR;
- The telephone numbers for each DEP regional office's main number and after hours emergency response telephone number.

The following is an expert from 25 Pa. Code Chapter 109 as it relates to the requirements for accredited laboratories:

25 Pa. Code Chapter 109, § 109.810. Reporting and notification requirements.

(a) Beginning November 13, 2009, a laboratory accredited under Chapter 252 (relating to environmental laboratory accreditation) shall electronically report to the Department on behalf of the public water supplier and in accordance with the reporting requirements under § 109.701(a) (relating to reporting and recordkeeping), the results of test measurements or analyses performed by the laboratory under this chapter using a secure computer application provided by the Department. In the event of a Department computer application failure, the Department will notify the laboratory of an alternate reporting method. In the event that a laboratory is unable to submit data electronically, due to circumstances beyond its control, the laboratory shall notify the Department prior to the applicable reporting deadline. If the Department

determines that the circumstances were beyond the control of the laboratory, the Department will specify a temporary, alternate reporting method the laboratory shall use to meet the reporting deadline.

(1) Unless a different reporting period is specified in this chapter, these results shall be reported within either the first 10 days following the month in which the result is determined or the first 10 days following the end of the required monitoring period as stipulated by the Department, whichever is shorter.

(2) Beginning November 23, 2009, an accredited laboratory and the public water supplier shall be given until the 10th of the following month to review and update submitted data using a secure computer application provided by the Department. Omissions and data errors remaining after the review period shall be considered reporting violations of the public water supplier.

(b) A laboratory accredited under Chapter 252 shall whenever the results of test measurements or analyses performed by the laboratory under this chapter indicate an MCL, MRDL or treatment technique performance requirements under § 109.202 (relating to State MCLs , MRDLs and treatment technique requirements) is exceeded, or an action level under § 109.1102 (a) (relating to lead and copper) is exceeded, or sample result requires the collection of check or confirmation samples under § 109.301 (relating to general monitoring requirements), or a sample collected under Subchapter M (relating to additional requirements for groundwater sources) is *E. Coli*-positive:

(1) Notify the public water supplier by telephone within 1 hour of the laboratory's determination. If the supplier cannot be reached within that time, notify the Department by telephone within 2 hours of the determination. If is necessary for the laboratory to contact the Department after the Department's routine business hours, the laboratory shall contact the appropriate Department's regional office's after-hours emergency response telephone number and provide information regarding the occurrence, the name of contact person and the telephone number where that individual may be reached in the event further information is needed. If the Department's appropriate emergency number cannot be reached, the laboratory shall notify the appropriate Department regional office by telephone within 1 hour of the beginning of the next business day. Each accredited laboratory shall be responsible for the following:

Obtaining and then maintaining the Department's current after-hours emergency response telephone numbers for each applicable regional office.

(i) Establishing or updating a standard operating procedure by November 8, 2002, and at least annually thereafter to provide the information needed to report the occurrences to the Department. The information regarding the public water system must include, but is not limited to, the PWSID number of the system, the system's name, the contaminant involved in the occurrence, the level of the contaminant found, where the sample was collected, the dates and times that the sample was collected and analyzed, the name and identification number of the certified laboratory, the name and telephone number of a contact person at the laboratory and what steps the laboratory took to contact the public water system before calling the Department.

(2) Notify the appropriate Department district office in writing within 24 hours of the determination. For the purpose of determining compliance with this requirement, the postmark, if the notice is mailed, or the date the notice is received by the Department, whichever is earlier, will be used. Upon approval by the Department, the notice may be made electronically to the Department as long as the information is received within the 24-hour deadline.

(c) A laboratory accredited under Chapter 252 shall meet the requirements under subsections (a) and (b), regarding the results of test measurements or analyses performed by the laboratory under this chapter, unless the laboratory assigns in writing the responsibility for reporting and notification to another accredited laboratory.

(d) A laboratory accredited under Chapter 252 shall be responsible for the accurate reporting of data required under the section to the Department.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE
FOR
THE DETERMINATION OF GROSS ALPHA
AND GROSS NON-VOLATILE BETA
IN WATER

(GL-RAD-A-001 Revision 20)

Applicable to Methods:
EPA 600/4-80-032 Method 900.0
US EPA SW-846 Method 9310

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1.0 STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF GROSS ALPHA AND GROSS NON-VOLATILE BETA IN WATER

2.0 METHOD OBJECTIVE, PURPOSE, CODE AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for gross alpha and gross non-volatile beta-emitting isotopes in water.

2.2 A sample is evaporated from a measured volume and then quantitatively transferred to a planchette. The planchette is flamed, allowed to cool, and weighed. The sample is then counted in a gas flow proportional counter at the appropriate voltage to simultaneously count alpha and beta activity.

3.0 METHOD SCOPE, APPLICABILITY, AND DETECTION LIMIT

3.1 Drinking water samples are processed according to source Method 900.0. This method has been modified for non-drinking water liquid samples from the source method EPA 600/4-80-032 for Prescribed Procedures for Measurement of Radioactivity in Drinking Water, August 1980, Method 900.0, and uses similar principles of radiochemical concentration and counting.

3.2 Procedures contained in this SOP may be used to analyze REMP samples.

3.3 Method Detection Limit (MDL): Typical Minimum Detectable Activity (MDA) for liquid samples analyzed for gross alpha and gross non-volatile beta is 5 pCi/L.

3.4 Analyst training records are maintained as quality records as outlined in GL-QS-E-008. Analysts training and proficiency in the method is outlined in the Quality SOP for the Method Validation and Initial and Continuing Demonstrations of Capability, GL-QS-E-011.

4.0 METHOD VARIATIONS

Some variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group Leader or Team Leader. Variations to a method will be documented with the analytical raw data. No method modifications are permitted for drinking water samples.

5.0 DEFINITIONS

5.1 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

6.0 INTERFERENCES

6.1 Due to the following sources of uncertainty, the results produced by this method could be biased slightly high or low when compared to isotopic results:

6.1.1 The varying solids that are contained in samples and the different attenuating properties of those solids.

6.1.2 Energies of the isotopes measured when compared to the calibration energies.

6.1.3 The presence of isotopes with short half-lives.

6.2 The sensitivity of the method is affected by the total solids concentration of each sample. The aliquot size is limited to that which will produce less than 100 mg of

solid residue in the counting planchet. When this method limitation prevents the laboratory from meeting the required detection limit, the samples will be counted for as long as the weekly background (500 minutes) in an effort to obtain the lowest possible detection limit.

6.3 Some types of dissolved solids, when converted to nitrate salts are quite hygroscopic. Samples counted when hygroscopic salts are present can result in inaccurate counting data. When there is evidence of hygroscopic salts in sample counting planchets, it is recommended that they be flamed for a few minutes to convert the nitrate salts to oxides before weighing and counting. The conversion to oxides stabilizes the sample weight and ensures that proper alpha/beta efficiencies are assigned for each sample. Volatile radioisotopes of carbon, hydrogen, technetium, polonium and cesium may be lost during sample heating.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for The Handling of Biological Materials.

7.4 This procedure utilizes Bunsen Burners, and all standard fire precautions should be used.

7.5 If there is any question regarding the safety of any laboratory practice, stop immediately, and consult qualified senior personnel such as a Group or Team Leaders.

7.6 Refer to GL-LB-N-001 the Safety, Health and Chemical Hygiene Plan for additional general safety and health information pertaining to the laboratory.

8.0 APPARATUS, EQUIPMENT AND INSTRUMENTATION

8.1 Stainless steel planchets (2" x 1/8"), concentric ring
8.2 Electric hot plates
8.3 Various sized beakers
8.4 Desiccator
8.5 Analytical balance
8.6 Drying Oven
8.7 Bunsen Burner

9.0 REAGENTS AND STANDARDS

9.1 Reagents

9.1.1 Deionized (DI) water

9.1.2 Concentrated Nitric Acid (16 M HNO_3)

9.1.3 1 M Nitric acid: Add 62 mL of concentrated nitric acid (16 M HNO_3) to 800 mL DI water and dilute to 1000 mL with water.

9.1.4 Tap water, Concentrated: Evaporate large volumes of tap water to near dry adding concentrated Nitric Acid if necessary to break up dissolved solids. Repeat until desired concentrated is obtained.

9.2 Standards

9.2.1 All standards used in this method must be NIST traceable.

9.2.2 Refer to GL-RAD-M-001 for instructions concerning the preparation of standard solutions.

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Water samples should be collected in plastic bottles and preserved with concentrated nitric acid to pH < 2.

10.2 Before beginning an analysis, the analyst should check the sample pH by removing a minimal amount of sample with transfer pipette and placing it on a pH strip. DO NOT insert pH strip into sample container. If the sample is received with a pH greater than 2, the analyst should contact the Group Leader or Team Leader. If approved by the client, the analyst should adjust the pH with concentrated nitric acid to a pH < 2. If the sample is pH adjusted, let the sample sit in the original container for a minimum of 24 hours before analysis.

11.0 SAMPLE PREPARATION

NOTE: Sample aliquot size may be estimated using the count time estimator spread sheet.

11.1 Transfer an aliquot to an appropriate sized beaker. Record the information. If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced. Prepare a MB and LCS by using DI water and concentrated nitric acid to a pH < 2. The MB and LCS volumes should be equivalent to the largest aliquot in the batch and should be recorded.

NOTE: A size should be chosen so that no more than 100 mg of total solids concentrate onto the planchet. If a sample contains sediment or is known to contain high levels of dissolved solids, a minimal amount of sample (approximately 5 mL) may be used to facilitate aliquot determination by taking it dry and calculating total amount of solids in desired aliquot.

11.2 Add an appropriate amount (typically 0.1 mL) of Th-230 and Sr-90 spike to MS, MSD, LCS and LCSD as applicable. Reference batch pull sheet for client requirements to determine appropriate spikes needed for the batch.

NOTE: Spiking steps should be witnessed by either another analyst qualified in this procedure or the Team Leader/Group Leader responsible for this procedure. After adding tracers and spikes, the witness must initial and record the date of witnessing.

11.3 Evaporate the aliquot to near dryness on a hot plate and add 5 mL concentrated nitric acid. Repeat the evaporation and addition of 5 mL concentrated nitric acid.

11.4 Add 10 mL 1 M HNO3 to the beaker and swirl to dissolve residue.

11.5 Quantitatively transfer the concentrate in small portions (not more than 5 mL at a time) to a pre-weighed planchet, evaporating each portion to near dryness.

11.6 Rinse the beaker with 1 M nitric acid and transfer to the planchet. Evaporate rinse to near dryness. Repeat rinse and take sample to dryness. Avoid splattering by reducing heat as necessary.

NOTE: Prior to flaming planchetes (Step 11.7) ensure that all equipment is functioning properly, all combustible materials are moved from the area, long hair is secured back. Do not ignite with matches (only use a lighter with extended nozzle).

11.7 Flame planchetted samples to a dull red color with a burner to convert the nitrate salts to oxides before weighing and counting. Rotate the samples over the flame to ensure a complete conversion to oxide. DO NOT LEAVE OPEN FLAMES UNATTENDED.

NOTE: You must turn off the gas immediately when the flaming process is complete.

11.8 FOR SAMPLES THAT ARE NOT FLAMED: Dry the sample residue in a drying oven for at least two hours. Cool in a desiccator, weigh, and count. Store the sample residue in a desiccator until ready for counting.

11.9 Allow the sample to cool and weigh the sample residue.

11.10 Submit samples and completed paperwork to count room for gas flow proportional counting analysis.

12.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

NOTE: CLIENT CONTRACTUAL QC REQUIREMENTS OVERRIDE THE REQUIREMENTS IN THIS SECTION.

12.1 Analyst and Method Verification Requirements
Refer to GL-RAD-D-002 for Analytical Methods Validation for Radiochemistry.

12.2 Method Specific Quality Control Requirements

12.2.1 A Matrix Spike (MS) should be run with every batch. The recovery should fall between 75-125%. If the sample result is > 5 times the MS nominal concentration then limits are not applicable.

12.2.2 A Duplicate (DUP) sample should be run with every batch. For drinking water samples a duplicate should be run once for every ten samples processed within the batch. The Relative Percent Difference (RPD) between the sample and the Duplicate should be less than or equal to 20% if both results are greater than 5 times the MDC. If both results are less than 5 times the MDC, the limit is 100%. If both results are less than the MDC then limits are not applicable.

12.2.3 A Method Blank (MB) should accompany each batch of 20 samples or less. The reported value should be less than or equal to the CRDL, or less than 5% of the least activity result (for RAD batches).

12.2.4 A Laboratory Control Sample (LCS) should be run with each batch of 20 samples or less. The recovery of the LCS should fall between 75-125%.

12.3 Actions required if the Quality Control Requirements are not met:

If any of the QC criteria from 12.2.1-12.2.4 cannot be satisfied, the analyst should inform their Group Leader and initiate a Data Exception Report as outlined in GL-QS-E-004.

12.4 The sensitivity of this method is affected by the total solids concentration of each sample. The aliquot size is limited to that which will produce less than 100 mg of solid residue in the counting planchet. When this method limitation prevents the laboratory from meeting the required detection limit, the samples will be counted for as long as the weekly background (500 minutes) in an effort to obtain the lowest possible detection limit. This will be noted in the applicable batch case narrative.

13.0 INSTRUMENT CALIBRATION, STANDARDIZATION AND PERFORMANCE

13.1 Calibration Source Preparation

NOTE: Source prep is only performed under the guidance of Team Leader or Group Leader.

NOTE: Sources are created using NIST traceable standards for both Th-230 and Sr-90 as well as a separate Po-210 source for crosstalk determination.

13.1.1 Evaporate tap water to achieve the desired calibration maximum of 100 mg of residue. To new labeled beakers containing tap water, add varying amounts of evaporated water to achieve a multi point calibration. 8 standards for the calibration with masses between 0 and slightly > 100 mg are normally run with a minimum of 7 points used in the calibration curve.

13.1.2 Add appropriate amount of applicable standard (~10,000 dpm) to each beaker.

13.1.3 Place samples on low heat, and add 5 mL concentrated nitric acid to beakers and reduce volume. This is repeated until nitrate conversion is complete and solution is clear.

13.1.4 Quantitatively transfer this solution to the pre-weighed planchetes. Keep on low heat and allow to dry.

13.1.5 Allow to cool, weigh planchetes, and calculate net residue weights.

13.1.6 Submit samples to count room for gas flow proportional counting analysis.

13.2 Verification Source Preparation

13.2.1 Sources are prepared using both Th-230 and Sr-90 on same planchet.

13.2.2 Follow the steps in 13.1 for preparation.

14.0 ANALYSIS AND INSTRUMENT OPERATION

Refer to GL-RAD-I-016 or GL-RAD-I-006 for instructions concerning gas flow proportional counters.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Refer to GL-RAD-I-010 for instructions concerning instrument maintenance.

16.0 DATA RECORDING, CALCULATION AND REDUCTION METHODS

Data recording, calculation and reduction takes place in accordance with GL-RAD-D-003 and GL-RAD-D-006.

17.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

Data are reviewed and packaged in accordance with GL-RAD-D-003 for Data Review, Validation and Data Package Assembly.

18.0 RECORDS MANAGEMENT

All data generated in the performance of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND DISPOSAL

Radioactive samples and materials are disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

20.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, USEPA, Method 900.0, pp. 1-9, August 1980.

20.2 Standard Methods for the Examination of Water and Wastewater, 14th Edition, American Public Health Association, Washington, DC, (1976).

20.3 1979 Annual Book of ASTM Standards, Part 31, American Society for Testing and Materials, Philadelphia, PA, (1979).

20.4 Friedlander, G., J. W. Kennedy, and J. Miller, Nuclear and Radiochemistry, John Wiley and Sons, Inc., New York, NY, (1964).

20.5 Youden, W. J. and F. J. Massey, Jr., Introduction to Statistical Analysis, 3rd edition, McGraw-Hill.

20.6 Hallden, N. A. and J. H. Harley, "An Improved Alpha-Counting Technique," Analytical Chemistry, Vol. 32:1861, (1960).

20.7 American National Standard, Calibration and Usage of Alpha/Beta Proportional Counters, ANSI N42.25 1997.

20.8 Gross Alpha and Gross Beta, SW-846 Method 9310, U.S. Environmental Protection Agency, September, 1986.

20.9 Manual for the Certification of Laboratories Analyzing Drinking Water. Criteria and Procedures Quality Assurance. Fifth Edition EPA 815-R-05-004 January 2005.

21.0 HISTORY

Revision 17: Reagents and standards, method specific and quality control requirements updated for clarification. 10% nitric acid changed to 1 M nitric acid in sample preparation.
Revision 18: Updated note on analyst witnessing during spiking.
Revision 19: Removed references to Queue sheets.
Revision 20: Updated Reagents section.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF GROSS ALPHA AND GROSS NON-VOLATILE BETA IN SOIL, FILTERS, SOLID MATRICES AND DIRECT COUNT AIR FILTERS

(GL-RAD-A-001B REVISION 20)

Applicable to Method:
EPA 600/4-80-032 Method 900.0 (Modified)
US EPA SW-846 Method 9310 (Modified)
SM 7110B (Modified)

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1.0 STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF GROSS ALPHA AND GROSS NON-VOLATILE BETA IN SOIL, FILTERS, SOLID MATRICES AND DIRECT COUNT AIR FILTERS

2.0 METHOD OBJECTIVE, PURPOSE, CODE AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for gross alpha and non-volatile beta emitting isotopes in soil, filters, direct count air filters, biological tissue, and other solid matrices.

2.2 This method has been modified on the basis of GEL's Performance Based Measurement System (PBMS).

2.3 Solid matrices are decomposed by digestion in accordance with GL-RAD-A-015 for Digestion for Soil. The digestate is evaporated to dryness and diluted with a nitric acid solution. The nitric acid solution is transferred to a concentric ring planchet for analysis.

3.0 METHOD SCOPE, APPLICABILITY AND DETECTION LIMIT

3.1 GEL Laboratories, LLC (GEL) utilizes methods that are derived from established sources. This method has been modified from the source method EPA 600/4-80-032 for Prescribed Procedures for Measurement of Radioactivity in Drinking Water, August 1980, Method 900.0, and uses the same principles of radiochemical concentration and counting.

3.2 Procedures contained in this SOP may be used to analyze REMP samples.

3.3 Method Detection Limits (MDL): Typical Minimum Detectable Activity (MDA) for solid samples analyzed for gross alpha is 4 pCi/g and non-volatile beta is 10 pCi/g. Typical Minimum Detectable Activity (MDA) for filter samples analyzed for gross alpha and non-volatile beta is 5 pCi/Filter.

3.4 Analyst training records are maintained as quality records as outlined in GL-QS-E-008. Analysts training and proficiency in the method is outlined in the Quality SOP for the Method Validation and Initial and Continuing Demonstrations of Capability, GL-QS-E-011.

4.0 METHOD VARIATIONS

4.1 Some variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group Leader or Team Leader. Variations to a method will be documented with the analytical raw data.

4.2 For solid matrices, GEL performs acid digestions according to SOP GL-RAD-A-015 which is a modification of SM7110B and EPA 900.0.

5.0 DEFINITIONS

5.1 Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel using the same lot(s) of reagents.

5.2 Deionized (DI) water: Type I water. Refer to GL-LB-E-016.

5.3 Laboratory Control Sample (LCS): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes.

5.4 Laboratory Duplicate (DUP): aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

5.5 Method Blank (MB): a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures.

5.6 Matrix Spike Duplicate (MSD): a second replicate matrix spike is prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

5.7 Matrix Spike (MS): prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

5.8 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

6.0 INTERFERENCES

6.1 Due to the following sources of uncertainty, the results produced by this method could be biased slightly high or low when compared to isotopic results:

6.1.1 The varying solids that are contained in samples and the different attenuating properties of those solids.

6.1.2 Energies of the isotopes measured when compared to the calibration energies.

6.1.3 The presence of isotopes with short half-lives.

6.2 The sensitivity of the method is affected by the total solids concentration of each sample. The aliquot size is limited to that which will produce less than 100 mg of solid residue in the counting planchet. When this method limitation prevents the laboratory from meeting the required detection limit, the samples will be counted for as long as the weekly background (8 hours) in an effort to obtain the lowest possible detection limit.

6.3 Some types of dissolved solids, when converted to nitrate salts, are quite hygroscopic. Samples counted when hygroscopic salts are present can result in inaccurate counting data. When there is evidence of hygroscopic salts in sample counting planchets it is recommended that they be flamed for a few minutes to convert the nitrate salts to oxides before weighing and counting. The conversion to oxides stabilizes the sample weight and ensures that proper alpha/beta efficiencies are assigned for each sample. Volatile radioisotopes of carbon, hydrogen, technetium, polonium and cesium may be lost during sample heating.

NOTE: Client requirements may specify that samples are not flamed.

NOTE: Client requirements may specify that samples are not flamed for an initial count to determine beta activity. The samples are returned to the lab and flamed for a second count to determine alpha activity in the sample.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for The Handling of Biological Materials.

7.4 This procedure utilizes Bunsen Burners, and all standard fire precautions should be used.

7.5 If there is any question regarding the safety of any laboratory practice, **stop immediately**, and consult qualified senior personnel such as a Group or Team Leader.

8.0 APPARATUS, EQUIPMENT, AND INSTRUMENTATION

8.1 Ancillary Equipment

8.1.1 Stainless steel planchets (2" x 1/8"), concentric ring

8.1.2 Electric hot plates

8.1.3 Desiccator

8.1.4 Analytical balance

8.1.5 100 mL Teflon® beakers or 50 mL polypropylene tubes

8.1.6 Bunsen burner

8.1.7 Flat stainless steel planchets (2” x 1/8”)

8.1.8 Watchglass of various sizes (Teflon or polypropylene)

8.1.9 Hoblock

9.0 REAGENTS AND STANDARDS

9.1 Reagents

9.1.1 Deionized (DI) water

9.1.2 Nitric acid, 1 M HNO_3: Add 62 mL of concentrated Nitric Acid (16 M HNO_3) to 800 mL of DI water and dilute to 1000 mL with DI water

9.1.3 Nitric Acid, concentrated (16 M HNO_3)

9.1.4 Tap Water, concentrated: Evaporate large volumes of tap water to near dryness, adding concentrated Nitric Acid if necessary to break up dissolved solids. Repeat until desired concentration is obtained.

9.2 Standards

9.2.1 All standards used in this method must be NIST traceable.

9.2.2 Refer to GL-RAD-M-001 for instructions concerning the preparation of standard solutions.

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 A representative sample must be collected from a source of soil and should be large enough (50-100 grams) so that adequate aliquots can be taken to obtain the required sensitivity. The container of choice should be plastic over glass to prevent loss due to breakage during handling.

10.2 Preservation is not required for filter samples.

10.3 Biological tissue and vegetation samples should be refrigerated for storage.

10.4 Typical hold time for samples covered in this method is 180 days.

11.0 SAMPLE PREPARATION

11.1 Sample Preparation Techniques

11.1.1 Transfer a representative aliquot (usually 0.1 gram) of the dried and homogenized sample into a Teflon beaker or polypropylene tube. Record aliquot. If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced. Record the aliquot for the MB and LCS as the largest aliquot in the batch.

11.1.2 Add an appropriate amount (typically 0.1 mL) of Th-230 and Sr-90 spike to MS, MSD, LCS and LCSD as applicable. Reference batch pull sheet for client requirements to determine appropriate spikes needed for the batch.

NOTE: Spiking and tracing steps should be witnessed by either another analyst qualified in this procedure or the Team Leader/Group Leader responsible for this procedure. After adding tracers and spikes, the witness must initial and record the date of witnessing.

11.1.3 Digest sample according to GL-RAD-A-015.

11.1.4 Evaporate the digested sample to less than 5 mL.

11.1.5 Transfer the sample to a labeled and pre-weighed planchet.

11.1.6 Evaporate to dryness on a low heat hot plate.

11.1.7 Rinse Teflon beaker or polypropylene tube with 1 M nitric acid onto planchet and evaporate to dryness.

11.1.8 Repeat step 11.1.7.

NOTE: All sample residue must be rinsed from the teflon beaker or polypropylene tube into the planchet. If two rinses are not sufficient to transfer the sample residue, more rinses may be performed.

11.1.9 Flame plancheted samples to a dull red color with a burner to convert the nitrate salts to oxides before weighing and counting. Rotate the samples over the flame to ensure a complete conversion to oxide. **DO NOT LEAVE OPEN FLAMES UNATTENDED**.

NOTE: You must turn off the gas immediately when flaming process is complete.

NOTE: Client requirements may specify that samples are not flamed.

11.1.10 For samples that are not flamed: Dry the sample residue in a drying oven for at least two hours. Cool in a desiccator, weigh, and count. Store the sample residue in a desiccator until ready for counting.

11.1.11 Allow the sample to cool and weigh the sample residue. The net solids should be less than 100 mg. If the weight is > 100 mg, then reprep sample with a smaller aliquot.

11.1.12 Submit samples and completed paperwork to the count room for Gas Flow Proportional counting.

11.2 Filters, Oils and Other Directly Plancheted Matrices

NOTE: For filters, this section applies to filters that have been previously digested and diluted according to GL-RAD-A-026.

NOTE: Filter aliquots can be determined using count time estimator spreadsheet and filter aliquot correction in LIMS. Aliquots will also vary due to the limited nature of filters and the number of other analysis required. See Team Leader or Group Leader for guidance in determining aliquots.

11.2.1 Select appropriate aliquot, and place directly onto pre-weighed planchet. If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced. Prepare a MB and LCS by using DI water and concentrated nitric acid to a pH < 2. The MB and LCS volume should be equivalent to the largest aliquot in the batch and should be recorded.

11.2.2 Add appropriate amount (typically 0.1 mL) of Th-230 and Sr-90 spike to MS, MSD, LCS and LCSD planchets as applicable. Reference batch pull sheet for client requirements to determine appropriate spikes needed for the batch.

NOTE: Spiking and tracing steps should be witnessed by either another analyst qualified in this procedure or the Team Leader/Group Leader responsible for this procedure. After adding tracers and spikes the witness must initial and record the date of witnessing.

11.2.3 If aliquot does not fill planchet, add 1 M nitric acid to disperse sample within planchet.

11.2.4 Take planchets to dryness on low heat to avoid splattering.

11.2.5 Flame plancheted samples to a dull red color with a burner to convert the nitrate salts to oxides before weighing and counting. Rotate the samples over the flame to ensure a complete conversion to oxide. **DO NOT LEAVE OPEN FLAMES UNATTENDED**.

NOTE: You must turn off the gas immediately when flaming process is complete.

NOTE: Client requirements may specify that samples are not flamed.

11.2.6 Allow the sample to cool, and weigh the sample residue. The net solids should be less than 100 mg. If the weight is > 100 mg, then reprep sample with a smaller aliquot.

11.2.7 Submit samples and completed paperwork to the count room for Gas Flow Proportional counting.

11.3 Direct Count Air Filters

11.3.1 If necessary, prepare a punch of the filter for analysis per GL-RAD-A-026.

11.3.2 Observe client special requirements for hold times prior to counting, when applicable.

11.3.3 Scan samples to batch and submit samples to count room for analysis. After analysis, store samples in a predetermined location for future composite analysis if required.

12.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

NOTE: Client contractual QC requirements override the requirements in this section.

12.1 Method Verification Requirements

Refer to GL-RAD-D-002 for instructions concerning the validation of analytical methods.

12.2 Method Specific Quality Control Requirements

12.2.1 A Matrix Spike (MS) should be run with every batch. The recovery should fall between 75-125%. If sample result is > 5 times the MS nominal concentration then limits are not applicable.

12.2.2 A duplicate of a sample should be run with every batch. The Relative Percent Difference (RPD) between the actual sample and the duplicate (DUP) should be less than or equal to 20% if both results are greater than 5 times the MDC or 100% if they are both less than 5 times the MDC. If both result are less than the MDC, then limits are not applicable.

12.2.3 A Method Blank (MB) should accompany each batch. The reported value should be less than or equal to the CRDL, or less than 5% of the least activity result (for RAD batches).

12.2.4 A Laboratory Control Sample (LCS) should be run with each batch. The recovery of the LCS should fall between 75-125%.

12.3 Actions Required if the Quality Control Requirements Are Not Met:

12.3.1 If any of the QC criteria cannot be satisfied, the analyst should inform the Group Leader and initiate a Nonconformance Report as outlined in GL-QS-E-004.

12.3.2 MS and RPD failures that are caused by non-homogeneous matrices will be noted in the applicable batch case narrative.

12.3.3 MS/MSD failures that are caused by the matrix of the sample will be noted in the applicable batch case narrative.

12.4 The sensitivity of this method is affected by the total solids concentration of each sample. The aliquot size is limited to that which will produce less than 100 mg of solid residue in the counting planchet.

13.0 INSTRUMENT CALIBRATION, STANDARDIZATION AND PERFORMANCE

Refer to GL-RAD-A-001 Section 13.0 for applicable instrument calibration.

14.0 ANALYSIS AND INSTRUMENT OPERATION

Refer to GL-RAD-I-016 or GL-RAD-I-006 for instructions concerning gas flow proportional counters.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Refer to GL-RAD-I-010 for instructions concerning instrument maintenance.

16.0 DATA RECORDING, CALCULATION AND REDUCTION METHODS

Data recording, calculation, and reduction takes place in accordance with GL-RAD-D-003 and GL-RAD-D-006.

17.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

Data are reviewed and packaged in accordance with GL-RAD-D-003 for Data Review, Validation and Data Package Assembly.

18.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND DISPOSAL

Laboratory waste is disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

20.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, USEPA, Method 900.0, pp. 1-9, (Aug. 1980).

20.2 Standard Methods for the Examination of Water and Wastewater, Mehod 7110B, 20th edition, American Public Health Association, Washington, DC (1996).

20.3 1979 Annual Book of ASTM Standards, Part 31, American Society for Testing and Materials, Philadelphia, PA (1979).

20.4 Friedlander, G., J. W. Kennedy, and J. Miller, Nuclear and Radiochemistry, John Wiley and Sons, Inc., New York, New York, (1964).

20.5 Youden, W. J. and F. J. Massey, Jr., Introduction to Statistical Analysis, 3rd edition, McGraw-Hill.

20.6 Hallden, N. A. and J. H. Harley, "An Improved Alpha-Counting Technique", Analytical Chemistry, p. 32:1861, (1960).

20.7 American National Standard, Calibration and Usage of Alpha/Beta Proportional Counters, ANSI N42.25-1997

20.8 “Methods for Determination of Radioactive Substances in Water and Fluvial Sediments.” USGS, Book 5, Chapter A5.

20.9 "Eastern Environment Radiation Facility Radiochemistry Procedures Manual." US EPA, June 1984.

21.0 HISTORY

Revision 16: Technical updates for SOP consistency as part of annual review.
Revision 17: Updated reagents section and method specific quality control requirements.
Revision 18: Removed reference to Queue Sheets. Added reference to refer to QAP for additional definitions.
Revision 19: Updated Reagents section.

Revision 20: Added the use of polypropylene tubes.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF TRITIUM

(GL-RAD-A-002 REVISION 23)

APPLICABLE TO METHODS:
EPA 600/4-80-032 Method 906.0

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF TRITIUM

2.0 METHOD OBJECTIVE, PURPOSE, CODE, AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for tritium in various matrices.

2.2 This method has been modified on the basis of GEL's Performance Based Measurement System (PBMS).

2.3 A sample is distilled in a flask in a basic potassium permanganate environment to avoid distilling organics and interfering radionuclides. Soil samples are either distilled with fossil water or the moisture is extracted from the soil using a vacuum or oven. The distilled tritium is transferred to a scintillation vial and counted in a liquid scintillation counter.

3.0 METHOD SCOPE, APPLICABILITY, AND DETECTION LIMIT

3.1 GEL Laboratories, LLC (GEL) utilizes methods that are derived from established sources. This method has been modified from the source method EPA 600/4-80-032 "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," August 1980, Method 906.0, and uses the same principles of radiochemical concentration and counting. EPA Method 906 is written for drinking water. This method has been modified to accommodate various matrices as discussed in section 11.0.

3.2 Procedures contained in this SOP may be used to analyze REMP samples.

3.3 Method Detection Limit (MDL): Typical Minimum Detectable Activity (MDA) for samples analyzed for tritium by standard distillation methods are 700 pCi/L for liquids and 6 pCi/g for solids.

4.0 METHOD VARIATIONS

Some variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group Leader or Team Leader. Variations to a method will be documented with the analytical raw data.

5.0 DEFINITIONS

5.1 Background: An instrument blank prepared with each batch using the same geometry as the samples being analyzed.

5.2 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel using the same lot(s) of reagents.

5.3 Deionized (DI) water: Type I DI water. Refer to GL-LB-E-016.

5.4 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes.

5.5 Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container under laboratory conditions, and processed and analyzed independently.

5.6 Matrix Spike (MS): Prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

5.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike is prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

5.8 Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures.

5.9 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

5.10 Refer to GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

6.0 INTERFERENCES/LIMITATIONS

6.1 Samples with color or chemical quenching agents may reduce the tritium counting efficiency. Generally, these problems are overcome by diluting the sample aliquot. However, in some cases distillation may be necessary.

6.2 Other beta emitters in the sample may bias the tritium results high.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for The Handling of Biological Materials.

7.4 If there is any question regarding the safety of any laboratory practice, stop immediately, and consult qualified senior personnel such as a Group or Team Leader.

8.0 APPARATUS, EQUIPMENT, AND INSTRUMENTATION

8.1 Apparatus and Equipment

8.1.1 20 mL plastic vials and caps (Liquid scintillation high density polyethylene vials)

8.1.2 5 mL Oxford® pipet or equivalent

8.1.3 10 mL Oxford® pipet or equivalent

8.1.4 Eppendorf® Repeater™ pipet or equivalent

8.1.5 Distillation apparatus

NOTE: All glassware used in this method must be washed then rinsed with DI water and dried in an oven at approximately 100° C prior to use.

8.1.6 Vacuum pump

8.1.7 Liquid Nitrogen Dewar

8.1.8 Anti-static cloth

8.1.9 Column rack

8.1.10 Extension funnels

8.1.11 Centrifuge tubes

8.1.12 Hot plate with stirring capabilities

8.1.13 Teflon coated magnetic stir bars

8.2 Instrumentation

8.2.1 Liquid Scintillation Counter

9.0 REAGENTS AND STANDARDS

9.1 Reagents

9.1.1 Type I deionized (DI) water

9.1.2 Background well water (fossil water or dead water)

9.1.2.1 When measuring tritium for low level analysis, fossil water from deep wells is used in the preparation of samples and blanks. This water has been isolated from natural generation of tritium from cosmic rays. The tritium concentration of this water is approximately 1,000 times lower than surface water.

9.1.2.2 To verify a new deep well location, a background must be prepared and compared to a background study from a previously accepted location as approved by a Group Leader.

9.1.3 Liquid scintillation cocktail (Ecoscint Ultra or equivalent)

9.1.4 Potassium permanganate, 1% $KMnO_4$: Dissolve 10 g of $KMnO_4$ in DI water and dilute to 1000 mL.

9.1.5 Sodium hydroxide pellets, reagent grade NaOH pellets

9.1.6 Liquid nitrogen

9.1.7 Quenching agent: Brown colorant, dissolve approximately 0.5 g of Sensient nut brown shade powder in 1000 mL of DI water.

9.1.8 Eichrom Tritium Columns, prepackaged

9.1.9 Methanol (CH_3OH)

9.2 Standards

9.2.1 NIST traceable Tritium standard.

9.2.2 Refer to GL-RAD-M-001 for instructions concerning the preparation of standard solutions.

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 The preferred method for sample collection is in a glass container with no preservatives added. This is preferred due to the possibility of tritium exchange between the sample and container if plastic is used. Plastic containers may be used if sample breakage is more probable in large solid samples.

10.2 Before beginning analysis, the analyst should check the liquid sample pH by removing a minimal amount of sample with transfer pipette and placing it on a pH strip. DO NOT insert pH strip into sample container. If the sample is received with a pH less than 7, the analyst should contact the Group Leader or Team Leader.

10.3 Soil Samples require no preservation and may be shipped in any suitable container.

11.0 SAMPLE PREPARATION

From the sample matrix and client requirements, determine the procedure to be used. The Project Manager, Group Leader or Team Leader may need to be consulted.

11.1 Determination of Tritium via the Direct Counting of the Sample in a Sample Vial

11.1.1 Prepare a background by adding 10 mL of fossil water and 13 mL of scintillation cocktail into a scintillation vial. Add quenching agent (normally 10 µL) to each vial. Cap the vial and shake vigorously to cause complete dissolution in the cocktail.

11.1.2 Transfer a known amount of sample (normally 10 mL) and 13 mL of liquid scintillation cocktail into a plastic scintillation vial. Record the Aliquot in Vial volume in LIMs.

NOTE: The proper ratio between sample volume and liquid scintillation cocktail must be maintained. If the sample aliquot is not clear and colorless, the amount of sample may be reduced with approval from a Group Leader or Team Leader. If the sample aliquot is less than 10 mL, fossil water must be added to the vial to maintain the calibration ratio.

11.1.3 Add an appropriate amount (typically 0.1 mL) of NIST traceable Tritium standard to the MS, MSD, LCS, LCSD.

NOTE: Spiking and tracing steps should be witnessed by either another analyst qualified in this procedure or the Team Leader/Group Leader responsible for this

procedure. After adding tracers and spikes, the witness must initial and record the date of witnessing.

11.1.4 Add quenching agent (normally 20 µL) to bring the quench value within the quench limits of the calibration. Cap the vial and shake vigorously to cause complete dissolution of the sample in the cocktail.

NOTE: If the sample aliquot in vial is not clear and colorless, quenching agent should not be added to the vial.

11.1.5 Wipe each sample vial with methanol and place in a counting rack.

11.1.6 Submit samples and completed paperwork to count room for Liquid Scintillation counting analysis.

11.2 Determination of Tritium Using an Air-cooled Distillation Apparatus

NOTE: Visually inspect all glassware prior to use. If scratches are visible, discard glassware.

11.2.1 For liquid samples: Weigh a known amount (typically 50 mL) of sample into an Erlenmeyer flask, recording the distillation rig number in LIMS. Record this weight as Initial Sample Aliquot.

11.2.1.1 If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample. Prepare a MB using fossil water and a LCS using DI Water. The MB and LCS volume should be equivalent to the largest aliquot in the batch. Record all aliquots.

11.2.2 For solid samples: Weigh a known amount of sample into an Erlenmeyer flask, recording the distillation rig number in LIMS. Record this weight as Initial Sample Aliquot.

NOTE: Soil sample aliquot size may be estimated using the count time estimator spreadsheet.

11.2.2.1 If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced. Prepare a MB using fossil water and a LCS using DI Water. The MB and LCS volume should be equivalent to the largest aliquot in the batch. Record all aliquots.

11.2.2.2 Add a known amount (typically 50 or 100 mL depending on aliquot size) of fossil water to the sample and record this as Volume Added for Distillation. The volume added to the MB and LCS flasks should be equal to that of the samples.

11.2.2.3 Add a Teflon coated magnetic stir bar to the flask.

NOTE: Solid samples are only run by this method when approved by the client.

11.2.3 Add 2 mL of 1% potassium permanganate and 5 to 10 sodium hydroxide pellets to each flask.

NOTE: If samples are suspected to contain high amounts of organic compounds, an additional 2 mL of 1% potassium permanganate can be added to samples to complete oxidation. Consult the Team Leader or Group Leader before adding 1% permanganate beyond this second addition.

11.2.4 Add an appropriate amount (typically 0.1 mL) of Tritium standard to the MS, MSD, LCS and LCSD as appropriate.

NOTE: Spiking and tracing steps should be witnessed by either another analyst qualified in this procedure or the Team Leader/Group Leader responsible for this procedure. After adding tracers and spikes, the witness must initial and record the date of witnessing.

11.2.5 Assemble the Erlenmeyer flask to the air condenser.

11.2.6 Heat the sample by placing the distillation flask on a hot plate at medium/high heat.

NOTE: Soil samples need to be placed on a hot plate with stirring capability.

11.2.7 Allow the inner container to fill then discard the distillate. Allow the inner container to refill and save for analysis.

11.2.8 Transfer a known amount of sample (normally 10 mL) and 13 mL of liquid scintillation cocktail into a scintillation vial. Record the Aliquot in Vial volume.

NOTE: The proper ratio between sample volume and liquid scintillation cocktail must be maintained. If the sample aliquot in vial is not clear and colorless, the amount of sample may be reduced with approval from a Group Leader or Team Leader. If the sample aliquot is less than 10 mL, fossil water must be added to the vial to maintain the calibration ratio.

11.2.9 Add quenching agent (normally 20 uL) to bring the quench value within the quench limits of the calibration. Cap the vial and shake vigorously to cause complete dissolution of the sample in the cocktail.

NOTE: If the sample aliquot in vial is not clear and colorless, quenching agent should not be added to the vial.

NOTE: A milky appearance is an indicator of cocktail loading. A volume should be chosen so that the vial appears clear. Consult the Group Leader or Team Leader if questions arise.

11.2.10 Prepare a background by adding 10 mL of fossil water and 13 mL of scintillation cocktail into a scintillation vial. Add quenching agent (normally 20 µL) to each vial. Cap the vial and shake vigorously to cause complete dissolution in the cocktail.

11.2.11 Wipe each sample vial with methanol and place in a counting rack.

11.2.12 Submit samples and completed paperwork to the count room for Liquid Scintillation counting analysis.

11.3 Determination of Tritium Using the Vacuum Rig

NOTE: These steps are used for large samples being analyzed for low level tritium.

NOTE: This procedure is used to remove approximately 10 mL or more of water from the sample.

11.3.1 All residual moisture in the distillation system must be removed. If droplets are present, dry areas with tissue or place in oven to dry. This must be accomplished before proceeding.

11.3.2 Weigh the sample container to be used and record this weight.

11.3.3 Add sample to the sample container and record this weight. This value can be used to calculate percent (%) moisture in a sample.

NOTE: The MB is prepared by pipetting 20 mL of fossil water into sample container and assembling to the vacuum distillation system.

NOTE: The LCS is prepared by pipetting 20 mL of fossil water into a sample container. Add an appropriate amount (typically 0.1 mL) of NIST traceable Tritium standard to the sample and assemble to the vacuum distillation system.

11.3.4 Assemble the vacuum distillation system. Check vacuum pump oil.

11.3.5 If a rig is not connected to a valve, slowly close that associated valve. Start the vacuum pump. When the pump has quieted, immerse the trap in liquid nitrogen and connect one end of the trap to the sample and the other end to the vacuum system.

NOTE: The sample trap MUST NOT be immersed in the liquid nitrogen before it is connected to the sample and the vacuum system.

11.3.6 Open or check to make sure all of the valves connected to a sample are open.

11.3.7 Heat the sample by placing it on a heating mantle at low to medium heat.

11.3.8 Allow the sample to distill until approximately 30 mL of water is collected.

11.3.9 Remove the heat source, close valves, and turn off the vacuum pump.

11.3.10 Remove sample trap from the liquid nitrogen.

NOTE: The sample trap MUST NOT stay immersed in the liquid nitrogen when it is not connected to the sample and the vacuum system.

11.3.11 Label the sample trap and allow sample to melt inside trap. Transfer sample to a 40 mL glass vial.

11.3.12 Place the sample container in the oven at approximately 100º C for at least 6 hours. If after 6 hours the sample does not appear dry, place in oven until dryness is obtained.

11.3.13 Allow sample to cool. Weigh sample container with dried sample and record this weight. This value can be used to calculate percent (%) moisture in a sample.

11.3.14 Wash all glassware and dry in oven at approximately 100º C. If high activity sample is run or sample splatter is evident, clean the section between the sample and the sample trap and dry in oven at approximately 100° C.

11.3.15 Transfer a known amount of distillate (usually 10 mL) and 13 mL of scintillation cocktail into a scintillation vial. Record the Aliquot in Vial in LIMS. Add an appropriate amount (typically 0.1 mL) of Tritium standard to the MS and MSD samples.

NOTE: The proper ratio between sample volume and liquid scintillation cocktail must be maintained. If the sample does contain enough moisture to extract the required 10 mL of distillate, the amount of sample in vial may be reduced with approval from the Group Leader or Team Leader. If the sample aliquot is less than 10 mL, fossil water must be added to the vial to maintain the calibration ratio.

11.3.16 Prepare a background by adding 10 mL of fossil water and 13 mL of scintillation cocktail into a scintillation vial. Add quenching agent (normally 20 µL) to each vial. Cap the vial and shake vigorously to cause complete dissolution in the cocktail.

11.3.17 Add quenching agent (normally 20 µL) to bring the quench value within the quench limits of the calibration. Cap the vial and shake vigorously to cause complete dissolution of the sample in the cocktail.

NOTE: If the sample aliquot in vial is not clear and colorless, quenching agent should not be added to the vial.

NOTE: A milky appearance is an indicator of cocktail loading. A volume should be chosen so that the vial appears clear. Consult the Group Leader or Team Leader if questions arise.

11.3.18 Wipe each sample vial with methanol and place in a counting rack.

11.3.19 Submit samples and completed paperwork to count room for Liquid Scintillation counting analysis.

11.4 Determination of Tritium Using the Oven

11.4.1 Weigh an empty paint can and record this weight.

11.4.2 Weigh a known amount of sample into the paint can and record this weight.

NOTE: The MB is prepared by pipetting 20 mL of fossil water into a paint can.

NOTE: The LCS is prepared by pipetting 20 mL of fossil water into a paint can. Add an appropriate amount (typically 0.1 mL) of Tritium standard to the sample.

11.4.3 Heat the sample by placing it in the oven. To collect the distillate, the sample flask is connected to a centrifuge tube using clear tubing. One end of the tubing is attached to the top of the container while the other end of the tubing is placed inside a labeled centrifuge tube outside the oven in an ice water bath.

NOTE: If sample matrix is a silica gel, platinum tubing must be used.

11.4.4 Allow the sample to distill until approximately 30 mL of water is collected. Leave container in oven for at least 6 hours when dry weight is needed. Record this weight.

NOTE: If client requires silica gel to be re-packaged for future collection, refer to Appendix 1 for packaging and assembly instructions.

11.4.5 Transfer a known amount of distillate (usually 10 mL) and 13 mL of scintillation cocktail into a scintillation vial. Record the Aliquot in Vialin LIMS. Add an appropriate amount (typically 0.1 mL) of Tritium standard to the MS and MSD samples.

NOTE: The proper ratio between sample volume and liquid scintillation cocktail must be maintained. If the sample does contain enough moisture to extract the required 10 mL of distillate, the amount of sample in vial may be reduced with approval from the Group Leader or Team Leader. If the sample aliquot is less than 10 mL, fossil water must be added to the vial to maintain the calibration ratio.

11.4.6 Add quenching agent (normally 20 uL) to bring the quench value within the quench limits of the calibration. Cap the vial and shake vigorously to cause complete dissolution of the sample in the cocktail.

NOTE: If the sample aliquot in vial is not clear and colorless, quenching agent should not be added to the vial.

NOTE: A milky appearance is an indicator of cocktail loading. A volume should be chosen so that the vial appears clear. Consult the Group Leader or Team Leader if questions arise.

11.4.7 Prepare a background by adding 10 mL of fossil water and 13 mL of scintillation cocktail into a scintillation vial. Add quenching agent (normally 20 µL) to each vial. Cap the vial and shake vigorously to cause complete dissolution in the cocktail.

11.4.8 Wipe each sample vial with methanol and place in a counting rack.

11.4.9 Submit samples and completed paperwork to count room for Liquid Scintillation counting analysis.

11.5 Determination of Tritium using Eichrom Columns for Removal of Organic Material and Interfering Anions and Cations.

11.5.1 If required, filter the sample through a 0.45 micron filter.

11.5.2 For each sample and QC, place a Tritium Column in the column rack.

11.5.3 Place a waste tray below the columns, remove the column caps and bottom plug from each column and allow to drain. Attach extension funnels to each column.

11.5.4 Pipet 10 mL of DI water into each column to condition resin and allow to drain.

NOTE: It is important to allow all rinse and sample solutions to completely drain through the column before proceeding to the next step. However, do not allow columns to sit long enough to begin to dry out.

11.5.5 Measure 25 mL of sample into a disposable centrifuge tube.

11.5.6 Add appropriate amount of Tritium standard (typically 0.1 mL) to MS, MSD, LCS, and LCSD. Swirl to mix.

NOTE: Spiking and tracing steps should be witnessed by either another analyst qualified in this procedure or the Team Leader/Group Leader responsible for this procedure. After adding tracers and spikes, the witness must initial and record the date of witnessing.

11.5.7 Add 5 mL of the sample to the Tritium Column and allow to drain to the waste tray.

11.5.8 Place a clean centrifuge tube beneath the column. Add the remaining 20 mL of sample to the column and collect in the clean centrifuge tube.

11.5.9 Remove an aliquot of sample collected in the centrifuge tube (normally 10 mL), record the volume in LIMS and add the aliquot to a plastic liquid scintillation vial.

11.5.10 Add the appropriate amount of LSC cocktail. Add quenching agent (normally 20 uL) to bring the quench value within the quench limits of the calibration. Cap and shake the vial to mix the sample and the cocktail.

11.5.11 Prepare a background by adding 10 mL of fossil water and 13 mL of scintillation cocktail into a scintillation vial. Add quenching agent (normally 20 µL) to each vial. Cap the vial and shake vigorously to cause complete dissolution in the cocktail.

11.5.12 Wipe each sample vial with methanol and place in a counting rack.

11.5.13 Submit samples and completed paperwork to the count room for liquid scintillation counting analysis.

12.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

NOTE: Client contractual QC requirements override the requirements in this section.

12.1 Analyst and Method Verification Requirements

Refer to GL-RAD-D-002 for information concerning method validation.

12.2 Method Specific Quality Control Requirements

12.2.1 A Matrix Spike (MS) should be run with every batch of 20 or less samples. The recovery of the spike should fall between 75 and 125%.

12.2.2 A sample DUP should be run with every batch of 20 or less samples. If both the sample and DUP values are greater than 5 times the Contract Required Detection Limit (CRDL), the allowable Relative Percent Difference (RPD) is less than or equal to 20%. If the sample and the DUP values are greater than or equal to the CRDL and less than 5 times the CRDL, the allowable RPD is less than or equal to 100%. The RPD is not applicable if either sample or DUP values are less than the CRDL.

12.2.3 A Method Blank (MB) should be run with each batch of 20 or less samples. The MB reported value should be less than or equal to the CRDL.

12.2.4 A Laboratory Control Sample (LCS) should be run with each batch of 20 or less samples. The LCS recovery should fall between 75 and 125%.

12.3 Actions Required if the Quality Control Requirements Are Not Met

If any of the above criteria cannot be satisfied, the analyst should inform the Group Leader and initiate a Data Exception Report (DER) as outlined GL-QS-E-004.

13.0 INSTRUMENT CALIBRATION, STANDARDIZATION AND PERFORMANCE

13.1 Instrument Calibration

NOTE: Source prep is only performed under the guidance of a Team Leader or Group

Leader.

NOTE: To optimize quench curve, a darker brown colorant quenching agent should be prepared by dissolving 0.05 g in 50 mL of DI water.

13.1.1 Prepare a set of standards consisting of 8 to 12 standards using the same matrix and cocktail as the samples to be measured. Add approximately 10,000 dpm to each standard, cap and shake. DO NOT add any quenching agent at this point.

13.1.2 Allow the standards to dark-adapt.

13.1.3 Using any available counting program, measure the observed cpm of each of the standards to verify accurate pipetting. All standards must agree within +/-5% of the mean. Discard any standards that do not meet this criterion.

13.1.4 Add varying amounts of quenching agent to each of the quench standards. DO NOT add quenching agent to the first standard.

13.1.5 Recount each of the standards to determine if the range of quench values covers the desired range of sample quench. If the range of the standards is not large enough, adjust the amount of quenching agent appropriately.

13.1.6 Once it has been determined that a valid set of quench standards have been prepared, submit the standards to the count room for calibration of the instrument.

13.1.7 Prepare a set of 8 to12 verification standards which are at or near the activity of the quench standards (approximately 10,000 dpm). If there is no standard of sufficient activity available, the Group Leader or designee can approve the use of a lower activity standard. The verification standards must be made with a different standard than was used for original quench standard set.

13.1.8 Add the same amounts of quenching agent to each of the verification standards that were added to the original quench standards, ensuring not to add quenching agent to the first standard.

13.1.9 Submit the verification standards to the count room for counting.

13.2 Instrument Performance Requirements

Refer to GL-RAD-I-004, for instrument performance requirements.

14.0 PROCEDURE FOR ANALYSIS AND INSTRUMENT OPERATION

Refer to GL-RAD-I-004 for performance requirements.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Refer to GL-RAD-I-004 for instructions concerning instrument maintenance.

16.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

Data recording, calculation and reduction take place in accordance with GL-RAD-D-006.

17.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

Data are reviewed and packaged in accordance with GL-RAD-D-003 for Data Review, Validation and Data Package Assembly.

18.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as Quality Documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND DISPOSAL

Laboratory waste is disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

20.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, USEPA, Method 906.0, August 1980.

20.2 Standard Methods for the Examination of Water and Wastewater, 14th Edition, American Public Health Association, Washington, DC, 1976.

20.3 Sample Preparation and Analysis of Tritiated Water Extracted from Solid Samples. Lockheed Analytical Services, 1994.

20.4 Eichrom Technologies, Inc. Analytical procedures. OTW02 rev 1.0 Tritium in Water.

20.5 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.3. May, 2019.

21.0 HISTORY

Revision 19: Updated SOP to include liquid scintillation high density polyethylene vials to apparatus and equipment section.
Revision 20: Updated SOP to include the inspection of glassware prior to use.
Revision 21: Updated amount of quenching agent used in sample preparation from 10 µL to 20 µL. Type II DI water to Type I. Equipment used in sample preparation updated.
Revision 22: Added Appendix 1 for the assembly and packaging for silica gel cartridges. Added current reference to DOD/DOE QSAS version 5.1 and 3.1
Revision 23: Removed the use of Queue Sheets and updated DOD QSM Version 5.3, May 2019.

APPENDIX 1: ATMOSPHERIC MOISTURE COLLECTION CANISTER PREPARATION

NOTE: Both new and waste silica gel require the following treatment steps prior to package and assembly of the cartridges. Inspect the waste silica gel for possible reuse. The waste silica gel may be reused as long as it has not begun to degrade (e.g. black particles have formed with the silica gel and/or blue color is dull).

Procedure:

1. Heat silica gel in a drying oven or muffle furnace for at least 6 hours at approximately 300° C.
2. Cap the drying container with a drying tube assembly and allow the silica gel to cool to room temperature.
3. Pour the dried silica gel into an atmospheric moisture collection canister.
4. Assemble the screw-top mechanism and clip the hose connectors together.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF RADIUM-226

(GL-RAD-A-008 REVISION 15)

APPLICABLE TO METHOD:
EPA 600/4-80-032 Method 903.1 (Modified)
DOE EML HASL-300 Method Ra-04-RC (Modified)

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF RADIUM-226

2.0 METHOD OBJECTIVE, PURPOSE, AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for Radium-226 in various matrices.

2.2 This method has been modified on the basis of GEL's Performance Based Measurement System (PBMS).

2.3 Solid matrices are decomposed by digestion in accordance with GL-RAD-A-015 for Digestion for Soil. The digestate is evaporated to dryness and diluted to known volume with nitric acid solution. A stream of nitrogen or helium gas is purged through the sample to initially remove radon from a water sample or solid sample digestate. The sample is then sealed and radon is allowed to ingrow. The radon, which is supported entirely by Ra-226 in the sample, is then purged with helium and trapped on a liquid nitrogen cold trap. The trap is sealed and warmed. The radon is then transferred by vacuum to a Lucas cell and counted after three hours in the cell.

3.0 METHOD SCOPE, APPLICABILITY AND DETECTION LIMIT

3.1 GEL Laboratories LLC (GEL) utilizes methods that are derived from established sources. This method has been modified from the source method EPA 600/4-80-032 "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," August 1980, Method 903.1, and uses the same principles of radiochemical concentration and counting. EPA Method 903.1 is written for drinking water. This method has been modified to accommodate various matrices as discussed in section 11.0.

3.2 Method Detection Limit (MDL): typical minimal detectable activity (MDA) for samples analyzed for Ra-226 is 1pCi/L or 1pCi/G.

4.0 METHOD VARIATIONS

Some variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group Leader or Team Leader. Variations to a method will be documented with the analytical raw data.

5.0 DEFINITIONS

5.1 AlphaLIMS: The data system used at GEL Laboratories LLC.

5.2 Batch: Environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

5.3 Deionized (DI) water: Type I DI water. Refer to GL-LB-E-016.

5.4 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes.

5.5 Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

5.6 Matrix Spike (MS): Prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

5.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike is prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

5.8 Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures.

5.9 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

6.0 INTERFERENCES

The analysis of samples for Ra-226 content by Rn-222 emanation is very specific using this procedure, and the separation of radium from other elements is not required. Sample losses can occur only as the result of improper sample transfer. Due to the specific nature of Ra-226 measurement by this method, the use of stable barium carrier or radioactive Ba-133 tracer for yield monitoring is not required.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Personnel performing this analytical procedure are trained to the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for Handling Biological Materials.

7.4 If there is any question regarding the safety of any laboratory practice, stop immediately, and consult qualified senior personnel such as a Group or Team Leader.

8.0 APPARATUS, EQUIPMENT AND INSTRUMENTATION

8.1 Apparatus and Equipment

8.1.1 De-emanation system with cold trap

8.1.2 Liquid nitrogen Dewars

8.1.3 1 Liter plastic bottles

8.1.4 Amber latex tubing

8.1.5 Small tubing clamps

8.1.6 Lucas cells

8.1.7 Teflon beakers

8.1.8 HI-pore diffusers

8.1.9 Graduated cylinder 500 mL

8.1.10 Teflon watch glasses

8.2 Instrumentation

8.2.1 Radon flask counter with scalar

9.0 REAGENTS AND STANDARDS

9.1 Reagents

9.1.1 All chemicals should be of reagent grade or equivalent whenever they are commercially available.

9.1.2 Deionized water (DI): Type I water

9.1.3 Concentrated nitric acid (16 M HNO_3)

9.1.4 Boric acid, granular, A.C.S. grade

9.1.5 Liquid nitrogen (LN)

9.2 Standards

9.2.1 NIST traceable Ra-226 standard

9.2.2 Refer to GL-RAD-M-001 for instructions concerning the preparation of standard solutions.

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Soil samples require no preservation and may be shipped in any suitable container.

10.2 Water samples should be collected in plastic bottles and preserved with concentrated nitric acid to pH < 2.

10.3 Before beginning an analysis, the analyst should check the sample pH by removing a minimal amount of sample with a transfer pipette and placing it on a pH strip. DO NOT insert pH strip into sample container. If the sample is received with a pH greater than 2, the analyst should adjust the pH with Nitric Acid to a pH < 2. If the sample pH is adjusted, let the sample sit in the original container for a minimum of 24 hours before analysis. This acidification should be documented on a batch history sheet and attached to the batch paper work.

11.0 SAMPLE PREPARATION

NOTE: Aliquot size may be estimated by using the count time estimator spreadsheet.

11.1 Solid matrices

NOTE: Alternatively, Ra-226 analysis in solid matrices can be completed as detailed in the Gamma Spectroscopy SOP, GL-RAD-A-013.

11.1.1 Transfer an appropriate aliquot (typically 1g) of sample to a labeled Teflon beaker. If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced on the Queue sheet. Record all aliquots on the Queue sheet. The Blank and LCS aliquot should be recorded on the Queue sheet to be the same aliquot as the largest sample in the batch. Prepare the MB and LCS with a small amount of nitric acid.

NOTE: Unless the client provides a blank filter for this analysis, there is no appropriate material identified for the MB and LCS.

11.1.2 Add 0.1 mL of working Ra-226 standard to MS, MSD, LCS and LCSD as applicable. Record standard IDs and volumes on the Queue sheet.

NOTE: The addition of tracers and spikes should be witnessed by either another analyst qualified on this procedure, a Team Leader or a Group Leader. After adding the tracers and spikes, the witness must initial and record the date of witnessing on the Queue sheet.

11.1.3 For analyses that require sample dissolution, digest solid samples as detailed in GL-RAD-A-015.

11.1.4 Dissolve the sample residue in 5 mL conc. nitric acid and transfer to a labeled de-emanation bottle. Dilute to 500 mL with DI water.

11.1.5 Proceed to Step 11.2.4 of this procedure.

11.2 Water samples

11.2.1 Transfer an appropriate aliquot (typically 500 mL) of sample to a labeled de-emanation bottle. Record aliquots on the Queue sheet.

NOTE: Each airtight cap should be placed on an empty nalgene bottle and checked for leaks before each use.

11.2.2 Prepare a MB and LCS using DI water and a small amount of Nitric acid to a pH<2. The volume should be the same as the largest volume of sample used in the batch and should be recorded on the Queue sheet.

11.2.3 Add 0.1 mL of working Ra-226 standard to MS, MSD, LCS and LCSD as applicable. Record standard IDs and volumes on the Queue sheet.

NOTE: The addition of tracers and spikes should be witnessed by either another analyst qualified on this procedure, a Team Leader or a Group Leader. After adding the tracers and spikes, the witness must initial and record the date of witnessing on the Queue sheet.

11.2.4 To remove radon from the sample, purge for at least 30 minutes with helium or nitrogen at a flow rate vigorous enough to remove radon from sample.

11.2.5 At the end of the degassing, seal the sample by connecting the inlet and outlet lines together. Record the date and time as the END INIT DEGAS DATE/TIME on the sample Queue sheet. Allow the sample to ingrow for a minimum of three days.

NOTE: Before proceeding to Step 11.2.6 it is advisable to begin acquiring background checks on the Lucas cells that will be used during the sample de-emanation process.

11.2.6 Fill the Dewars with liquid nitrogen. Lift the platform holding the Dewars to completely submerge the cold trap in LN. Allow the cold trap to equilibrate before proceeding.

11.2.7 Refer to Figure 1 for Operation of Radon Emanation Line. Connect the sample to lines V-3 and V-4 and ensure that the connections are secure. Turn valves V-3 and V-4 to the sample position. Bubbles should be visible as the helium is now purging the radon into the cold trap. Monitor the purging of the sample. Allow the helium to flow for approximately 15 minutes. Afterwards, record the date and time of the sample de-emanation as the END LN DE-EM DATE/TIME on the Queue sheet.

11.2.8 After approximately 15 minutes, turn valves V-5 and V-6 to the closed position. This will seal the cold trap that now contains the sample radon. The cold trap contains brass filings to create surface area for radon condensation. Turn valves V-3 and V-4 to the bypass position.

11.2.9 Connect the Lucas cell to the system. Pull a vacuum on the system by turning on the vacuum pump and opening valve V-7. With cold trap still under LN quickly open and close valve V-6 to remove excess helium.

11.2.10 Ensure that valves V-5 and V-6 are closed. Pull a vacuum on the system and the Lucas cell by turning on the vacuum pump and opening the valve V-7.

11.2.11 Close valve V-7 and turn off the vacuum pump. Check the system for leaks by observing the vacuum gauge for approximately 30 seconds. The vacuum gauge should hold vacuum at -20 to -30 psi. If the vacuum does not hold, notify your Group Leader or Team Leader.

11.2.12 Remove the LN Dewar and gently warm the trap with warm water and/or a hot air gun. The trap should feel warm to the touch before proceeding.

11.2.13 Open valve V-6 to the vacuum system. Place hands on valves V-5 and V-6. Keep eyes on the vacuum gauge. Open valve V-5 and close valve V-6 just before the vacuum pressure goes to zero.

NOTE: The pressure will drop fast so be alert to the clockwise direction required to close valve V-6.

NOTE: If the zero (atmospheric pressure) is slightly passed the sample may still be counted. The analyst is trying to avoid creating a large positive pressure within the Lucas cell, which may cause the cell to leak or rupture.

11.2.14 Allow the radon to equilibrate in the line for approximately 30 seconds. Disconnect the Lucas cell and allow the radon daughters to equilibrate for a minimum of three hours before counting the cell. Place the cell in the counter for approximately 5 minutes before beginning the sample count.

11.2.15 Count each sample for a minimum of 15 minutes. Record the date and time the count is started, the count time and the gross counts observed as the START COUNT DATE/TIME on the Queue sheet.

NOTE: Sample activity levels can be verified using a re-transfer technique. This is done by taking a sample that has been previously transferred to a de-emanation bottle and repeating steps 11.2.4 through 11.2.15.

11.2.16 The Lucas cell should be cleaned as soon as possible after the sample count is completed. The Lucas cell cleaning apparatus is connected to the helium and the vacuum.

11.2.17 Connect the Lucas cell to the cleaning apparatus. Turn on the vacuum pump and the helium inlet valve. Turn on the relay to flush and evacuate the cell for at least two minutes.

11.2.18 Store the cell under a slightly positive helium pressure until the next use. The cell should be stored for a minimum of three hours prior to use for sample analysis.

12.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

NOTE: Client contractual QC requirements override the requirements in this section.

12.1 Analyst and Method Verification Requirements

Refer to GL-RAD-D-002 for instructions concerning the validation of analytical methods.

12.2 Method Specific Quality Requirements

12.2.1 A Method Blank (MB) should accompany each batch of 20 or less samples. The reported value of the blank should be less than or equal to the CRDL (contract required detection limit).

12.2.2 The tracer added to all samples issued to calculate the method recovery. The method recovery of all samples should be between 25-125% when compared to the reference standard.

12.2.3 A Matrix Spike (MS) should be run with each batch of 20 or less samples. The recovery of the MS should be between 75-125%.

12.2.4 A Duplicate sample should be run with each batch of 20 or less samples. The relative percent difference (RPD) between the actual sample and the QC DUP results should be less than or equal to 20% if both the sample and QC DUP results are greater than 5 times the LLD or 100% if either result is less than 5 times the LLD.

12.2.5 A Laboratory Control Sample (LCS) should be run with each batch of 20 or less samples. The recovery of the LCS should fall between 75-125%.

12.3 Actions required if the Quality Control Requirements Are Not Met

12.3.1 If any of the QC criteria from 12.2.1 through 12.2.5 cannot be satisfied, the analyst should inform their group leader and initiate a Nonconformance Report as outlined in GL-QS-E-004.

13.0 INSTRUMENT, CALIBRATION, STANDARDIZATION AND PERFORMANCE

13.1 Ludlum Model 2000 operating voltage, plateau generation and standard deviation:

13.1.1 Place a sealed Lucas Cell Ra-226 source of sufficient activity on the detector approximately 5 minutes before counting. Set the front panel discriminator to 50 volts. Count the source and record the counts.

13.1.2 Step the front panel discriminator up in 50-volt increments and acquire counts at the increasing voltages up to 2000 volts and record counts. Plot the gross counts on the y-axis and the voltage on the x-axis and determine the “knee” of the plateau.

13.1.3 The knee is determined by drawing straight lines along the rising slope and the plateau portions of the curve. The knee is the point where these two lines intersect. The operating voltage should be selected at 50 – 150 volts above the “knee.”

13.1.4 Put a copy of the plateau for model 2000 scaler/radon flask counter in the Ra-226 Calibration File.

13.1.5 To determine the control limits (standard deviation), place a sealed Lucas Cell Ra 226 source of sufficient activity on the detector. Acquire twenty counts and record each count. If the operating voltage remains the same there is no need to establish new control limits.

13.1.6 Put a copy of the counts and calculation of standard deviation in the Ra-226 Calibration File.

13.2 Calibration, cell constant, efficiency and verification of the Lucas Cell:

13.2.1 The analyst should determine which cells need to be calibrated. Calibration is done annually or when a new Lucas cell is received. Give yourself at least 3 weeks before old calibration has expired. Calibration dates are stored in LIMS and are updated by a Group Leader or a Team Leader after the calibration is complete.

13.2.2 Each Lucas Cell needs to be given a two or three digit number (old numbers can be reused). With the first number to each cell will be the detector and rig it goes to. (For example, 120 will go into detector 1 and rig 1, 220 will go into detector 2 and rig 2.) Each lucas cell has one detector it can be counted on and one rig that it can be transferred on.

13.2.3 A background count is performed on each cell before every calibration and verification run and each count is recorded in the logbook.

13.2.4 Each counting cell is calibrated by spiking a 500 mL DI water sample with a known dpm of Ra-226 activity. The sample is carried through the entire procedure. The procedure is performed 3 separate times to each cell. Record each count.

13.2.5 Put information from the three runs in an excel spreadsheet to calculate cell constant, average and standard deviation. Standard deviation needs to be less that 10 % of the cell constant average. Put the Ra-226 cell constant spreadsheet in the Calibration File.

13.2.6 Each counting cell will be verified by spiking 500 mL of DI water with a known dpm of Ra-226 activity. Each verification sample is carried through the entire procedure. Acceptance criteria is 100% ± 25%.

13.2.7 After processing verification, put the spreadsheet in the Ra-226 Calibration File.

13.2.8 When calibration file is complete, the Group Leader or Team Leader will update the CELLEFF file to change the old cell efficiency to the new cell efficiency. The new calibration date will be updated in LIMS and should also be placed on the rig itself at this time.

14.0 ANALYSIS AND INSTRUMENT OPERATION

Refer to GL-RAD-I-007 for instrument operating instructions.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Refer to GL-RAD-I-007 for equipment and instrument maintenance.

16.0 DATA RECORDING, CALCULATION AND REDUCTION METHODS

Date recording, calculation and reduction takes place in accordance with GL-RAD-D-006.

17.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

Data is reviewed and packaged in accordance with GL-RAD-D-003 for Data Review, Validation and Data Package Assembly.

18.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND DISPOSAL

Laboratory waste is disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

20.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, USEPA, Method 903.1, August, 1980.

20.2 Mathieu, G.G., Biscaye, P.E., Lupton, R.A. "A System for Measurement of Rn-222 at Low Levels in Natural Waters." Health Physics, Vol. 55, No.6, pp. 989-992. 1988.

20.3 Key, R.M., Brewer, R.L., Stockwell, J.H., Guinasso, N.L., Schink, D.R., "Some Improved Techniques for Measuring Radon and Radium in Marine Sediments and Seawater. Marine Chemistry, pp. 251-264. October 30, 1978.

20.4 Special thanks to Dr Bill Burnett and his associates at Florida State University for their help in building the radon de-emanation system.

20.5 EML procedures manual. HASL-300-Ed. 28, 1997, Ra-04-RC, Vol. 1.

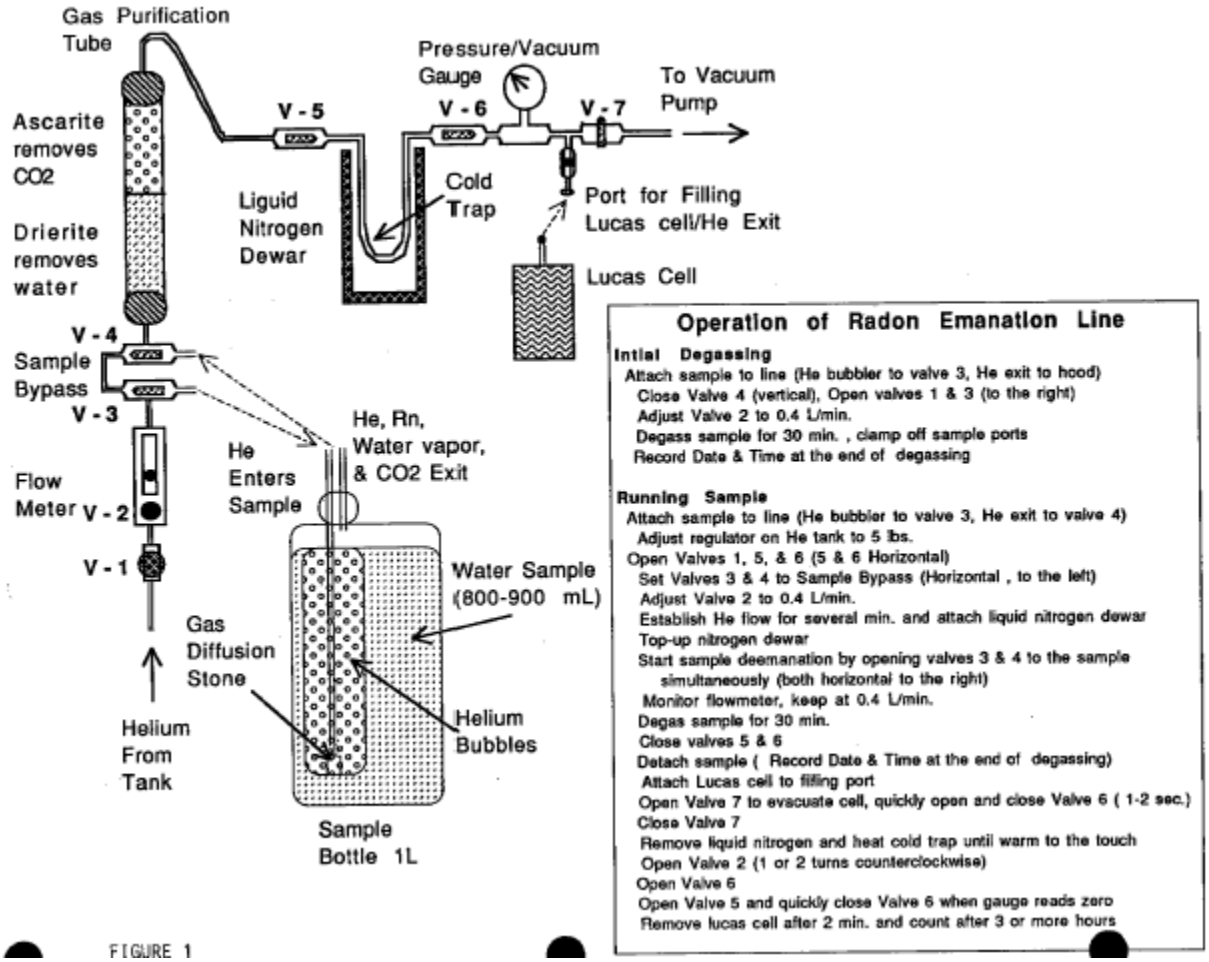
21.0 HISTORY

Revision 13: Texas audit finding, updates made to comply with NELAC standard.

Revision 14: Updated water sample preservation to pH<2. Type II to type I DI water.

Revision 15: Added a NOTE: for verification of sample activity level using re-tranfer technique.

FIGURE 1



Operation of Radon Emanation Line

Intial Degassing

Attach sample to line (He bubbler to valve 3, He exit to hood)
Close Valve 4 (vertical), Open valves 1 & 3 (to the right)
Adjust Valve 2 to 0.4 L/min.
Degass sample for 30 min. , clamp off sample ports
Record Date & Time at the end of degassing

Running Sample

Attach sample to line (He bubbler to valve 3, He exit to valve 4)
Adjust regulator on He tank to 5 lbs.
Open Valves 1, 5, & 6 (5 & 6 Horizontal)
Set Valves 3 & 4 to Sample Bypass (Horizontal , to the left)
Adjust Valve 2 to 0.4 L/min.
Establish He flow for several min. and attach liquid nitrogen dewar
Top-up nitrogen dewar
Start sample deemanation by opening valves 3 & 4 to the sample simultaneously (both horizontal to the right)
Monitor flowmeter, keep at 0.4 L/min.
Degas sample for 30 min.
Close valves 5 & 6
Detach sample (Record Date & Time at the end of degassing)
Attach Lucas cell to filling port
Open Valve 7 to evacuate cell, quickly open and close Valve 6 (1-2 sec.)
Close Valve 7
Remove liquid nitrogen and heat cold trap until warm to the touch
Open Valve 2 (1 or 2 turns counterclockwise)
Open Valve 6
Open Valve 5 and quickly close Valve 6 when gauge reads zero
Remove lucas cell after 2 min. and count after 3 or more hours

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE
FOR
THE DETERMINATION OF RADIUM-228
IN WATER AND SOLIDS

(GL-RAD-A-009 REVISION 17)

APPLICABLE TO METHOD:
EPA 600/4-80-032, Method 904.0 (Modified)

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1.0 STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF RADIUM-228 IN WATER AND SOLIDS

2.0 METHOD OBJECTIVE, PURPOSE, CODE AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for Radium-228 in water and solids.

2.2 The modifications to this method are based on GEL's Performance Based Measurement System (PBMS).

2.3 Liquid samples are preconcentrated by a Barium Sulfate precipitation and converted to a Barium Carbonate. Solid samples are digested according to GL-RAD-A-015 then concentrated with a Carbonate precipitation. Both types of samples are then dissolved in weak Nitric Acid for column separation and final source preparation.

3.0 METHOD SCOPE, APPLICABILITY AND DETECTION LIMIT

3.1 Although this method has been modified from EPA 600/4-80-032 Method 904.0 and EPA 520/5-84-006, it uses the same principles of final source preparation, radiochemical concentration and counting. This method is also similar in concept to the source method from "Radiochemical Analytical Procedures for Analysis of Environmental Samples," EPA Environmental Monitoring and Support Laboratory, Las Vegas, 1979.

3.2 Method Detection Limit (MDL): Typical Minimum Detectable Activity (MDA) for samples analyzed for Ra-228 is 3 pCi/L or 3 pCi/g.

3.3 Analyst training records are maintained as Quality Records. Refer to GL-QS-E-008. Analyst training and proficiency in the method is outlined in GL-QS-E-011 for Method Validation and Initial and Continuing Demonstrations of Capability.

4.0 METHOD VARIATIONS

Some variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group Leader or Team Leader. Variations to a method will be documented with the analytical raw data.

5.0 DEFINITIONS

5.1 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel using the same lot(s) of reagents.

5.2 Deionized (DI) water: Type I water. Refer to GL-LB-E-016.

5.3 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes.

5.4 Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

5.5 Matrix Spike (MS): Prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

5.6 Matrix Spike Duplicate (MSD): A second replicate matrix spike is prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

5.7 Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures.

5.8 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

6.0 INTERFERENCES/LIMITATIONS

6.1 When converting Barium Sulfate to the Carbonate it is important to remove excess Sulfate or the Potassium Carbonate will be consumed by the reaction:

$$K_2CO_3 + H_2SO_4 \text{ --> } K_2SO_4 + H_2O + CO_2$$

6.2 Samples with high Sr-90 may cause interference in the Ac-228 beta count. This problem occurs because of Y-90 present that may follow the Ac-228 chemically. It is best to confirm high Ra-228 (i.e. greater than 5 pCi/L) by Gamma Spectroscopy.

6.3 Samples with elevated radioactive Lead may cause interference in the Ac-228 beta count. It is best to confirm high Ra-228 (i.e. greater than 5 pCi/L) by Gamma Spectroscopy.

6.4 Th-234 would potentially interfere with Ac-228 beta counting. Its presence could be confirmed with a decay curve analysis.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Personnel performing this analytical procedure are trained to the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for The Handling of Biological Materials.

7.4 If there is any question regarding the safety of any laboratory practice, stop immediately, and consult qualified senior personnel such as a Group or Team Leader.

8.0 APPARATUS, EQUIPMENT, AND INSTRUMENTATION

8.1 Apparatus and Equipment

8.1.1 Watch glasses

8.1.2 Centrifuge

8.1.3 50 mL centrifuge tubes

8.1.4 Beakers-glass and Teflon of various sizes

8.1.5 Stirring rods

8.1.6 Stainless steel planchets

8.1.7 Disposable filter funnels

8.1.8 1 1/4" x 0.16" stainless steel disc

8.1.9 47 mm glass fiber filters

8.1.10 Hot plate

8.1.11 Titration apparatus

8.1.12 LN Spec resin (Eichrom)

8.1.13 Microwave

8.1.14 Freezer

8.1.15 TRU spec resin (Eichrom)

8.2 Instrumentation

8.2.1 Gross Alpha/Beta Proportional Counting System

8.2.2 Gamma Spectrometer and associated electronics and data reduction package.

9.0 REAGENTS AND STANDARDS

9.1 Reagents

NOTE: All chemicals should be of reagent grade or equivalent whenever they are commercially available.

9.1.1 Acetic Acid, glacial (CH_3COOH)

9.1.2 1.5 M Ammonium Sulfate [1.5 M $(NH_4)_2SO_4$]: Dissolve 200 g Ammonium Sulfate in 1 L DI water.

9.1.3 Barium Carrier (16 mg Ba/mL): Dissolve 28.46 grams reagent grade Barium Chloride ($BaCl_2 \bullet 2H_2O$) in 800 mL DI water. Add 5 mL concentrated Nitric Acid and dilute to 1 L with DI water.

9.1.4 Cerium Carrier (500 mg/L): Preferably, use Ce 500 mg/L o2si standard. Alternatively, dissolve 0.155 g Cerium in 100 mL DI water.

9.1.5 1 M Citric Acid ($C_6H_8O_7$): Dissolve 192.13 g Citric Acid anhydrous powder in 1 L DI water.

9.1.6 Deionized (DI) water—Type I water

9.1.7 Deionized (DI) water, pH 10. Add Ammonium Hydroxide (NH_4OH) dropwise until pH of 10 is reached.

9.1.8 80% Ethanol: Dilute 400 mL Ethanol to 500 mL with DI water.

9.1.9 3 M Hydrochloric Acid: Add 250 mL concentrated Hydrochloric Acid to 500 mL DI water and dilute to 1 L with DI water.

9.1.10 12 M Hydrochloric Acid, concentrated (HCl)

9.1.11 49% Hydrofluoric Acid, concentrated (HF)

9.1.12 0.090 M Nitric Acid (HNO_3): Add 5.5 mL concentrated Nitric Acid to 500 mL DI water and dilute 1000 mL with DI water in volumetric flask.

9.1.13 0.35 M Nitric Acid (HNO_3): Add 11.0 mL concentrated Nitric Acid to 200 mL DI water and dilute to 500 mL with DI water in volumetric flask.

9.1.14 0.5 M Nitric Acid: Add 32 mL concentrated Nitric Acid to 500 mL DI water and dilute to 1 L with DI water.

9.1.15 8 M Nitric Acid (HNO_3): Add 500 mL concentrated Nitric Acid to 400 mL DI water, allow to cool, then dilute to 1000 mL with DI water.

9.1.16 16 M Nitric Acid, concentrated (HNO_3)

9.1.17 Phenolphthalein indicator

9.1.18 50% (w/w) Potassium Carbonate (K_2CO_3)

9.1.19 0.75 M Sodium Carbonate (Na_2CO_3): Add 79.5 g Sodium Carbonate to 500 mL DI water and dilute to 1000 mL with DI water.

9.1.20 6 N Sodium Hydroxide (NaOH): Cautiously add 120 g Sodium Hydroxide pellets to approximately 300 mL with DI water. When cool, dilute to 500 mL with DI water.

9.1.21 Thymol Blue indicator

9.2 Standards

Refer to GL-RAD-M-001 for instructions concerning the preparation of standard solutions.

9.2.1 NIST traceable Ba-133 standard

9.2.2 NIST traceable Ra-228 standard

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Water samples should be collected in plastic bottles and preserved with concentrated Nitric Acid to a pH < 2.

10.2 Before beginning an analysis, the analyst should check the sample pH by removing a minimal amount of sample with transfer pipette and placing it on a pH strip. **DO NOT** insert pH strip into sample container. If the sample is received with a pH greater than 2, the analyst should contact the Group Leader or Team Leader. If approved by the client, the analyst should adjust the pH with Nitric

Acid to a pH < 2. If the sample is pH adjusted, let the sample sit in the original container for a minimum of 24 hours before analysis.

11.0 SAMPLE PREPARATION

NOTE: Sample aliquot size may be estimated using the count time estimator spread sheet.

11.1 Sample Preparation Techniques for Gas Flow Proportional Counting in Water

11.1.1 Measure an appropriate aliquot of water sample into a beaker. If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced on the Queue sheet. Prepare a MB and LCS by using DI water and concentrated Nitric Acid to a pH < 2. The MB and LCS volume should be equivalent to the largest aliquot in the batch and should be recorded on the Queue sheet.

NOTE: If liquid samples contain sediment, they should be filtered through a glass fiber filter (collecting liquid portion) prior to analysis.

11.1.2 Add Ba-133 tracer (typically 0.1 mL) to all samples and add an appropriate amount (typically 0.1 mL) of Ra-228 spike to MS, MSD, LCS and LCSD as applicable.

NOTE: Spiking and tracing steps should be witnessed by either another analyst qualified in this procedure or the Team Leader/Group Leader responsible for this procedure. After adding tracers and spikes, the witness must initial and record the date of witnessing.

11.1.3 Then add to all samples: 1 mL Barium Carrier ($BaC1_2$), 10 mL glacial Acetic Acid, 5 mL 1 M Citric Acid, 10 mL 1.5 M Ammonium Sulfate. Let sit overnight or until the precipitate settles.

11.1.4 Decant or aspirate the clear supernate. Transfer the remaining precipitate to a 50 mL centrifuge tube with DI water, let precipitate settle, and centrifuge.

11.1.5 Decant centrifuge tube and remove excess Sulfate by washing the precipitate with DI water from a wash bottle. Let precipitate settle.

11.1.6 Centrifuge and decant the DI water wash. Check the pH of the wash solution with a pH strip.

11.1.7 Repeat the washing as necessary until a pH of approximately 6 is observed.

11.1.8 Add 2 mL of 50% Potassium Carbonate (K_2CO_3) to the precipitate making sure the precipitate is completely submerged in the solution.

11.1.9 Heat in water bath at approximately 90° F for approximately 4 hours.

11.1.10 Wash the slurry with approximately 50 mL DI water, let precipitate settle, centrifuge and decant the supernate. Check the pH of the wash

solution. It should initially be around 12. If a high pH is not observed consult the appropriate Group Leader or Team Leader.

11.1.11 Wash the precipitate with approximately 50 mL of DI water, let precipitate settle, centrifuge and decant. Repeat washings until the pH of the wash solution is approximately 7.

11.1.12 Dissolve the precipitate in 10 mL of 0.090 M Nitric Acid solution. Centrifuge the solution and decant into a 20 mL scintillation vial. Record date and time of Actinium ingrowth on the Queue sheet.

11.1.13 Add Ba-133 tracer (typically 0.1 mL) to 10 mL of 0.090 M Nitric solution in a 20 mL liquid scintillation vial. This solution will serve as the reference for standard yield determination.

11.1.14 Count the samples and the reference vial on a Gamma Spectrometer to determine Ba-133 yield.

11.1.14.1 Typically, samples and reference are counted on Gamma Wizard. Refer to GL-RAD-I-018 for operation.

11.1.14.2 Samples and Reference can also be counted on high purity Germanium detectors. Refer to GL-RAD-I-001. The samples and reference should be given a sample identification number, an identical reference date and counting geometry. Divide the result by the reference result to determine the chemical yield.

NOTE: Reference the date, time, geometry, and sample volume. The volume must be the same for all samples and reference standard in order to perform yield determination by direct comparison.

11.1.15 Allow the sample to ingrow for approximately 30 hours from the time the 10 mL of 0.090 M Nitric Acid was added to the centrifuge tubes (this is also the time of ingrowth recorded on the Queue sheet).

NOTE: The following steps should be performed as rapidly as possible to avoid decay of unsupported Ac-228 with a half-life of 6.13 hours.

11.1.16 Pre-rinse a LN Spec column with two 5 mL rinses of 0.090 M Nitric Acid.

11.1.17 Load sample onto the column and record elution time on Queue sheet. Rinse with 9 mL of 0.090 M Nitric Acid by adding in 3 mL increments allowing previous volume to completely drain. Collect the effluent into a labeled centrifuge tube and save in the event reanalysis is required.

11.1.18 Elute the Ac-228 with 15 mL of 0.35 M Nitric Acid into labeled plastic centrifuge tube.

11.1.19 Add 200 µL of 500 mg/L Cerium carrier to the samples and swirl. Add 2 mL of concentrated HF, swirl and allow to stand for at least 30 minutes.

11.1.20 Place disposable filter funnel onto filter rig. Check to ensure proper placement of filter in funnel.

11.1.21 Rinse the filter and funnel under vacuum with 80% Ethanol. With minimum delay, add the sample to the filtering apparatus and rinse the centrifuge tube several times into the funnel with DI water. Complete the filtering by rinsing the funnel with 80% Ethanol after the entire sample has passed through the filter.

11.1.22 Label a 47 mm flat planchet. Place double sided tape on the planchet and place a 1¼" x 0.16" stainless steel disc with double sided tape on one side in the middle of the planchet. Carefully place the filter (precipitate side up) on the middle of the disc. Care should be taken to make the filter as flat as possible on the disc.

11.1.23 Turn filters and completed paperwork into countroom for Gas Flow Proportional counting analysis.

11.2 Re-elution Technique

NOTE: Re-elution may be used to verify sample activity or in the event of reanalysis.

11.2.1 Count the sample saved in step 11.1.17 on the Gamma Spectrometer along with a reference that contains the same volume.

11.2.2 Allow the sample to ingrow for at least 30 hours from the time of the last elution. Record the date and time on the Queue sheet as the ingrowth time.

11.2.3 Pre-rinse an LN Spec column with 10 mL of 0.090 M Nitric Acid.

11.2.4 Load the sample onto the column and record the elution time when the sample is approximately halfway through the column. Add an additional 5 mL of 0.090 M Nitric Acid. Repeat this step for a total of 10 mL. Collect and save the effluent. Proceed to step 11.1.18.

11.3 Re-precipitation Technique

NOTE: Re-precipitation may be used to verify activity or in the event of reanalysis when re-elution has already taken place.

11.3.1 Add 2 drops Thymol Blue and add 6 N Sodium Hydroxide (NaOH) dropwise until sample turns blue.

11.3.2 Add 5 mL of 0.75 M Sodium Carbonate (Na_2CO_3). Microwave for 30 seconds or until you see precipitation. Allow to cool.

11.3.3 Centrifuge and decant supernate.

11.3.4 Proceed to step 11.1.12.

11.4 Procedure for Sample Preparation of Soils and Difficult Matrices

11.4.1 For solid samples, transfer an aliquot to analyze to a glass beaker. Record aliquot information on Queue sheet. If required, the DUP, MS and MSD

should be the same aliquot as the appropriate sample referenced on the Queue sheet. Record the aliquot for the MB and LCS as the largest aliquot in the batch on the Queue sheet.

11.4.2 Add Ba-133 tracer (typically 0.1 mL) to all samples and spike MS, MSD, LCS, and LCSD as appropriate, with Ra-228 standard (typically 0.1 mL).

NOTE: Spiking and tracing steps should be witnessed by either another analyst qualified in this procedure or the Team Leader/Group Leader responsible for this procedure. After adding tracers and spikes, the witness must initial and record the date of witnessing.

11.4.3 It is recommended that the samples be ashed in a muffle furnace as specified in GL-RAD-A-021B and digested as specified in GL-RAD-A-015. Once digested, add 5 mL of concentrated Nitric Acid to Teflon beaker to dissolve residue.

NOTE: If sample aliquot used is greater than approximately 0.1 g or sample contains significant amount of Iron, use the following step. If not, proceed to step 11.4.5. Determining the precipitation routine is based on analyst experience with the matrix and sample composition.

11.4.4 Transfer the 5 mL concentrated Nitric Acid solution to a glass beaker and dilute to approximately 300 mL with DI water. Proceed to step 11.1.3 or alternatively proceed to step 11.4.6.

11.4.5 Transfer the 5 mL concentrated Nitric Acid solution to a disposable centrifuge tube.

11.4.6 Add 1 mL Barium Carrier and dilute to approximately 20 mL with DI water.

11.4.7 Add 2 drops of Phenolphthalein solution. Add 6 M Sodium Hydroxide dropwise until the sample turns pink. Add 10 mL of 0.75 M Sodium Carbonate.

11.4.8 Microwave samples for approximately 15 seconds.

11.4.9 Allow the centrifuge tube to cool then centrifuge for 5 minutes.

11.4.10 Pour off the supernate then rinse the precipitate with pH 10 DI water. Centrifuge again for 5 minutes and decant.

11.4.11 Dissolve the precipitate completely in 0.090 M Nitric Acid. This may require gentle heating and up to 20 to 35 mL of 0.090 M Nitric Acid.

11.4.12 Record date and time of Actinium ingrowth. Centrifuge solution and decant into a 20 mL scintillation vial. Proceed to step 11.1.14.

11.5 Procedure for Difficult Liquid Samples Containing Large Amount of Sediment

11.5.1 Measure an appropriate aliquot into a beaker. Record the volume on the Queue sheet. If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced on the Queue sheet.

Prepare a MB and LCS by using DI water and concentrated Nitric Acid to a pH < 2. The MB and LCS volume should be equivalent to the largest aliquot in the batch and should be recorded on the Queue sheet.

11.5.2 Add Ba-133 tracer (typically 0.1 mL) and 1.0 mL Barium Carrier ($BaCl_2$) to all samples. Spike appropriate QC samples with Ra-228 standard (typically 0.1 mL).

NOTE: Spiking and tracing steps should be witnessed by either another analyst qualified in this procedure or the Team Leader/Group Leader responsible for this procedure. After adding tracers and spikes, the witness must initial and record the date of witnessing.

11.5.3 Heat samples on a hot plate and evaporate to dryness. Muffle samples as specified in GL-RAD-A-021B for at least four hours.

11.5.4 Add 10 mL of concentrated Nitric Acid and 10 mL of concentrated Hydrochloric Acid. Reflux for at least three hours.

11.5.5 Heat samples and evaporate to dryness. Repeat addition of 10 mL of concentrated Nitric Acid and 10 mL of Hydrochloric Acid. Reflux for 30 minutes or until all solids have leached off the glass.

11.5.6 Transfer leachate to centrifuge tube using 8 M Nitric Acid. Centrifuge and pour liquid into a glass beaker, then heat samples and evaporate to dryness. Transfer pellet into a Teflon beaker using Nitric Acid.

11.5.7 To the liquid portion, add 10 mL of concentrated Nitric Acid, heat samples and evaporate to dryness. Dissolve residue in 10 mL of Nitric Acid.

11.5.8 Digest the pellet according to GL-RAD-A-015 until completely digested. Dissolve the residue in 10 mL of Nitric Acid and combine with the liquid portion.

11.5.9 Transfer sample to a centrifuge tube using 8 M Nitric Acid. Put centrifuge tubes in the freezer for approximately 15 minutes. After samples have cooled, there should be a visible precipitate. Centrifuge and discard supernate.

11.5.10 Add 2 mL of concentrated Nitric Acid and dilute to 30 mL with DI water. Add 2 to 3 drops of Phenolthalein indicator, and titrate with 6 N Sodium Hydroxide until the sample turns pink. Add 5 mL of 0.75 M Sodium Carbonate. Digest in hot water bath until precipitate settles. Centrifuge and discard supernate.

11.5.11 Dissolve pellet in 15 mL of concentrated Nitric Acid and put back in freezer for approximately 15 minutes. Centrifuge and discard supernate.

11.5.12 Repeat step 11.5.11.

11.5.13 Dissolve pellet in 10 mL of 0.090 M Nitric Acid. Record date and time of Actinium ingrowth. Proceed to step 11.1.14.

12.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

NOTE: CLIENT CONTRACTUAL QC REQUIREMENTS OVERRIDE THE REQUIREMENTS IN THIS SECTION.

12.1 Analyst and Method Verification Requirements

Refer to GL-RAD-D-002 for instructions concerning the validation of analytical methods.

12.2 Method Specific Quality Control Requirements

12.2.1 A Method Blank (MB) should accompany each batch of 20 or less samples. The reported value of the blank should be less than or equal to the Contract Required Detection Limit (CRDL).

12.2.2 The Ba-133 tracer added to all samples is used to calculate the method recovery. The method recovery of all samples should be between 15-125% when compared to the reference standard.

12.2.3 A Duplicate (DUP) sample should be run with each batch of 20 or less samples. The Relative Percent Difference (RPD) between the actual sample and the DUP should be less than or equal to 20% if both the sample and the DUP results are greater than 5 times MDC or 100% if both results are less than 5 times MDC. If both results are less than MDC, then limits are not applicable.

12.2.4 A Laboratory Control Sample (LCS) should be run with each batch of 20 or less samples. The recovery of the LCS should fall between 75-125%.

12.3 Actions Required if the Quality Control Requirements Are Not Met

If any of the QC criteria from 12.2.1 through 12.2.4 cannot be satisfied, the analyst should inform the Group Leader and initiate a Data Exception Report as outlined in GL-QS-E-004.

13.0 INSTRUMENT CALIBRATION, STANDARDIZATION AND PERFORMANCE

13.1 Instrument Calibration Source Preparation for Gas Flow Proportional Counters for Ra-228.

NOTE: Source prep is only performed under guidance of Team Leader or Group Leader.

13.1.1 Pre-rinse the same number of Tru-Spec column as detectors that will be calibrated.

13.1.2 Add 5 mL Ra-228 standard in Teflon beaker. Take to dry, and then bring up to 5 mL with 0.5 M Nitric Acid.

13.1.3 Pre-rinse with 5 mL of 0.5 Nitric Acid. Load sample. Rinse twice with 2 mL of 0.5 M Nitric Acid.

13.1.4 Elute with 15 mL of 3 M Hydrochloric Acid.

13.1.5 Proceed to steps 11.1.19 through 11.1.23.

13.2 Verification Source Preparation

Verification sources are prepared using the entire sample preparation process as outlined in section 11.0.

14.0 PROCEDURE FOR ANALYSIS AND INSTRUMENT OPERATION

14.1 Refer to GL-RAD-I-001 or GL-RAD-I-018 for instructions concerning the analysis of the Ba-133 tracer.

14.2 Refer to the appropriate gas flow proportional counting procedure GL-RAD-I-006 or GL-RAD-I-016 for instructions concerning the analysis of the Ac-228.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Refer to GL-RAD-I-010 for instrument maintenance.

16.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

Data recording, calculation, and reduction take place in accordance with GL-RAD-D-003 and GL-RAD-D-006.

17.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

Data are reviewed and packaged in accordance with GL-RAD-D-003 for Data Review, Validation and Data Package Assembly.

18.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND DISPOSAL

Laboratory waste is disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

20.1 “Radiochemical Analytical Procedures for Analysis of Environmental Samples.” March 1979. EPA EMSL.

20.2 “Radiochemistry Procedures Manual.” EPA 520/5-84-006, December 1987, Method Ra-05.

20.3 “Prescribed Procedures for Measurement of Radioactivity in Drinking Water.” EPA 600/4-80-032, August 1980, Method 904.0.

20.4 “Test Methods for Evaluating Solid Waste,” US EPA, June 1997, SW-846.

20.5 Special thanks to Dr. Bill Burnett and his associates for their development of this method at Florida State University.

21.0 HISTORY

Revision 16: Update method recovery from 25% to 15%. Replace nonconformance reports to data exception reports.

Revision 17: Technical updates for SOP consistency as part of annual review.

APPENDIX 1

Ac-228 Separation

Use LN resin column

Column Work

_____ 5 mL 0.090 M HNO_3 (conditioning)

_____ 5 mL 0.090 M HNO_3 (conditioning)

_____ Load sample onto colum and collect in C-tube. Record the Ac-228 separation time on Queue sheet

_____ 3 mL rinse 0.090 M HNO_3, collect in C-tube

_____ 3 mL rinse 0.090 M HNO_3, collect in C-tube

_____ 3 mL rinse 0.090 M HNO_3, collect in C-tube

_____ Cap C-tube and keep for possible Re-Elution

_____ **Elute:** 15 mL 0.35 M HNO_3 and collect in C-tube

_____ Add 200 µL Cerium (500 mg/L) and swirl

_____ Add 2 mL concentrated HF and swirl

_____ Let stand at least 30 min. and filter

APPENDIX 2

Ac-228 Separation by Re-Elution

Use LN resin column and 25 mL column funnel extension

Column Work:

_____ 10 mL 0.090 M HNO_3 (conditioning)

_____ Load sample and collect in C-tube. Record Ac-228 separation time when solution has passed approximately half way through column.

_____ Rinse: 5 mL 0.090 M HNO_3 and collect in C-tube

_____ Rinse: 5 mL 0.090 M HNO_3 and collect in C-tube

_____ Cap C-tubes and keep for possible reprecipitation

_____ **Elute:** 15 mL 0.35 M HNO_3 and collect in C-tube

_____ Add 200 µL Cerium (500 mg/L) and swirl

_____ Add 2 mL concentrated HF and swirl

_____ Let stand at least 30 min. and filter

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

THE ISOTOPIC DETERMINATION OF AMERICIUM, CURIUM, PLUTONIUM, AND URANIUM

(GL-RAD-A-011 REVISION 27)

APPLICABLE TO METHODS:
DOE RP800 1997 (Modified)
EML HASL-300 U-02-RC (Modified)
EML HASL-300 Am-05-RC (Modified)
DOE HASL-300 Pu-11-RC (Modified)
EPA SW-846 3050B (Modified)

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1.0 STANDARD OPERATING PROCEDURE FOR THE ISOTOPIC DETERMINATION OF AMERICIUM, CURIUM, PLUTONIUM, AND URANIUM

2.0 METHOD OBJECTIVE, PURPOSE, CODE, AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for isotopic americium, curium, plutonium, and uranium in a variety of liquid, filter and solid matrices. This method also gives specific guidance on determining U-232, Pu-242 and Am-243, which are typically used as isotopic tracers.

2.2 A soil sample is aliquoted and digested according to GL-RAD-A-015, if necessary. The elements are then separated through ion exchange resins. For liquid samples, transuranic elements are scavenged by coprecipitation with iron hydroxide. The precipitate is dissolved, and separation of elements is accomplished through ion exchange resins. The elements are then prepared for the measurement of radioactive isotopes by coprecipitation with neodymium fluoride. The neodymium fluoride precipitate is trapped on a filter, mounted on a metal disk and placed in a partially evacuated chamber for measurement of isotopic alpha emission.

2.3 This method has been modified from the source method from EML Methods Manual HASL-300 U-02-RC, Am-05-RC, and Pu-11-RC and uses similar principles of radiochemical separation and counting. Modifications include chemical separations utilizing Eichrom TEVA and TRU resins to facilitate separation of various elements. There are also variations in the concentrations of acids, as well as the application of these acids.

2.4 This method is also very similar in concept to the source method from the DOE Methods Manual for Evaluating Environmental and Waste Management Samples, 1997 Edition, RP800, "Sequential Separation of Americium and Plutonium by Extraction Chromatography."

2.5 This method has been modified on the basis of GEL's Performance Based Measurement System (PBMS).

2.6 This method also contains a special procedure for digestion of samples in accordance with EPA method SW-846 3050B (Modified).

3.0 METHOD SCOPE, APPLICABILITY, AND DETECTION LIMIT

3.1 Method Detection Limit: Typical minimum detectable activity (MDA) for samples analyzed for Am/Cm/Pu/U is 1 pCi/L or 1 pCi/g for all isotopes.

3.2 Analyst training records are maintained as quality records as outlined in GL-QS-E-008. Analyst training and proficiency in the method is outlined in the Quality SOP for the Method Validation and Initial and Continuing Demonstrations of Capability, GL-QS-E-011.

3.3 Applicable matrices to this SOP are liquids, drinking water, vegetation, tissues, air filters, and solids.

NOTE: This method is not an EPA approved method for the analysis of drinking water.

4.0 METHOD VARIATIONS

Some variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group or Team Leader. Variations to a method will be documented with the analytical raw data.

5.0 DEFINITIONS

5.1 AlphaLIMS: Laboratory Information Management System used at GEL.

5.2 Batch: Environmental samples prepared and/or analyzed together with the same process and personnel using the same lot(s) of reagents.

5.3 Deionized (DI) Water: Type I water, Refer to GL-LB-E-016.

5.4 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes.

5.5 Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

5.6 Matrix Spike (MS): Prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

5.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike is prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

5.8 Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures.

5.9 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

5.10 Solid Reference Material (SRM): A solid material containing known and verified amounts of analytes.

5.11 Tracer: A known quantity of a radioisotope that is added to each sample of a chemically equivalent radioisotope of unknown concentration so that the yield of the chemical separation can be calculated.

6.0 INTERFERENCES

6.1 Internal tracer standards may have ingrown daughters that may interfere with the analysis. For example Th-228 will be present in aged U-232 standard, Fr-221 will be present in Th-229, which will interfere with the curium analysis, and U-232 will be present in Pu-236. These problems are overcome by running separate aliquots of sample for thorium analysis, or by mathematical compensation for the interference.

6.2 Short lived radioactive progeny may ingrow on prepared filters. For example, the Ra-224 alpha peak will be present if the Th-228 parent is present. These interferences are minimized by counting sample as soon as possible after separation chemistry.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for The Handling of Biological Materials.

7.4 If there is any regarding the safety of any laboratory practice, **stop immediately**, and consult qualified senior personnel such as a Group or Team Leader.

8.0 APPARATUS, EQUIPMENT, AND INSTRUMENTATION

8.1 Apparatus and Equipment

8.1.1 Silicon surface barrier detectors with associated electronics, vacuum chambers, and data reduction capabilities

8.1.2 Eichrom Technologies TEVA Resin, 100 – 150 µm particle size

8.1.3 Eichrom Technologies TRU Resin, 100 – 150 µm particle size

8.1.4 Vacuum pump and filtration apparatus

8.1.5 Disposable filter funnels (containing 25 mm polypropylene filters with 0.1 µm pore size)

8.1.6 Metal disks, 29 mm diameter

8.1.7 Stainless steel tweezers

8.1.8 Polypropylene centrifuge tube (50 mL)

8.1.9 Sample drying and ashing apparatus

8.1.10 Sample homogenization apparatus

8.1.11 AG 1X8 anion exchange resin, 100 – 200 mesh

8.1.12 Hot plate

8.1.13 Beakers (Glass and Teflon of various sizes)

8.1.14 2.5 cm^3 column

8.1.15 25 mL column funnel extension

8.1.16 Watch glasses (various sizes)

8.1.17 Digestion vessel

8.1.18 Reflux cap

8.1.19 Ribbed watch glass

8.1.20 Hot block

8.1.21 2.0 µm pore size plunger filter (PTF grade)

9.0 REAGENTS AND STANDARDS

9.1 Reagents

9.1.1 Neodymium carrier (500 mg/L)

9.1.2 Neodymium carrier (10,000 mg/L)

9.1.3 Carbon Colorant: Place four 47 mm cellulose nitrate filters in a beaker and add 5 mL concentrated sulfuric acid. Cover and heat on a hot plate with medium-high heat for approximately 2 to 4 hours. Cool dark residue completely. Slurry the residue in DI water and dilute to 1 L with DI water.

9.1.4 Hydrochloric acid (9 M HCl): Add 750 mL of concentrated hydrochloric acid to 100 mL of DI water. Allow to cool and dilute to

1 L with DI water.

9.1.5 Hydrochloric acid (3 M HCl): Add 250 mL of concentrated hydrochloric acid to 500 mL DI water. Allow to cool and dilute to 1 L with DI water.

9.1.6 Hydrochloric acid, concentrated (12 M HCl).

9.1.7 9 M Hydrochloric acid/0.05 M Ammonium iodide: Dissolve 7.24 g of ammonium iodide in 750 mL of concentrated hydrochloric acid and add to 100 mL of DI water. Allow to cool and dilute to 1 L with DI water. PREPARE DAILY.

9.1.8 Hydrochloric acid (6 M HCl): Add 500 mL of concentrated hydrochloric acid to 500 mL of DI water.

9.1.9 6 M Hydrochloric acid/0.52 M Hydrofluoric acid: Add 500 mL of concentrated hydrochloric acid and 18.6 mL of 49% hydrofluoric acid to 300 mL of DI water. Allow to cool and dilute to 1 L with DI water.

9.1.10 25% Hydrazine dihydrochloride: Dissolve 25 g of hydrazine dihydrochloride in 75 mL of DI water and dilute to 100 mL with DI water.

9.1.11 9 M Hydrochloric acid/0.04% Hydrogen peroxide: Add 8 drops of 30% hydrogen peroxide to 1 L of 9 M hydrochloric acid. PREPARE DAILY.

9.1.12 Ethyl alcohol (80% EtOH): Dilute 800 mL ethanol to 1 L with DI water.

9.1.13 Hydrochloric acid (0.1 M HCl): Add 8.3 mL of concentrated hydrochloric acid to 500 mL of DI water. Allow to cool and dilute to

1 L with DI water.

9.1.14 Hydrofluoric acid, concentrated (49% HF)

9.1.15 Hydrogen peroxide (30% H_2O_2)

9.1.16 Iron Carrier (10 mg/mL): Dissolve 62.7 g of $Fe(NO_3)_3 \bullet 6H_2O$ or 72.3 g of $Fe(NO_3)_3 \bullet 9H_2O$ in 800 mL DI water and dilute to 1 L with DI water.

9.1.17 Nitric acid concentrated (16 M HNO_3)

9.1.18 Nitric acid (2 M HNO_3): Add 125 mL of concentrated nitric acid to 500 mL of DI water. Allow to cool and dilute to 1 L with DI water.

9.1.19 Nitric acid (1 M HNO_3): Dilute 62.5 mL concentrated nitric acid to 500 mL of DI water. Allow to cool and dilute to 1 L with DI water.

9.1.20 2 M Nitric acid/1 M Aluminum nitrate: Dissolve 375.13 g of aluminum nitrate nonahydrate, $Al(NO_3)_3 \bullet 9H_2O$, in 300 mL of DI water. Add 125 mL of concentrated nitric acid to the DI water. Allow to cool and dilute to 1 L with DI water.

9.1.21 Titanium (III) chloride, 10-20% reagent

9.1.22 Hydrochloric acid (2 M HCl): Add 167 mL of concentrated hydrochloric acid to 500 mL DI water. Allow to cool and dilute to 1 L with DI water.

9.1.23 Nitric acid (1 M HNO_3): Add 62.5 mL of concentrated nitric acid to 500 mL of DI water. Allow to cool and dilute to 1 L with DI water.

9.1.24 1.25 M Calcium nitrate: Dissolve 205 g of anhydrous calcium nitrate or 295 g hydrated calcium nitrate, $Ca(NO_3)_2 \bullet 4H_2O$, in 500 mL of DI water. Dilute to 1L with DI water.

9.1.25 Phosphoric acid, concentrated (H_3PO_4)

9.1.26 Lanthanum (10,000 mg/L)

9.1.27 Sulfuric acid (0.1 M H_2SO_4): Add 5 mL concentrated sulfuric acid to 800 mL of DI water. Allow to cool and dilute to 900 mL.

9.1.28 Formic acid, concentrated

9.1.29 4 M Ammonium thiocyanate/0.1 M Formic acid: Add 60 g of ammonium thiocyanate and 1.0 mL of concentrated formic acid to a graduated cylinder and dilute to 200 mL with DI water. Prepare fresh daily.

9.1.30 1.5 M Ammonium thiocyanate/0.1 M Formic acid: Add 9.5 g of Ammonium thiocyanate and 0.5 mL of concentrated formic acid to a graduated cylinder and dilute to 100 mL with DI water. Prepare fresh daily.

9.1.31 Substrate suspension: Dilute 4 mL of neodymium chloride (10,000 mg/L), 80 mL of concentrated hydrochloric acid and 40 mL of carbon colorant to 1500 mL with DI water. Add 40 mL 49% hydrofluoric acid while swirling and dilute to 2 L with DI water.

9.1.32 Sulfuric acid, concentrated (18 M H_2SO_4).

9.1.33 Cellulose nitrate filters (47 mm)

9.1.34 Ammonium hydroxide concentrated (14 N NH_4OH)

9.1.35 Acetone

9.2 Standards

9.2.1 NIST traceable standards: Am-241, Am-243, Cm-244, Pu-242, Pu-239, Pu-238, Pu-236, U-232, U-236, U-238.

9.2.2 Refer to GL-RAD-M-001.

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Samples should be collected in a plastic bottle and preserved to approximately pH< 2 with nitric acid.

10.2 Before beginning an analysis, the analyst should check the sample pH by removing a minimal amount of sample with a transfer pipette and placing it on a pH strip. DO NOT insert pH strip into sample container. If the sample is received with a pH greater than 2, the analyst should contact the Group Leader or Team Leader. If approved by the client, the analyst should adjust the pH with nitric acid to a pH< 2. If the sample pH is adjusted, let the sample sit in the original container for a minimum of 24 hours before analysis. This acidification should be documented on a batch history sheet and attached to the batch paper work.

10.3 If the sample has exceeded the hold time the analyst should contact the Group Leader before continuing with the batch.

10.4 Soil and filter matrices require no preservation and may be shipped in any suitable container.

11.0 SAMPLE PREPARATION

NOTE: Aliquots may be estimated by using the count time estimator spreadsheet.

11.1 Soil Sample Preparation:

11.1.1 If not already done, dry and homogenize the sample by performing GL-RAD-A-021.

11.1.2 Measure an appropriate aliquot of soil (usually 0.2 g to 1.0 g) in a glass container or digestion vessel. If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced. Record all aliquots. Add approximately 4 to 6 drops of iron carrier to the Blank and LCS beakers. The Blank and LCS aliquot should be recorded to be the same aliquot as the largest sample in the batch. For soils and other special matrices, such as vegetation, air filters, tissue, etc., Deionized water is a suitable matrix for use as the MB and LCS aliquot. Iron carrier may also be added to all samples in the batch, if necessary, based on the appearance and iron content of each sample. If Solid Reference Material is required, weigh out approximately 0.1 g into the LCS beaker and record the exact weight.

11.1.3 Add a certified dpm of the appropriate tracer to each of the samples (usually between 5 to 10 dpm). Add a certified dpm (usually between 5 to 10 dpm) of the appropriate spike to the MS, MSD, LCS and LCSD as applicable. Reference the pull sheet for client requirements to determine appropriate tracer and spike.

11.1.3.1 For the determination of isotopic americium/curium, Am-243 is typically used as the tracer, and Am-241/Cm-244 are typically used as the spike.

11.1.3.2 For the determination of isotopic plutonium, Pu-242 is typically used as the tracer and Pu-239 is typically used as the spike. Pu-236 is an acceptable tracer provided no significant impurities are present.

NOTE: If Pu-241 is run in tandem, a separate MS and LCS is required to quantify Pu-241 spike recovery.

11.1.3.3 For the determination of isotopic uranium, U-232 is typically used as the tracer, and U-238 is typically used as the spike.

NOTE: The addition of tracers and spikes should be witnessed by either another analyst qualified on this procedure, a Team Leader or a Group Leader. After adding the tracers and spikes, the witness must initial and record the date of witnessing.

11.1.3.4 When running samples sequentially with Sr, all Sr carriers and spikes should be added prior to leach or digestion. See step 11.10.2 regarding collection procedures for Sr analysis.

11.1.4 If the analysis of the sample calls for quantification of U-232, Pu-242 or Am-243, the following steps shall be taken:

11.1.4.1 The sample will be run normally with the tracer indicated in sections 11.1.3 or 11.2.2.

11.1.4.2 A second run of the sample shall be made with a different tracer isotope such as U-236, Pu-236 or Cm-244. The quantification of the isotope that was normally the tracer can then be made. If there is any quantifiable activity a correction can be made to the initial run by calculating a correction ratio for the tracer recovery of the first run from the second run results.

NOTE: If prescribed to analyze by EPA method 3050B (Modified), proceed Appendix 7.

11.1.5 It is recommended that the samples be ashed in a muffle furnace as specified in GL-RAD-A-021B.

11.1.6 For uranium analysis, digest aliquot as specified in GL-RAD-A-015 and proceed to step 11.2.8.

11.1.7 A separate Am/Cm/Pu aliquot is treated with an aggressive acid leach of 6M or 9M hydrochloric acid depending on matrix and sample aliquot as described in the following steps. Uranium should not be run by this leaching technique.

NOTE: Determining the leaching routine is based on analyst experience with the matrix. The concentration required to obtain the leached sample will vary depending on the type of material, size of aliquot, muffling of sample, and other factors. The influence of these factors generally can be established by good judgment and experience with the materials being tested.

11.1.7.1 Place the sample in a beaker and add approximately 10 to 20mL of appropriate hydrochloric acid concentration per gram of sample with a minimum of 10 mL.

11.1.7.2 Heat the samples on medium heat and cover with a watch glass. Allow to leach for a minimum of 2 hours. Agitate the sample periodically to enhance the leaching process.

11.1.7.3 Allow the sample to partially cool and transfer to a centrifuge tube. Centrifuge the sample to separate the solid and leached portions.

11.1.7.4 Decant the leachate to a clean labeled beaker, and rinse the solid phase with DI water. Centrifuge the sample and decant the leachate into the beaker.

11.1.7.5 Evaporate the solution to dryness on medium heat.

11.1.7.6 Proceed to step 11.2.8.

11.2 Aqueous Sample Preparation:

11.2.1 Add an appropriate aliquot of sample to a labeled beaker. Prepare a Blank and LCS using DI water and a small amount of concentrated nitric acid to a pH < 2. The volume of DI water used should be the same as the largest volume of sample in the batch. If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced. Record all aliquots.

11.2.2 Add a certified dpm of the appropriate tracer to each of the samples (usually between 5 to 10 dpm). Add a certified dpm (usually between 5 to 10 dpm) of the appropriate spike to the MS, MSD, LCS and LCSD as applicable. Reference the pull sheet for client requirements to determine appropriate tracer and spike.

11.2.2.1 For the determination of isotopic americium/curium, Am-243 is typically used as the tracer, and Am-241/Cm-244 are typically used as the spike.

11.2.2.2 For the determination of isotopic plutonium, Pu-242 is typically used as the tracer, and Pu-239 is typically used as the spike. Pu-236 is an acceptable tracer, provided no significant impurities are present.

NOTE: If Pu-241 is run in tandem, a separate MS and LCS is required to quantify Pu-241 spike recovery.

11.2.2.3 For the determination of isotopic uranium, U-232 is typically used as the tracer, and U-238 is typically used as the spike.

11.2.2.4 When running samples sequentially with Sr, all Sr carriers and spikes should be added prior to initial iron precipitation to scavenge actinides. See section 11.10 regarding collection procedures for Sr analysis.

NOTE: The addition of tracers and spikes should be witnessed by either another analyst qualified on this procedure, a Team Leader or a Group Leader. After adding the tracers and spikes, the witness must initial and record the date of witnessing.

11.2.3 If the analysis of the sample calls for quantification of U-232, Pu-242 or Am-243, the following steps shall be taken:

11.2.3.1 The sample will be run normally with the tracer indicated in sections 11.1.3 or 11.2.2.

11.2.3.2 A second run of the sample shall be made with a different tracer isotope such as U-236, Pu-236 or Cm-244. The quantification of the isotope that was normally the tracer can then be made. If there is any quantifiable activity a correction can be made to the initial run by calculating a correction ratio for the tracer recovery of the first run from the second run results.

11.2.4 If samples contain large amounts of sediment that the client requires analyzed with the liquid portion of the sample, proceed to step 11.9.

NOTE: Other sample matrices, such as vegetation, air filters, tissue, etc. are prepared as outlined in GL-RAD-A-026. The analyst must ensure that the appropriate tracer(s) are added to these other matrices as discussed in sections 11.1.3 or 11.2.2.

11.2.5 Add 1 mL of iron carrier (10 mg/mL).

11.2.6 Add concentrated ammonium hydroxide until turbidity persists, or

pH > 9. Then add approximately 2 mL in excess. Heat to boiling for approximately 10 minutes or until precipitate breaks into fine particles. Allow to settle and cool.

11.2.7 Decant excess supernate and discard. Collect the remaining precipitate by centrifugation in a 50 mL centrifuge tube and discard the supernate.

NOTE: Exercise care in this step because finely divided material that contains the actinides may also be present in addition to the large iron hydroxide flocks.

11.2.8 Dissolve the precipitate from step 11.2.7 or residue from step 11.1.6 or 11.1.7.5 in 10 to 15 mL of 9 M hydrochloric acid /0.04% hydrogen peroxide solution.

NOTE: Samples may be dissolved with 10 to 15 mL of 9 M hydrochloric acid and then add 1 drop of 30% hydrogen peroxide as an alternative to dissolving with 9 M hydrochloric acid /0.04% hydrogen peroxide. This may also be done by dissolving samples with 10 to 15 mL 9 M hydrochloric acid and adding approximately 1 mL of DI water to approximately 1 mL of 30% hydrogen peroxide, mixing and adding one drop to each sample.

NOTE: If uranium only is required, the load solution is 10 to 15 mL of 9 M hydrochloric acid.

11.2.9 Slurry AG 1x8 anion resin (Cl form 100-200 mesh) in a squirt bottle with DI water. Transfer the resin to a small column to obtain a settled resin bed of approximately 2.5 mL.

11.2.10 Condition the column with 10 mL of 9 M hydrochloric acid.

11.2.11 Pass the sample solution from step 11.2.8 through the column and collect the eluate in a labeled, disposable 50 mL centrifuge tube for americium/curium analysis.

11.2.12 Rinse the column with 5 mL of 9 M hydrochloric acid and collect with the americium/curium fraction. Proceed to step 11.3.

11.2.13 Rinse the column with an additional 15 mL of 9 M hydrochloric acid and collect in a drip pan for disposal.

11.2.14 Elute plutonium by adding 10 mL of 9 M hydrochloric acid /0.05 M ammonium iodide solution, catching the plutonium elution in a labeled, disposable 50 mL centrifuge tube. Proceed to step 11.5 for plutonium microprecipitation for alpha spectroscopy. This elution may be omitted if plutonium analysis is not required.

11.2.15 Rinse the column with 15 mL of 6 M hydrochloric acid /0.52 M hydrofluoric acid and collect in a drip pan for disposal.

11.2.16 Rinse the column with 5 mL of 6 M hydrochloric acid and collect in a drip pan for disposal.

11.2.17 Place a labeled, disposable 50 mL centrifuge tube under each column. Elute uranium from the column using 15 mL of 0.1 M hydrochloric acid. Proceed to step 11.6 for uranium microprecipitation for alpha spectroscopy.

11.3 Americium/Curium Separation via TRU Resin:

NOTE: If sample aliquot is small or liquid sample is clean and free of particulates continue with step 11.3.1 and TRU column work. If not, proceed to step 11.3.5 for additional clean-up steps and TRU column work.

11.3.1 Precondition a 2 mL TRU column with 5 mL of 9 M hydrochloric acid.

11.3.2 Pass the sample solution from step 11.2.12 through the column collecting in a drip pan for disposal.

11.3.3 Rinse the column with 5 mL of 9 M hydrochloric acid collecting in a drip pan for disposal.

11.3.4 Place a labeled, disposable 50 mL centrifuge tube under each column. Elute americium and curium from the column using 20 mL of 3 M hydrochloric acid. Proceed to step 11.4 Americium/Curium microprecipitation for alpha spectroscopy.

11.3.5 Add 0.5 mL of 1.25 M calcium nitrate to the elution from step 11.2.12.

11.3.6 Add 1.0 mL of phosphoric acid. Swirl to mix.

11.3.7 Dilute to approximately 30 mL with DI water.

11.3.8 Add 28-30% ammonium hydroxide to pH of 8 to 10 to precipitate calcium phosphate. Do not over precipitate.

11.3.9 Allow to cool then spin samples in a centrifuge and pour off supernate.

11.3.10 Add approximately 25 mL of DI water to centrifuge tube, cap, and shake vigorously to break up precipitate.

11.3.11 Spin samples in a centrifuge and pour off supernate.

11.3.12 Add 15 mL of 2 M nitric acid/1 M aluminum nitrate to centrifuge tube and dissolve precipitate. Gently heat if necessary. Solution should be clear.

11.3.13 Precondition a 2 mL TRU column with 10 mL of 2 M nitric acid, collecting the rinse in a drip pan for disposal.

11.3.14 Pass the sample solution from step 11.3.12 through the column, collecting the load solution in a drip pan for disposal.

11.3.15 Rinse the column twice with 5 mL of 2 M nitric acid and collect the rinse in a drip pan for disposal.

11.3.16 Rinse the column with 5 mL of 1 M nitric acid and collect the rinse in a drip pan for disposal.

11.3.17 Place a labeled, disposable 50 mL centrifuge tube under each column. Elute americium and curium from the column using 20 mL of 3 M hydrochloric acid. If rare earth elements are suspected in the sample proceed to step 11.8.1 to separate rare earth elements via TEVA resin, otherwise, continue with step 11.4.

11.4 Americium/Curium Microprecipitation:

11.4.1 Dilute americium elution from step 11.3.4, 11.3.17, or 11.8.11 to approximately 40 mL with DI water. Add 0.1 mL of neodymium carrier (500 mg/L) to the solution and swirl to mix. Add 5 mL of 49% hydrofluoric acid and swirl to precipitate fluorides. Allow solution to sit for approximately 30 minutes, then proceed to step 11.7.1.

11.5 Plutonium Microprecipitation

11.5.1 Dilute plutonium elution from step 11.2.14 to approximately 40 mL with DI water. Add 0.1 mL of neodymium carrier (500 mg/L) and swirl. Add approximately 3 to 4 drops of 25% hydrazine dihydrochloride and swirl to mix. Let the solution sit for approximately 10 minutes, and add 5 mL of 49% hydrofluoric acid. Swirl to mix. Allow solution to sit for approximately 30 minutes, then proceed to step 11.7.1.

11.6 Uranium Microprecipitation:

11.6.1 Dilute uranium elution from step 11.2.17 to approximately 40 mL with DI water. Add 0.1 mL of neodymium carrier solution (500 mg/L) and swirl to mix. Add 0.5 mL of titanium (III) chloride solution and allow the sample to sit for approximately 30 seconds. Add 5 mL of 49% hydrofluoric acid to precipitate fluorides. Allow the solution to sit for approximately 30 minutes, then proceed to step 11.7.1.

11.7 Sample Filtration:

11.7.1 Place a disposable filter funnel on the filter support screen. Wet the filter with 80% ethyl alcohol and apply vacuum.

11.7.2 Add 5 mL of substrate suspension. After solution has passed through filter, add another 5 mL of substrate suspension.

11.7.3 Add 1 mL of the carbon colorant.

11.7.4 Filter the fluoride precipitated solution through the filter paper. Rinse the centrifuge tube with approximately 5 mL DI water and pass through filter.

11.7.5 Rinse the funnel with 80% ethyl alcohol.

CAUTION: Directing a stream of liquid onto the filter will disturb the distribution of the precipitate on the filter and render the sample unsuitable for alpha spectrometry resolution.

11.7.6 Without turning off the vacuum, remove the funnel.

11.7.7 Turn off vacuum and remove filter. Mount filter on a labeled 29 mm flat planchet. Ensure that the filter is centered and as flat as possible on the planchet.

NOTE: Care should be taken not to touch the active area of the filter with tweezers.

11.7.8 Place the mounted filter under a heat lamp for approximately 5 minutes or allow to air dry completely prior to alpha spectrometry measurement.

11.7.9 Submit samples for Alpha Spec counting.

NOTE: After Alpha Spec counting and review is complete, if Pu-241 analysis is required, proceed to SOP GL-RAD-A-035 step 11.2.30.

11.8 Separation of Americium from the Rare Earth Elements via TEVA Resin:

11.8.1 Transfer the elution from Step 11.3.17 to a clean beaker and add 0.3 mL of lanthanum. Gently cook dry on low heat.

11.8.2 Once the samples have cooled, add 5 mL of concentrated nitric acid and approximately 2 mL of 30% hydrogen peroxide. Heat on a hot plate at low heat to dryness. Cool and repeat.

11.8.3 Dissolve residue in approximately 1 ml of 0.1 M sulfuric acid. Evaporate until a very small amount of acid remains.

11.8.4 Dissolve residue in approximately 1 mL of concentrated formic acid. Evaporate until a very small amount of acid remains.

11.8.5 Repeat step 11.8.4, and evaporate the sample under low heat until the beaker is gently dry.

11.8.6 Dissolve the sample in 10 mL of 4 M ammonium thiocyanate/0.1 M formic acid. Be sure that the 4 M ammonium thiocyanate/0.1 M formic acid is prepared fresh daily.

11.8.7 Condition a TEVA column with 5 mL of 4 M ammonium thiocyanate/0.1 M formic acid, collecting the rinse in a drip pan for disposal.

11.8.8 Load the sample onto the TEVA column, collecting the load in a drip pan for disposal.

11.8.9 Rinse the beaker with 5 mL of 4 M ammonium thiocyanate/0.1 M formic acid and add to the column, collecting the rinse in a drip pan for disposal.

11.8.10 Rinse lanthanum and other rare earth elements from the column with 10 mL of 1.5 M ammonium thiocyanate/0.1 formic acid, collecting the rinse in a drip pan for disposal. Be sure that the 1.5 M ammonium thiocyanate/0.1 formic acid is prepared fresh daily.

11.8.11 Place a labeled, disposable 50 mL centrifuge tube under each column. Elute americium with 20 mL of 2 M hydrochloric acid.

11.8.12 Proceed to Step 11.4 to precipitate and filter samples.

11.9 Samples Containing Large Amounts of Sediment

NOTE: When aliquoting samples that contain large amounts of sediment, ensure that the sample is thoroughly homogenized.

11.9.1 Evaporate to dryness on medium to low heat.

11.9.2 Muffle in a furnace at approximately 550˚ C for a minimum of 2 hours.

11.9.3 If uranium analysis is required, leach for approximately 30 minutes and proceed to step 11.1.6.

11.9.4 If americium, curium, or plutonium analyses are required, proceed to step 11.1.7.

NOTE: Samples requiring americium extraction MUST be separated from rare earth elements via TEVA resin.

11.10 Preparation technique for Sr samples run in tandem with americium, plutonium, or uranium analysis.

11.10.1 Supernate from step 11.2.7 should be decanted into a clean, labeled beaker for further Sr analysis. Do not discard.

11.10.2 Elution from steps 11.2.11 and 11.2.12 should be collected in a clean, labeled centrifuge tube.

11.10.3 If americium/curium analysis is not required sample should be combined with supernate from step 11.10.1. Then proceed to appropriate SOP for Sr analysis.

11.10.4 If americium/curium analysis is needed proceed to step 11.3. Elution from steps 11.3.2 and 11.3.3 should be collected in a clean, labeled centrifuge tube. Elution should be combined with supernate from step 11.10.1. Then proceed to appropriate SOP for Sr analysis.

12.0 QUALITY CONTROL REQUIREMENTS

NOTE: Client contractual QC requirements override the requirements in this section.

12.1 Analyst and Method Verification Requirements

Refer to GL-RAD-D-002 for instructions concerning the validation of analytical methods.

12.2 Method Specific Quality Requirements

12.2.1 A method blank (MB) should accompany each batch of 20 or less samples. The reported value of the blank should be less than or equal to the contract required detection limit (CRDL).

12.2.2 The tracer added to all samples is used to calculate the method recovery. The method recovery of all samples should be between 15-125% when compared to the reference standard.

12.2.3 A duplicate (DUP) sample should be run with each batch of 20 or less samples. The relative percent difference (RPD) between the actual sample and the DUP should be less than or equal to 20% if both the sample and DUP results are greater than 5 times the minimal detectable concentration (MDC), or 100% if they are both less than 5 times MDC. If both results are less than the MDC, then limits are not applicable.

12.2.4 A laboratory control sample (LCS) should be run with each batch of 20 or less samples. The recovery of the LCS should fall between 75-125%.

12.3 Actions Required if the Quality Control Requirements Are Not Met

If any of the QC criteria from 12.2.1 through 12.2.4 cannot be satisfied, the analyst should inform the Group Leader and initiate a Data Exception Report (DER) as outlined in GL-QS-E-004.

13.0 INSTRUMENT CALIBRATION AND PERFORMANCE

For direction on calibration and instrument performance refer to GL-RAD-I-009.

14.0 ANALYSIS AND INSTRUMENT OPERATION

For analysis and instrument operation refer to GL-RAD-I-009.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

For maintenance of system refer to GL-RAD-I-010.

16.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

Data recording, calculation, and reduction take place in accordance with GL-RAD-D-003 and GL-RAD-D-006.

17.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

Refer to GL-RAD-D-003 for instructions concerning the data review process, approval, and transmittal.

18.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND WASTE DISPOSAL

Radioactive samples and material shall be handled and disposed of as outlined in the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

20.1 EPA Environmental Monitoring and Support Laboratory. Las Vegas. Radiochemical Analytical Procedures for Analysis of Environmental Samples. March 1979.

20.2 EML Procedures Manual HASL-300, Volume I February 2000, Method U-02-RC, Revision 1.

20.3 DOE Methods Manual for Evaluating Environmental and Waste Management Samples, 1997 Edition, RP800, "Sequential Separation of Americium and Plutonium by Extraction Chromatography."

20.4 Analytical Chemistry. Rapid Determination of Thorium-230 in Mill Tailings by α Spectrometry. UNC Geotech, Grand Junction Projects Office. Steve Donivan, Mark Hollenbach, and Mary Costello. Vol. 59, No. 21, 1987.

20.5 Los Alamos Health and Environmental Chemistry: Analytical Techniques. LA-10300-M Vol. 1, September 1987.

20.6 Special thanks to Dr. Bill Burnett and his associates for assistance in developing this method at Florida State University.

20.7 EML Procedures Manual HASL-300, Volume II February 1997, Method Am-05-RC.

20.8 U.S. Department of Energy, Environmental Measurements Laboratory Procedures Manual HASL-300, Section 4.5.4, Vol. 1, Pu-11-RC, 28th Ed., 1997

21.0 HISTORY

Revision 27: Removed reference to the use of Queue sheets
Revision 26: Added Appendix 7 to include steps of digestion of soil using EPA Method 3050B (Modified).
Revision 25: 1 mL of Titanium chloride to 0.5 mL in sample preparation section and checklist.

Revision 24: Updated Appendix 1. Combined steps 11.3.18 with step 11.3.17 for clarification.

Revision 23: Added DOE HASL-300 Pu-11-RC (modified) to Applicable methods on title page. Section 2.3 added Pu-11-RC as a source method. Updated reagent section. Added U-236 to section 9.2.1. Added section 11.1.4 regarding tracers. Note added after section 11.2.2.2 regarding Pu-241 analysis if run in tandem. Omitted section 11.2.3.2 and 11.2.3.3. Removed plutonium cookdown from sections 11.2.14 and 11.5. Removed MS requirement from section 12.2. Updated section 16.0.

APPENDIX 1

AMERICIUM, CURIUM, PLUTONIUM, AND URANIUM

Use a 2.5 cm^3 column with 1X8 anion resin (Cl^- form 100-200 mesh)

COLUMN WORK

____ 10 mL 9 M HCl (Conditioning)

____ Load solution: 10 to 15 mL 9 M HCl / 0.04% H_20_2 (Catch in C-Tube for Am/Cm)
NOTE: If U only is required the load solution is 10 to 15 mL of 9 M HCl

____ 5 mL 9 M HCl (Catch in C-Tube for Am/Cm then proceed to Appendix 2 or 3 as appropriate for Am/Cm procedure)

____ 15 mL 9 M HCl (Rinse)

____ **Elute** Pu: 10 mL 9 M HCl / 0.05 M NH_4I (Catch in C-Tube then proceed to Appendix 4 Plutonium Precipitation)

____ 15 mL 6 M HCl / 0.52 M HF (Rinse)

____ 5 mL 6 M HCl (Rinse)

____ **Elute** U: 15 mL 0.1 M HCl (Catch in C-Tube)

____ Proceed to Appendix 4 for Uranium Precipitation

APPENDIX 2

AMERICIUM / CURIUM CONTINUATION

AMERICIUM / CURIUM

____ 0.5 mL 1.25 M Calcium nitrate

____ 1.0 mL Phosphoric acid and swirl

____ Dilute to approximately 30 mL with DI water

____ Concentrated NH_4OH to pH of 8 to 10

____ Centrifuge samples and pour off supernate

____ Add approximately 25 mL DI water and shake samples to break up precipitate

____ Centrifuge samples and pour off supernate

____ 10 mL 2 M HNO_3 (Condition 2 mL TRU Resin Column)

____ Load Solution: 15 mL 2 M HNO_3 / 1 M $Al(NO_3)_3$

____ 5 mL 2 M HNO_3 (Rinse)

____ 5 mL 2 M HNO_3 (Rinse)

____ 5 mL 1 M HNO_3 (Rinse)

____ **Elute** Am/Cm: 20 mL 3 M HCl (Catch in C-Tube)

____ Proceed to Appendix 4 for Am/Cm precipitation

APPENDIX 3

AMERICIUM / CURIUM CONTINUATION

AMERICIUM / CURIUM

___ 5 mL 9 M HCl (Condition 2 mL TRU Resin Column)

___ Load solution from Appendix 1 (catch in drip pan)

___ 5 mL 9 M HCl (Rinse)

___ **Elute** Am/Cm: 20 mL 3 M HCl (Catch in C-tube)

___ Proceed to Appendix 4 for Am/Cm precipitation

APPENDIX 4

AMERICIUM / CURIUM PRECIPITATION

____ Dilute elution with DI water to approximately 40 mL

____ 0.1 mL 500 mg/L Neodymium and swirl

____ 5 mL 49% HF and swirl

____ Wait approximately 30 minutes

____ Filter

PLUTONIUM PRECIPITATION

____ Dilute elution with DI water to approximately 40 mL

____ 0.1 mL 500 mg/L Neodymium and swirl

____ Approximately 3 to 4 drops 25% Hydrazine dihydrochloride and swirl

____ Wait approximately 10 minutes

____ 5 mL 49% HF and swirl

____ Wait approximately 30 minutes

____ Filter

URANIUM PRECIPITATION

____ Dilute elution with DI water to approximately 40 mL

____ 0.1 mL 500 mg/L Neodymium and swirl

____ 0.5 mL Titanium chloride and swirl

____ Wait approximately 30 seconds

____ 5 mL 49% HF and swirl

____ Wait approximately 30 minutes

____ Filter

APPENDIX 5

RARE EARTH CLEAN-UP

____ Transfer elution from TRU column to a clean beaker and add 0.3 ml of lanthanum

____ Evaporate to dryness on low heat

____ 5 mL concentrated HNO_3 and approximately 2 mL of 30% H_2O_2. Evaporate to dryness on low heat.

____ 5 mL concentrated HNO_3 and approximately 2 ml of 30% H_2O_2. Evaporate to dryness on low heat.

____ Approximately 1 mL of 0.1 M Sulfuric Acid. Evaporate to dryness on low heat

____ Approximately 1 mL of concentrated Formic Acid. Evaporate to dryness on low heat

____ Approximately 1 mL of concentrated Formic Acid. Evaporate to dryness on low heat

____ 5 mL 4 M Ammonium thiocyanate/0.1 M Formic acid (Condition 2 mL TEVA column)

____ Load Solution: 10 mL 4 M Ammonium thiocyanate/0.1 M Formic acid

____ 5 mL 4 M Ammonium thiocyanate/0.1 M Formic acid (Rinse)

____ 10 mL 1.5 M Ammonium thiocyanate/0.1 M Formic acid (Rinse)

____ **ELUTE** Am: 20 mL of 2 M HCl (catch in C-tube)

____ Proceed to Appendix 4 for Am/Cm precipitation

APPENDIX 6

SAMPLE CLEANUP FROM AN ALPHA SPEC FILTER

1. Remove the filter from the mounting disc by wetting the filter with a small amount of acetone and pulling the filter off the disc using tweezers. Place the filter in a labeled small glass beaker.

2. Add 4-6 drops of iron carrier (10 mg/L), 10 mL of concentrated hydrochloric acid and 1.0 mL of 5% boric acid solution.

3. Fill the bulb end of a disposable pipette with DI water and turn upside down. Place on the filter in the glass beaker to ensure the filter remains submerged.

4. Heat on a hot plate for 30 minutes frequently stirring the filter, flipping it over then back etc. Use the disposable pipette to stir and flip.

5. Remove the filter from the solution and rinse with DI water. Do this over the glass beaker so the DI water rinse falls back into the beaker.

6. Evaporate to dryness.

7. Proceed to section 11.2.8 and perform separations as specified.

APPENDIX 7

SPECIAL PROCEDURE: DIGESTION OF SOILS AND SEDIMENTS BY EPA METHOD 3050B (MODIFIED)

— Complete Steps 11.1.1 thru 11.1.4 of this procedure

— Add 5 mL of [HNO_3] and 5 mL of Type I DI water to the samples and quality control samples

— Gently swirl the sample and acid mixture

— Cover the sample with a reflux cap or watch glass and heat the sample in a hot block at 95° +/- 5° C. Reflux the sample for 10 to 15 minutes

— Remove the samples from the hot block and allow the samples to cool

— Add 5 mL of [HNO_3], return samples to hot block, replace the watch glass, reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by nitric acid, add an additional 5 mL [HNO_3] until no brown fumes are given off by the sample.

— Using a ribbed watch glass or reflux cap, allow the solution to evaporate to approximately 5 mL, without boiling, or heat for 2 hours.

— Remove the sample from the hot block and allow to cool

— Add 2 mL of Type I DI water and 3 mL of 30% H_2O_2, return samples to hot block and allow the peroxide reaction to occur. Continue to add H_2O_2 in 1 mL increments until effervescence subsides. Do not add more than 10 mL of H_2O_2.

— Cover the samples with ribbed watch glass or reflux cap and heat the samples at 95° +/- 5° C for 2 hours, without boiling.

— Remove from hot block and allow the samples to cool

— Cap the samples and shake well

— Filter each sample with a 2.0 µm pore size plunger type filter (PTF grade) or allow to settle overnight.

— Transfer liquid phase to clean labeled centrifuge tube

— Proceed to Step 11.2.6 of this procedure

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF GAMMA ISOTOPES

(GL-RAD-A-013 REVISION 27)

APPLICABLE TO METHODS:
EPA 600/4-80-032 Method 901.1
DOE EML HASL-300 Section 4.5.2.3
DOE EML HASL-300 Ga-01-R

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1.0 STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF GAMMA ISOTOPES

2.0 METHOD OBJECTIVE, PURPOSE, AND SUMMARY

2.1 This standard operating procedure (SOP) provides the necessary instructions to conduct the analysis for gamma isotopes in water, soil, urine, filters, drinking water and miscellaneous matrices.

2.2 Water samples are typically counted in Marinelli beakers. Soil samples are typically sealed in aluminum cans, which can be counted immediately if Ra-226 is not desired. If Ra-226 is desired, the sealed can is set aside for minimum of 20 days to allow equilibrium between Rn-222 and Bi-214 to become re-established. Ra-226 is then quantified using the 609 keV line of Bi-214.

2.3 This method is based on the source method EPA 600/4-80-032 "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," August 1980, Method 901.1, and the Department of Energy (DOE) EML Procedures Manual source method for Gamma PHA in environmental samples, HASL-300 Section 4.5.2.3 and Ga-01-R, Gamma Radioassay.

2.4 This SOP is applicable for analyzing samples that contain radionuclides emitting gamma photons with energies ranging from about 5 to 2000 keV (including I-131).

3.0 METHOD SCOPE, APPLICABILITY, AND DETECTION LIMIT

3.1 Minimum Detectable Activity (MDA): The MDA is based upon sample volume, Compton background, instrument efficiency, count time, and other statistical factors, as well as specific isotopic values such as abundance and half-life. A typical detection limit is 10 pCi/L or 0.1 pCi/g (based on Cs-137). The MDA for drinking water samples is 10 pCi/L (based on Cs-137). Typical aliquot for drinking waters is 2 liters. Typical count time for drinking waters is 2-4 hours, to ensure the required sensitivity (specified by the National Primary Drinking Water Regulations) is achieved.

3.2 Method Precision: Typical Relative Percent Difference (RPD) is 20% or less or 100% or less if the activity is less than five times the MDA.

3.3 Method Bias (Accuracy): The method accuracy requirement for gamma, measured by running a Laboratory Control Sample (LCS) with each batch, is 25% of the true value. For drinking water samples, laboratory fortified blanks (LFB, equivalent to LCS) recoveries should be between 90-110% of the known value.

3.4 Procedures contained in this SOP may be used to analyze REMP samples.

3.5 Analysts training records are maintained as quality records as outlined in GL-QS-E-008. Analysts training and proficiency in the method is outlined in the Employee Training SOP GL-HR-E-002.

3.6 For drinking water samples, analyst initial and ongoing demonstrations of proficiency will follow critical elements for radiochemisrtry, chapter VI, section 1.5, of The Manual for the Certification of Laboratories Analyzing Drinking Water (reference 20.5).

3.7 Sensitivity studies will follow critical elements for radiochemistry, chapter VI, section 7.3 of The Manual for the Certification of Laboratories Analyzing Drinking Water (reference 20.5).

4.0 METHOD VARIATIONS

4.1 Some variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group Leader or Team Leader. Variations to a method will be documented with the analytical raw data.

4.2 Filter samples can either be counted directly, or digested prior to counting. If filters are digested, they are digested in accordance with GL-RAD-A-026.

4.3 No method modifications are permitted for drinking water samples.

5.0 DEFINITIONS

5.1 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

5.2 Deionized (DI) water: Type I water.Refer to GL-LB-E-016.

5.3 AlphaLIMS: GEL's Laboratory Information Management System.

5.4 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

5.5 Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures.

5.6 Laboratory Duplicate (DUP): For soils, when sufficient sample is available, a separate duplicate will be prepared. For liquid samples and when sufficient sample is not available for solids, an independent count of the sample container will be performed to show precision.

5.7 Laboratory Control Sample (LCS): A sample matrix, similar to the batch of associated samples (when available) that is free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes. The LCS is equivalent to a Fortified Blank in the EPA drinking water compliance manual (See to section 20.5).

5.8 Refer to SOP GL-QS-B-001 the Quality Assurance Plan for additional lab-wide used definitions.

6.0 INTERFERENCES

6.1 Some gamma isotopes emit gamma lines that may overlap with other isotopes. If the energies of the two isotopes are within the energy tolerance setting, the peaks may not be resolvable and may give a positive bias to the result. This problem is minimized by careful review of the peak search.

6.2 Soil samples may vary in density from the standard used for calibration. A density correction is applied to the "CAN" geometry. This correction was determined using solids with weights varying between 54 g and 192 g.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Keep hands free from moving parts of canning device and gamma shields.

7.2 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.3 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.4 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for The Handling of Biological Materials.

7.5 If there is any question regarding the safety of any laboratory practice, **stop immediately**, and consult qualified senior personnel such as a Group or Team Leader.

8.0 APPARATUS, EQUIPMENT, AND INSTRUMENTATION

8.1 Ancillary Equipment

8.1.1 100 cc aluminum cans with lids for soil and miscellaneous samples

8.1.2 10 cc Gelman Sciences Petri dish for soil, filters and miscellaneous samples

8.1.3 2 L and 500 mL Marinelli beakers for water samples

8.1.4 Air displacement pipettes

8.1.5 Can sealing tool

8.1.6 Graduated cylinder

8.1.7 25 cc VWR Petri for soil and miscellaneous samples

8.1.8 250 mL plastic jar for filters, soil, and miscellaneous samples

8.1.9 Hot plate

8.1.10 Teflon beakers and lids

8.1.11 1 L Marinelli beaker for soil samples

8.2 Instrumentation

8.2.1 High purity germanium detector, with associated electronics and data reduction software

8.2.2 Top loader balance

9.0 REAGENTS, CHEMICALS, AND STANDARDS

9.1 NIST traceable mixed gamma standard in 100 cc aluminum can

9.2 NIST traceable mixed gamma standard in 2.0 L Marinelli beaker

9.3 NIST traceable mixed gamma standard in 0.5 L Marinelli beaker

9.4 NIST traceable mixed gamma standard in Gelman Sciences 10 cc Petri dish

9.5 NIST traceable mixed gamma standard in 13, 47 mm glass fiber filter composites in Gelman Sciences Petri dish.

9.6 NIST traceable mixed gamma standard in 0.4 L jar

9.7 NIST traceable mixed gamma standard in 0.25 L jar

9.8 NIST traceable mixed gamma standard in 1, 47 mm glass fiber filter

9.9 NIST traceable mixed gamma standard in Impregnated Charcoal Sample Cartridge.

9.10 NIST traceable mixed gamma standard in VWR (53 mm x 15 mm) Petri dish (approximately 25 cc)

9.11 NIST traceable mixed gamma standard in aqueous solution

9.12 NIST traceable mixed gamma standard in 1.0 L Marinelli beaker

9.13 NIST traceable mixed gamma standard in 20 mL liquid scintillation vial

9.14 16 M Nitric acid, reagent grade (HNO_3)

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 For soil samples, 500 g of sample should be collected, preferably in a plastic container to avoid breakage.

10.2 For water samples, 2 L of sample should be collected in a plastic container and preserved to a pH < 2 with nitric acid.

10.2.1 Before beginning an analysis, the analyst should check the sample pH by removing a minimal amount of sample with a transfer pipette and placing it on a pH strip. DO NOT insert pH strip into sample container. If the sample is received with a pH greater than 2, the analyst should contact the Group Leader or Team Leader.

NOTE: If the analysis is requesting I-131 (or any other iodine isotopes) Analysis without preserving is acceptable. If a sample is preserved with acid without stabilizing the iodine, Iodine may volatilize and escape the solution as a gas.

10.2.2 If approved by the client, the analyst should adjust the pH with nitric acid to a pH < 2. If the sample pH is adjusted, let the sample sit in the original container for a minimum of 24 hours before analysis. This

acidification should be documented on a batch history sheet and attached to the batch paperwork.

10.3 For filters no preservation is necessary.

11.0 SAMPLE PREPARATION

11.1 Solid Sample Preparation.

11.1.1 Prepare the sample for gamma counting in accordance with SOP GL-RAD-A-021, Soil Sample Preparation for the Determination of Radionuclides.

11.1.2 Fill the appropriate container with sample prepared from step 11.1.1 using the following steps as a guideline:

11.1.2.1 If Ra-226 analysis is required, the sample is placed in a 100 cc can for in-growth.

NOTE: It is recommended that in-growth be allowed 20 days to quantify Ra-226. Shorter ingrowth periods can be used at the request of the client. However, shorter in-growth periods may decrease the accuracy of the data. If there is insufficient mass of sample to fill the 100 cc can, contact the Team or Group Leader.

11.1.2.2 If sufficient mass is available, homogenized samples should be placed in the 100 cc can. Determine the net weight of the sample. If the net weight is less than 54 g or greater than 192 g, contact the Team or Group Leader to determine the appropriate counting container. Record sample weight and date in AlphaLIMS and on sample container.

11.2 Water Sample Preparation

11.2.1 Place the appropriate labeled Marinelli beaker (typically 500 mL or 2 L) on a balance and tare the balance.

11.2.2 If less than approximately 1.1 L is available, sample should be poured into a 500 mL Marinelli beaker.

11.2.3 Transfer the appropriate volume to the tared container and record the volume of the sample on the Queue sheet.

NOTE: If there is insufficient sample to fill the Marinelli, record the exact amount of sample volume on the container and on the Queue sheet. Dilute the sample to the appropriate volume to maintain the calibration geometry. Record the volume the sample was diluted to on the sample container, also.

11.2.4 The MB should be recorded on the Queue sheet to be the same aliquot as the largest sample in the batch. An empty Marinelli beaker should be labeled as the MB and submitted with each batch of samples.

11.2.5 Submit the Marinellis and completed paperwork to the count room for gamma counting analysis.

11.3 Urine Sample Preparation

11.3.1 Refer to GL-RAD-B-030.

11.4 Preparation of Miscellaneous Matrices

11.4.1 Prepare the sample in accordance with GL-RAD-A-026 for The Preparation of Special Matrices for the Determination of Radionuclides.

11.4.2 If sample(s) was (were) received from the client in a container that matches a calibrated geometry, a direct count of the sample can be performed.

12.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

Refer to GL-RAD-D-003.

13.0 INSTRUMENT CALIBRATION, STANDARDIZATION, AND PERFORMANCE

Refer to GL-RAD-I-001.

14.0 ANALYSIS AND INSTRUMENT OPERATION

Refer to GL-RAD-I-001.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Refer to GL-RAD-I-010.

16.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

Data recording, calculation and reduction take place in accordance with SOP GL-RAD-D-003 and GL-RAD-D-006.

17.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

Data are reviewed and packaged in accordance with GL-RAD-D-003 for Data Review, Validation, and Data Package Assembly.

18.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as Quality Documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND DISPOSAL

Radioactive samples and material shall be handled and disposed of as outlined in the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

20.1 USEPA. Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Method 901.1, August 1980.

20.2 Canberra Nuclear Genie System Spectroscopy, Applications and Display User's Guide, Vol. I and II, May 1991.

20.3 DOE EML Procedures Manual, HASL-300, 27th Edition. (Section 4.5.2.3)

20.4 DOE EML Procedures Manual, HASL-300, 28th Edition. (Ga-01-R)

20.5 Manual for the Certification of Laboratories Analyzing Drinking Water. Criteria and Procedures Quality Assurance. Fifth Edition EPA 815-R-05-004 January 2005.

20.6 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.0, July 2013 and Version 5.1, January 2017; DOE QSAS 3.0, July 2013 and Version 3.1 January 2017.

21.0 HISTORY

Revision 23: Procedure updated to include requirements for drinking water samples.

Revision 24: Changed recovery limit for laboratory fortified blank from 90-100% to 90-110% in section 3.3.

Revision 25: Type II to type I water.

Revision 26: Removed reference to obsolete software. Updated the reagents and standards section. Updated sample prep section to current practices.

Revision 27: Added clarification of aliquots volume and count times for samples analyzed for drinking water methods.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR THE ISOTOPIC DETERMINATION OF THORIUM

(GL-RAD-A-038 REVISION 18)

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR THE ISOTOPIC DETERMINATION OF THORIUM

2.0 METHOD OBJECTIVE, PURPOSE, AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for isotopic thorium in a variety of matrices.

2.2 A soil/solid sample is aliquoted and digested, if necessary. The elements are then separated through ion exchange resins. For liquid samples, actinide elements are scavenged by coprecipitation with iron hydroxide. The precipitate is dissolved, and separation of elements is accomplished through ion exchange resins. The elements are then prepared for the measurement of radioactive isotopes by coprecipitation with neodymium fluoride. The neodymium fluoride precipitate is trapped on a filter, mounted on a metal disk and placed in a partially evacuated chamber for measurement of isotopic alpha emission.

2.3 GEL utilizes methods that are derived from established sources. This method is based on the source method from DOE EML Methods Manual HASL 300 PU-02, 03 and uses similar principles of radiochemical separation and counting. This method is also very similar in concept to the source method from the DOE Methods Manual for Evaluating Environmental and Waste Management Samples, 1997 Edition, RP800: "Sequential Separation of Americium and Plutonium by Extraction Chromatography." This method is also based on the source method EPA 053917 EMSL LV 1979 "Isotopic Determination of Plutonium, Uranium, and Thorium in Water, Soil, Air, and Biological Tissue" and in some cases this method is referenced as EPA RA-LV-PI.

2.4 This method has been modified on the basis of GEL's Performance Based Measurement System (PBMS).

3.0 METHOD APPLICABILITY

3.1 Method Detection Limit (MDL): Typical minimum detectable activity (MDA) for samples analyzed for thorium is 1 pCi/L or 1 pCi/g for all isotopes.

3.2 Analyst training records are maintained as quality records outlined in GL-QS-E-008. Analyst training and proficiency in the method is outlined in GL-QS-E-011 for Method Validation and Initial and Continuing Demonstrations of Capability.

3.3 Applicable matrices to this SOP are liquids, drinking water, vegetation, tissues, air filters, and solids.

NOTE: This method is not an EPA approved method for the analysis of drinking water.

4.0 METHOD VARIATIONS

Some variations may be necessary due to special matrices encountered in the lab. These

variations may be used with approval from a Group or Team Leader. Variations to a method will be documented with the analytical raw data.

5.0 DEFINITIONS

5.1 AlphaLIMS: GEL's Laboratory Information Management System.

5.2 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel using the same lot(s) of reagents.

5.3 Deionized (DI) water: Type I water, Refer to GL-LB-E-016.

5.4 Laboratory Control Sample (LCS): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes.

5.5 Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

5.6 Matrix Spike (MS): Prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

5.7 Matrix Spike Duplicate (MSD): A second replicate matrix spike is prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

5.8 Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures.

5.9 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

5.10 Solid Reference Material (SRM): A solid material containing known and verified amounts of analytes.

5.11 Tracer: A known quantity of a radioisotope that is added to each sample of a chemically equivalent radioisotope of unknown concentration so that the yield of the chemical separation can be calculated.

5.12 Refer to the SOP GL-QS-B-001 the Quality Assurance Plan for the additional lab-wide definitions.

6.0 INTERFERENCES

6.1 Internal tracer standards may have ingrown daughters that may interfere with the analysis. For example, Th-228 will be present in aged U-232 standard. This

problem is overcome by not performing thorium and uranium analysis in tandem.

6.2 Short-lived radioactive progeny may ingrow on prepared filters. For example, the Ra-224 alpha peak will be present if the Th-228 parent is present. These interferences are minimized by counting samples as soon as possible after separation chemistry.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for The Handling of Biological Materials.

7.4 If there is any Question regarding the safety of any laboratory practice, **stop immediately,** and consult qualified senior personnel such as a Group or Team Leader.

8.0 APPARATUS, EQUIPMENT, AND INSTRUMENTATION

8.1 Apparatus and Equipment

8.1.1 Silicon surface barrier detectors with associated electronics, vacuum chambers, and data reduction capabilities

8.1.2 Vacuum pump and filtration rig

8.1.3 Disposable filter funnels (containing 25 mm filters with 0.1 µm pore size)

8.1.4 Metal disks, 29 mm diameter

8.1.5 Stainless steel tweezers

8.1.6 Polypropylene centrifuge tube (50 mL)

8.1.7 Sample drying and ashing apparatus

8.1.8 Sample homogenization apparatus

8.1.9 Analytical Grade 1X8 anion exchange resin, 100-200 mesh

8.1.10 Beakers (Glass and Teflon of various sizes)

8.1.11 2.5 cm^3 column

8.1.12 25 mL column funnel extension

8.1.13 Watch glasses (various sizes)

8.1.14 Hot plate

8.1.15 Pipettes

8.1.16 Balances

8.1.17 Disposable transfer pipettes

8.1.18 pH strips

9.0 REAGENTS AND STANDARDS

9.1 Reagents

9.1.1 Hydrogen Peroxide (30% H_2O_2)

9.1.2 Neodymium (500 mg/L Nd)

9.1.3 Neodymium (10,000 mg/L Nd)

9.1.4 Ethyl alcohol (80% EtOH): Dilute 400 mL ethanol to 500 mL with DI water.

9.1.5 Hydrochloric Acid, concentrated (12 M HCl)

9.1.6 Hydrofluoric Acid, concentrated (49% HF)

9.1.7 Iron Carrier (10 mg/mL): Dissolve 62.7 g of $Fe(NO_3)_3 \bullet 6H_2O$ or 72.3 g $Fe(NO_3)_3 \bullet 9H_2O$ in 800 mL DI water and dilute to 1 L with DI water.

9.1.8 Hydrochloric Acid (9 M HCl): Add 750 mL of concentrated hydrochloric acid to 100 mL of DI water. Allow to cool and dilute to 1 L with DI water.

9.1.9 Hydrochloric Acid (2 M HCl): Add 167 mL of concentrated hydrochloric acid to 500 mL of DI water. Allow to cool and dilute to 1 L with DI water.

9.1.10 Nitric Acid, concentrated (16 M HNO_3)

9.1.11 Nitric Acid (8 M HNO_3): Add 500 mL concentrated nitric acid to 500 mL DI water.

9.1.12 Cellulose Nitrate Membrane filters (47 mm)

9.1.13 Substrate Suspension: Dilute 4 mL of neodymium (10,000 mg/L) and 80 mL concentrated hydrochloric acid to 1500 mL with DI water. Add, while stirring, 40 mL of 49% hydrofluoric acid and dilute to 2 L with DI water.

9.1.14 Sulfuric Acid, concentrated (36 M H_2SO_4)

9.1.15 Ammonium Hydroxide, concentrated (28-30% NH_4OH)

9.1.16 Saturated Boric Acid, 5%: Dissolve 50 g of H_3BO_3 per liter of DI water.

9.2 Standards

9.2.1 NIST traceable standards: Th-229, Th-230, Th-232, Ac-227.

9.2.2 Refer to GL-RAD-M-001.

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Liquid samples should be preserved to pH < 2 with concentrated nitric acid and collected in a plastic bottle.

10.2 Before beginning an analysis, the analyst should check the sample pH by removing a minimal amount of sample with a transfer pipette and placing it on a pH strip. DO NOT insert pH strip into sample container. If the sample is received with a pH > 2, the analyst should contact the Group Leader or Team Leader. If approved by the client, the analyst should adjust the pH with concentrated nitric acid to a pH < 2. If the sample pH is adjusted, let the sample sit in the original container for a minimum of 24 hours before analysis. This acidification should be documented on a batch history sheet and attached to the batch paperwork.

10.3 If the sample has exceeded the hold time, the analyst should contact the Group Leader before continuing with the batch.

10.4 Soil samples require no preservation and may be shipped in any suitable container.

11.0 SAMPLE PREPARATION

NOTE: Aliquots may be estimated by using the count time estimator.

11.1 Soil/Solids Sample Preparation

11.1.1 If not already done, dry and homogenize the sample by performing GL-RAD-A-021.

11.1.2 Measure an appropriate aliquot of soil/solids (usually 0.2 g to 1.0 g) in a suitable container (glass or Teflon beaker). If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced on the sheet. Record all aliquots. Add approximately 4 to 6 drops of iron carrier to the MB and LCS beakers. The MB and LCS aliquots should be recorded to be the same aliquot as the largest sample in the batch. Iron carrier may also be added to all samples in the batch, if necessary, based on the appearance and iron content of each sample. If solid reference material is required, weigh out approximately 0.1 g into the LCS beaker and record the exact weight.

11.1.3 Add a certified dpm of the appropriate tracer to each of the samples (usually between 5 to 10 dpm). Add a certified dpm (usually between 5 to 10 dpm) of the appropriate spike to the MS, MSD, LCS and LCSD as applicable. Reference the batch pull sheet for client requirements to determine appropriate tracer and spike.

11.1.3.1 For the determination of isotopic thorium, Th-229 is typically used as the tracer, and Th-232 is typically used as the spike.

NOTE: The addition of tracers and spikes should be witnessed by either another analyst qualified on this procedure, a Team Leader or a Group Leader. After adding the tracers and spikes, the witness must initial and record the date of witnessing.

11.1.4 If samples are to be place in a muffle furnace (recommended for miscellaneous solid samples), samples shall be in a glass beaker (not Teflon). Refer to GL-RAD-A021B for instructions.

11.1.5 For thorium analysis, digest as specified in GL-RAD-A-015.

11.1.6 Proceed to step 11.2.6.

11.2 Aqueous Sample Preparation

11.2.1 Add an appropriate aliquot of sample to a labeled beaker. Prepare a MB and LCS using DI water and a small amount of concentrated nitric acid to a pH < 2. The volume of DI water used should be the same as the largest volume of sample in the batch. If required, the DUP, MS and MSD should be the same aliquot as the appropriate sample referenced. Record all aliquots.

11.2.2 Add a certified dpm of the appropriate tracer to each of the samples

(usually between 5 to 10 dpm). Add a certified dpm (usually between 5 to 10 dpm) of the appropriate spike to the MS, MSD, LCS and LCSD as applicable. Reference the batch pull sheet for client requirements to determine appropriate tracer and spike.

11.2.2.1 For the determination of isotopic thorium, Th-229 is typically used as the tracer, and Th-232 is typically used as the spike.

NOTE: The addition of tracers and spikes should be witnessed by either another analyst qualified on this procedure, a Team Leader or a Group Leader. After adding the tracers and spikes, the witness must initial and record the date of witnessing.

NOTE: Other sample matrices, such as vegetation, air filters, tissue, etc., are prepared as outlined in GL-RAD-A-026. The analyst must ensure that the appropriate tracer(s) is added to these other matrices as discussed in section 11.1.3 and 11.2.2.

NOTE: If samples contain large amounts of sediment and client requires inclusion with the liquid portion of the sample, proceed to section 11.3.

11.2.3 Add 1 mL of iron carrier (10 mg/mL).

11.2.4 Add concentrated ammonium hydroxide until turbidity persists, or the pH > 9. Add approximately 2 mL in excess. Heat to boiling for approximately 10 minutes or until precipitate breaks into fine particles. Allow to settle and cool.

11.2.5 Decant excess supernate and discard. Collect the remaining precipitate by centrifugation in a 50 mL centrifuge tube and discard supernate.

NOTE: Exercise care in this step because finely divided material that contains the actinides may also be present in addition to large iron hydroxide flocks.

11.2.6 Dissolve the precipitate from step 11.2.5 or residue from step 11.1.6 in 10 to 15 mL of 8 M nitric acid.

NOTE: If all of the precipitated iron solids do not go into solution, it may be necessary to place samples in a hot water bath for approximately 10-15 minutes before proceeding to column work.

11.2.7 Slurry Analytical Grade 1X8 anion exchange resin in DI water. Transfer the resin to a small column to obtain a settled resin bed of approximately 2.5 mL.

11.2.8 Condition the column with 15 mL of 8 M nitric acid.

11.2.9 Pass the solution from step 11.2.6 through the column, and collect in a

drip pan for disposal.

NOTE: If the samples were traced with Ac-227, annotate the separation date and time when the load solution has passed through the column.

11.2.10 Rinse the column with 5 mL of 8 M nitric acid, and collect in a drip pan for disposal.

11.2.11 Rinse the column with 15 mL of 8 M nitric acid, and collect in a drip pan for disposal.

11.2.12 Elute the thorium from the column by adding 20 mL of 9 M hydrochloric acid, collecting the elution in a labeled, disposable centrifuge tube.

11.2.13 Transfer the sample to a beaker using DI water. Add approximately 4 to 6 drops of iron carrier. Evaporate the sample to dryness on medium heat.

11.2.14 Add 10 mL of concentrated nitric acid and slowly add approximately 2 to 3 mL hydrogen peroxide. Evaporate samples to dryness on medium heat.

11.2.15 Add 2 mL of concentrated hydrochloric acid and evaporate samples to dryness on medium heat.

11.2.16 Dissolve the residue with 4 mL of 2 M hydrochloric acid and transfer the sample to a clean centrifuge tube using DI water.

11.2.17 Add 0.1 mL of 500 mg/L neodymium and swirl. Add 2.0 mL of 49% hydrofluoric acid and swirl. Wait approximately 30 minutes to allow fluorides to coprecipitate with thorium.

11.2.18 Place the disposable filter funnel on the filter rig and apply vacuum.

11.2.19 Rinse the funnel with 80% ethyl alcohol.

11.2.20 Add 5 mL substrate suspension. After solution has passed through filter, add another 5 mL of substrate suspension.

11.2.21 Filter the fluoride precipitated solution through the filter paper. Rinse the centrifuge tube with approximately 5 mL DI water and pass through filter.

11.2.22 Rinse the funnel with 80% ethyl alcohol.

CAUTION: Directing a stream of liquid onto the filter will disturb the distribution of the precipitate on the filter and render the sample unsuitable for alpha spectrometry resolution.

11.2.23 Without turning off the vacuum, remove the funnel.

11.2.24 Turn off vacuum and remove filter. Mount filter on a labeled 29 mm flat planchet. Ensure that the filter is centered and as flat as possible on the planchet.

NOTE: Care should be taken not to touch the active area of the filter with tweezers.

11.2.25 Place the mounted filter under a heated lamp to dry (usually for 10-20 minutes).

11.2.26 Submit samples for alpha spectrometer counting.

11.3 Samples Containing Large Amounts of Sediment:

NOTE: When aliquoting samples that contain large amounts of sediment, ensure sample is thoroughly homogenized.

11.3.1 Dry on medium to low heat.

11.3.2 Muffle in a furnace at approximately 550° C for a minimum of 2 hours.

11.3.3 Proceed to step 11.1.5.

12.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

NOTE: Client contractual QC requirements override the requirements in this section.

12.1 Method Verification Requirements

Refer to GL-RAD-D-002 for instructions concerning the validation of analytical methods.

12.2 Method Specific Quality Requirements

12.3 Actions Required if the Quality Control Requirements Are Not Met

If any of the QC criteria from 12.2.1 through 12.2.4 cannot be satisfied, the analyst should inform the Group Leader and initiate a Data Exception Report as outlined in GL-QS-E-004.

13.0 INSTRUMENT CALIBRATION AND PERFORMANCE

For direction on calibration and instrument performance, refer to GL-RAD-I-009.

14.0 ANALYSIS AND INSTRUMENT OPERATION

For analysis and instrument operation, refer to GL-RAD-I-009.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

For maintenance of system, refer to GL-RAD-I-010.

16.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

Data recording, calculation, and reduction take place in accordance with GL-RAD-D-003 and GL-RAD-D-006.

17.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

Refer to GL-RAD-D-003 for instructions concerning the data review process, approval, and transmittal.

18.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND WASTE DISPOSAL

Radioactive samples and material are disposed as outlined in the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

20.1 EPA Environmental Monitoring and Support Laboratory, Las Vegas. Radiochemical Analytical Procedures for Analysis of Environmental Samples. March 1979.

20.2 EML Procedures Manual HASL-300, 1982.

20.3 Analytical Chemistry. Rapid Determination of Th-230 in Mill Tailings by Alpha Spectroscopy. UNC Geotech, Grand Junction Projects Office. Steve Donivan, Mark Hollenbach, and Mary Costello. Vol. 59, No. 21, 1987.

20.4 Los Alamos Health and Environmental Chemistry: Analytical TechniQueues. LA-10300-M Vol. 1, September 1987.

20.5 Special thanks to Dr. Bill Burnett and his associates for assistance in developing this method at Florida State University.

20.6 U.S. DOE RP 800:, Methods for Evaluating Environmental and Waste Management Samples, “Sequential Separation of Americium and Plutonium by Extraction Chromatography”, 1997.

20.7 U.S. EPA, EMSL LV 053917 (EPA RA-LV-PI), “ Isotopic Determination of Plutonium, Uranium, and Thorium in Water, Soil, Air, and Biological Tissue”, 1979.

21.0 HISTORY

Revision 14: Added section 2.3 and references for certification.

Revision 15: Updated reference to calculation SOP and DI water.

Revision 16: Technical updates for SOP consistency as part of annual review. Added Appendix 3 regarding clean up steps.

Revision 17: Updated SOP to current practices.

Revision 18: Remove the reference to queue sheets.

APPENDIX 1

THORIUM

Use a 2.5 cm^3 column with 1 x 8 anion resin (Cl^- form 100-200 mesh)

_____ 15 mL 8 M HNO_3 (Condition Column)
_____ 10–15 mL 8 M HNO_3 (Load)
_____ 5 mL 8 M HNO_3 (Rinse)
_____ 15 mL 8 M HNO_3 (Rinse)
_____ **Elute Th:** 20 mL 9 M HCl (Catch in C-Tube)
_____ Transfer to a clean beaker. Add approximately 4-6 drops of Fe carrier and evaporate to dryness on medium heat
_____ 10 mL of concentrated HNO_3 and approximately 2–3 mL H_2O_2. Evaporate to dryness on medium heat.
_____ 2 mL of concentrated HCl and evaporate to dryness on medium heat.
_____ Dissolve with 4 mL of 2 M HCl and transfer to centrifuge tube with DI water.
_____ Proceed to Appendix 2 for thorium precipitation

APPENDIX 2

THORIUM PRECIPITATION

_____ 0.1 mL 500mg/L neodymium and swirl

_____ 2.0 mL 49% HF and swirl

_____ Wait approximately 30 minutes

_____ Filter

APPENDIX 3

SAMPLE CLEANUP FROM AN ALPHA SPEC FILTER

1. Remove the filter from the mounting disc by wetting the filter with a small amount of acetone and pulling the filter off the disk using tweezers. Place the filter in a labeled glass beaker.
2. Add 4-6 drops of iron carrier (10 mg/L), 10 mL of concentrated hydrochloric acid and 1.0 mL of 5% boric acid solution.
3. Fill the bulb end of a disposable pipette with DI water and turn upside down. Place on the filter in the glass beaker to ensure the filter remains submerged.
4. Heat on a hot plate for 30 minutes frequently stirring the filter, flipping it over then back, etc. Use the disposable pipette to stir and flip.
5. Remove the filter from the solution and rinse with 9M HCl. Do this over the glass beaker so the 9M HCl rinse falls back into the beaker.
6. Evaporate to dryness.
7. Convert with concentrated Nitric Acid and evaporate to dryness.
8. Proceed to section 11.2.6 and perform separations as specified.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

SAMPLE ACCEPTANCE POLICY, SAMPLE LOGIN AND STORAGE

(GL-SR-E-001 REVISION 48)

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GEL Proprietary

1.0 STANDARD OPERATING PROCEDURE FOR SAMPLE ACCEPTANCE POLICY, SAMPLE LOGIN AND STORAGE

2.0 PURPOSE

To describe the routine operational procedures for the receipt, login, and storage of samples received by GEL Laboratories, LLC (GEL).

3.0 DISCUSSION

3.1 Sample custody is a pre-planned mechanism for tracking a sample from the collection of the sample in the field through the release of the finished analytical data to the client. At the collection site, the sample containers are filled with sample and the chain of custody (CoC) form is initiated. The sample collector fills out the form, which includes the name of the client, the requested analysis parameters, sample location, the date and time of collection, sampling technique, preservatives used, and any comments or remarks that may be useful in the analytical work or data interpretation that will follow. Proper sample receipt, login and storage assure accurate chain of custody.

3.2 Custody is defined as:

3.2.1 Being in your physical possession, or

3.2.2 Being in your view, after being in your possession, or

3.2.3 Being locked up after being in your possession, or

3.2.4 Being in a designated secure area

3.3 Upon arrival at the laboratory, sampling personnel, delivery services and carriers relinquish the samples to sample management personnel. The samples and chain of custody documents are evaluated for sample acceptance, rejection, or qualification, based upon the requirements in GEL's Quality Assurance Plan GL-QS-B-001 Sample Storage and Preservation Requirements and any additional requirements provided by the client or regulatory authorities. Each sample container receives a unique sample identifier that is assigned electronically by AlphaLIMS (GEL's Laboratory Information Management System). AlphaLIMS tracks the status and location of each sample container, and serves as the database for analytical results.

4.0 DEFINITIONS

4.1 AlphaLIMS: The Laboratory Information Management System used at GEL.

4.2 Chain of Custody (CoC): A written record of sample transfer and possession.

4.3 Custody Seal: Security seals that are attached to sample containers and/or bottles that are used to detect unauthorized tampering.

4.4 Holding Time: The period of time between sample collection and preparation or analysis.

4.5 Labeled Package: A package containing radioactive material labeled with a Radioactive White-I, Radioactive Yellow-II or Radioactive Yellow-III label as specified in US Department of Transportation Regulations, 49 CFR 172.403 and 172.436-440.

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4.6 Limited Quantity-Excepted Package (UN2910): A packaging and its radioactive contents that meet reduced quantity restrictions and relaxed packaging specifications under the Department of Transportation's Hazardous Materials Regulations, 49 CFR 173.400, Subpart I.

4.7 Material Safety Data Sheet (MSDS): A document that may accompany samples of known chemical characteristics. (Refer to GEL's Safety, Health and Chemical Hygiene Plan for more information on MSDSs.)

4.8 Matrix: The physical appearance or make-up of a sample (groundwater, drinking water, wastewater, soil, sludge, etc.) as determined by the client or Project Manager.

4.9 Preservative: Additives that are introduced to a sample at the time of collection to help retard chemical and biological changes that may occur.

4.10 Sample: Any item that has been submitted for analysis to GEL.

4.11 Sample Delivery Group (SDG): One or more samples (typically not to exceed 20 samples) from a specific client that are reported by the laboratory at the same time.

4.12 Sample Receipt Review (SRR): A form used to document a sample's arrival and the condition of its arrival at the laboratory.

4.13 Turn Around Time (TAT): A numeric designation to the degree of attention a sample should receive. This designation is used to convey the client's requested data delivery dates to the laboratory.

5.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

5.1 All samples must be handled with care during the login process. Wear protective gear such as gloves, safety glasses and laboratory coats when handling all samples. Some samples may be accompanied by MSDSs that contain vital information on potential hazards. The sample description and client labels may also give this information.

5.2 If there is a spill of a known hazard (based on historical results, MSDSs, and/or sample description), immediately contact the Group Leader, Laboratory Waste Manager, or Radiation Safety Officer as appropriate.

5.3 All sample management personnel are required to read and understand GEL's Safety, Health and Chemical Hygiene Plan, which is found on GEL's Intranet.

6.0 SAMPLE PACKAGE RECEIPT

6.1. All sample packages submitted to GEL are received by sample management personnel. Samples are received from a number of carriers including GEL field staff, GEL couriers, individual clients, and public and private shipping companies.

6.2. Upon arrival, all sample packages will be inspected for integrity. Note any unusual physical damage, signs of leakage, or evidence that custody seals have been tampered with. If the package appears to be leaking or has any unusual odor, place it under the fume hood and notify the Group Leader, Laboratory Waste Manager, Radiation Safety Officer, or Project Manager as appropriate before continuing. As appropriate, the client should be contacted for further direction.

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6.3. All sample packages are screened for external contact radiation exposure. This screening is accomplished by performing a spot check on the external surfaces of each package (top, bottom, all sides). This screening is performed to determine the possible presence of radionuclide(s) that may require special handling. When a radioactive labeled package, a Limited Quantity UN2910 package, or any package that exceeds 0.5 mR/hr on contact is received, the RSO group is notified, and the package is segregated in the sample receiving area. The RSO or designee will unpack the package following the procedures described in GL-RAD-S-007 for Receiving Radioactive Packages.

6.4. Clients may notify GEL that they are submitting samples potentially contaminated with beryllium or asbestos. Sample receiving documents may also indicate the presence or potential presence of these contaminants. Personnel identifying samples such as these must notify the Safety group. The Safety group will determine what special handling requirements are needed and provide specific instructions. These handling requirements may vary from unpacking the shipping container under an enclosure in login to transferring control of the container to the Safety Group. When transferred to the Safety Group, these samples are handled as Safety Controlled Samples as described in SOP GL-RAD-S-016 (Work Permits).

6.5. Some packages received by the laboratory from sources outside the continental United States contain soil samples that are regulated by the US Department of Agriculture (USDA). GEL holds a valid foreign soil permit issued by the USDA authorizing the laboratory to receive, handle, treat and dispose of these foreign samples under the specific conditions stated in the signed Compliance Agreement between GEL and the USDA. When packages are received from outside the continental US, the login technician must refer to GL-SR-E-004, Control of Foreign Soils, to ensure full compliance with the additional regulatory requirements promulgated for foreign soils. The login technician shall continue to follow this SOP for receipt procedures and take the supplemental steps contained in GL-SR-E-004 in parallel.

6.6. Bioassay and Low Level Mercury (LLHg) sample packages are initially received and segregated in the GEL login area. Following package screening, they are then transported to the bioassay or LLHg login area for inspection, login, and storage. Bioassay staff will refer to the checklist in Appendix 3 or a similar client-specific checklist for sample inspection on Bioassay samples. Bioassay staff will then follow login and storage procedures starting at section 7.0. LLHg staff performs the same sample inspection, login, and storage requirements as noted in this SOP using the Sample Review Receipt (SRR) Form in Appendix 1.

6.7. The remaining packages are further inspected to identify any samples intended to be received under the authority of GEL's Radioactive Material License.

6.7.1. In addition to "labeled" radioactive material, radioactive material is any material that meets the following criteria: Any material shipped and received that is marked as radioactive (i.e. conventional trefoil, yellow and magenta tape, etc), or has otherwise been declared radioactive by the cosigner on the accompanying

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documents, or may be intended for receipt under the authority of a radioactive materials license although it was shipped under DOT exemption for radioactive material.

6.7.2. Materials identified as "radioactive" shall be handled in accordance with the handling procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

6.7.3. Copies of the CoC and SRR for radioactive samples are made available for the RSO group to review.

6.8. All discrepancies noted during receipt and inspection shall be recorded using a SRR form in Appendix 1.

6.8.1. Client-specific Sample Receipt Review forms may be created by the Project Management Group. These checklist are created because additional sample management comments and checks are required in order to meet quality objectives established for these project samples. Sample management personnel are responsible for using any client required receipt forms.

6.9. Open all shipping containers (excluding Bioassay and LLHg samples) under the high volume exhaust duct located in Sample Receiving.

NOTE: It is only necessary to open Bioassay and LLHg samples under a fume hood when the integrity of the containers is suspected/determined to be compromised.

6.10. All samples received (excluding bioassay) must be screened for radioactivity using a Geiger-Muller pancake probe. Results for the highest reading samples in the sample receipt group are to be noted on the SRR form. The Radiation Safety Group shall be notified when for any individual nonradioactive sample, readings exceed 2X background.

6.10.1. All samples from sites that have a history of radioactive material that are to be shipped to another facility without a radioactive material license are to be further screened by the Radiation Safety Group. If the sample is found to have activity for alpha beta above LLD, as determined by gas flow analysis in GEL SOP GL-RAD-S-001, the sample will be handled as radioactive material and shipping is described in GEL SOP GL-SR-E-002. If the activity is below the LLD for alpha and beta, the sample will be forwarded to the other facility as non-radioactive material as described in the same SOP.

6.11. The CoC should accompany all samples received by the Sample Management Group. The CoC documentation includes sample identification (e.g., MW-1; Lagoon 17; #1234567), sampling date and time, sample collector, requested parameters to be tested, sample location, preservation type and any special comments. If a nonradioactive sample arrives without this documentation, the Sample Management Group upon receipt can initiate the CoC. Identify this initiation by printing "INITIATED ON RECEIPT" on the CoC form. Alternately, the Project Manager may contact the customer to obtain a

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chain of custody. If a radioactive sample arrives without a chain of custody, the sample will be placed on hold until a chain of custody is submitted.

6.12. Compare the sample labels to the chain of custody: compare sample descriptions, collection dates, collection times, number and type of containers and any other available information. Note any discrepancies between the CoC and samples on the SRR and inform the Project Manager. Sign and date (including time) the CoC in the appropriate box.

NOTE: The labeling system is to be unique and is to include the use of water- resistant labels and indelible ink.

7.0 PRESERVATION CHECKS

7.1. Analytical procedure may require preservation of the sample to ensure that changes in the sample's chemistry or biology do not occur. The two predominant preservation techniques used are changing the pH of the sample and cooling the sample to 0° ≤ 6° C. It is important to check and document the holding time, preservation, and temperature of the samples upon arrival to the laboratory. The GEL generated barcode label is utilized to record and document the observed, or checked preservation via the AlphaLIMS system using the 'container management application'. The application captures the container type, preservative, temperature, technician, date and time. The correct methods of sample storage, container type, minimum volume/mass, chemical preservation, and maximum holding times are shown in GEL's Quality Assurance Plan GL-QS-B-001. Those samples determined to be nonconforming shall additionally be documented on the SRR and the Project Manager notified. Rad II and Rad III samples may only be opened in a HEPA-filtered enclosure with Rad technician interface.

NOTE: Any sample for the Department of Energy requiring thermal preservation which cannot be received and immediately taken to its final storage location shall be placed in temporary thermal storage until the sample labels are available to complete the receiving process. If samples are not placed in temporary storage or taken directly to the final sample storage location, the Department of Energy client shall be notified in writing.

7.2. Sample receipt temperature measurement shall be verified through the use of a temperature blank for **each** transport container (such as a cooler) or other sample container measurement when temperature blank is not available. An IR gun or immersion thermometer may be used.

7.2.1. Open the sample cooler.

7.2.2. Remove the Temperature Validation Container (TVC) if provided.

7.2.3. Open the TVC and immerse a thermometer with a valid calibration into the TVC.

7.2.4. Allow the thermometer reading to equilibrate, and read the thermometer result while it is still immersed in the TVC.

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7.2.5. Alternately, the receipt temperature can be measured with a calibrated infrared temperature (IR) gun by selecting the TVC or another sample within the shipment for receipt/shipping temperature check.

NOTE: Calibration checks are performed daily on each IR gun prior to use. The IR gun reading is compared to an immersion thermometer and the temperature of both devices is recorded in the calibration check logbook. The IR gun reading must agree within ± 0.5 °C to be acceptable for use.

NOTE: If the thermometer or IR gun is labeled with a correction factor ('Add' or 'Subtract') this value must be either added or subtracted from the displayed value on the thermometer or IR gun prior to recording the temperature value.

7.2.6. Record the observed reading using the 'container management application'. The Sample Receipt Review form (Appendix 1), and the CoC may also be used, if a space is provided: i.e. "TEMP 4° C UPON ARRIVAL."

7.2.7. Temperature verification results of 0 ≤ 6° C, are considered conforming for those samples listed as requiring storage at 4° C. The EPA has extended this range from just above the freezing temperature of water to 6° C.

7.2.8. If the initial temperature verification result is determined to be nonconforming, select multiple sample containers (if available) from the shipping container and re-perform the temperature measurements. Document all measurements.

7.2.9. Record the confirmation temperatures using the 'container management application'. Also use the SRR as well as on the CoC if a space is provided. Label the temperature as a confirmation temperature (i.e., CT = 7.0° C).

7.2.10. If another container is not available within the shipment to verify the temperature, the secondary temperature verification is not performed and duly noted.

NOTE: Samples that are hand delivered to the laboratory on the same day that they are collected may not meet these criteria. In these cases, the samples may be considered acceptable if there is evidence that the chilling process has begun (such as arrival on ice).

7.3. Verify and document pH preservation using the following procedure:

7.3.1. Open the container and remove an aliquot of the original sample. Immerse a pH strip into the removed aliquot. When the likelihood that the potential for spilling a sample exists by pouring, a Pasteur pipette should be used to obtain sample to perform the pH check. Pipettes containing pH test strips are single-use and may be placed into sample containers to withdraw enough sample for pH strip testing.

7.3.2. Observe the pH as indicated on the pH strip, and properly discard pH strip and any secondary containers or glassware used in testing.

NOTE: Never reuse a pH strip or one that has been contaminated.

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NOTE: Use the pH strip appropriate for the range being tested.

7.3.3. Document results on the preservation verification for each distinct container in the AlphaLIMS system via the 'container management application'. Document the overall receipt issues on the appropriate line of the SRR form.

NOTE: If the pH of the sample is determined to be nonconforming, place the sample on hold and notify the Project Manager. The Project Manager will call the client for further direction.

7.3.4. If direction is given to adjust the preservation, continue processing the sample, and chemically preserve the sample with the appropriate preservative. Record the lot # of preservative used on the SRR.

7.3.5. After adding the appropriate preservative to the sample, wait at least 2 minutes and perform steps 7.3.1 through 7.3.2 again. The preserved sample should now be places on the preservation adjustment hold shelf located in AlphaLIMS as "preservation 24-hour hold shelf" (sample receiving). This ensures that the 16-hour holding time for metals samples and the 24-hour holding time for radiochemistry samples are met following preservation or adjustment. Additionally, sample management time is met. Document this on the SRR: "SAMPLE PRESERVED UPON ARRIVAL."

7.3.6. The following is a list of tests that require pH verification upon arrival:

TEST	pH
Ammonia	≤ 2
COD	≤ 2
Cyanide	≥ 12
Hardness	≤ 2
Hydrazine	≤ 2
Metals	≤ 2
Nitrate/Nitrite	≤ 2
Phenols	≤ 2
Phosphorous, Total	≤ 2
Radiochemistry (all except Tritium, C-14, Rn-222, I-129, I-131)	≤ 2
Sulfide	≥ 9
TKN	≤ 2
TOC/TIC/DOC	≤ 2

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NOTE: The pH of all aqueous sample fractions, preserved and unpreserved, shall be checked during sample login for the following National Nuclear Security Administration (NNSA) (formerly known as DOE-Albuquerque):

- Los Alamos National Laboratories
- Pantex Plant
- Sandia National Laboratories, Albuquerque

NOTE: Exceptions to the pH check are C-14, TPH-GRO, EDB/DBCP, Rn-222, tritium, iodine, VOC, TOX, oil and grease, and urine samples.

NOTE: The preservative verification is made only when the client sample labels indicate either the analytical fraction or the chemical preservative.

7.4. Project Managers may specify via client specific SRRs that aqueous organic analysis sample containers (excluding volatile 40 mL vials) be checked for the presence of residual chlorine at the time of sample receipt. Residual chlorine is checked by using the following procedure:

7.4.1. Pour an aliquot of the sample into a secondary container. Immerse a potassium iodide/starch paper strip into the secondary container to test the sample. The presence of residual chlorine may be alternatively determined by removing a very small aliquot of the sample using disposable glassware. The aliquot is tested using potassium iodide/starch paper.

7.4.2. A blue color on the starch paper indicates the presence of residual chlorine. Discard the test strip and any secondary container or glassware used in testing.

7.5. If residual chlorine is present, document this on the SRR and inform the Project Manager. The Project Manager may specify that samples with residual chlorine require the addition of sodium thiosulfate.

8.0 ALPHALIMS LOGIN

8.1. A copy of the chain of custody may be printed (colored paper may be used as a practice to identify originals vs. copies) to facilitate the login process of the samples. The originals can be retained with the samples in the sample receipt area. Once completed the completed original CoC and SRR are delivered to the appropriate Project Manager.

8.2. The Project Manager or Project Manager Assistant pre-logs the data from the CoC into AlphaLIMS. Once samples are pre-logged into the system, the data are verified, and the samples are logged-in. Unique bar code labels are generated for each sample container upon completion of the log-in. Details of the Project Management process for pre-log and login may be found in GL-CS-M-001 and GL-CS-E-008.

8.3. The bar code labels are ready to be affixed to the appropriate containers.

8.3.1. Sample bar code labels are color-coded as follows:

8.3.2. Yellow for radioactive I

8.3.3. Purple for radioactive II

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8.3.4. Red for radioactive III

8.3.5. Solid white for nonradioactive samples

8.3.6. Orange for material required special waste handling.

8.4. Compare the sample description on the printed GEL bar code label to the client sample bottle label before attaching labels to containers. Wherever possible, the GEL label should not cover the client's label or any other information provided by the client or sample collector.

8.5. If the sample is a solid submitted for volatiles or TCLP VOA analysis and a single container is provided, a designation is generated on the barcode label indicating, "Volatiles must aliquot sample first." It is then stored in the appropriate storage location until removed for volatiles or TCLP volatiles testing. Once the volatiles lab takes its required aliquot the container will be marked with the analyst's initials and the date completed. The sample container will then be placed in the appropriate walk-in cooler and released for other laboratory analyses. Note exception in Section 9.2.1.

NOTE: Clients may request that a sample(s) previously received, be logged in for additional testing and that they are composited for the creation of a new sample (e.g., weekly filters composited to create a quarterly sample). These samples should also follow the steps outlined above or the relog function in LIMS which can be used to transfer the information previously submitted.

8.6. Situations may occur that delay the login process of samples. Examples include: awaiting client direction in response to a nonconformance, discrepancies between chain of custody and sample label information, broken, contaminated, or damaged containers, etc. Once a delay is identified, a Project Management team member will identify any samples requiring thermal preservation and place them into temporary refrigerated storage until such a time that they are ready to be labeled. At the end of each shift, a Project Management team member will perform an inspection documenting any unlabeled sample containers. The results of this inspection will be emailed to members of the Project Management Group and the Client Services Manager.

8.7. Project Managers and the Client Services Manager will be notified daily of any containers remaining in the hold cooler to include relogs, subcontractor samples, or any other sample containers placed in the temporary storage location. This process will be repeated daily until the sample issue is resolved and the sample containers in question are either relocated to proper storage locations or properly packed for shipment.

9.0 SAMPLE STORAGE

9.1. Properly labeled samples are scanned into the electronic tracking system in AlphaLIMS. The samples are placed in the appropriate storage areas located within the laboratory in a secure facility with limited access. Refer to GL-LB-E-012 for Verifying the Maintenance of Sample Integrity.

NOTE: Samples requiring immediate analysis or those with very quick turn around times (TAT) may be made available to the laboratory prior to label application. In these

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cases, the label is applied to any remaining sample container after the sample has been made available for analysis. This sample type includes VOA "EnCores" which require immediate preservation by the VOA group. Solid samples submitted for volatile analysis that are collected in "EnCore" containers shall be delivered to the volatiles laboratory immediately after unpacking to help ensure preparation hold times are met.

9.2. Samples are placed in numerical order in the appropriate storage locations throughout the facility. Containers are 'loaded' into the system by container type and size (i.e., 1000 mL Nalgene), preservative (i.e., sulfuric acid), and storage area of destination.

9.2.1. Samples requiring analysis of volatile organics shall be segregated from other samples by placing them in either the radioactive or nonradioactive coolers, which are located in the Volatiles are and maintained at $0 \leq 6°$ C. EnCore samples are placed in the designated freezer. Encore kits containing 40 mL vials are placed in the freezer at a slight tilt or a 45° angle to prevent breakage due to the expansion of liquid.

NOTE: Samples requiring volatile analyses known to contain high concentrations of organic solvents or hydrocarbons should not be stored in the volatiles coolers. Place these samples in the general use walk-in cooler.

9.2.2. Samples requiring radiochemical analyses only are stored, in numerical order, in ambient storage. Radioactive and nonradioactive samples are segregated in these storage areas.

9.2.3. Samples requiring thermal preservation (other than volatile organics samples) are stored in numerical order in general use walk-in coolers, which are maintained at $0 \leq 6°$ C. Radioactive and nonradioactive samples are segregated in these storage areas.

9.3. Coolers are monitored in accordance with GL-LB-E-004, Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators, and Other Similar Devices, for requirements associated with temperature monitoring and temperature monitoring devices.

10.0 RECORDS MANANGMENT

10.1 The Sample Receipt Review form is attached to the chain of custody and forwarded to the Project Manager.

10.2 Cooler temperature logs are reviewed in AlphaLIMS. Refer to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators, and Other Similar Devices.

11.0 REFERENCES

11.1 Example Standard Operating Procedures for Contract Laboratory Program (CLP), National Enforcement Investigations Center (NEIC), Contract Evidence Audit Team (CEAT-TechLaw), EPA Contract 68-01-6838, 1986.

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11.2 Dept. of Defense (DOD), Dept. of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories DOD QSM Version 5.2, December, 2018.

11.3 Table 4-1 of SW-846 Chapter 4, Rev 4, February 2007-PCB hold times.

11.4 Section 8, SW-846 Method 8082A, February 2007-PCB hold times.

12.0 HISTORY

Revision 48: Revised test. Updated sample receipt and review form, updated DoD QSM Version 5.2 requirements.

Revision 47: Updated Appendix 1 with current form. Updated Reference Section for current DoD QSM Version 5.2, December, 2018.

Revision 46: Added a Note after section 7.1 to address preservation for DOE samples.
Revision 45: Updated the Sample Receipt & Review form in Appendix 1.
Revision 44: Clarify and segregate receipt activities, remove sample storage and preservation table available in QAP.
Revision 43: Updated errors and clarification of preservation requirements for the following parameters: Hardness (EDTA titration), Hardness (calculation), Hydrazine, Odor, pH, Total Organic Halides, Poylnuclear Aromatic Hydrocarbons, added footnote 9.

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APPENDIX 1: SAMPLE RECEIPT AND REVIEW FORM (FOR ILLUSTRATIVE PURPOSE ONLY)

GEL Laboratories LLC

SAMPLE RECEIPT & REVIEW FORM

Client:	**SDG/AR/COC/Work Order:**
Received By:	**Date Received:**
Carrier and Tracking Number	Circle Applicable: FedEx Express FedEx Ground UPS Field Services Courier Other

Suspected Hazard Information	**Yes**	**No**	*If Net Counts > 100cpm on samples not marked "radioactive", contact the Radiation Safety Group for further investigation.
A)Shipped as a DOT Hazardous?			Hazard Class Shipped: UN#: If UN2910, Is the Radioactive Shipment Survey Compliant? Yes___ No___
B) Did the client designate the samples are to be received as radioactive?			COC notation or radioactive stickers on containers equal client designation.
C) Did the RSO classify the samples as radioactive?			Maximum Net Counts Observed* (Observed Counts - Area Background Counts): _____ **CPM / mR/Hr** **Classified as: Rad 1 Rad 2 Rad 3**
D) Did the client designate samples are hazardous?			COC notation or hazard labels on containers equal client designation.
E) Did the RSO identify possible hazards?			If D or E is yes, select Hazards below. PCB's Flammable Foreign Soil RCRA Asbestos Beryllium Other:

	Sample Receipt Criteria	**Yes**	**NA**	**No**	**Comments/Qualifiers (Required for Non-Conforming Items)**
1	Shipping containers received intact and sealed?				Circle Applicable: Seals broken Damaged container Leaking container Other (describe)
2	Chain of custody documents included with shipment?				Circle Applicable: Client contacted and provided COC COC created upon receipt
3	Samples requiring cold preservation within (0 ≤ 6 deg. C)?*				Preservation Method: Wet Ice Ice Packs Dry ice None Other: *all temperatures are recorded in Celsius **TEMP:**_____
4	Daily check performed and passed on IR temperature gun?				**Temperature Device Serial #:**_____ Secondary Temperature Device Serial # (If Applicable):
5	Sample containers intact and sealed?				Circle Applicable: Seals broken Damaged container Leaking container Other (describe)
6	Samples requiring chemical preservation at proper pH?				Sample ID's and Containers Affected: If Preservation added, Lot#:
7	Do any samples require Volatile Analysis?				If Yes, are Encores or Soil Kits present for solids? Yes___ No___ NA___(If yes, take to VOA Freezer) Do liquid VOA vials contain acid preservation? Yes___ No___ NA___(If unknown, select No) Are liquid VOA vials free of headspace? Yes___ No___ NA___ Sample ID's and containers affected:
8	Samples received within holding time?				ID's and tests affected:
9	Sample ID's on COC match ID's on bottles?				ID's and containers affected:
10	Date & time on COC match date & time on bottles?				Circle Applicable: No dates on containers No times on containers COC missing info Other (describe)
11	Number of containers received match number indicated on COC?				Circle Applicable: No container count on COC Other (describe)
12	Are sample containers identifiable as GEL provided?				
13	COC form is properly signed in relinquished/received sections?				Circle Applicable: Not relinquished Other (describe)

Comments (Use Continuation Form if needed):

PM (or PMA) review: Initials _____ Date _____ Page _____ of _____

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Example Only

APPENDIX 2: SAMPLE RECEIPT AND REVIEW CONTINUATION FORM

(FOR ILLUSTRATIVE PURPOSE ONLY)

GEL Laboratories LLC

SAMPLE RECEIPT & REVIEW CONTINUATION FORM

Client: _____ **Received By:** _____ **Date Received:** _____ **SDG/AR/COC/Work Order:** _____

Example Only

PM (or PMA) review: Initials _____ Date _____ Page _____ of _____

APPENDIX 3: BIOASSAY SAMPLE RECEIPT AND REVIEW FORM (FOR ILLUSTRATIVE PURPOSE ONLY)

GEL Laboratories LLC

Bioassay Sample Receipt & Review Form

Client:	Work Order/SDG:
Date Received:	PM (A) Review:
Received By:	GEL Cooler / Client Cooler / Box / Other (Circle one)

	Sample Review Criteria	Yes	No	Comments/Qualifiers (Required for Non-Conforming Items)
1	Were all shipping containers intact and sealed?			
2	Were all chain of custody documents included?			
3	Were all chain of custody documents completed correctly?			
4	Were all sample containers listed on the chain of custody received?			
5	Were all sample containers intact, sealed, and properly labeled?			
6	Were all samples received within holding time?			
7	Were samples weighed upon receipt, weights recorded on chain of custody? (Tare weights: Brown wide mouth in box = 225 g, clear wide mouth = 217 g, clear small opening box = 210 g, 500 mL bottle = 67 g, 250 mL bottle = 38 g)			
8	Airbill, Tracking #'s, and Additional Comments?			

Example Only

APPENDIX 4: REMP SAMPLE RECEIPT AND REVIEW FORM

(FOR ILLUSTRATIVE PURPOSE ONLY)

GEL Laboratories LLC

REMP Sample Receipt & Review Form

Client:	**Work Order/SDG:**
Date Received:	**PM(A) Review:**
Received By:	**GEL Cooler / Client Cooler / Box / Other (Circle one)**

	Sample Review Criteria	Yes	No	Comments/Qualifiers (Required for Non-Conforming Items)
1	Were all shipping containers intact and sealed?			
2	Were all chain of custody documents included?			
3	Were all chain of custody documents completed correctly?			
4	Were all sample containers listed on the chain of custody received?			
5	Were all sample containers intact, sealed and properly labeled?			
6	Were all sample IDs and collection dates and times matching between the chain of custody and the bottles?			
7	Were all samples received within holding time?			
8	Were samples marked Radioactive or Hazardous? (If so, contact PM or Rad Safety, samples may need to be returned to Login)			
9	Were SONG drinking water samples preserved with 25mg NaHSO3 and 20mL HCl upon receipt?			
10	Airbill, Tracking #'s, and Additional Comments?			

Example Only