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August 25, 2011

United States Army Corps of Engineers
Kansas City District
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ATTN:	CENWK-PM-ES/Buckrucker
CONTRACT:	W912DQ-08-D-0018
PROJECT:	Lower Passaic River Restoration Project Remedial Investigation/Feasibility Study Oversight Lower Passaic River Study Area, New Jersey
SUBJECT:	Final Quality Assurance Project Plan, Addendum #9 River Mile 10.9 Characterization Study

Dear Ms. Buckrucker:

CDM Federal Programs Corporation (CDM) is pleased to submit this electronic copy of the Final Quality Assurance Project Plan, Addendum No. 9 for Oversight of the Remedial Investigation/ Feasibility Study, River Mile 10.9 Characterization in support of the Lower Passaic River Restoration Project in the Lower Passaic River Study Area, New Jersey. This document is based on the CPG's *Quality Assurance Project Plan/ Remedial Investigation River Mile 10.9 Characterization Study, Revision 2* dated August 2011.

If you have any comments concerning this submittal, please contact me at (212) 377-4056.

Very truly yours,
CDM FEDERAL PROGRAMS CORPORATION

Frank Tsang, P.E.
Program Manager

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623560

Contract No.: W912DQ-08-D-0018
Task Order No.: 014

U. S. Army Corps of Engineers
Kansas City District

Final Quality Assurance Project Plan Addendum No.9 River Mile 10.9 Characterization

Lower Passaic River Restoration Project

Remedial Investigation/Feasibility Study Oversight

Lower Passaic River Study Area, New Jersey

August 25, 2011

CDM

LOWER PASSAIC RIVER RESTORATION PROJECT

OPERABLE UNIT (OU) 2

Remedial Investigation/Feasibility Study Oversight
Final Quality Assurance Project Plan
Addendum No. 9

River Mile 10.9 Characterization
Lower Passaic River Study Area, New Jersey

USACE CONTRACT No. W912DQ-08-D-0018

TASK ORDER No. 014

August 25, 2011

Prepared for:
U.S. Army Corps of Engineers
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Note:

Worksheets not included herein are included in the Physical Water Column Monitoring/Generic Final QAPP dated March 9, 2010.

Acronyms

%	percent
%D	percent difference
%R	percent recovery
µg/g	microgram per gram
µg/L	microgram per liter
A	analytical
AAS	atomic absorption spectrometry
ABS	absolute difference
AES	atomic emission spectrophotometry
ANSETS	Analytical Services Tracking System
ASC	analytical services coordinator
ASTM	American Society of Testing and Materials
BS	Bachelor of Science
CA	corrective action
CAS	Chemical Abstract Service
CCV	continuing calibration verification
CD	compact disk
CDM	Camp, Dresser & McKee
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CHMM	Certified Hazardous Materials Manager
CIH	certified industrial hygienist
CLP	Contract Laboratory Program
COC	chain of custody
COPC	compound of potential concern
CPG	Cooperating Parties Group
CRM	certified reference material
CRQL	contract required quantitation limits
CVAFS	cold vapor atomic fluorescence spectrometry
DESA	Division of Environmental Science and Assessment
DL	detection limit
DOC	dissolved organic carbon
DoD	Department of Defense
DQA	data quality assessment
DQI	data quality indicators
DQL	data quality level
DQO	data quality objectives
DV	data validation

EDD	electronic data deliverable
EPA	United States Environmental Protection Agency
EQL	estimated quantitation limit
ESAT	EPA data validation contractor
FAR	Federal Acquisition Regulations
FASTAC	Field and Analytical Services Teaming Advisory Committee
FID	flame ionization detector
FS	feasibility study
FSP	field sampling plan
FTL	field task leader
GC/MS	gas chromatograph / mass spectroscopy
H&S	health and safety
H&SM	health and safety site manager
HASP	Health and Safety Plan
HDPE	high density polyethylene
HPLC	High Pressure Liquid Chromatography
HQ	headquarters
HRGC/HRMS	High Resolution Gas Chromatography / High Resolution Mass Spectrometry
HRGC/LRMS	High Resolution Gas Chromatography / Low Resolution Mass Spectrometry
ICAL	initial calibration
ICP	inductively coupled plasma
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ID	identification
IPR	initial precision and recovery
IR	infra-red
KC	Kansas City
LAN	local area network
LC	lethal concentration
LCS	laboratory control samples
LCSD	laboratory control sample duplicates
LPR	Lower Passaic River
Ltd.	limited
MDL	method detection limit
mg/kg	milligram per kilogram
mg/L	milligram per liter
MPI	Malcolm Pirnie Inc.
MS	matrix spike
MS/ MSD	matrix spikes /matrix spike duplicate

NA	not available or not applicable
ng/g	nanogram per gram
ng/kg	nanogram per kilogram
NJ	New Jersey
NJDEP	New Jersey Department of Environmental Protection
NJDOT	New Jersey Department of Transportation
NOAA	National Oceanic Atmospheric Administration
NY	New York
^{o}C	degrees Celsius
OPR	ongoing precision and recovery
OU	operable unit
oz	ounce
PAH	polycyclic aromatic hydrocarbon
PAL	project action limit
PCB	polychlorinated biphenyl
PCDD/PCDF	polychlorodibenzodioxin /polychlorodibenzofurans
pg/g	picogram per gram
PPE	Personal Protection Equipment
ppt	parts per thousand (salinity unit)
PQL	project quantitation limit
PQLG	project quantitation limit goal
PQO	project quality objective
PREmis	Passaic River Estuary Management Information System
PRP	potentially responsible party
PT	Performance Test
QA	quality assurance
QAC	quality assurance coordinator
QAPP	quality assurance project plan
QC	quality control
QCS	quality control sample
QL	quantitation limit
QP	quality procedure
RA	remedial action
RAS	routine analytical services
RI/FS	Remedial Investigation / Feasibility Study
RL	reporting limit
RPD	relative percent difference
RPM	remedial project manager
RSCC	Regional Sample Control Coordinator

RSD	relative standard deviation
S&A	sampling and analytical
SA	self assessment
SDG	Sample Delivery Group
SM	Standard Method
SOP	standard operating procedure
SOW	scope of work
SVOC	semivolatile organic compound
TAL	target analyte list
TBD	to be determined
TCL	target compound list
TOC	total organic carbon
TOM	task order manager
TSOP	Technical Standard Operating Procedure
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
WS	worksheet

Dioxin and Furans:

HpCDD	hepta-chlorodibenzo-*p*-dioxin
HpCDF	hepta-chlorodibenzofuran
HxCDD	hexa-chlorodibenzo-*p*-dioxin
HxCDF	hexa-chlorodibenzofuran
OCDD	octa-chlorodibenzo-*p*-dioxin
OCDF	octa-chlorodibenzofuran
PeCDD	penta-chlorodibenzo-*p*-dioxin
PeCDF	penta-chlorodibenzo-furan
TCDD	tetrachloro-dibenzo-*p*-dioxin
TCDF	tetrachloro-dibenzo-furan

Introduction

CDM Federal Programs Corporation (CDM) will perform oversight and accept split sediment samples from the Cooperating Parties Group (CPG) during the August 2011 River Mile 10.9 Characterization study in the Lower Passaic River Study Area (LPRSA).

This Final Quality Assurance Project Plan (QAPP) Addendum No.9 and the *Lower Passaic River Remedial Investigation / Feasibility Study (RI/FS) Oversight Final QAPP, Physical Water Column Monitoring and Generic Information for Upcoming Tasks*, dated March 2010 (hereafter referred to as the Final QAPP) are the governing documents for execution of this characterization event conducted as part of the RI/FS. CDM will use the various plans prepared by the CPG contractors to verify proper execution of the study's sample handling, preservation and shipment.

The CDM Final QAPP indicated that future oversight tasks assigned to CDM would be appended with selected worksheets. The following worksheets are included in this addendum to reflect only the analytical procedures and requirements of the CPG's QAPPs written by AECOM, *Quality Assurance Project Plan, Lower Passaic River Restoration Project, River Mile 10.9 Characterization* dated July 2011, Revision 2:

- Worksheet No. 1 contains the title and approval pages for the addendum
- Worksheet No. 2 contains the QAPP identifying information
- Worksheet No. 3 provides the distribution list
- Worksheet No. 10 describes the specific problem definition
- Worksheet No. 11 provides the project quality objectives
- Worksheet No. 14 provides a summary of project tasks
- Worksheet No. 16 provides the schedule and timeline
- Worksheet No. 18 provides the proposed survey locations
- Worksheet No. 37 provides the usability assessment (field summary report)

Worksheets 12, 15, 19, 20, 23, 24, 28, 30, and 36 are also included in this addendum to address the sampling and analytical requirements of this event. The CPG's Characterization QAPP provides procedures for conducting the sampling.

1.1 Summary of Sediment Samples Collection

CDM's oversight program is designed to provide technical review, verify the accuracy of the CPG's sediment sample results, and evaluate the CPG-implemented QAPPs for sediment sampling.

Oversight will include field observation and acceptance of split sediment samples from a sampling grid developed for the RM 10.9 sampling area. The CPG's sampling purpose is to provide representative nature and extent coverage and to gather data on physical characteristics to further the understanding of sediment stability over the study area and radiological samples to provide information on historic depositional patterns. Grab samples from the surface of the sediment and sediment cores (low resolution) will be split with the CPG field team.

Split samples will be analyzed for select groups of contaminants as requested by EPA and USACE.

Group A includes:

- PCB congeners and homologs
- Polychlorinated dibenzo-dioxin and furans (PCDD/PCDF) congeners
- Organochlorine pesticides
- Polyaromatic hydrocarbon (PAH) compounds
- Semi-volatile organic compounds SVOCs
- Herbicides
- Volatile organic compounds (VOCs)
- Metals (including low level mercury)
- Total petroleum hydrocarbons (TPH) extractables
- Total organic carbon (TOC)

Butyltins, cyanide, grain size, percent moisture, specific gravity, and sulfides will also be collected by the CPG during the investigation, but will not be split by CDM.

Group B includes nutrients such as Ammonia-nitrogen, phosphorus, and TKN as well as AVS/SEM. As with components of Group A, Group B will not be split by CDM.

Group R includes radiochemistry components such as Pb-210 and Cs-137. CDM will not initially split these samples. EPA is requesting that the CPG retain the radiological samples for potential recount by EPA's subcontract laboratory if the counting results suggest that a recount is required.

Additional oversight activities will include review of CPG-selected sampling locations and supporting documents as well as observation of field procedures. This oversight QAPP details the planning and execution processes for conducting field oversight, and accepting, preparing, and shipping samples for analysis and evaluation of data.

QAPP Worksheet #1
Title and Approval Page

Document Title: **LPR Restoration Project Final Quality Assurance Project Plan (QAPP) River Mile 10.9 Characterization**

Lead Organization: United States Army Corps of Engineers (USACE) – Northwestern Division

Preparer's Name and Organizational Affiliation: Jeniffer Oxford, CDM

Preparer's Address, Telephone Number, and E-mail Address: 14 Wall Street, Suite 1702
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Preparation Date (Day/Month/Year): August 25, 2011

Investigative Organization's Project Manager/Date: 8/25/11
Signature

Frank Tsang/CDM

Investigative Organization's Project QA Manager/Date: for Jo Nell Mullins 8/25/11
Signature

Jo Nell Mullins/CDM

Lead Organization's Project Manager/Date: _____
Signature

Elizabeth Buckrucker/USACE – KC District

EPA Remedial Project Manager /Date: _____
Signature

Stephanie Vaughn

EPA Quality Assurance Officer /Date: _____
Signature

William Sy

Document Control Numbering System: Not Applicable (N/A)

QAPP Worksheet #2
QAPP Identifying Information

Site Name/Project Name: Lower Passaic River (LPR) Restoration Project	**Title**: QAPP Addendum No. 9, River Mile 10.9 characterization
Site Location: LPR study area, New Jersey	**Revision Number:** 0
Site Number/Code: NJD 980528996	**Revision Date:** NA
Operable Unit (OU): OU2	**Contractor Name:** Camp, Dresser, & McKee (CDM)
Contractor Number: W912DQ-08-D-0018	
Contract Title: Unrestricted Indefinite Delivery/Indefinite Quantity, Multiple Award Contract, for Architect-Engineer Environmental Services for EPA Region 2 and the Corps of Engineers Northwestern Division.	
Task Order Number: 14	

1. Regulatory program: Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (Superfund)

2. Approval entity: United States Army Corps of Engineers (USACE)

3. The QAPP is (select one): Generic **√ Project Specific**

4. Dates of negotiation: NA

5. Dates and titles of QAPP documents written for previous and current site work, if applicable:

Title	Approval Date
See Final QAPP for a full list of previous QAPP prepared for site work	
Lower Passaic River RI/FS Oversight Final QAPP, Physical Water Column Monitoring and Generic Information for Upcoming Tasks (PWCM/Generic QAPP) (referred to herein as Final QAPP)	March 2010
LPR RI/FS Oversight QAPP, Final Addendum No.1: *Avian Community Survey*	August 6, 2010
LPR RI/FS Oversight QAPP, Final Addendum No.2: *Fish Community Survey*	June 8, 2010
LPR RI/FS Oversight QAPP, Final Addendum No.3: *Benthic Invertebrate Community Survey*	June 8, 2010
LPR RI/FS Oversight QAPP, Addendum No.4: *Surface Sediment Sampling Co-located with the Small Forage Fish Tissue Samples during the Summer 2010 Benthic Community Survey oversight*	July 12, 2010
LPR RI/FS Oversight QAPP, Addendum No.5: *Fish Tissue Analysis*	August 24, 2010
LPR RI/FS Oversight QAPP, Addendum No.6: *Habitat Identification Survey*	August 9, 2010
LPR RI/FS Oversight QAPP, Addendum No.7: *Caged Bivalve Study*	April 29, 2011
LPR RI/FS Oversight QAPP, Addendum No.8: *Small Volume Chemical Water Column Monitoring Study*	August 2, 2011

6. Organizational partners (stakeholders) and connection with lead organization: United States Environmental Protection Agency (EPA), USACE, New Jersey Department of Environmental Protection (NJDEP), New Jersey Department of Transportation (NJDOT), National Oceanic Atmospheric Administration (NOAA), United States Fish and Wildlife Service (USFWS)

7. Data users: EPA, USACE, Partner Agencies, CDM, Louis Berger Group, Inc., HydroQual, Inc., and stakeholders

8. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusions below: the Final Generic QAPP provides all the required worksheets. *This addendum addresses only the River Mile 10.9 Characterization oversight, therefore only worksheets pertinent to this task and information not previously provided are included.*

QAPP Worksheet #3
Distribution List

QAPP Recipients	Title	Organization	Telephone Number	Fax Number	E-mail Address
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Candice Navaroli	Project Manager	Axys Analytical Services limited (Ltd.)	(250) 655-5800 or (888) 373-0881	250-655-5811	cnavaroli@axys.com
John Birri	Laboratory Contact	DESA Laboratory	219-769-8378	(732) 906-6886	Birri.John@epamail.epa.gov
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Problem Definition
QAPP Worksheet #10

The problem to be addressed by the project:

Sediment sampling: Oversight will include field observation and acceptance of surface and core sediment split samples from River Mile 10.9 in order to better characterize that region of the LPR. CDM will provide oversight and analysis of split samples collected from the LPR Study Area to verify the CPG's compliance with their approved project plans and accuracy of derived data.

Oversight will include:

- Technical Review and evaluation of CPG's project plans
- Documentation of field activities observations and deficiencies
- Acceptance of split sediment samples
- Sample handling, packaging and shipping to off-site laboratories
- Review of CPG-selected sampling locations
- Comparison of data sets to determine any analytical bias

Additional information is provided on Worksheet 11.

The environmental questions being asked:

- Is the CPG contractor complying with the approved plans?
- Does the CPG data adequately describe the site conditions and is it representative for project decisions?
- Is the CPG and CDM data complete and accurate?
- Are data sets comparable?
- Does the data show any analytical bias?
- Are the CPG versus CDM data relative percent difference (RPD)'s within the measurement performance criteria?

Secondary data: See Worksheet #13 of the CPG River Mile 10.9 Characterization QAPP (AECOM 2011)

The possible classes of contaminants and the affected matrices:

Split sediment samples will be collected for the following chemical analyses:

- Polychlorinated biphenyl (PCB) congeners and homologs using EPA Method 1668A
- Polychlorinated dibenzo-dioxin and furans (PCDD/PCDF) congeners using EPA Method 1613B

Problem Definition
QAPP Worksheet #10

- Organochlorinated pesticides (excluding toxaphene) using Axys SOP MLA-028
- PAHs, and alkyl PAHs based on California EPA Air Resources Board Method 429 and NOAA ORCA 130 Method (Axys Lab SOP)
- SVOCs using EPA Method 8270C
- Chlorinated Herbicides using EPA Method 8151A
- Volatile organic compounds (VOCs) using EPA Method 8260B
- Metals (including low-level mercury) and titanium using EPA Method 6010C and EPA Method 1631
- Total petroleum hydrocarbons (TPH) extractables using NJDEP Method OQA-QAM-025-02/08
- Total organic carbon (TOC) using the Lloyd Kahn Method

Split samples will not be accepted for the following analytes to be analyzed by the CPG contractors: butyltins, cyanide, sulfide, total phosphorus, total Kjeldahl nitrogen, ammonia, acid volatile sulfide/simultaneously extracted metals, bulk density, specific gravity, percent moisture, and grain size. Moisture analysis will be conducted routinely only as part of the analytical procedure to report results as dry weight.

The rationale for inclusion of chemical and non-chemical analyses:

The split samples will be used to support the goals of the oversight program. The analyses selected to be split were determined to be more critical for oversight evaluation; the analyses that will not be split are ancillary parameters and not major risk drivers. The field observations and split sample data will enable CDM to perform technical review and evaluation on the CPG field program, analytical data and reports and to qualitatively assess any potential bias in the CPG dataset.

Project decision conditions ("If..., then..." statements):

- If field work is inconsistent with the CPG QAPPs, then the field oversight staff will verify tasks with respect to the CPG's QAPPs, and HASP and note deviations with the CPG's field project leader and document such discussions in the Daily Field Summary Reports submitted to EPA. The CDM Project Manager, USACE PM and EPA RPM will be informed if there are deviations.
- If the CPG team needs to relocate survey locations, or there are any changes to the planned field program, CDM will communicate this change to the USACE and document it on the Daily Field Summary Reports.

CDM will present data findings in a Report and submit it to the USACE and EPA, who will then determine if any additional actions are required.

QAPP Worksheet #11
Project Quality Objectives /Systematic Planning Process Statements

Who Will Use the Data? USACE, EPA and other partner agencies, CDM, and stakeholders (as necessary).

What Will the Data be Used For?

The CPG will use the sediment data to:

- Characterize the stability of sediments in the RM 10.9 sediment deposit in the LPRSA
- Determine the nature and extent of contamination in the RM 10.9 sediment deposit
- Assess the potential for sediments and associated COPCs to be transported from this location to downstream areas of the river
- Develop an understanding of physical and chemical characteristics of the RM 10.9 sediment deposit
- Develop a comprehensive conceptual site model

Oversight activities will monitor the CPG-implemented sediment sampling program to verify that elements of the approved RI/FS QAPPs are fulfilled. The oversight field crew will also review the CPG-selected sampling locations. CDM's split sample results will be compared to data obtained by the CPG to determine if a bias exists in data produced by the CPG and if data are complete and accurate and compliant with the approved QAPPs.

A comparison of the split sample data and the CPG parent sample data will only be completed for parameters that were analyzed and detected by both the CPG program and the oversight program. Data comparison will not be conducted on concentrations that are non-detect. (Note that if a consistent bias in detections is observed in either the split samples or CPG samples, an evaluation of detection limits will be completed.) The data comparison will be presented in a table showing the relative percent difference for values that are 5 times the quantitation limits. As appropriate, alternative data comparisons will be provided. For each location, a mean and variance of the sample concentrations may also be calculated. These statistics will be compared to the CPG samples. For analytical groups that contain multiple parameters (e.g., congeners), data comparison will be completed on select parameters per chemical class. Parameters will be selected by the project chemist/and analytical service coordinator to cover a range of concentrations from non-detects to high concentrations. In addition, analytes of greater risk or of greater concern will be selected for comparison over other analytes. This selection will be made with the consensus of the USACE and EPA.

Because of the overlap of the SVOC and PAH chemical classes, some analytes will be reported twice in the split sample program. For data comparison, PAH results reported by Axys Analytical Services using the HRGC/LRMS method will take precedence over the PAH data generated

QAPP Worksheet #11
Project Quality Objectives /Systematic Planning Process Statements

during the SVOC analysis.

CDM's QC data will be used to determine CDM's split samples data quality and comparability with the CPG's data and whether sample results are acceptable based on the established project data quality objectives (DQOs). QC sample results will be compared to the measurement performance criteria (MPC) of data quality indicators (DQIs).

To further achieve these objectives, CDM field personnel will observe the CPG's contractors field implementation of the RI/FS QAPPs and note any deviations. Deviations will be brought to the attention of the CPG's contractor, and reported to the CDM project manager who will communicate this information to the USACE PM and EPA RPM. These will be documented in the Daily Field Summaries and in the Final Report and include a discussion of the impact of the deviation(s) on data quality. The CPG contractor's activities will be documented in the field logbook.

What Type of Data is Needed?

CDM will observe and document the sediment sampling activities conducted by the CPG's contractor to facilitate verification of the chemical data suitability for the project objectives listed on Worksheet No. 10. Split samples will be collected at random locations selected by the CDM Field team or as directed by the CDM Deputy project manager or the USACE/EPA project managers. Analyte splits to be collected include PCB congeners, PCDD/PCDF congeners, organochlorine pesticides, VOCs, PAHs and Alkyl PAHs, SVOCs, chlorinated herbicides, metals including titanium and total low level mercury, TPH extractables, and TOC. Low limits are required for mercury as shown on QAPP Worksheet # 15.

How much data are needed?

Oversight observations will be made at the locations shown on Figure 1 of the CPG's Characterization QAPP, River Mile 10.9 Characterization. CDM will observe the CPG's Contractor sampling at all locations and will accept split samples at approximately 10 percent of the sampling locations. Locations will be selected by the field oversight personnel in consultation with the deputy project manager and EPA. Worksheets # 11 and 18 and Figure 1 of the CPG's QAPP show the planned locations for sampling. Oversight activities are listed in Worksheet 10. Field duplicates will be analyzed for each sample event.

QAPP Worksheet #11
Project Quality Objectives /Systematic Planning Process Statements

How "good" do the data need to be in order to support the environmental decision?

The oversight observation will mirror the CPG locations to allow data comparability. CDM's oversight staff will document whether the sampling program is consistent with the CPG's QAPP. The representativeness of data is dependent on the sampling design.

Definitive level data are required for full validation of data. Fixed based laboratories with EPA, Environmental Laboratory Accreditation Program or national Environmental Laboratory Accreditation Program certifications and qualification will be used to generate the analytical data. CDM has attempted to use comparable methods and obtain similar reporting limits to the CPG's.

CDM's oversight staff will document whether the River Mile 10.9 Characterization study is in compliance with the CPG's QAPP. The representativeness of data is dependent on the sampling design established by the CPG.

The laboratory reporting limits or quantitation limits (QLs), need to be below or equal to the CPG's project required detection limits or the CPG's achievable laboratory quantitation limits. CDM will notify DESA or the CDM subcontract laboratory and request lower reporting limits to achieve the project data quality objectives for sensitivity as needed.

Validation of data will be performed by DESA/ EPA; however samples analyzed by a subcontract laboratory will be validated by CDM.

In addition, to ensure that measurement performance criteria for usability (criteria for measures of precision, accuracy, representativeness, comparability, completeness, and sensitivity) are met, all CDM data will be subject to a data usability assessment. The inputs will be the EPA generated validation reports and subcontract laboratory QC summaries. Measurement performance criteria for the assessment are presented in Worksheets #12, 28, 35 and 36. The results will be presented in a CDM data report.

The data usability assessment will evaluate whether appropriate field procedures were followed and whether data met the approved QAPP and project DQOs and are usable for the stated project needs.

QAPP Worksheet #11
Project Quality Objectives /Systematic Planning Process Statements

Where, when, and how should the data be collected?

When - The sediment samples will be collected by the CPG's contractor and split with the CDM oversight staff during the characterization study. Oversight will be performed according to the CPG's schedule. The field event started on August 22, 2011; oversight sampling will begin on August 29, 2011.

Where - The survey locations are shown in the CPG Characterization QAPP, Figure 1. At locations selected by CDM in consultation with the USACE and EPA, additional sediment mass will be collected to generate sufficient mass for both sample sets.

How - Field sampling procedures are described in the CPG characterization QAPP, which details the sampling procedures and how the samples will be collected. CDM will accept the split samples and prepare them for shipment. Split samples will be obtained by the alternate filling of the sample bottles with the CPG's contractor with sufficient volume to fulfill analytical needs.

Who will collect and generate the data?

CDM oversight staff will record field observations in logbooks and accept splits of the selected locations while the field sampling program is being conducted by the CPG. The CPG's contractor will provide a split of a portion of the sediment samples to CDM who will label, pack and ship to the appropriate laboratories. The analytical laboratories outlined in this QAPP will generate data.

How will the data be reported?

- Field observations and accepted splits will be recorded as described in CDM's Final QAPP using field logbooks in accordance with TSOP 4-1 provided in Appendix C of the CDM Final QAPP.
- Results will be reported in text format and will include a discussion of data quality, deviations from the QAPP, and oversight data comparability with the CPG's data. This review will be used to evaluate the accuracy of the CPG data.
- Sample results generated by the DESA laboratory will be e-mailed to CDM for use in data assessment and evaluation
- Sample results generated by CDM's subcontract laboratory will be e-mailed to CDM for review and validation.
- Data reporting is further covered in the CDM Final QAPP.

QAPP Worksheet #11
Project Quality Objectives /Systematic Planning Process Statements

How will the data be archived?

- Hard copies of data will be kept in the CDM Edison office until archived in the project file; if requested, survey data will be uploaded to the EarthSoft Environmental Quality Information System (EQuIS) database.

The CDM March 2010 Final QAPP contains other archival information.

QAPP Worksheet #12-a
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	VOCs
Concentration Level	Low

Sampling Procedure	**Analytical Method/ SOP**	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria[1] (MPC)**	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)**
CPG Group's SOP, and QAPP CDM will accept split samples	SW-846 Method 8260B	Precision	RPD ≤ 40% if concentration ≥5 CRQL	Split samples and field duplicates	S & A
		Precision	RPD ≤30%	MS/MSD	S & A
		Precision	%RPD <30% or ±QL for samples <10x QL	LCS/LCSD	A
		Accuracy	70-130% Recovery	LCS/LCSD; MS/MSD	A; S & A
		Sensitivity/ accuracy	≤ QLs (WS#15)	Field rinsate blanks/ Method blanks/ DV and DQA	S & A – Rinsate blank A – Method blank
		Accuracy	Per laboratory SOP	Surrogates	A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S & A
		Completeness	≥ 90%	Evaluated during Data Quality Assessment	S & A

Note:
1. The assigned laboratory will perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable laboratory SOP.

QAPP Worksheet #12-b
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	SVOC
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1] (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	SW-846 Method 8270D	Precision	RPD ≤ 40% if concentration ≥5 CRQL	Split samples and field duplicates	S & A
		Precision	Per laboratory SOP	LCS/LCSD; MS/MSD	A; S & A
		Accuracy/Bias	Per laboratory SOP (compound specific)	LCS; MS/MSD	A; S & A
		Accuracy	Per laboratory SOP	Surrogate	A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S & A
		Comparability	Comparable units, and methods	Evaluated during Data Quality assessment	S & A
		Completeness	≥ 90%	Evaluated during Data Quality Assessment	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15)	Field rinsate blanks/ Method blanks/ DV and DQA	S & A

Note:
1. The designated laboratory will perform the analysis, and meet the measurement performance and QC criteria in their SOP or Statement of Work.

QAPP Worksheet #12-c
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	PAHs and Alkyl PAHs
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1] (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	Axyx SOP MLA-021 based on GC/MS Isotope dilution Method is confidential	Precision	RPD ≤ 40% if concentration ≥10 QL	Split samples and field duplicates	S & A
		Precision	±20% of mean if concentration >10DL	Laboratory duplicate or MS/MSD	A
		Accuracy/Bias	50-200 %recovery (see laboratory SOP for individual limits)	Matrix Spike	S & A
		Accuracy/Bias	15-130% recovery (See SOP for individual limits)	Perdeuterated Surrogate	A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S
		Comparability	Comparable units, and methods	Evaluated during Data Quality assessment	S & A
		Completeness	≥ 90%	Evaluated during Data Quality Assessment	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15)	Field rinsate blanks/ Method blanks/ DV and DQA	S & A

Note:
The assigned laboratory will perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable laboratory SOP.

QAPP Worksheet #12-d
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	Organochlorine pesticides
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1] (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	Axys SOP: MLA-028 Isotope Dilution Method is confidential	Precision	RPD ≤ 40% if concentration ≥10 QL	Split samples and field duplicates	S & A
		Precision	±20% of mean if concentration >10DL	Laboratory duplicate	A
		Accuracy/Bias	Per laboratory SOP ±20%	Certified Reference Material or Spike Reference Standard	A
		Accuracy/Bias	60-150% R for E1 pesticides and 50-130% R for E2 pesticides (See SOP for compound list and individual recoveries ranges)	On-going Precision and Recovery /Matrix Spike	A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S
		Accuracy/Bias	20-150% recovery (See SOP for individual limits)	Surrogate	A
		Comparability	Comparable units, and methods	Evaluated during Data Quality Assessment	S & A
		Completeness	≥ 90%	Evaluated during Data Quality Assessment	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15 and SOP)	Field rinsate blanks/Method blanks/ DV checked during DQA	S & A

Note:
The assigned laboratory must perform and meet all the quality assurance requirements specified in MLA-028 including: performance of initial and ongoing studies, calibration verification, addition of internal standards, analyses of blanks and determination of detection limits.

QAPP Worksheet #12-e
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	PCB Congeners
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1] (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	EPA Method 1668A Lab SOP MLA-010 Method is confidential	Precision	RPD ≤ 40% if concentration ≥10 CRQL	Split samples and field duplicates	S & A
		Precision	≤ 40% RPD; ±QL for samples <10x QL	Laboratory (analysis) duplicate	A
		Accuracy/Bias	70 -130 %recovery. This value will be superceded by supplier provided limits.	Certified Reference Material; Calibration Verification Sample	A
		Accuracy/Bias	60-140 %recovery 20-135 %recovery – varies by compound	Initial Precision and Recovery Labeled compounds	A
		Precision	RSD ≤ 40%		
		Accuracy/Bias	Per laboratory SOP Warning 70-130%R; Accept 50-150 %recovery	LCS or Ongoing Precision and Recovery	A
		Accuracy	50-150 %recovery in Calibration verification and 15-140% Recovery in ongoing verification standards	Surrogates	A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S
		Comparability	Comparable units, and methods	Data Quality assessment	S & A
		Completeness	≥ 90%	Data Quality Assessment	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15)	Field rinsate blanks/ Method blanks/ DV and DQA	S & A

Note:
The assigned laboratory will perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable laboratory SOP.

QAPP Worksheet #12-f
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	Herbicides
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1] (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	SW-846 Method 8151A Laboratory SOP S-SV-022	Precision	RPD ≤ 40% if concentration ≥5 CRQL	Split samples and field duplicates	S & A
		Precision	≤ 20% RPD; ±QL for samples <10x QL	Laboratory duplicate	A
		Accuracy/Bias Precision	35-155 %recovery (See laboratory SOP for individual limits)	MS/MSD	S & A
		Accuracy/Bias		LCS	A
		Accuracy/Bias	Per laboratory limits	Surrogates	A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks /Data validation (DV)	S
		Comparability	Comparable units, and methods	Data Quality assessment	S & A
		Completeness	≥ 90%	Data Quality Assessment	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15)	Field rinsate blanks/ Method blanks/ DV and DQA	S & A

Note:
1. The assigned laboratory will perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable laboratory SOP.

QAPP Worksheet #12-g
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	TPH Extractables
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1] (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	New Jersey Method OQA-QAM-025-10/91 Laboratory SOP No. EDS-GCS-011	Precision	RPD ≤ 40% if concentration ≥5 CRQL	Split samples and field duplicates	S & A
		Precision	≤ 20% RPD; ±QL for samples <10x QL	Laboratory duplicate	A
		Accuracy/Bias Precision	70 -130 %recovery	MS/MSD	S & A
		Precision	RSD ≤ 40%		
		Accuracy/Bias	60-140 %recovery	LCS	A
		Accuracy/Bias	Per laboratory SOP	Surrogates	A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S
		Comparability	Comparable units, and methods	Data Quality assessment	S & A
		Completeness	≥ 90%	Data Quality Assessment	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15)	Field rinsate blanks/ Method blanks/ DV and DQA	S & A

Note:

1. The assigned laboratory will perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable laboratory SOP.
2. The information above may change dependent on the assigned laboratory.

QAPP Worksheet #12-h
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	PCDD/PCDF Congeners
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1] (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	USEPA Method 1613B – Axys Analytical Services SOP MLA-017 using Dean Stark extraction Method is confidential	Precision	RPD ≤ 40% if concentration ≥10 CRQL	Split samples and field duplicates	S & A
		Precision	±20 of mean if concentration >10DL	Laboratory duplicate	A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S
		Precision	Per laboratory SOP	Initial precision and recovery	A
		Accuracy/Bias	70-130% recovery or per laboratory SOP	Ongoing precision and recovery	A
		Accuracy/Bias	17-130% recovery	Sample surrogates	A
		Comparability	Comparable units, and methods	Evaluated during Data Quality Assessment	S & A
		Completeness	≥ 90%	Evaluated during Data Quality Assessment	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15)	Field rinsate blanks/ Method blanks/ DV and DQA	S & A

Note:
The assigned laboratory will perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable laboratory SOP.

QAPP Worksheet #12-i
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	Metals
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1] (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	SW-846 Method 6010C ICP-AES Lab SOP: S-IM-022	Precision	RPD ≤ 40% if concentration ≥5 CRQL	Split samples and field duplicates	S & A
		Precision	RPD ≤ 35% if concentration ≥5 CRQL – Lab limit: 20% RPD	Laboratory duplicate	A
		Accuracy/Bias	80-120 %recovery	LCS	A
		Accuracy/Bias	75-125 %recovery	MS/MSD	S & A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S & A
		Comparability	Comparable units, and methods	Evaluated during Data Quality assessment	S & A
		Completeness	≥ 90%	Evaluated during Data Quality Assessment	S & A
		Sensitivity/ accuracy	≤ CRQLs (WS#15)	Field rinsate blanks/ Method blanks/ DV and DQA	S & A

Note:
The assigned laboratory will perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in the applicable laboratory SOP.

QAPP Worksheet #12-j
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	Total low level mercury
Concentration Level	Trace (ng/g)

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1] (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	EPA Method – 1631 Microbac SOP Hg-1631	Precision	RPD ≤ 40% if concentration ≥5 CRQL	Split samples and field duplicates	S & A
		Accuracy	RPD ≤ 24% for values ≥10 MDL. No more than 35% of RSDs >25%	Laboratory duplicate	A
		Accuracy/Bias	71-126 %recovery	MS/MSD	S & A
		Precision	RPD ≤ 24%	MS/MSD	S & A
		Accuracy/Bias	77-123 %recovery	Blank Spike (QC Sample)	A
		Precision	RPD ≤ 20%	Blank Spike Duplicate	A
		Accuracy	Laboratory LIMS or 70-130%R; 75-125%R	Ongoing Precision and Recovery; Standard Reference Material	A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S & A
		Comparability	Comparable units, and methods	Evaluated during Data Quality assessment	S & A
		Completeness	≥ 90%	Evaluated during Data Quality Assessment	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15) ≤ 5MDLs	Field rinsate blanks/ Method blanks/ DV and DQA	S & A

Note:
The assigned laboratory must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in USEPA Method 1631. If DESA performs the analysis, they will meet the measurement performance and QC criteria in their SOP.

QAPP Worksheet #12-k
Measurement Performance Criteria Table

Matrix	Sediment
Analytical Group	TOC
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria[1] (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	EPA Method - Lloyd Kahn DESA SOP C-88. Rev. 2	Precision	RPD ≤ 40% if concentration ≥5 CRQL	Split samples and field duplicates	S & A
		Accuracy/Bias	75-125 %recovery	Laboratory Fortified Blank or AQCs or QCS	A
		Precision	RPD ≤20%		A
		Precision	RPD ≤50%	Sample matrix duplicates	S & A
		Sensitivity/ accuracy	≤ 100 mg/kg (WS#15)	Field rinsate blanks/ Preparation blank/ DV and DQA	S & A
		Accuracy/ Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S & A
		Comparability	Comparable units, and methods	Evaluated during Data Quality assessment	S & A
		Completeness	≥ 90%	Evaluated during Data Quality Assessment	S & A

QAPP Worksheet #14
Summary of Project Tasks

Sampling Tasks:
As part of the LPR Restoration Project, the CPG is characterizing an area at River Mile 10.9 to support the RI/FS. On behalf of the USACE and EPA, CDM will provide oversight and will record observations at all locations. The oversight program is designed to provide technical review and evaluation of CPG-implemented field sampling plans. Worksheet #10 discusses the oversight activities that will occur; and Worksheet #11 provides details on data to be collected. CDM's task is to observe and document the sampling conducted during the surveys.

CDM will also accept split samples from the CPG's sampling contractor during the River Mile 10.9 sampling investigation. CDM's oversight staff will package, label and ship samples and QC samples to the DESA laboratory and the subcontract laboratories outlined on QAPP Worksheet 30.

Analysis Tasks:
Split samples will be collected during oversight of the River Mile 10.9 sampling conducted during from Mid August through the fall 2011. Oversight will be documented in the field logbooks by CDM's oversight staff. Analyses of sediment split samples will include VOCs, SVOCs, PAHs and Alkyl PAHs, organochlorinated pesticides, PCB congeners and homologs, herbicides, PCDD/PCDF, TPH extractables, metals (total including titanium), mercury (total low level), and TOC.

Quality Control Tasks: Field duplicate samples will be collected as outlined on Worksheet #20. CDM will observe CPG's calibration, testing and maintenance of their GPS units. CDM will document observations of the survey in the field logbooks. The CDM Deputy project manager or designee will review the logs to ensure that the required information has been documented.

Secondary Data: Since this is an oversight project, no secondary data are being used directly by CDM. Data generated by the CPG - field program will be used as shown on Worksheet #11 of the CPG's QAPP.

Data Management Tasks:
Analytical data generated by the various laboratories will be managed according to the procedures described in the CDM Final QAPP. The

QAPP Worksheet #14
Summary of Project Tasks

information will be uploaded to the EQuIS database.

Documentation and Records: Records of the River Mile 10.9 sediment characterization field oversight will be documented in the field logbooks. All field activity, deviations and additional information will be documented in project logbooks.

Records of accepted sediment cores and grab samples will be documented in field logbooks. Oversight observations, notes and results will be documented in the following:

1. Field logs/logbooks
2. Data Validation reports
3. COCs, ANSETS, and Trip Report
4. Oversight summary report
5. Data Quality and Usability Summary Report

All procedures will be documented in accordance with TSOP 4-1 provided in Appendix C of the CDM Final QAPP.

Assessment/Audit Tasks: See CDM Final QAPP for assessment tasks (CDM 2009)

Data Review Tasks: The CPG's Data Summary Report will be reviewed by CDM. A data quality evaluation will be performed based on the CPG's compliance with their approved QAPP. A comparison of CDM's and the CPG's sediment sample results will be included in the data quality evaluation and submitted to the USACE.

QAPP Worksheet #15-a
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: VOCs by 8260B
Concentration Level: Low (mg/kg)

Analyte	CAS Number	Project Action Limit [1]	Project Quantitation Limit Goal (PQLG) [2]	Analytical Method		Achievable Laboratory Limits[3, 4]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
1,1,1-Trichloroethane	71-55-6	290	0.0050	0.005	NL	0.00034	0.005
1,1,2,2-Tetrachloroethane	79-34-3	0.56	0.0050	0.005	NL	0.00044	0.005
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	4300	0.0050	0.005	NL	0.0021	0.005
1,1,2-Trichloroethane	79-00-5	0.16	0.0050	0.005	NL	0.00057	0.005
1,1-Dichloroethane	75-34-3	3.3	0.0050	0.005	NL	0.00046	0.005
1,1-Dichloroethene	75-35-4	24	0.0050	0.005	NL	0.0004	0.005
1,2,3-Trichlorobenzene	87-61-6	4.9	0.0050	0.005	NL	0.00036	0.005
1,2,4-Trichlorobenzene	120-82-1	0.91	0.0050	0.005	NL	0.00045	0.005
1,2-Dibromo-3-chloropropane	96-12-8	0.0054	0.0050	0.005	NL	0.00092	0.005
1,2-Dibromoethane	106-93-4	0.034	0.0050	0.005	NL	0.00048	0.005
1,2-Dichlorobenzene	95-50-1	0.013	0.0050	0.005	NL	0.00022	0.005
1,2-Dichloroethane	107-06-2	0.26	0.0050	0.005	NL	0.00055	0.005
1,2-Dichloropropane	78-87-5	0.333	0.0050	0.005	NL	0.00039	0.005
1,3-Dichlorobenzene	541-73-1	0.12	0.0050	0.005	NL	0.00017	0.005
1,4-Dichlorobenzene	106-46-7	0.11	0.0050	0.005	NL	0.00024	0.005
1,4-Dioxane	123-91-1	4.9	0.10	0.005	NL	0.03	0.05
2-Butanone	78-93-3	2800	0.010	0.005	NL	0.0043	0.01
2-Hexanone	591-78-6	21	0.005	0.005	NL	0.0015	0.01
4-Methyl-2-pentanone	108-10-1	530	0.010	0.005	NL	0.00049	0.01
Acetone	67-64-1	6100	0.010	0.005	NL	0.0011	0.02
Benzene	71-43-2	1.1	0.0050	0.005	NL	0.00028	0.005
Bromochloromethane	74-97-5	16	0.0050	0.005	NL	0.00012	0.005
Bromodichloromethane	75-27-4	0.27	0.0050	0.005	NL	0.00036	0.005

QAPP Worksheet #15-a
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: VOCs by 8260B
Concentration Level: Low (mg/kg)

Analyte	CAS Number	Project Action Limit [1]	Project Quantitation Limit Goal (PQLG) [2]	Analytical Method		Achievable Laboratory Limits [3, 4]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Bromoform	75-25-2	0.492	0.0050	0.005	NL	0.00064	0.005
Bromomethane	74-83-9	0.00137	0.00139	0.005	NL	0.0007	0.005
Carbon Disulfide	75-15-0	82	0.0050	0.005	NL	0.00059	0.005
Carbon Tetrachloride	56-23-5	0.61	0.0050	0.005	NL	0.00059	0.005
Chlorobenzene	108-90-7	0.035	0.0050	0.005	NL	0.00029	0.005
Chloroethane	75-00-3	220	0.0050	0.005	NL	0.00099	0.005
Chloroform	67-66-3	0.121	0.0050	0.005	NL	0.00036	0.005
Chloromethane	74-87-3	4	0.0050	0.005	NL	0.00024	0.005
cis-1,2-Dichloroethene	156-59-2	16	0.0050	0.005	NL	0.00024	0.005
cis-1,3-Dichloropropene	10061-01-5	1.7	0.0050	0.005	NL	0.00029	0.005
Cyclohexane	110-82-7	31000	0.0050	0.005	NL	0.00067	0.005
Dibromochloromethane	124-48-1	0.68	0.0050	0.005	NL	0.00035	0.005
Dichorodifluoromethane	75-71-8	9.4	0.0050	0.005	NL	0.00083	0.005
Ethylbenzene	100-41-4	0.064	0.0050	0.005	NL	0.00039	0.005
Isopropylbenzene	98-82-8	210	0.0050	0.005	NL	0.00023	0.005
m, p-Xylene	136777-61-2	6.3	0.0050	0.005	NL	0.00021	0.005
Methyl Acetate	79-20-9	7800	0.0050	0.005	NL	0.00098	0.005
Methyl tert-Butyl Ether	1634-04-4	43	0.0050	0.005	NL	0.0004	0.005
Methylcyclohexane	108-87-2	NA	0.0050	0.005	NL	0.00041	0.005
Methylene Chloride	75-09-2	0.159	0.0050	0.005	NL	0.00024	0.005
o-Xylene	95-47-6	0.12	0.0050	0.005	NL	0.00008	0.005
Styrene	100-42-5	0.254	0.0050	0.005	NL	0.00018	0.005
Tetrachloroethene	127-18-4	0.45	0.0050	0.005	NL	0.00046	0.005

QAPP Worksheet #15-a
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: VOCs by 8260B
Concentration Level: Low (mg/kg)

Analyte	CAS Number	Project Action Limit [1]	Project Quantitation Limit Goal (PQLG) [2]	Analytical Method		Achievable Laboratory Limits[3, 4]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Toluene	108-88-3	0.45	0.0050	0.005	NL	0.00035	0.005
Trans-1,2-Dichloroethene	156-60-5	0.654	0.0050	0.005	NL	0.00054	0.005
Trans-1,3-Dichloropropene	10061-02-6	1.7	0.0050	0.005	NL	0.00029	0.005
Trichloroethene	79-01-6	0.122	0.0050	0.005	NL	0.00064	0.005
Trichlorofluoromethane	75-69-4	79	0.0050	0.005	NL	0.00055	0.005
Vinyl Chloride	75-01-4	0.06	0.0050	0.005	NL	0.00033	0.005

Notes:

1. At this time, project-specific action levels have not been developed. The values in mg/kg listed are data Quality Levels (DQLs) taken from the CPG RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011

2. The target PQLGs listed in mg/kg are the lower of the CPG's DQLs and the Sediment reporting limits (RLs) listed in the CPG's QAPP. These sediment RLs are taken from Tables 2-1 through 2-21 (MPI QAPP, Lower Passaic River Restoration Project, August 2005).

3. The QLs and MDLs are based on Shealy Laboratory data. Except for bromomethane, the laboratory's QL is low enough to allow comparison of the split sample data to the CPG data.

4. Laboratory results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

QAPP Worksheet #15-b
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: SVOCs by SW-846, 8270C
Concentration Level: Low (mg/kg)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method[3]			Achievable Laboratory Limits	
				MDLs	8270 QLs[3]	SOM01.2 CRQLs	MDLs[4]	QLs[4]
1,1'-Biphenyl	92-52-4	80	0.0033	NA	NA	0.17	0.03	0.01
1,2,4,5-Tetrachlorobenzene	95-94-3	1.252	0.17	NA	NA	NA	Not listed	NA
1,4-Dioxane	123-91-1	4.9	0.10	NA	NA	NA	Done as VOA	NA
2,2'-Oxybis (1-Chloropropane)	108-60-1	NA	0.17	NA	0.66	0.17	Not listed	NA
2,4,5-Trichlorophenol[5]	95-95-4	0.003	0.003	NA	0.66	0.17	0.033	0.093
2,4,6-Trichlorophenol[5]	88-06-2	0.006	0.006	NA	0.66	0.17	0.033	0.098
2,4-Dichlorophenol[5]	120-83-2	0.005	0.005	NA	0.66	0.17	0.033	0.010
2,4-Dimethylphenol	105-67-9	0.304	0.17	NA	0.66	0.17	0.033	0.012
2,4-Dinitrophenol[5]	51-28-5	0.00621	0.00621	NA	3.3	0.33	0.170	0.110
2,4-Dinitrotoluene[5]	121-14-2	0.0144	0.0144	NA	0.66	0.17	0.067	0.018
2,6-Dinitrotoluene	606-20-2	6.1	0.17	NA	0.66	0.17	0.067	0.017
2-Chloronaphthalene	91-58-7	0.417	0.17	NA	0.66	0.17	0.033	0.011
2-Chlorophenol[5]	95-57-8	0.008	0.008	NA	0.66	0.17	0.033	0.0092
2-Methylnaphthalene	91-57-6	0.0202	0.0033	NA	0.66	0.17	0.033	0.0099
2-Methylphenol	95-48-7	310	0.17	NA	0.66	0.17	0.033	0.006
2-Nitroaniline	88-74-4	61	0.17	NA	3.3	0.33	0.067	0.023
2-Nitrophenol	88-75-5	1830	0.17	NA	0.66	0.17	0.067	0.018
3,3'-Dichlorobenzidine	91-94-1	1.08	0.17	NA	1.3	0.17	0.170	0.036
3-Nitroaniline	99-09-2	1.83	0.33	NA	3.3	0.33	0.067	0.039
4,6-Dinitro-2-methylphenol	534-52-1	0.611	0.33	NA	3.3	0.17	0.170	0.130
4-Bromophenyl-phenylether	101-55-3	NA	0.17	NA	0.66	0.17	0.033	0.0098
4-Chloro-3-methylphenol	59-50-7	610	0.17	NA	1.3	0.17	0.033	0.0084
4-Chloroaniline	106-47-8	24.4	0.17	NA	1.3	0.17	0.033	0.0068
4-Chlorophenyl-phenyl ether	7005-72-3	NA	0.17	NA	0.66	0.17	0.033	0.011
4-Methylphenol	106-44-5	31	0.17	NA	0.66	0.17	0.067	0.012
4-Nitroaniline	100-01-6	23.2	0.33	NA	NA	0.33	0.067	0.019

QAPP Worksheet #15-b

Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: SVOCs by SW-846, 8270C
Concentration Level: Low (mg/kg)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method[3]			Achievable Laboratory Limits	
				MDLs	8270 QLs[3]	SOM01.2 CRQLs	MDLs[4]	QLs[4]
4-Nitrophenol	100-02-7	1800	0.17	NA	3.3	0.33	0.170	0.096
Acenaphthene[5]	83-32-9	0.00671	0.0033	NA	0.66	0.17	0.033	0.011
Acenaphthylene[5]	208-96-8	0.00587	0.0033	NA	0.66	0.17	0.033	0.010
Acetophenone	98-86-2	NA	0.17	NA	NA	0.17	0.033	0.018
Anthracene	120-12-7	0.0469	0.003	NA	0.66	0.17	0.033	0.0074
Atrazine	1912-24-9	2.1	0.17	NA	NA	0.17	0.033	0.017
Benzaldehyde	100-52-7	780	0.17	NA	NA	0.17	0.033	0.017
Benzo(a)anthracene	56-55-3	0.0317	0.0033	NA	0.66	0.17	0.033	0.0088
Benzo(a)pyrene	50-32-8	0.015	0.0033	NA	0.66	0.17	0.033	0.0093
Benzo(b)fluoranthene	205-99-2	0.15	0.0033	NA	0.66	0.17	0.033	0.0096
Benzo(g,h,i)perylene	191-24-2	0.17	0.0033	NA	0.66	0.17	0.033	0.012
Benzo(k)fluoranthene	207-08-9	0.24	0.0033	NA	0.66	0.17	0.033	0.0095
bis-(2-Chloroethoxy)methane	111-91-1	18	0.17	NA	0.66	0.17	0.033	0.010
bis-(2-Chloroethyl)ether	111-44-4	0.21	0.17	NA	0.66	0.17	0.033	0.0092
bis(2-Ethylhexyl)phthalate	117-81-7	0.182	0.0033	NA	0.66	0.17	0.033	0.012
Butylbenzylphthalate	85-68-7	0.063	0.0033	NA	0.66	0.17	0.067	0.022
Caprolactam	105-60-2	3100	0.17	NA	NA	0.17	0.033	0.017
Carbazole	86-74-8	24	0.0033	NA	NA	0.17	0.033	0.014
Chrysene	218-01-9	0.0571	0.0033	NA	0.66	0.17	0.033	0.011
Dibenzo(a,h)-anthracene[5]	53-70-3	0.00622	0.0033	NA	0.66	0.17	0.033	0.0091
Dibenzofuran	132-64-9	NA	0.17	NA	0.66	0.17	0.033	0.010
Diethylphthalate [5]	84-66-2	0.006	0.006	NA	0.66	0.17	0.033	0.011
Dimethylphthalate	131-11-3	46	0.17	NA	0.66	0.17	0.033	0.011
Di-n-butylphthalate [5]	84-74-2	0.058	0.058	NA	NA	0.17	0.033	0.018
Di-n-octylphthalate	117-84-0	46	0.0033	NA	0.66	0.17	0.067	0.032
Fluoranthene	206-44-0	0.111	0.0033	NA	0.66	0.17	0.033	0.011
Fluorene	86-73-7	0.0190	0.0033	NA	0.66	0.17	0.033	0.009
Hexachlorobenzene [5]	118-74-1	0.002	0.0020	NA	0.66	0.17	0.033	0.015
Hexachlorobutadiene [5]	87-68-3	0.0013	0.0013	NA	0.66	0.17	0.033	0.011
Hexachloroethane	67-72-1	0.073	0.073	NA	0.66	0.17	0.033	0.0089

QAPP Worksheet #15-b

Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: SVOCs by SW-846, 8270C
Concentration Level: Low (mg/kg)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method[3]			Achievable Laboratory Limits	
				MDLs	8270 QLs[3]	SOM01.2 CRQLs	MDLs[4]	QLs[4]
Hexachlorocyclopentadiene[5]	77-47-4	0.007	0.0070	NA	0.66	0.17	0.170	0.025
Indeno(1,2,3-cd)-pyrene	193-39-5	0.2	0.0033	NA	0.66	0.17	0.033	0.0097
Isophorone	78-59-1	0.432	0.17	NA	0.66	0.17	0.033	0.0074
Naphthalene	91-20-3	0.0346	0.0033	NA	0.66	0.17	0.033	0.010
Nitrobenzene	98-95-3	0.145	0.0033	NA	0.66	0.17	0.033	0.0054
n-Nitroso-di-n-propylamine	621-64-7	0.069	0.069	NA	0.66	0.17	0.033	0.013
n-Nitrosodiphenylamine	86-30-6	99	0.0033	NA	0.66	0.17	0.033	0.0083
Pentachlorophenol[5]	87-86-5	0.017	0.0033	NA	3.3	0.33	0.170	0.140
Phenanthrene	85-01-8	0.0419	0.0033	NA	0.66	0.17	0.033	0.009
Phenol	108-95-2	0.0491	0.17	NA	0.66	0.17	0.033	0.0091
Pyrene	129-00-0	0.053	0.0033	NA	0.66	0.17	0.033	0.013

1. At this time, project-specific action levels have not been developed. The values in mg/kg listed are Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011.

2. The target PQLGs listed are based on the CPG's goals and are taken from the sediment RLs listed in Tables 2-1 through 2-21 (MPI QAPP, Lower Passaic River Restoration Project, August 2005).

3. Specific MDLs are not given in the listed method.

4. Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing the analytical method. Actual MDLs and QLs were obtained from the Shealy subcontract Laboratory.

5. The project action limits for highlighted cells are below some of the laboratory quantitation limits as shown above. The laboratory QL of 0.018 mg/kg meets the MPI sediment RL which is 0.17 mg/kg; the CPG's lab achievable limit is also 0.17 mg/kg, therefore the din-butylphthalate split results are expected to be comparable. The laboratory achievable limits are generally expected to be low enough to allow comparison of the split sample data to the CPG data.

Additional note:

Some analytes listed above will also be reported from the lower limits GC/MS-SIM method for PAH analysis; the PAH method results will take precedence over SW846 Method 8270C results.

QAPP Worksheet #15-c
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PAH and Alkyl PAHs by Axys SOP MLA-021
Concentration Level: Low (µg/kg)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method[3]		Achievable Laboratory Limits[4]	
				MDLs	QLs	MDLs	QLs
1-Methylnaphthalene	90-12-0	22,000	5,590	NA	NA	NA	3.3
1-Methylphenanthrene	832-69-9	1,700,000	3.3	NA	NA	0.28	3.3
2,3,5-Trimethylnaphthalene	2245-38-7	3,600	3.3	NA	NA	0.60	3.3
2,6-Dimethylnaphthalene	581-42-0	3,600	3.3	NA	NA	0.25	3.3
2-Methylnaphthalene	91-57-6	20.2	3.3	NA	NA	0.29	3.3
Acenaphthene	83-32-9	6.71	3.3	NA	NA	0.37	1.7
Acenaphthylene	208-96-8	5.87	3.3	NA	NA	0.37	1.7
Anthracene	120-12-7	46.9	3.3	NA	NA	0.41	1.7
Benzo[a]anthracene	56-55-3	31.7	3.3	NA	NA	0.36	1.7
Benzo[a]pyrene	50-32-8	15.0	3.3	NA	NA	0.37	1.7
Benzo[b]fluoranthene	205-99-2	150	3.3	NA	NA	0.37	1.7
Benzo[e]pyrene	192-97-2	170,000	3.3	NA	NA	0.36	1.7
Benzo[g,h,i]perylene	191-24-2	170	3.3	NA	NA	0.36	3.3
Benzo[j]fluoranthene	205-82-3	240	3.3	NA	NA	0..39	1.7
Benzo[k]fluoranthene	207-08-9	240	3.3	NA	NA	0..39	1.7
Chrysene	218-01-9	57.1	3.3	NA	NA	0.37	1.7
Dibenzo[a,h]anthracene	53-70-3	6.22	3.3	NA	NA	0.37	3.3
Dibenzothiophene	135-65-0	NA	3.3	NA	NA	0.41	3.3
Fluoranthene	206-44-0	111	3.3	NA	NA	0.38	1.7
Fluorene	86-73-7	19	3.3	NA	NA	0.45	1.7
Indeno[1,2,3-c,d]-pyrene	193-39-5	200	3.3	NA	NA	0.36	3.3
Naphthalene	91-20-3	34.6	3.3	NA	NA	1.50	1.7
Perylene	198-55-0	170,000	3.3	NA	NA	0.37	3.3
Phenanthrene	85-01-8	41.9	3.3	NA	NA	0.37	1.7
Pyrene	129-00-0	53	3.3	NA	NA	0.38	1.7
C1-Benzanthracene/chrysenes	NA	NA	NA	NA	NA	NA	NA
C1-Dibenzothiophenes	NA	NA	NA	NA	NA	NA	NA
C1-Fluorenes	NA	NA	NA	NA	NA	NA	NA
C1-Phenanthrene/anthracenes	NA	NA	NA	NA	NA	NA	NA

QAPP Worksheet #15-c
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PAH and Alkyl PAHs by Axys SOP MLA-021
Concentration Level: Low (µg/kg)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method[3]		Achievable Laboratory Limits[4]	
				MDLs	QLs	MDLs	QLs
C1-Pyrene/fluoranthenes	NA	NA	NA	NA	NA	NA	NA
C2-Benzanthracene/chrysenes	NA	NA	NA	NA	NA	NA	NA
C2-Dibenzothiophenes	NA	NA	NA	NA	NA	NA	NA
C2-Fluorenes	NA	NA	NA	NA	NA	NA	NA
C2-Naphthalenes	NA	NA	NA	NA	NA	NA	NA
C2-Phenanthrene/anthracenes	NA	NA	NA	NA	NA	NA	NA
C3-Benzanthracene/chrysenes	NA	NA	NA	NA	NA	NA	NA
C3-Dibenzothiophenes	NA	NA	NA	NA	NA	NA	NA
C3-Fluorenes	NA	NA	NA	NA	NA	NA	NA
C3-Naphthalenes	NA	NA	NA	NA	NA	NA	NA
C3-Phenanthrene/anthracenes	NA	NA	NA	NA	NA	NA	NA
C4-Benzanthracene/chrysenes	NA	NA	NA	NA	NA	NA	NA
C4-Dibenzothiophenes	NA	NA	NA	NA	NA	NA	NA
C4-Naphthalenes	NA	NA	NA	NA	NA	NA	NA
C4-Phenanthrenes/anthracenes	NA	NA	NA	NA	NA	NA	NA

Notes:

1. At this time, project-specific action levels have not been developed. The values in µg/kg listed are Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011.
2. The target PQLGs listed are based on the CPG's QAPP values. The project QL goals were selected as the lower of the DQL and the Sediment RL. Sediment RLs are from Tables 2-1 through 2-21 (MPI QAPP, Lower Passaic River Restoration Project, August 2005).
3. Specific MDLs are not given in the listed methods.
4. Achievable MDLs listed are the statistically-derived MDLs and are based on the analysis of a 10 g dry weight sample size. QLs are based on the analysis of a 3 g dry sample size, as routinely required for Passaic River samples in order to reduce matrix effects. These MDLs and QLs are based on Axys Analytical Service typical sample specific detection limits. Results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects. MDLs and QLs are limits that an individual laboratory can achieve when performing the analytical method.

QAPP Worksheet #15-d
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: Organochlorinated Pesticides by AXYS MLA-028 [EPA 1613B/1699 Modified]
Concentration Level: Low (ng/g) (µg/kg)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method		Achievable Laboratory Limits[4]	
				MDLs	CLP Method QLs[3]	MDLs	QLs
2,4'-DDD	53-19-0	2	0.2	NA	NL	0.008	0.07
2,4'-DDE	3424-82-6	1.42	0.2	NA	NL	0.006	0.07
2,4'-DDT	789-02-6	1	0.2	NA	NL	0.008	0.07
4,4,-DDD	72-54-8	2	0.2	NA	3.3	0.008	0.07
4,4,-DDE	72-55-9	1.42	0.2	NA	3.3	0.009	0.07
4,4,-DDT	50-29-3	1	0.2	NA	3.3	0.010	0.07
Aldrin	309-00-2	2	0.2	NA	1.7	0.079	0.07
alpha-BHC	319-84-6	0.94	0.2	NA	1.7	0.027	0.07
beta-BHC	319-85-7	0.94	0.2	NA	1.7	0.015	0.07
cis-Chlordane (alpha Chlordane)	5103-71-9	0.02	0.02	NA	1.7	0.024	0.07
cis-Nonachlor	5103-73-1	200	0.02	NA	NL	0.027	0.07
delta-BHC	319-86-8	0.94	0.2	NA	1.7	0.007	0.17
Dieldrin	60-57-1	0.02	0.02	NA	3.3	0.019	0.17
Endosulfan I	959-98-8	37,000	0.04	NA	3.3	0.029	0.17
Endosulfan II	33213-65-9	37,000	0.04	NA	3.3	0.057	0.17
Endosulfan sulfate	1031-07-8	37,000	0.2	NA	3.3	0.052	0.17
Endrin	72-20-8	2.22	0.2	NA	3.3	0.031	0.17
Endrin Aldehyde	7421-93-4	2.67	0.2	NA	3.3	0.027	0.17
Endrin ketone	53494-70-5	2.67	0.2	NA	3.3	0.029	0.17
gamma-BHC (Lindane)	58-89-9	0.94	0.2	NA	1.7	0.012	0.07
Hexachorobenzene	118-74-1	2	2	NA	On SVOC list	0.009	0.03
Heptachlor	76-44-8	0.6	0.2	NA	1.7	0.024	0.07
Heptachlor Epoxide	1024-57-3	0.6	0.2	NA	1.7	0.014	0.17
Methoxychlor	72-43-5	6	0.3	NA	17	0.005	0.33
Toxaphene	8001-35-2	NL	NL	NA	170	NA	NA
Oxychlordane	27304-13-8	0.02	0.02	NA	NL	0.043	0.07
Trans-Chlordane (gamma Chlordane)	5103-74-2	0.02	0.02	NA	1.7	0.015	0.07
Trans-Nonachlor	3734-49-4	0.02	0.02	NA	NS	0.021	0.07

Notes:

1. At this time, project-specific action levels have not been developed. The values in µg/kg listed are Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011. The split sample data should be low enough for data comparison. Differences in laboratory limits will be considered in data comparison.
2. The target PQLGs listed are based on the CPG's QAPP values. The project QL goals were selected as the lower of the DQL and the Sediment RL. Sediment RLs are from Tables 2-1 through 2-21 (MPI QAPP, Lower Passaic River Restoration Project, August 2005.
3. Method QLs are not listed in Method 1613B.
4. MDLs are statistically-derived and are based on the analysis of a 10 g dry weight sample size. QLs are based on the analysis of a 3 g dry sample size, as routinely required for Passaic River samples in order to reduce matrix effects; these limits are from Axys Analytical Services. Results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
Monochlorobiphenyl	27323-18-8	2.27E04	3000	NA	NA	NA	NA
Dichlorobiphenyl	25512-42-9	2.27E04	3000	NA	NA	NA	NA
Trichlorobiphenyl	25323-68-6	2.27E04	3000	NA	NA	NA	NA
Tetrachlorobiphenyl	26914-33-0	2.27E04	3000	NA	NA	NA	NA
Pentachlorobiphenyl	25429-29-2	2.27E04	3000	NA	NA	NA	NA
Hexachlorobiphenyl	26601-64-9	2.27E04	3000	NA	NA	NA	NA
Heptachlorobiphenyl	28655-71-2	2.27E04	3000	NA	NA	NA	NA
Octachlorobiphenyl	55722-26-4	2.27E04	3000	NA	NA	NA	NA
Nonachlorobiphenyl	53742-07-7	2.27E04	3000	NA	NA	NA	NA
Decachlorobiphenyl	2051-24-3	2.27E04	3000	NA	NA	NA	NA
PCB-1		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-2		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-3		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-4		2.27E04	0.2 through 2	See Method	See Method	0.47	0.7
PCB-5		2.27E04	0.2 through 2	See Method	See Method	0.25	0.7
PCB-6		2.27E04	0.2 through 2	See Method	See Method	0.25	0.7
PCB-7		2.27E04	0.2 through 2	See Method	See Method	0.30	0.7
PCB-8		2.27E04	0.2 through 2	See Method	See Method	0.74	0.7
PCB-9		2.27E04	0.2 through 2	See Method	See Method	0.25	0.7
PCB-10		2.27E04	0.2 through 2	See Method	See Method	0.25	0.7
PCB-11		2.27E04	0.2 through 2	See Method	See Method	0.56	0.7
PCB-12 (Co-elutes with PCB-13)		2.27E04	0.2 through 2	See Method	See Method	0.5	0.7
PCB-13 (Co-elutes with PCB-12)		2.27E04	0.2 through 2	See Method	See Method	0.5	0.7
PCB-14		2.27E04	0.2 through 2	See Method	See Method	0.25	0.7
PCB-15		2.27E04	0.2 through 2	See Method	See Method	0.37	0.7

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
PCB-16		2.27E04	0.2 through 2	See Method	See Method	0.36	0.3
PCB-17		2.27E04	0.2 through 2	See Method	See Method	0.38	0.3
PCB-18 (Co-elutes with PCB-30)		2.27E04	0.2 through 2	See Method	See Method	0.67	0.3
PCB-19		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-20 (Co-elutes with PCB-28)		2.27E04	0.2 through 2	See Method	See Method	0.94	0.3
PCB-21 (Co-elutes with PCB-33)		2.27E04	0.2 through 2	See Method	See Method	0.5	0.3
PCB-22		2.27E04	0.2 through 2	See Method	See Method	0.35	0.3
PCB-23		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-24		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-25		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-26 (Co-elutes with PCB-29)		2.27E04	0.2 through 2	See Method	See Method	0.5	0.3
PCB-27		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-28 (Co-elutes with PCB-20)		2.27E04	0.2 through 2	See Method	See Method	0.94	0.3
PCB-29 (Co-elutes with PCB-26)		2.27E04	0.2 through 2	See Method	See Method	0.5	0.3
PCB-30 (Co-elutes with PCB-18)		2.27E04	0.2 through 2	See Method	See Method	0.67	0.3
PCB-31		2.27E04	0.2 through 2	See Method	See Method	0.82	0.3
PCB-32		2.27E04	0.2 through 2	See Method	See Method	0.27	0.3
PCB-33 (Co-elutes with PCB-21)		2.27E04	0.2 through 2	See Method	See Method	0.5	0.3
PCB-34		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-35		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-36		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-37		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-38		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-39		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-40 (Co-elutes with PCB-41, PCB-71)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
PCB-41 (Co-elutes with PCB-40, PCB-71)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-42		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-43		2.27E04	0.2 through 2	See Method	See Method	0.87	0.3
PCB-44 (Co-elutes with PCB-47, PCB-65)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-45 (Co-elutes with PCB-51)		2.27E04	0.2 through 2	See Method	See Method	0.57	0.3
PCB-46		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-47 (Co-elutes with PCB-44, PCB-65)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-48		2.27E04	0.2 through 2	See Method	See Method	0.28	0.3
PCB-49 (Co-elutes with PCB-69)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-50 (Co-elutes with PCB-53)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-51 (Coleutes with PCB-45)		2.27E04	0.2 through 2	See Method	See Method	0.57	0.3
PCB-52		2.27E04	0.2 through 2	See Method	See Method	0.44	0.3
PCB-53 (Co-elutes with PCB-50)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-54		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-55		2.27E04	0.2 through 2	See Method	See Method	0.32	0.3
PCB-56		2.27E04	0.2 through 2	See Method	See Method	0.27	0.3
PCB-57		2.27E04	0.2 through 2	See Method	See Method	0.31	0.3
PCB-58		2.27E04	0.2 through 2	See Method	See Method	0.41	0.3
PCB-59 (Co-elutes with PCB-62, PCB-75)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-60		2.27E04	0.2 through 2	See Method	See Method	0.51	0.3
PCB-61 (Co-elutes with PCB-70, PCB-74, PCB-76)		2.27E04	0.2 through 2	See Method	See Method	1.1	0.3
PCB-62 (Co-elutes with PCB-59, PCB-75)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-63		2.27E04	0.2 through 2	See Method	See Method	0.26	0.3
PCB-64		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
PCB-65 (Co-elutes with PCB-44, PCB-47)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-66		2.27E04	0.2 through 2	See Method	See Method	0.68	0.3
PCB-67		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-68		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-69 (Co-elutes with PCB-49)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-70 (Co-elutes with PCB-61, PCB-74, PCB-76)		2.27E04	0.2 through 2	See Method	See Method	1.1	0.3
PCB-71 (Co-elutes with PCB-40, PCB-41)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-72		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-73		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-74 (Co-elutes with PCB-61, PCB-70, PCB-76)		2.27E04	0.2 through 2	See Method	See Method	1.1	0.3
PCB-75 (Co-elutes with PCB-59, PCB-62)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-76(Co-elutes with PCB-61, PCB-70, PCB-74)		2.27E04	0.2 through 2	See Method	See Method	1.1	0.3
PCB-77		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-78		2.27E04	0.2 through 2	See Method	See Method	0.36	0.3
PCB-79		2.27E04	0.2 through 2	See Method	See Method	0.42	0.3
PCB-80		2.27E04	0.2 through 2	See Method	See Method	0.32	0.3
PCB-81		2.27E04	0.2 through 2	See Method	See Method	0.27	0.3
PCB-82		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-83 (Co-elutes with PCB-99)		2.27E04	0.2 through 2	See Method	See Method	0.60	0.3
PCB-84		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-85 (Co-elutes with PCB-116, PCB-117)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-86 (Co-elutes with PCB-87, PCB-97,		2.27E04	0.2 through 2	See Method	See Method	1.50	0.3

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
PCB-108, PCB-119, PCB-125)							
PCB-87 (Co-elutes with PCB-86, PCB-97, PCB-108, PCB-119, PCB-125)		2.27E04	0.2 through 2	See Method	See Method	1.50	0.3
PCB-88 (Co-elutes with PCB-91)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-89		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-90 (Co-elutes with PCB-101, PCB-113)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-91 (Co-elutes with PCB-88)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-92		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-93 (Co-elutes with PCB-95, PCB-98, PCB-100, PCB1-02)		2.27E04	0.2 through 2	See Method	See Method	4.30	0.3
PCB-94		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-95 (Co-elutes with PCB-93, PCB-98, PCB-100, PCB-102)		2.27E04	0.2 through 2	See Method	See Method	4.30	0.3
PCB-96		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-97 (Co-elutes with PCB-86, PCB-87, PCB-108, PCB-119, PCB-125)		2.27E04	0.2 through 2	See Method	See Method	1.50	0.3
PCB-98 (Co-elutes with PCB-93, PCB-95, PCB-100, PCB-102)		2.27E04	0.2 through 2	See Method	See Method	4.30	0.3
PCB-99 (Co-elutes with PCB-83)		2.27E04	0.2 through 2	See Method	See Method	0.60	0.3
PCB-100 (Co-elutes with PCB-93, PCB-95, PCB-98, PCB-102)		2.27E04	0.2 through 2	See Method	See Method	4.30	0.3
PCB-101 (Co-elutes with PCB-90, PCB-113)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-102 (Co-elutes with PCB-93, PCB-95, PCB-98, PCB-100)		2.27E04	0.2 through 2	See Method	See Method	4.30	0.3
PCB-103		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-104		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
PCB-105		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-106		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-107 (Co-elutes with PCB-124)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-108 (Co-elutes with PCB-86, PCB-87, PCB-97, PCB-119, PCB-125)		2.27E04	0.2 through 2	See Method	See Method	1.50	0.3
PCB-109		2.27E04	0.2 through 2	See Method	See Method	0.27	0.3
PCB-110 (Co-elutes with PCB-115)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-111		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-112		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-113 (Co-elutes with PCB-90, PCB-101)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-114		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-115 (Co-elutes with PCB-110)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-116 (Co-elutes with PCB-85, PCB-117)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-117 (Co-elutes with PCB-85, PCB-116)		2.27E04	0.2 through 2	See Method	See Method	0.75	0.3
PCB-118		2.27E04	0.2 through 2	See Method	See Method	0.48	0.3
PCB-119 (Co-elutes with PCB-86, PCB-87, PCB-97, PCB-108, PCB-125)		2.27E04	0.2 through 2	See Method	See Method	1.50	0.3
PCB-120		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-121		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-122		2.27E04	0.2 through 2	See Method	See Method	0.26	0.3
PCB-123		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-124 (Co-elutes with PCB-107)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-125 (Co-elutes with PCB-86, PCB-87, PCB-97, PCB-108, PCB-119)		2.27E04	0.2 through 2	See Method	See Method	1.50	0.3

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
PCB-126		2.27E04	0.2 through 2	See Method	See Method	0.29	0.3
PCB-127		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-128 (Co-elutes with PCB-166)		2.27E04	0.2 through 2	See Method	See Method	0.81	0.3
PCB-129 (Co-elutes with PCB-138, PCB-160, PCB-163)		2.27E04	0.2 through 2	See Method	See Method	1.20	0.3
PCB-130		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-131		2.27E04	0.2 through 2	See Method	See Method	0.32	0.3
PCB-132		2.27E04	0.2 through 2	See Method	See Method	0.31	0.3
PCB-133		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-134 (Co-elutes with PCB-143)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-135 (Co-elutes with PCB-151 PCB-154)		2.27E04	0.2 through 2	See Method	See Method	1.4	0.3
PCB-136		2.27E04	0.2 through 2	See Method	See Method	0.42	0.3
PCB-137		2.27E04	0.2 through 2	See Method	See Method	0.42	0.3
PCB-138 (Co-elutes with PCB-129, PCB-160, PCB-163)		2.27E04	0.2 through 2	See Method	See Method	1.20	0.3
PCB-139 (Co-elutes with PCB-140)		2.27E04	0.2 through 2	See Method	See Method	0.58	0.3
PCB-140 (Co-elutes with PCB-139)		2.27E04	0.2 through 2	See Method	See Method	0.58	0.3
PCB-141		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-142		2.27E04	0.2 through 2	See Method	See Method	0.36	0.3
PCB-143 (Co-elutes with PCB-134)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-144		2.27E04	0.2 through 2	See Method	See Method	0.29	0.3
PCB-145		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-146		2.27E04	0.2 through 2	See Method	See Method	0.37	0.3
PCB-147 (Co-elutes with PCB-149)		2.27E04	0.2 through 2	See Method	See Method	0.62	0.3

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
PCB-148		2.27E04	0.2 through 2	See Method	See Method	0.31	0.3
PCB-149 (Co-elutes with PCB-147)		2.27E04	0.2 through 2	See Method	See Method	0.62	0.3
PCB-150		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-151 (Co-elutes with PCB-135, PCB-154)		2.27E04	0.2 through 2	See Method	See Method	1.4	0.3
PCB-152		2.27E04	0.2 through 2	See Method	See Method	0.31	0.3
PCB-153 (Co-elutes with PCB-168)		2.27E04	0.2 through 2	See Method	See Method	0.67	0.3
PCB-154 (Co-elutes with PCB-135, PCB-151)		2.27E04	0.2 through 2	See Method	See Method	1.4	0.3
PCB-155		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-156 (Co-elutes with PCB-157)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-157 (Co-elutes with PCB-156)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-158		2.27E04	0.2 through 2	See Method	See Method	0.26	0.3
PCB-159		2.27E04	0.2 through 2	See Method	See Method	0.29	0.3
PCB-160 (Co-elutes with PCB-129, PCB-138, PCB-163)		2.27E04	0.2 through 2	See Method	See Method	1.20	0.3
PCB-151 (Co-elutes with PCB-135, PCB-154)		2.27E04	0.2 through 2	See Method	See Method	1.4	0.3
PCB-152		2.27E04	0.2 through 2	See Method	See Method	0.31	0.3
PCB-153 (Co-elutes with PCB-168)		2.27E04	0.2 through 2	See Method	See Method	0.67	0.3
PCB-154 (Co-elutes with PCB-135, PCB-151)		2.27E04	0.2 through 2	See Method	See Method	1.4	0.3
PCB-155		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-156 (Co-elutes with PCB-157)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-157 (Co-elutes with PCB-156)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-158		2.27E04	0.2 through 2	See Method	See Method	0.26	0.3

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
PCB-159		2.27E04	0.2 through 2	See Method	See Method	0.29	0.3
PCB-160 (Co-elutes with PCB-129, PCB-138, PCB-163)		2.27E04	0.2 through 2	See Method	See Method	1.20	0.3
PCB-161		2.27E04	0.2 through 2	See Method	See Method	0.31	0.3
PCB-162		2.27E04	0.2 through 2	See Method	See Method	0.30	0.3
PCB-163 (Co-elutes with PCB-129, PCB-138, PCB-160)		2.27E04	0.2 through 2	See Method	See Method	1.20	0.3
PCB-164		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-165		2.27E04	0.2 through 2	See Method	See Method	0.33	0.3
PCB-166 (Co-elutes with PCB-128)		2.27E04	0.2 through 2	See Method	See Method	0.81	0.3
PCB-167		2.27E04	0.2 through 2	See Method	See Method	0.46	0.3
PCB-168 (Co-elutes with PCB-153)		2.27E04	0.2 through 2	See Method	See Method	0.67	0.3
PCB-169		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-170		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-171 (Co-elutes with PCB-173)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-172		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-173 (Co-elutes with PCB-171)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-174		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-175		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-176		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-177		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-178		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-179		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-180 (Co-elutes with PCB-193)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-181		2.27E04	0.2 through 2	See Method	See Method	0.72	0.3

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
PCB-182		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-183 (Co-elutes with PCB-185)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-184		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-185 (Co-elutes with PCB-183)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-186		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-187		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-188		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-189		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-190		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-191		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-192		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-193 (Co-elutes with PCB-180)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-194		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-195		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-196		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-197 (Co-elutes with PCB-200)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-198 (Co-elutes with PCB-199)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-199 (Co-elutes with PCB-198)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-200 (Co-elutes with PCB-197)		2.27E04	0.2 through 2	See Method	See Method	0.50	0.3
PCB-201		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-202		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-203		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-204		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-205		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3

QAPP Worksheet #15-e
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCB Congeners by 1668A
Concentration Level: Low (picogram per gram [pg/g])

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[3]		Achievable Laboratory Limits[4, 5]	
				MDLs	QLs	MDLs	QLs
PCB-206		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-207		2.27E04	0.2 through 2	See Method	See Method	0.27	0.3
PCB-208		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3
PCB-209		2.27E04	0.2 through 2	See Method	See Method	0.25	0.3

Notes:

1. At this time, project-specific action levels have not been developed. The values in pg/g listed are Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011.
2. The target PQLG listed in pg/g is based on the CPG's QAPP. The project QL goal is selected as the lower of the DQL and the Sediment RL. Sediment RL from 2005 CPG's QAPP is listed as 2.00E-07 to 2.00-E06 for individual congeners PCB-1 through PCB-209. Note that the reference value of 2.00E-06 was used for comparing achievable laboratory limits to the project QL goal.
3. Method MDLs are listed EPA 1668A.

   The MDLs listed are the statistically-derived MDLs and are based on the analysis of a 10 g dry weight sample size. QLs are based on the analysis of a 3 g dry sample size as routinely required for Passaic River samples in order to reduce matrix effects, and quantified using a 6 point calibration series. These MDLs and QLs listed were obtained from Axys Analytical Services.
4. Achievable QLs listed are based on typical Axys Analytical Services laboratory detection limits expected to range from 0.1 to 2.0 pg/g, with exceptions (particularly co-eluting congeners). The assigned laboratory will report PCB congeners to sample specific detection limits, which may be different depending upon the samples. The achievable QLs shown above are generally below the PQLGs listed in the CPG RI/FS QAPP, so that split sample data should be suitable for comparison. Laboratory results will be reported in dry weight.
5. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

QAPP Worksheet #15-f
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: Herbicides by Method 8151
Concentration Level: Low (mg/kg)

Analyte	CAS Number	Project Action Limit [1]	Project Quantitation Limit Goal (PQLG) [2]	Analytical Method		Achievable Laboratory Limits [3, 4]	
				MDLs	Method QLs	MDLs	QLs
2,4-D	94-75-7	69	0.14	0.11 (ECD)	NA	0.017	0.040
2,4-DB	94-82-6	49	0.16	NA	NA	0.013	0.080
2,4,5-T	93-76-5	12.3	0.020	NA	NA	0.0014	0.010
2,4,5-TP (Silvex)	93-72-1	0.675	0.020	0.28 (ECD)	NA	0.0043	0.010

Notes:

1. At this time, project-specific action levels have not been developed. The values in mg/kg listed are Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011.

2. The target PQLGs listed in mg/kg are based on the CPG's QAPP values and are the lower of the DQL and the Sediment RLs taken from Tables 2-1 through 2-21 (MPI QAPP, Lower Passaic River Restoration Project, August 2005).

3. The QLs and MDLs are based on the Shealy subcontract laboratory. The laboratory's QL is low enough to allow comparison of the split sample data to the CPG data.

4. Laboratory results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

QAPP Worksheet #15-g
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: TPH Extractables by NJ Method OQA-QAM-025-10/91
Concentration Level: Low (mg/kg)

Analyte	CAS Number	Project Action Limit [1]	Project Quantitation Limit Goal (PQLG) [2]	Analytical Method		Achievable Laboratory Limits[3, 4]	
				MDLs (mg/kg)	Method QLs (mg/kg)	MDLs (mg/kg)	QLs (mg/kg)
Total Petroleum Hydrocarbons [extractable]	NA	20	20	10	30	As per Laboratory work instruction, EDS-WI-071	6.7

Notes:

1. At this time, there are no project-specific screening levels or action levels approved by the EPA for this parameter for this project. The PAL values in the QAPP are Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011. There was no listed value for TPH.

2. The target PQLGs are taken from the CPG's RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011. These PQLGs are the lower of the DQL and the Sediment RL. Since there is no TPH extractables PAL or DQL, the PQLG defaults to the RL taken from Tables 2-1 through 2-21 (MPI QAPP, Lower Passaic River Restoration Project, August 2005).

3. The QL is the reporting limit listed in the Test America method SOP. MDLs are detailed in the laboratory's work instruction and may be obtained and included in the Final QAPP, however the laboratory's QL is low enough to allow comparison of the split sample data to the CPG data.

4. Laboratory results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

QAPP Worksheet #15-h
Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: PCDD/PCDF by EPA 1613B
Concentration Level: Low (ng/kg = nanogram per kilogram)

Analyte	CAS Number	Project Action Limit[1]	Project Action Levels[1]	Project Quantitation Limit Goals (PQLGs)[2]	Analytical Method[3]		Achievable Laboratory Limits	
					MDLs[3]	Method QLs[3]	MDLs[4]	QLs[4]
2378-TCDD	1746-01-6	TBD	0.12	0.12	NA	1.0	0.031	0.17
12378-PeCDD	40321-76-4	TBD	4.5	2.5	NA	5.0	0.13	0.33
123678-HxCDD	57653-85-7	TBD	45	2.5	NA	5.0	0.18	0.33
123478-HxCDD	39227-28-6	TBD	45	2.5	NA	5.0	0.19	0.33
123789-HxCDD	19408-74-3	TBD	45	2.5	NA	5.0	0.17	0.33
1234678-HpCDD	35822-46-9	TBD	450	2.5	NA	5.0	0.17	0.33
OCDD	3268-87-9	TBD	15,000	5.0	NA	10	0.83	1.67
2378-TCDF	51207-31-9	TBD	45	0.50	NA	1.0	0.028	0.17
12378-PeCDF	57117-41-6	TBD	150	2.5	NA	5.0	0.095	0.33
23478-PeCDF	57117-31-4	TBD	15	2.5	NA	5.0	0.096	0.33
123678-HxCDF	57117-44-9	TBD	45	2.5	NA	5.0	0.12	0.33
123789-HxCDF	72918-21-9	TBD	45	2.5	NA	5.0	0.093	0.33
123478-HxCDF	70648-26-9	TBD	45	2.5	NA	5.0	0.091	0.33
234678-HxCDF	60851-34-5	TBD	45	2.5	NA	5.0	0.12	0.33
1234678-HpCDF	67562-39-4	TBD	450	2.5	NA	5.0	0.099	0.33
1234789-HpCDF	55673-89-7	TBD	450	2.5	NA	5.0	0.088	0.33
OCDF	39001-02-0	TBD	15,000	5.0	NA	10	0.28	1.67

Notes:

1. Project-specific action levels have not been developed. The PALs shown above are actually Data Quality Levels (DQLs) for the individual PCDD/PCDF Congeners from the CPG's RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing data.

2. The target PQLG listed is based on the CPG's QAPP value. The project QL goal was selected as the lower of the DQL and the Sediment RL. Sediment RL are from Tables 2-1 through 2-21 (MPI QAPP, Lower Passaic River Restoration Project, August 2005.

3. Specific MDLs for solids are not given in USEPA Method 1613B, but the QLs listed are the minimum levels published in Table 2 of USEPA Method 1613B. The actual detection limits are usually dependent on the level of interference rather than instrument limitations.

4. The MDLs listed are the statistically-derived MDLs and are based on the analysis of a 10 g dry weight sample size. QLs are based on the analysis of a 3 g dry sample size as routinely required for Passaic River samples in order to reduce matrix effects. These MDLs and QLs listed were obtained from Axys Analytical Services.

5. The project action limit for the highlighted cell is below the QL. The laboratory achievable limit is expected to be low enough to allow comparison of the split data to the CPG data.

QAPP Worksheet #15-i

Reference Limits and Evaluation Table

Matrix: Sediment

Analytical Group: Metals SW-846, 6010C [Shealy does6010C for all]

Concentration Level: Low (mg/kg)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method[5]		Achievable Laboratory Limits[4]		
				MDLs[3]	QLS	MDLs	QLs[4, 5]	CPG Achievable QLs
Aluminum	7429-90-5	7,700	20	NL	NA	1.3	10	2.0
Antimony	7440-36-0	2.0	1.0	NL	NA	0.18	0.5	0.050
Arsenic	7440-38-2	0.39	0.25	NL	NA	0.19	**0.5**	**0.50**
Barium	7440-39-3	1,500	5.0	NL	NA	0.0091	1.3	0.050
Beryllium	7440-41-7	16	0.25	NL	NA	0.028	0.2	0.020
Cadmium	7440-43-9	0.6	0.25	NL	NA	0.011	0.1	0.020
Calcium	7440-70-2	NA	500	NL	NA	18	250	10
Chromium	7440-47-3	26	1.0	NL	NA	0.051	0.25	0.20
Cobalt	7440-48-4	2.3	0.50	NL	NA	0.092	1.3	0.020
Copper	7440-50-8	16	1.0	NL	NA	0.048	0.25	0.10
Iron	7439-89-6	5,500	10	NL	NA	1.6	5.0	4.0
Lead	7439-92-1	31	0.50	NL	NA	0.093	0.5	0.050
Magnesium	7439-95-4	NA	500	NL	NA	18	250	4.0
Manganese	7439-96-5	2660	0.50	NL	NA	0.058	0.75	0.050
Nickel	7440-02-0	16	0.50	NL	NA	0.15	2.0	0.20
Potassium	7440-09-7	NA	500	NL	NA	250	11	80
Selenium	7782-49-2	1.0	0.50	NL	NA	0.17	0.5	**1.0**
Silver	7440-22-4	0.5	0.25	NL	NA	0.042	0.25	0.020
Sodium	7440-23-5	NA	500	NL	NA	17	250	40
Thallium	7440-28-0	0.078	0.50	NL	NA	0.25	**2.5**	0.02
Titanium	7440-28-0	100,000	100	NL	NA	0.51	2.5	2
Vanadium	7440-62-2	38.1	0.50	NL	NA	0.15	2.5	0.2
Zinc	7440-66-6	120	1.0	NL	NA	0.34	2.5	0.5

Notes:

1. At this time, project-specific action levels have not been developed. The values in mg/kg listed are Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011.

2. The target PQLGs listed in mg/kg are based on the CPG's QAPP values and are the lower of the DQL and the Sediment RLs taken from Tables 2-1 through 2-21 (MPI QAPP, Lower Passaic River Restoration Project, August 2005).

3. Method MDLs are not specified.

4. The achievable QLs listed are for Shealy Laboratory by ICP-AES.

5. Laboratory results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

QAPP Worksheet #15-j

Reference Limits and Evaluation Table

Matrix: Sediment
Analytical Group: Mercury (low level) by EPA 1631
Concentration Level: Mercury Trace (ng/g)

Analytical Group: TOC by EPA Lloyd Kahn (DESA SOP C-88)
Concentration Level: Low (mg/kg)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal (PQLG)[2]	Analytical Method		Achievable Laboratory Limits[4, 5]		Laboratory
				MDLs[3]	Method QLs	MDLs	QLs	
Mercury (low level)	7439-97-6	150	30 ng/g	NA	NA See EPA 1631	0.014 ng/g	1 ng/g	Microbac
TOC	D3590-89-02	Not Available	100 mg/kg	Not listed	100 mg/kg	99.7579 mg/kg	100 mg/kg	DESA

Notes:

1. At this time, project-specific action levels have not been developed. The values listed are Data Quality Levels (DQLs) taken from the CPG RI/FS QAPP, *River Mile 10.9 Characterization*, July 2011.

2. The target PQLGs listed are based on the CPG's QAPP values and are the lower of the DQL and the Sediment RLs taken from Tables 2-1 through 2-21 (MPI QAPP, Lower Passaic River Restoration Project, August 2005).

3. Method MDLs are not specified for TOC.

4. The achievable QLs listed are for Microbac and DESA Laboratories.

5. Laboratory results will be reported in dry weight. Actual QLs may be higher and are dependent on the sample moisture content and matrix effects.

QAPP Worksheet #16
Project Schedule Timeline Table

Activities	Organization	Anticipated Date(s) of Initiation	Anticipated Date of Completion	Deliverable	Deliverable Due Date
Prepare and submit: Oversight QAPP Addendum for River Mile 10.9 Sediment Sampling to EPA and USACE	CDM	August 1, 2011	August 12, 2011	UFP-QAPP addendum	August 12, 2011
Prepare and submit: Revised oversight QAPP Addendum for River Mile 10.9 Sediment Sampling to EPA and USACE	CDM	As soon as comments are received	August 25, 2011	UFP-QAPP addendum	August 25, 2011
Oversight/ acceptance of splits and sample handling activities	CDM	Mid August 2011 - TBD	10 days after commencement date	Summary report of field chemical data	To be determined
Laboratory Analysis	DESA and subcontract laboratories (Shealy, Microbac and Axys)	August through September 2011	January 2012	Data Package	To be determined; For standard analyses, 21 – 30 days after the last sample is received; however, specialized analyses may take additional time – see worksheet 30
Validation and verification of sample data	CDM	September 2011	March 2012	Validated data report	To be determined
Oversight /Data Evaluation	CDM	August 2011	March 2012	Oversight Summary Report/ Data Quality Summary Report	To be determined
Review CPG Characterization Summary Report	CDM	Upon receipt	1 month after receipt of report	Comments on CPG Characterization Report	1 month after receipt of report

QAPP Worksheet #18
Sampling Locations and Methods/SOP Requirements Table

Survey Location ID	Depth	Analytical Group	Concentration Level	Estimated Number of Samples (identify field duplicates)	Sampling SOP Reference	Rationale for Sampling Location
Refer to July 2011 RM 10.9 Characterization QAPP prepared by AECOM for the CPG	Sediment split samples (See worksheet 18 of AECOM QAPP for depths of individual station locations)	Analytical group for split samples includes: VOCs, SVOCs, PAHs and alkyl PAHs, organochlorinated pesticides, PCB congeners and homologs, herbicides, TPH extractables, PCDD/PCDF, metals (including titanium and low level mercury), and TOC	Low	All sampling locations will be observed. Approximately 10 percent of CPG samples will be split.	Appendix B of CPG River Mile 10.9 Characterization QAPP (SOP-Collection and Processing of Sediment Grab Samples) of CPG QAPP (AECOM 2011)	Sediment split samples will be collected judgmentally by the on-site oversight staff in consultation with the project manager, deputy project manager and USACE/EPA

Notes:
Refer to Worksheets # 10, 17 and 18, Appendix B and Figure 1 for sampling information in the QAPP prepared by AECOM for the CPG (July 2011).

QAPP Worksheet #19
Analytical SOP Requirements Table

Matrix	Analytical Group	Concentr-ation Level	Analytical and Preparation Method/SOP Reference	Sample Volume	Containers (number, size, and type)[1]	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Sediment – Shealy/	VOCs	Low	5035A/ SW846 Method 8260B	Minimum mass = 15 g each	(4) 40 mL glass vials with magnetic stir bars and PTFE-lined septa/open top screw cap (1 vial is for moisture determination)	Cool to 4 ^{C}C ± 2 ^{C}C	48 hours for lab preservation (freezing); 14 days from sample collection for preparation and analysis
	SVOCs	Low	SW846 Method 8270C	Minimum mass = 30 grams	2- 8 oz glass jar (ship one jar for metals, SVOC, herbicides, and percent moisture and one jar for TPH and percent moisture)	Cool to 4 ^{C}C ± 2 ^{C}C	14 days to extraction; 40 days to analysis at 4 ^{C}C
	Herbicides	Low	EPA 8151A Lab SOP S-SV-022	Minimum mass = 50 g			
Test America Edison	TPH Extractables	Low	New Jersey OQA-QAM-025-02/08; Lab SOP EDS-GCS-011	100 g			
Shealy	Metals	Low	SW846 Method 6010C	Minimum mass = 20 g	1- 8 oz glass jar (see combined glassware in SVOC row)	Cool to 4 ^{C}C ± 2 ^{C}C and freeze as soon as possible	6 months for prep and analysis 1 year [if aliquoted, weighed and frozen at <-15 ^{C}C]
Microbac	Low level mercury	Low	EPA 1631	Minimum mass = 20 g	1- 2 oz pre-tared fluoropolymer, glass or polyethylene jar	Cool to 4 ^{C}C ± 2 ^{C}C Aliquoted, weighed and frozen at <-15 ^{C}C by laboratory.	Analysis within 1 year of collection.
DESA	TOC	Low	Lloyd Kahn DESA SOP C-88	35 g + 5 g for moisture	1- 2 oz glass jar	Cool to 4 ^{C}C ± 2 ^{C}C	14 days per Lloyd Kahn (Per DESA SOP no holding time applies)

Notes:

1. The actual jar size may vary depending on the need of the laboratory. The sampler should confirm sample volumes with the laboratory prior to mobilizing to the field.

QAPP Worksheet #19
Analytical SOP Requirements Table

Matrix	Analytical Group	Concentr -ation Level	Analytical and Preparation Method/SOP Reference	Sample Volume	Containers (number, size, and type) [1]	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Sediment - Axys	PAH and Alkyl PAHs	Low	Axys SOP MLA-021 Rev 10.02	Minimum mass = 45 g	1-4 oz amber glass jar (ship one jar for pesticides, PCBs, PCDDs/PCDFs, and PAHs/Alkyl PAHs)	Maintain in the dark at less than 4 degrees Celsius (^{C}C) from collection until receipt at the laboratory Upon arrival at lab: store at <-10°C in the dark	14 days to extraction, 40 days to analysis at 4^{o}C (For this study PAH samples can be stored 199 days if frozen.)
	Organochlorine Pesticides	Low	Axys SOP summary MLA-028 Rev 06.02	Minimum mass = 50 g			14 days to extraction, 40 days to analysis at 4^{o} C. Organochlorine pesticide samples can be stored 299 days if frozen.
	PCB Congeners and Homologs	Low	EPA 1668A for HRGC/HRMS Axys SOP MLA-010 Rev 10.02				If stored at less than -10^{o} C solid multiphase samples can be stored for up to one year. Sample extracts can be stored at less than -10 degrees Celsius for up to one year
	PCDD/PCDF Congeners	Low	EPA 1613B for HRGC/HRMS using Dean-Stark extraction with toluene Axys SOP MLA-017, Rev 20	20 g			If stored at less than -10^{o}C, solid multiphase samples can be stored up to one year. Sample extracts can be stored at less than -10^{o}C for up to one year

Notes:

1. The actual jar size may vary depending on the need of the laboratory. The sampler should confirm sample volumes with the laboratory prior to mobilizing to the field.

QAPP Worksheet #20
Field Quality Control Sample Summary Table

Matrix	Analytical Group	Concentra-tion Level	Analytical and Preparation SOP Reference	No. of Split Sampling Locations	No. of Field Duplicate Pairs	No. of Extra Volume Laboratory QC (e.g., MS/MSD) Samples	No. of Equipment Blanks	No. of Trip. Blanks	No of PE Samples	Total No. of Samples
Sediment	VOCs	Low	EPA 5035A /8260B (Collection/analysis); Shealy SOP S-VO-002	16	1 per 20 (total of 1 duplicate)	1	0	0	0	17
	TCL SVOCs	Low	SW846 Method 8270D Shealy SOP S-SV-021 and S-EX-017	38	2	2	0	0	0	40
	PAHs and Alkyl PAHs	Low	Modified SW-846 Method 8270C (Axys SOP MLA-021)	38	2	2	0	0	0	40
	Organochlorinated Pesticides	Low	EPA Method 1699 Modified (HRGC/HRMS) Axys SOP MLA-028	33	2	2	0	0	0	35
	PCB congeners and homologs	Low	EPA 1668A for HRGC/HRMS (Axys SOP MLA-010)	33	2	2	0	0	0	35
	Herbicides	Low	EPA 8151A Shealy SOP S-SV-022 and S-EX-004	33	2	2	0	0	0	35
	TPH-Extractables	Low	New Jersey OQA-QAM-025-02/08 Lab SOP EDS-GCS-011	38	2	2	0	0	0	40
	PCDD/PCDF congeners	Low	EPA Method 1613B for HRGC/HRMS Axys SOP MSU-020/ summary SOP MLA-017	33	2	2	0	0	0	35
	TAL metals + titanium	Low	Method 6010C [analysis] /3050B; [extraction]; Shealy SOP S-IM-022 and S-IM-013	38	2	2	0	0	0	40

QAPP Worksheet #20
Field Quality Control Sample Summary Table

Matrix	Analytical Group	Concentra-tion Level	Analytical and Preparation SOP Reference	No. of Split Sampling Locations	No. of Field Duplicate Pairs	No. of Extra Volume Laboratory QC (e.g., MS/MSD) Samples	No. of Equipment Blanks	No. of Trip. Blanks	No of PE Samples	Total No. of Samples
Sediment	Mercury (total + low level)	Low	Microbac SOP for EPA Method 1631	38	2	2	0	0	0	40
	TOC	Low	EPA Method Lloyd Kahn (DESA SOP C-88)	38	2	2	0	0	0	40

Notes:

1. The Field and Analytical Services Teaming Advisory Committee (FASTAC) decision process is required for obtaining laboratory services. However, for this project it is critical for CDM to mirror the CPG's analytical procedures in addition to maintaining similar volumes to provide comparable data and detection limits. This limits the number of laboratories and the methods which can be used. Low concentrations and flexibility are required for the Passaic project. Also, due to the difficulty of analyzing the sample matrix for the selected analyses subcontract laboratories are being used to supplement DESA services to ensure accurate results, to reduce uncertainties in the measurements and to obtain data comparable with data from previous and future surveys and with the CPG's data. PAH/ alkyl PAH, organochlorinated pesticides, PCB congeners, and dioxin/furans will be analyzed by Axys laboratory. CDM subcontracted one of its master services agreement laboratories, Shealy, to obtain analytical services for the metals; TPH extractables, and low level mercury will be analyzed by Test America and Microbac laboratory, respectively. DESA has been requested to perform the TOC analysis.
2. CDM will split 10% of the Low Resolution Cores samples for Group A analyses. Split samples will consist of both grab and core samples.
3. The exact number of samples to be split will be determined in the field and is based on the CPG collection of sufficient volume during the late summer 2011 effort.

QAPP Worksheet #23
Analytical SOP References Table

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work?
8260B Shealy SOP: S-VO-022	*SOP GC/MS Volatiles Analysis based on EPA Method 8260B and 624, Prepared by EPA Method 5030B, 5035 and 3585*. Rev 11, July 2011.	Definitive	VOCs in extracts from solid and aqueous matrices	GC/MS	Shealy	No
EPA 8270D Shealy SOP: S-SV-021	*Analysis of Base /Neutral and Acid Compounds in Aqueous, Soil/ Sediment and Waste Oil/Waste Organic Solvent Samples*. *SOP GC/MS Analysis based on EPA Method 8270D, Prepared by EPA Method 3520C, 3550C and 3580A*. Rev 6, March 2011.	Definitive	SVOCs in extracts from solid and aqueous matrices	GC/MS	Shealy	No
EPA Methods 8270C/D Axys SOP: MLA-021	*Analytical Method for the Determination of Polycyclic Aromatic Hydrocarbons (PAH), and Alkylated PAHs and Alkanes*, Laboratory SOP MLA-021, Revision 10.02, March 2011.	Definitive	PAH and Alkyl PAH	Low-resolution mass spectrometry (LRMS)	Axys Analytical Services Laboratory 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone:1-888-373-0881	No
Axys SOP SOP: MLA-028	*Analytical Method for the Analysis of Organochlorine Pesticides by Isotope Dilution HRGC/HRMS*, Laboratory SOP MLA-028, Revision 6, Version 2. May 2011	Definitive	Organochlorinated Pesticides	High-resolution gas chromatograph / high-resolution mass spectrometry (HRGC/HRMS)		Analyte list per WS#15
EPA 1668 for HRGC/HRMS Axys SOP: MLA-10	*Analytical Method for the Determination of: 209 PCB Congeners by EPA Method 1668A or CBC01.2*. Laboratory SOP MLA-010, Revision 10, Version 2. June 2011.	Definitive	PCB Congeners	HRGC/HRMS		No
EPA 1613B Axys SOP: MSU-020 SOP Summary MLA-017	*Analytical Method for the Determination of Polychlorinated Dibenzodioxins and Dibenzofurans* Laboratory SOP Summary MLA-017, Revision 20, January 2011.	Definitive	PCDD/PCDF Congeners	HRGC/HRMS		No
EPA 8151A Shealy SOP S-SV-022 and S-EX-004	*SOP Gas Chromatographic Analysis based on EPA Methods 8000B and 8151A*. Rev 2, April 2011.	Definitive	Herbicides	GC	Shealy	TBD

QAPP Worksheet #23
Analytical SOP References Table

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work?
New Jersey DEP OQA-QAM-025-02/08 Lab SOP EDS-GCS-011	*Quantitation of Semi-volatile Petroleum Products in Water, Soil, Sediment and Sludge* [by GC/FID]. Revision 3. June 2008.	Definitive	TPH Extractables	GC/FID	Test America, Edison	No
EPA Method 6010C S-IM-022 6010C Rev. 3	*SOP for Inductively Coupled Plasma-Atomic Emission Spectroscopy and Spectrometric Method for Trace Element Analysis* 6010C. Revision 3. July. 2011.	Definitive	Metals	ICP-AES	Shealy	No
EPA 1631 Microbac SOP	*SOP for Mercury using Automatic Fluorescence Spectroscopy*. Revision 2. August 2009 (Microbac). *Appendix to Method 1631, Total Mercury in Tissue, Sludge, Sediment and soil by Acid Digestion and BrCl Oxidation*. January 2001 (EPA)	Definitive	Total low level mercury	CVAFS	Microbac	No
C-88	*Total Organic Carbon-Sediment*. Rev 2.2. February 2011.	Definitive	TOC	Carbon Analyzer	DESA	No
Lloyd Kahn	*Determination of TOC in Sediment*. July 1998 and Attachment B, *Supplemental Technical Direction and Additional QC Procedures*					

Notes:

The titles above may change dependent on the assigned laboratories.

1: As necessary, the assigned laboratories will perform additional clean-up of split samples (via gel permeation chromatography) prior to analysis of organic compounds.

QAPP Worksheet #24
Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
TOC Analyzer	Per vendor, instrument manual and laboratory SOP	Check daily	Calibration and corrective action as per laboratory SOP and Manufacturer's instruction. No samples shall be analyzed if instrument calibration exceeds the acceptance criteria.		Laboratory analyst / QA officer - TBD	Lloyd Kahn SOP DESA - C-88
HRGC/ HRMS and HRGC/LRMS	Initial Calibration and calibration verification check: Per laboratory SOP	After set up, prior to run and after instrument changes or failures of checks.	% RSD and % recovery per laboratory SOPs.	Check, correct; re-calibrate and rerun all samples analyzed after last valid calibration check	Laboratory analyst / QA officer - TBD	Axys SOP for PAH analysis: MLA-021 Axys SOP for Chlorinated pesticides: MLA-028 Axys SOP for PCDD/ PCDF by EPA 1613B: MLA-017 Axys SOP for PCB Congeners by EPA 1668A: MLA-010
	Calibration checks: CCVs per laboratory SOP	Daily: Beginning of run and after every 10 samples and at end of analytical run	% recovery per laboratory SOP	Check, correct; re-calibrate and rerun all samples analyzed after last valid cal check	Laboratory analyst / QA officer - TBD	
GC/MS GC GC/FID	Initial calibration: 5 points standards	Upon award of the contract, whenever the laboratory takes corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement, etc.), or if the continuing calibration acceptance criteria have not been met.	relative response factor (RRF) ≥ minimum acceptable RRF listed in Table 5 of procedure; All target compounds, initial relative standard deviation (RSD) ≤ 10% or 20% and correlation coefficient (r)> 0.995. %RSD ≤ value in Table 5 of SOM01.2 or other laboratory SOP as applicable.	Inspect system for problems (e.g., clean ion source, change the column, service the purge and trap device), correct problem, re-calibrate.	Laboratory Technician	for VOC/SVOC - SW-846 8260/8270/8151
GC/MS and GC GC/FID	Continuing calibration (CCV)	Once every 12 hours or as per laboratory SOPs	%D ≤15% or <30% or as per laboratory SOPs	Inspect system; correct problem; recalibrate the instrument, reanalyze affected samples and standards.	Laboratory GC/MS Technician	8260/8270C

QAPP Worksheet #24
Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
GC/MS	Calibration Standards Verification	Each lot of standards	As per laboratory established control limits	Inspect system; correct problem; re-run standard and affected samples	Laboratory GC/MS Technician	8260/8270C /8151
GC/MS	Tuning	Daily: every 12 hours	Response factors and RRF as method specified	Inspect system; correct problem; re-run standard and affected samples	Laboratory GC/MS Technician	All MS instruments
GC/FID	Mass Discrimination Check	Every 12 hours	RF ratio of C32/C20 should be >0.8	Per laboratory SOP	Laboratory GC/FID Technician	NJ OQA-QAMS/ EDS-GCS-011
CVAFS	Per method and laboratory SOP	Calibration	Per method/ laboratory SOP. ICAL ≤15%RSD.	Inspect the system, correct problem, re-calibrate, and re-analyze samples.	Assigned laboratory personnel	EPA 1631 Microbac SOP: Hg-1631
		ICV: Check daily when instrument is in use	85-115% R for Total mercury			
		CCV: Beginning and after every 10 samples	77-123% R for total mercury			
ICP-AES	See Method and SOPs; as per instrument manufacturer's recommended procedures	Initial calibration: daily or once every 24 hours and each time the instrument is set up.	ICP-AES: As per instrument manufacturer's recommended procedures, with at least 2 standards.	Inspect the system, correct problem, re-calibrate, and re-analyze samples.	TBD DESA Laboratory, or Subcontractor	SW-846, 6010
	Initial calibration	Daily; after tuning and optimizing instrument	r >0.995; minimum of 3 standards and a blank	Repeat analysis; re-prepare calibration standards and reanalyze	ICP-AESTechnician/ analyst / QA officer	Shealy SOP: S-IM-022

QAPP Worksheet #24
Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
	ICV	Before sample analysis	90-110% recovery; source of standard separate from calibration standards	Re-calibrate instrument; prepare fresh ICV standards; do not analyze samples until problem is corrected		
ICP-AES	Reporting Limit Standard	After initial calibration verification standard	80-120% recovery or concentration ≤ 30% difference (from true value)	Re-analyze failed standard	TBD	SW-846, 6010B/6020 Shealy SOP: S-IM-022
	CCV	Every 10 samples and at end of analytical sequence	90-110% recovery; source of standard separate from calibration standards	Re-check; re-calibrate and rerun all samples analyzed after last valid CCV	DESA Laboratory, or Subcontractor	
ICP-MS	Continuing calibration	Beginning and end of run; 10% frequency or every 2 hours during an analysis run	As per instrument manufacturer's recommended procedures, with at least 2 standards. A minimum of three replicate integrations are required for data acquisition.		ICP-AES Technician/ analyst / QA officer	

Notes:

1. General GC/MS calibration requirements are presented. Instruments used for analyses follow the calibration frequencies outlined in the method SOPs (Appendix P of this Oversight QAPP, Addendum No. 9). Laboratory specific calibration information is maintained by the laboratories; method specific calibration information is detailed in the methods. The laboratory standard calibration procedures will dictate.

QAPP Worksheet #28-a
QC Samples Table

Matrix	Sediment
Analytical Group	VOCs
Concentration Level	Low (mg/L)
Sampling SOP(s)	See Worksheet #21
Analytical Method/SOP Reference	EPA 8260B/S-VO-002
Sampler's Name	TBD
Field Sampling Organization	CDM
Analytical Organization	Axys Analytical Services Ltd.
No. of Sample Locations	See Worksheet # 20

QC Sample:	Frequency/ Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per sample batch	Per laboratory SOP	Results>PQL, reanalyze blank and associated samples.	Laboratory Analyst	Accuracy/ Sensitivity	No analyte > QL
LCS/ LCSD	Per sample batch	70-130% recovery; 60-140% recovery for select compounds and marginal limits and per laboratory SOP	Identify source of problem, make other adjustments; redigest if needed and reanalyze per lab SOP	Laboratory Analyst	Accuracy	Per method/laboratory SOP
					Precision	Individual laboratory established limits per SOP
MS/ MSD	Per sample batch	70-130% recovery	Per laboratory SOP	Laboratory Analyst	Accuracy	70-130% recovery
		RPD ≤30%			Precision	RPD ≤30%
Surrogate	Every field and QC sample, standards, blanks	Per laboratory SOP Table IX and LIMS	Per laboratory SOP	Laboratory Analyst	Accuracy	Per laboratory SOP Table IX and LIMS
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	Laboratory Analyst	Accuracy/bias	≤ 10 degrees Celsius for data validation

QAPP Worksheet #28-b
QC Samples Table

Matrix	Sediment
Analytical Group/ SOP Reference	SVOCs by 8270D/ S-SV-021
Concentration Level	Low
Sampling SOP(s)	Split of CPG samples
Sampler's Name	TBD
Field Sampling Organization	CDM
Analytical Organization	Shealy Laboratory
No. of Sample Locations	See Worksheet #20

QC Sample:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria**
Method Blank	per extract batch	Per laboratory SOP	Results>PQL, reanalyze blank and associated samples.	Laboratory Analyst	Accuracy/ Sensitivity	No analyte > QL
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	Laboratory Analyst	Accuracy/bias	≤ 10 degrees Celsius for data validation
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
MS/MSD	1 per 20 samples or each group of samples	Per method/laboratory SOP	Investigate and correct; reanalyze affected samples. Flag outliers Document in case narrative	Laboratory Analyst	Precision	Individual limits listed as per laboratory established limits
MS/MSD and LCS					Accuracy	
DMC/Surrogates	Every field and QC sample, standards, blanks	Per method/laboratory SOP:	Identify source of problem, make adjustments and reanalyze as required	Laboratory Analyst	Accuracy	Recovery - See Laboratory SOP limits

Notes: The assigned laboratory also must perform the QA/QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs as specified in 8270, such as matrix spike duplicates for precision, matrix spikes, surrogates for accuracy, and blanks and method detection limits for sensitivity. The laboratory personnel must follow all the corrective actions required by the laboratory SOP or subcontract Statement of work (SOW).

QAPP Worksheet #28-c
QC Samples Table

Matrix	Sediment
Analytical Group	PAHs and Alkyl PAHs
Concentration Level	Low
Sampling SOP(s)	See Worksheet #21 – split of CPG samples
Analytical Method/SOP Reference	Laboratory SOP, MLA-021
Sampler's Name	TBD
Field Sampling Organization	CDM
Analytical Organization	Axys Analytical Services Ltd.
No. of Sample Locations	See Worksheet #20

QC Sample:	Frequency/ Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	per extract batch	Per laboratory SOP	Investigate and correct per laboratory SOP	Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
Laboratory Duplicate (MS/MSD)	1 per 20 samples	Per laboratory SOP	Investigate and correct; reanalyze affected samples. Flag outliers	Laboratory Analyst	Precision	± 20% of mean if sample concentration >10x DL
Matrix Spike	1 per 20 samples or with each group of field samples	Per laboratory SOP	Investigate and correct. Document in data summary	Laboratory Analyst	Accuracy/Precision	50-200% Recovery per laboratory SOP
Perdeuterated Surrogate	Every field and QC sample, standards	Per laboratory SOP	Identify source of problem, make other adjustments and reanalyze	Laboratory Analyst	Accuracy	15-130% Recovery - See Laboratory SOP
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 10*QL)

Note:

The assigned laboratory also must perform the QA/QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs, such as laboratory duplicates and matrix spike duplicates for precision, matrix spikes, Deuterated monitoring compounds for accuracy, and blanks and method detection limits for sensitivity. The laboratory personnel must follow all the corrective actions required by the laboratory SOP.

QAPP Worksheet #28-d
QC Samples Table

Matrix	Sediment
Analytical Group	Organochlorinated Pesticides
Concentration Level	Low
Sampling SOP(s)	See Worksheet #21 – split of CPG samples
Analytical Method/SOP Reference	OC Pesticides/MLA-028
Sampler's Name	TBD
Field Sampling Organization	CDM
Analytical Organization	Axys Analytical Services Ltd.
No. of Sample Locations	See Worksheet #20

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	per extract batch	Per laboratory SOP	Investigate and correct per laboratory SOP	Laboratory Analyst	Accuracy/ Sensitivity	No analyte > QL
Laboratory Duplicate	1 per 20 samples	Per laboratory SOP	Investigate and correct; Flag outliers	Laboratory Analyst	Precision	± 20% of mean if sample concentration >10x DL
Reference Standard/Sample	With each batch or as requested	Per laboratory SOP	Investigate and correct; Flag outliers	Laboratory Analyst	Accuracy	Per laboratory SOP
Ongoing Precision and Recovery/ MS	1 per batch of 20 samples prior to sample analysis	60-150% R for E1 pesticides and 50-130% R for E2 pesticides (See SOP Tables 6 and 7 for compound list and individual recoveries)	Identify source of problem, make other adjustments as per laboratory SOP	Laboratory Analyst	Accuracy	See method limits; for individual compound limits see laboratory SOP
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 10QL)

Notes:
The assigned laboratory also must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in laboratory SOP; such as performance of initial and ongoing studies, calibration verification, addition of internal standards, analyses of blanks and determination of detection limits.

QAPP Worksheet #28-e
QC Samples Table

Matrix	Sediment
Analytical Group	PCB Congeners
Concentration Level	Low (pg/g)
Sampling SOP(s)	See Worksheet #21
Analytical Method/SOP Reference	EPA 1668A / MLA-010
Sampler's Name	TBD
Field Sampling Organization	CDM
Analytical Organization	Axys Laboratory
No. of Sample Locations	See Worksheets #20

QC Sample:	Frequency/ Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per 20 samples	< QL	If samples non-detect or if lowest sample result is >10 times the blank-no action; otherwise redigest and reanalyze	Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
Laboratory Duplicate	1 per 20 samples	≤ 20% RPD; ±QL for samples <10x QL	Flag outliers	Laboratory Analyst	Precision	RPD ≤ 40%
Certified Reference Material or QC Sample	Periodically at least quarterly	Criteria will depend on which CRM is requested to be analyzed - TBD	Check standards; recalibrate if required	Laboratory Analyst	Accuracy	Criteria will depend on which CRM is requested to be analyzed – TBD. Also see Worksheet 12-e
Calibration Verification Sample	Beginning of each 12-hour shift	70-130%R for native analytes and 50-150%R for surrogates	Adjust and/or recalibrate	Laboratory Analyst	Accuracy/bias	70-130%R for native analytes and 50-150%R for surrogates
Initial Precision and Recovery	Prior to sample analysis	Per laboratory SOP	Investigate and correct	Laboratory Analyst	Accuracy	60-140%R ≤ 40% RSD
Ongoing Precision and Recovery	1 per batch of 20 samples	Per laboratory SOP	Identify source of problem, recalibrate if needed/ make other adjustments and reanalyze	Laboratory Analyst	Accuracy	Warning 70-130%R; Accept 50-150%R for native analytes, and 15-140% for surrogates
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 10QL)

QAPP Worksheet #28-f
QC Samples Table

Matrix	Sediment
Analytical Group	Herbicides
Concentration Level	Low (mg/L)
Sampling SOP(s)	See Worksheet #21
Analytical Method/SOP Reference	EPA 8151/S-SV-022
Sampler's Name	TBD
Field Sampling Organization	CDM
Analytical Organization	Axys Analytical Services Ltd.
No. of Sample Locations	See Worksheet # 20

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per 20 samples	Per laboratory SOP	If samples non-detect or if lowest sample result is >10 times the blank-no action; otherwise redigest and reanalyze	Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
Laboratory Duplicate	1 per 20 samples	Per laboratory SOP	Investigate and correct; Flag outliers	Laboratory Analyst	Precision	± 20% of mean if sample concentration >10x DL otherwise ±QL
MS	1 per batch of 20 samples	Per laboratory limits	Investigate and correct	Laboratory Analyst	Accuracy	Individual laboratory established limits
LCS	1 per batch of 20 samples		Identify source of problem, make other adjustments; redigest if needed and reanalyze	Laboratory Analyst	Accuracy	
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	Laboratory Analyst	Accuracy/bias	≤ 10 degrees Celsius for data validation

QAPP Worksheet #28-g
QC Samples Table

Matrix	Sediment
Analytical Group	TPH Extractables
Concentration Level	Low (mg/L)
Sampling SOP(s)	See Worksheet #21
Analytical Method/SOP Reference	NJ OQA-QAM Lab SOP EDS-GCS-011
Sampler's Name	TBD
Field Sampling Organization	CDM
Analytical Organization	Axys Analytical Services Ltd.
No. of Sample Locations	See Worksheet #20

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per 20 samples	Per laboratory limits	If samples non-detect or if lowest sample result is >10 times the blank-no action; otherwise redigest and reanalyze	Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
Laboratory duplicate	1 per 20 samples	Per laboratory limits	Investigate and correct; Flag outliers	Laboratory Analyst	Precision	± 20% of mean if sample concentration >10x DL
MS/MSD	Prior to sample analysis; 1 per 20 samples	Per laboratory limits	Investigate and correct	Laboratory Analyst	Accuracy/ Precision	70-130% recovery /RPD ≤30 %
LCS	1 per batch of 20 samples	Per laboratory limits	Identify source of problem, Dilute, make other adjustments; redigest if needed and reanalyze	Laboratory Analyst	Accuracy	60-140% recovery
Surrogate	Every sample, standard	Per laboratory limits		Laboratory Analyst	Accuracy	Per laboratory limits
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	Laboratory Analyst	Accuracy/bias	≤ 10 degrees Celsius for data validation

QAPP Worksheet #28-h
QC Samples Table

Matrix	Sediment
Analytical Group	PCDD/PCDF
Concentration Level	Low (mg/L)
Sampling SOP(s)	See Worksheet #21
Analytical Method/SOP Reference	EPA 1613B/ MLA-017
Sampler's Name	TBD
Field Sampling Organization	CDM
Analytical Organization	Axys Analytical Services Ltd.
No. of Sample Locations	See Worksheet #20

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per 20 samples	Per laboratory SOP	If samples are non-detect or if lowest sample result is >10 times the blank-no action; otherwise redigest and reanalyze	Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
Laboratory Duplicate	1 per 20 samples	Per laboratory SOP	Investigate and correct; Flag outliers	Laboratory Analyst	Precision	± 20% of mean if sample concentration >10x DL
Initial Precision and Recovery	Prior to sample analysis	Per laboratory SOP	Investigate and correct	Laboratory Analyst	Accuracy	Per method/laboratory SOP
Ongoing Precision and Recovery	1 per batch of 20 samples	Per laboratory SOP	Identify source of problem, make other adjustments; redigest if needed and reanalyze	Laboratory Analyst	Accuracy	Individual laboratory established limits per SOP
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 10QL)
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	Laboratory Analyst	Accuracy/bias	≤ 10 degrees Celsius for data validation

Notes:
The assigned laboratory also must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in EPA Method 1613B.

QAPP Worksheet #28-i
QC Samples Table

Matrix	Sediment
Analytical Group	Metals + titanium (no mercury)
Concentration Level	Low
Sampling SOP(s)	See Worksheet #21 – split of CPG samples
Analytical Method/SOP Reference	SW-846 6010C/ S-IM-022
Sampler's Name /Organization	TBD /CDM
Analytical Organization	Shealy
No. of Sample Locations	See Worksheet #20

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note in laboratory narrative. CDM will use more coolant; check packing procedure	Laboratory Analyst	Accuracy/bias	≤ 10 degrees Celsius for data validation
Preparation Blank	1 per 20 samples	No constituent > QL	Suspend analysis until source rectified; re-digest and reanalyze affected samples	Laboratory Analyst	Accuracy/ Sensitivity	No result > QL
Laboratory duplicate	1 per 20 samples or each group	± 20% RPD	Investigate and correct; Flag outliers; Note in case narrative	Laboratory Analyst	Precision	≤ 35% RPD if result >5QL
Spike	1 per 20 samples	75-125%R	Flag outliers	Laboratory Analyst	Accuracy	75-125%R
Post-Digestion Spike	after any analyte (except Ag) fails spike %R	75-125%R	Flag outliers	Laboratory Analyst	Accuracy	75-125%R
Interference Check Sample	beginning, end and periodically during run (twice each 8 hr)	± 2 *QL of true value or ± 20% , whichever is greater	Check calculations and instruments, reanalyze affected samples	Laboratory Analyst	Sensitivity	± 2 * QL of true value or ± 20% of true value, whichever is greater
Laboratory Control Sample	1 per 20 samples	Lab Control limits	Suspend analysis rectify source; re-digest and reanalyze affected samples	Laboratory Analyst	Accuracy	90-110%R

Notes:

The assigned laboratory also must perform the QA/QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs as specified in the method or laboratory SOP and or subcontract Statement of work (SOW) as applicable.

QAPP Worksheet #28-j
QC Samples Table

Matrix	Sediment
Analytical Group	Low Level Total Mercury
Concentration Level	Trace
Sampling SOP(s)	See Worksheet #21 – split of CPG samples
Analytical Method/SOP Reference	EPA 1631
Sampler's Name /Organization	TBD /CDM
Analytical Organization	CDM Subcontract Laboratory-TBD
No. of Sample Locations	See Worksheet #18 & 20

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
Temperature Blank	1 per cooler	≤ 6 degrees Celsius or frozen as applicable	Note in laboratory narrative. CDM will use more coolant; check packing procedure	Laboratory Analyst	Accuracy/bias	≤ 10 degrees Celsius or per WS 19 and 37 for data validation
Preparation Blank	3 per 20 samples or batch	Per laboratory SOP	Reanalyze. Suspend analysis until source rectified; re-distill and reanalyze affected samples if results are <10 times the blank	Laboratory Analyst	Accuracy/Sensitivity	No result > 5MDL
Laboratory duplicate	1 per 20 samples	Per laboratory SOP	Investigate and correct; Flag outliers; Note in case narrative. Multiple failures require re-distillation and reanalysis.	Laboratory Analyst	Precision	≤ 35% RPD if result >5CRQL
CRM and Ongoing Precision and Recovery Samples	1 per 20 samples	Per laboratory SOP	Check calculations and instruments, reanalyze affected samples. Report in case narrative.	Laboratory Analyst	Accuracy	70-130%R for OPR <20 RSD for IPR 75-125%R for CRM/IPR
MS/MSD	1 per 20 samples or	Per laboratory SOP	Investigate matrix effects and note in data narrative.	Laboratory Analyst	Accuracy	70-130%R
					Precision	RPD ≤35% (30 per method)

Notes:

The assigned laboratory also must perform the QA/QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs as specified in the method or laboratory SOP and or subcontract Statement of work (SOW) as applicable.

QAPP Worksheet #28-k
QC Samples Table

Matrix	Sediment
Analytical Group	TOC
Concentration Level	Low
Sampling SOP(s)	See Worksheet #21 – split of CPG samples
Analytical Method/SOP Reference	Lloyd Kahn – DESA SOP C-88
Sampler's Name	TBD
Field Sampling Organization	CDM
Analytical Organization	DESA
No. of Sample Locations	See Worksheet #18 & 20

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Preparation Blank	per extract batch	≤ 100 mg/kg	Determine source; recalibrate and rerun prior to analyzing samples	Laboratory Analyst	Accuracy/Sensitivity	No result > QL
Sample matrix duplicate	1 per 20 samples or with each group of field samples	≤ 50% RPD	Reanalyze affected samples. Flag outliers and document in case narrative	Laboratory Analyst	Precision	≤ 50% RPD
Laboratory fortified blank/AQCs/QCS	per batch	± 25% of true value	Recalibrate and reanalyze prior to running samples.	Laboratory Analyst	Accuracy	± 25% of true value
		RPD ≤20 %			Precision	RPD ≤20 %
Sample splits and field duplicates	1 per 20 samples	None	Rerun. Flag and note in narrative. Data assessor to inform PM if MPC is exceeded; address in data quality assessment	Laboratory Analyst / CDM ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	Laboratory Analyst	Accuracy/bias	≤ 10 degrees Celsius for data validation

Notes:

The assigned laboratory also must perform the QA/QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs as specified in the method or laboratory SOP and or subcontract Statement of work (SOW) as applicable.

Corrective action driven by laboratory SOP or as noted above.

Worksheet 30
Analytical Services Table

Matrix	Analytical Group	Concentra-tion Level	Sample Location/ ID Numbers	Analytical SOP	Validated Data Package Turnaround Time Laboratory/Data Validation	Laboratory/ Organization (Name and Address, Contact person and Telephone Number)	Backup Laboratory/Organization (Name and Address, Contact person and Telephone Number
Sediment	PAHs and Alkyl PAHs	Low	TBD	Axys SOP MLA-021	65 days (35 days /30 days)[2]	Axys Analytical Services Ltd 2045 Mills Road West Sidney, BC V8L 5X2, Canada 1-888-373-0881	TBD
Sediment	Organochlorine pesticides	Low		Axys SOP MLA-028	65 days (35 days for laboratory analysis/ 30 days for data validation)[2]		TBD
Sediment	PCB Congeners	Low		EPA Method 1668A Axys SOP MLA-010	65 days (35 days /30 days)[2]		TBD
Sediment	PCDD/PCDF	Low		EPA Method 1613B Axys SOP MLA-017	65 days (35 days /30 days)[2]		TBD
Sediment	VOCs	Low		SW846 Method 8260B Shealy SOP S-VO-002	51 days (21 days / 30 days)	Shealy Environmental Services Inc. 106 Vantage Point Drive West Columbia, SC 29172 Attention: Nisreen Saikaly 1-800-673-9375 [TPH samples will be shipped by Shealy to Test America, Edison]	EPA CLP
Sediment	SVOCs	Low		SW846 Method 8270D Shealy SOP S-SV-021	51 days (21 days / 30 days)		EPA CLP
Sediment	Herbicides	Low		SW846 Method 8151A Shealy SOP S-SV-022	51 days (21 days / 30 days)		EPA CLP
Sediment	TPH extractables	Low		NJ OQA-QAM-025-02/08 Lab SOP EDS-GCS-011	51 days (21 days / 30 days)		DESA
Sediment	Metals including titanium	Low		SW846 Method 6010C Shealy SOP S-IM-022	51 days (21 days / 30 days)		EPA CLP

Worksheet 30

Analytical Services Table

Matrix	Analytical Group	Concentra-tion Level	Sample Location/ ID Numbers	Analytical SOP	Validated Data Package Turnaround Time Laboratory/Data Validation	Laboratory/ Organization (Name and Address, Contact person and Telephone Number)	Backup Laboratory/Organization (Name and Address, Contact person and Telephone Number
Sediment	Low level Total Mercury	Low	TBD	EPA Method 1631	51 days (21 days / 30 days)	Microbac 250 West 84th Drive Merrillville, IN 46410 Attention: Kevin Falvey 219-769-8378	TBD
Sediment	TOC	Low		Lloyd Kahn DESA SOP C-88	51 days (21 days / 30 days)	DESA 2890 Woodbridge Avenue Edison, NJ 08837 732-906-6161/6171 DESA contact: John Birri 732-906-6886	Shealy

Notes:

1: Sediment matrix refers to sediments split sample analyzed for sediment chemical concentration.

2: Subcontract laboratories will communicate with the ASC on split sample status and potential analytical difficulties (if any arise). With the approval of the ASC and Task Leader, the turn-around-time for the laboratory data package deliverable can be adjusted to account for re-analysis or additional quality control as necessary.

QAPP Worksheet #36
Validation (Steps IIa and IIb) Summary Table

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria[1, 3]	Data Validator (title and organizational affiliation)
IIa /IIb	Sediment	VOCs by 8260B	Low	Region 2 – Data Validation Guidelines SOP HW-34, rev 1 or National Functional Guidelines	CDM ASC, Scott Kirchner or designee
IIa /IIb		SVOCs by 8270D	Low	Region 2 – Data Validation Guidelines SOP HW-35, rev 1 or National Functional Guidelines	CDM ASC, Scott Kirchner or designee
IIa /IIb		PAH – Axys Laboratory SOP	Low-trace	National Functional Guidelines	CDM ASC, Scott Kirchner or designee
IIa /IIb		Organochlorinated Pesticides – Axys SOP	Low-trace	National Functional Guidelines	CDM ASC, Scott Kirchner or designee
IIa /IIb		PCB Congeners – EPA 1668A	Low	Region 2 - Data Validation Guidelines SOP HW-46, rev 1 or National Functional Guideline	EPA Region 2
IIa /IIb		Herbicides – 8151A	Low	EPA SOP HW-17, Validating Chlorinated Herbicides by GC, Revision 3 or National Functional Guidelines	CDM ASC, Scott Kirchner or designee
IIa /IIb		TPH-Extractables – NJ OQA-QAM	Low	National Functional Guidelines	CDM ASC, Scott Kirchner or designee
IIa /IIb		PCDD/PCDF Congeners – EPA 1613B	Low	EPA SOP HW-19 or 25, Validating PCDD/PCDF by HRGC/HRMS, Revision 1 or National Functional Guidelines	CDM ASC, Scott Kirchner or designee
IIa /IIb		Metals - 6010C	Low/Medium	Region 2 - Data Validation Guidelines SOP HW-2, rev 13 or National Functional Guidelines	CDM ASC, Scott Kirchner or designee
IIa /IIb		Total Mercury - EPA 1631	Trace	National Functional Guidelines modified by QAPP Worksheets 12,15,19 and 24	CDM ASC, Scott Kirchner or designee
IIa /IIb		TOC - Lloyd Kahn (DESA SOP C-88)	Low	DESA validation SOP or CDM 029A SOP modified by QAPP Worksheets #12,15,19 and 24	DESA or CDM ASC, Scott Kirchner or designee

Notes:

1. Results will be validated if analyzed by a subcontract laboratory by the process of data verification and assessment utilizing the laboratory QC summaries.
2. All validation procedures will utilize the measurement performance criteria in the QAPP and any additional method requirements.

QAPP Worksheet #37
Usability Assessment

An Oversight Summary Report and Data Quality Summary Report will be prepared by CDM personnel. Frank Tsang, Project Manager, will be responsible for its content and for assigning this task to CDM personnel. The data comparability review and usability assessment will be conducted on validated data. The effectiveness of control actions will be evaluated during the laboratory review of data, data validation and data evaluation and data quality assessment process. Data information will be documented in the laboratory narrative, data validation report and in the Data Comparability Report. The report will include an overall assessment of the CPG's analytical data using the results of the split sampling and field oversight including the field oversight observations of deficiencies and compliance; and an assessment of the split sampling data quality. The following items will be assessed for CDM split samples and conclusions drawn based on their results:

Precision – Results of laboratory duplicates will be assessed during data validation and data will be qualified according to data validation procedures cited on Worksheet #36. Split samples will be compared by matrix using the relative percent difference (RPD) for each pair of results reported above quantitation limits (QL) or for organic and inorganic analyses respectively. RPD acceptance criteria of less than or equal those listed in this QAPP will be used to access sampling precision. Absolute difference will be used when one or both results are at or below the QL. An absolute difference of less than five times the QL will be the acceptance criteria. A discussion summarizing the results of laboratory precision and any limitations on the use of data will be described in the report.

Accuracy/Bias Contamination – Results for all laboratory blanks will be assessed as part of data validation. During the validation process, the validator will qualify data following the procedures described on Worksheet #36. A discussion summarizing the results of laboratory accuracy and bias based on contamination will be presented and any limitations on the use of data will be described in the report.

Representativeness –The representativeness of the survey data will be evaluated based on the ability to implement the sediment sampling as written in the QAPP. A determination will be made based on the observations completed during the surveys, whether data results accurately represent the sediment concentrations in the study area during the River Mile 10.9 survey, and whether the results are comparable with those made in previous events.

Comparability –The results of this oversight will be used in conjunction with the CPG's data to support the investigation results. Data will be handled, analyzed and reported in a manner that is comparable to the CPG's data set. The RPD between CDM's and the CPG's data will be calculated.

Completeness – A completeness check will be performed on the split sample data generated by the laboratories. Completeness will be determined based on whether all CPG planned (or modified) sampling locations were sampled at the pre-determined frequencies and the obtained data set compared to the project completeness goal of 90 percent. A discussion summarizing the results of project completeness and any limitations on the use of data will be described in the report.

For sampling, completeness will be calculated as the number of samples collected and analyzed divided by the number of planned for collection. For each analyte, completeness will also be calculated as the number of data points that meet measurement performance criteria divided by the total number of data points for that analyte. A discussion summarizing the results of project completeness and any limitations on the use of data will be described in the report.

The results will be presented in text of the Data Comparability Report. Data gaps will be evaluated if requested by USACE/EPA. The report will discuss the completeness of the planned and collected data and the affect on the data objective of evaluating the accuracy of the CPG's data.

Sensitivity – Data results will be compared to project action limits provided on Worksheet #15. A discussion summarizing any conclusions about sensitivity of the analyses will be presented, and any limitations on the use of data will be described in the report.

Reconciliation – The PQLGs presented in Worksheet #12 will be examined to determine if the objectives were met. This examination will include a combined overall assessment of the results of each analysis pertinent to an objective. Each analysis will first be evaluated separately in terms of major impacts observed from data validation, data quality indicators and measurement performance criteria assessments. Based on the results of these assessments, the quality of data will be determined. Based on the quality determined, the usability of data for each analysis will be determined. Based on the combined usability of data from all analyses for an objective, it will be determined if the PQLG was met and whether project goals were achieved. As part of the reconciliation of each objective, conclusions will be drawn and any limitations on the usability of any of data will be described.

The following equations will be used:

1. To calculate split sample precision: $RPD = 100 * 2 |X1 - X2| / (X1 + X2)$

where X1 and X2 are the reported concentrations for each duplicate or replicate

2. To calculate split data completeness:

% Completeness = V/n * 100 - where V= number of measurements judged valid; n = total number of measurements made and

% Completeness = C/x * 100 - where C= number of samples collected; x = total number of measurements planned

The investigation results will be presented in table and figures and in the text of the Data Comparability Report. Data gaps will be evaluated if requested by USACE/EPA. The report will discuss the completeness of the planned and collected data and the affect on the data objective of evaluating the accuracy of the CPG's data.

References:

AECOM. 2011. Quality Assurance Project Plan, River Mile 10.9 Characterization, Lower Passaic River Restoration Project. Revision 2. August.

Malcolm Pirnie, Inc. 2008. Final Quality Assurance Project Plan for CPG Oversight, Lower Passaic River Restoration Project, 2008 Sediment Coring. July.

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Appendix O

Lower Passaic River

River Mile 10.9 Characterization Study

Figure 1 Excerpted from AECOM QAPP

July 2011, Revision 1

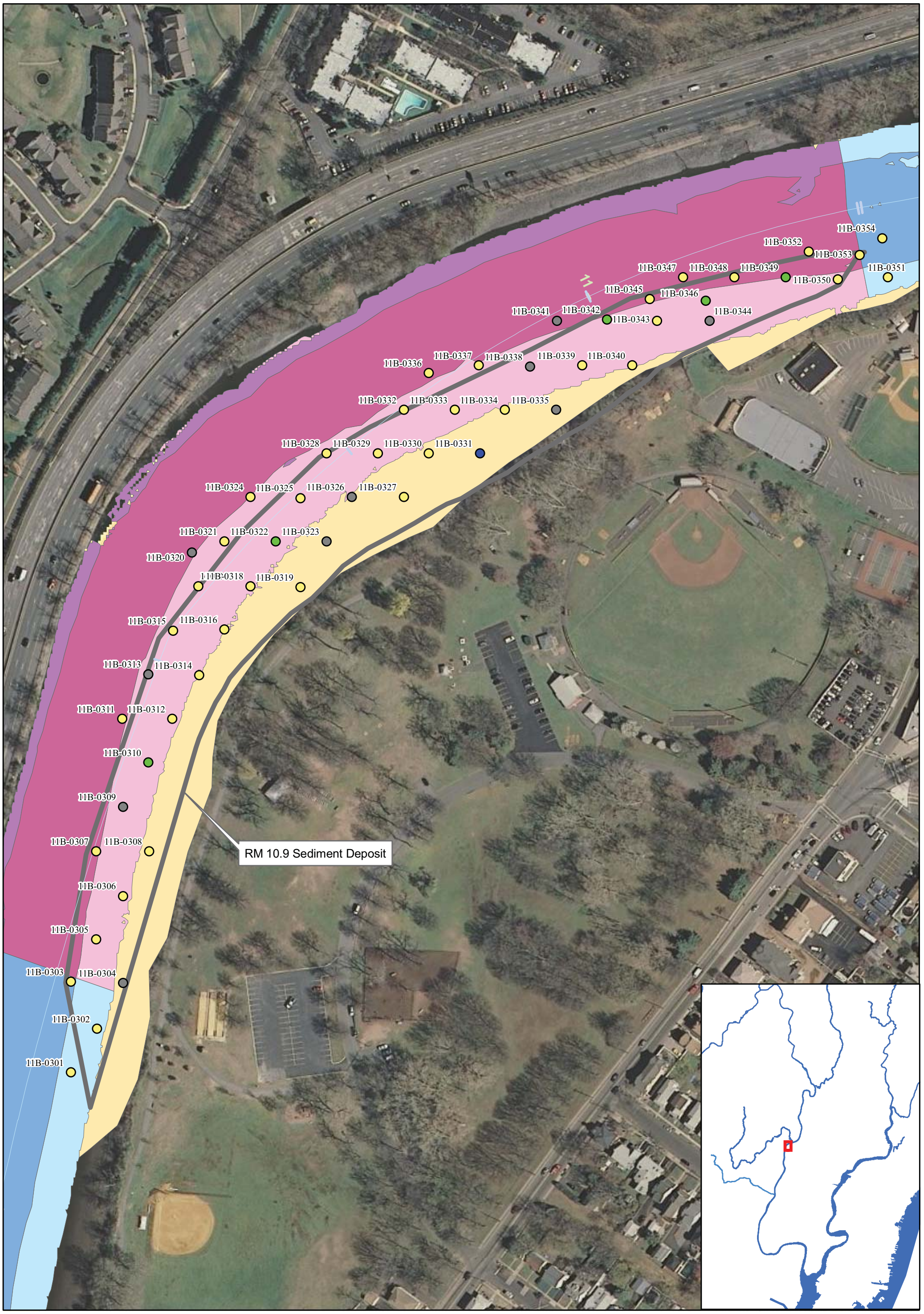

Figure 1. RM 10.9 Characterization Study
Sediment Sampling Locations

0 50 100 200 300 Feet

N

- Core & Grab
- Core, Grab, AVS/SEM, & Nutrients
- Core, Grab, & HR Core
- Core, Grab, HR Core, AVS/ SEM, & Nutrients

Geomorphic Region (2007)

center channel | side channel | nearshore | bend channel | outer bend | point bar

AECOM

June, 2011
Orthophoto: NJGIS, 2007

Nearshore = As defined by the 2007 Geomorphic Region plus the area between point bar and approximate shoreline

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Appendix P

Laboratory Standard Operating Procedures

Lower Passaic River

River Mile 10.9 Characterization Study

PAHs / Alkyl PAHs - Axys

Organochlorinated Pesticides - Axys

PCB Congeners - Axys

PCDDs/PCDFs – Axys

VOCs – Shealy

SVOCs – Shealy

Herbicides – Shealy

TAL Metals + titanium - Shealy

Low Level Mercury - Microbac

TPH Extractables – Test America

TOC – DESA

Appendix P

Laboratory SOPs

Axys SOP

PAHs / Alkyl PAHs

MLA-021

AXYS | Axys Analytical Services Ltd

2045 MILLS ROAD WEST
SIDNEY, BRITISH COLUMBIA, CANADA V8L 5X2

TEL 250-655-5800 FAX 250-655-5811
E-MAIL: analytical@axys.com

December 16, 2010

Re: AXYS ANALYTICAL SERVICES LTD. – Update to quantification references for AXYS Method MLA-021 "Analytical Method for the Determination of Polycyclic Aromatic Hydrocarbons (PAH), Alkylated Polycyclic Aromatic Hydrocarbons and Alkanes"

Historically, AXYS Method MLA-021 has used d8-Acenaphthylene as the quantification reference for 2-Methylfluorene, Dimethylfluorenes and C1 to C3-Fluorenes. Through continual improvement processes AXYS has identified d10-Phenanthrene as a more appropriate quantification reference. The above listed target analytes are observed to behave in a manner more similar to this compound.

This method improvement will provide data with greater accuracy and precision, and will result in a better adherence to method acceptance criteria. The impact to data reporting is minimal. Quantification references and relative retention time references on data reports will be updated to reflect this change, where appropriate.

The attached table provides AXYS Ongoing Precision and Recovery (OPR) data obtained September 1, 2009 to August 31, 2010. Data quantified against both d8-Acenaphthylene and d10-Phenanthrene are presented and the data illustrates the benefit of this method improvement. Recoveries in bold, italicized text do not meet method acceptance criteria. Data quantified against d10-Phenanthrene adheres much more strongly to method acceptance criteria.

If you have any questions or comments on the process, please do not hesitate to ask.

Sincerely
AXYS ANALYTICAL SERVICES LTD.

Richard Grace
Director - Sales, Marketing, and Service

Georgina Brooks
Client Services Supervisor

Teresa Rawsthorne
Sales and Marketing Coordinator

Dale Hoover
Quality Assurance Manager

Supporting Documentation to Method MLA-021 Quantification Update
Ongoing Precision and Recovery (OPR) Data
September 1, 2009 to August 31, 2010

AXYS ID	WG30468-102	WG30481-102	WG30496-102	WG30766-102	WG30785-102	WG30924-102	WG30924-103	WG31018-102	WG31300-102
Matrix	SOLID	SOLID	SOLID	TISSUE	FILTER	AQUEOUS	TISSUE	TISSUE	AQUEOUS
Results quantified against D8-Acenaphthylene* (% Recovery)									
2-Methylfluorene	***519***	***154***	139	***180***	***213***	***167***	***154***	***177***	147
1,7-Dimethylfluorene	***604***	***184***	***154***	***176***	***288***	***214***	***169***	***230***	***172***
Results quantified against d10-Phenanthrene (% Recovery)									
2-Methylfluorene	115	91	97	104	99	87	98	95	97
1,7-Dimethylfluorene	134	109	108	101	134	111	108	123	113
Labeled Quantification Standard Results (% Recovery)									
D8-Acenaphthylene	13	44	45	35	9	24	28	18	33
D10-Phenanthrene	61	76	67	63	19	48	47	39	50

AXYS ID	WG31319-102	WG31531-102	WG31764-102	WG32198-104	WG32198-106	WG32198-107	WG32267-102	WG32418-102	WG32430-102
Matrix	SOLID	SOLID	AQUEOUS	AQUEOUS	AQUEOUS	AQUEOUS	EXTRACT	SOLID	AQUEOUS
Results quantified against D8-Acenaphthylene* (% Recovery)									
2-Methylfluorene	128	***250***	***188***	138	***151***	***178***	133	***212***	142
1,7-Dimethylfluorene	***163***	***382***	***240***	***174***	***201***	***229***	***166***	***243***	***171***
Results quantified against d10-Phenanthrene (% Recovery)									
2-Methylfluorene	86	81	93	83	83	82	93	96	85
1,7-Dimethylfluorene	110	123	119	105	111	105	116	110	102
Labeled Quantification Standard Results (% Recovery)									
D8-Acenaphthylene	57	52	35	33	30	22	50	28	38
D10-Phenanthrene	86	34	69	54	55	47	69	62	60

****Results in bold, italicized text indicate recoveries that did not meet the method acceptance criteria of 50-150%***

Summary of AXYS Method MLA-021 Rev 10.02:

ANALYTICAL METHOD FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH), ALKYLATED POLYCYCLIC AROMATIC HYDROCARBONS, AND ALKANES

AXYS Method MLA-021 describes the determination of concentrations of PAHs, alkylated PAHs and alkanes in solid (sediment, soil, ash), tissue (including blood), aqueous, XAD-2 column (resin and filters), air, and oil samples and in solvent extracts.

The method may be used for analysis of samples where USEPA Methods 1625B or 8270C/D have been requested **provided the modifications described in this document are permitted by contract**.

This summary document covers only the analysis of PAHs and alkylated PAHs.

Target Analytes

PAHs and alkylated PAHs determined by multi-point calibration

PAHs

Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benz(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(j/k)fluoranthenes
Benzofluoranthenes
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
Dibenzo(ah)anthracene
Indeno(1,2,3-cd)pyrene
Benzo(ghi)perylene

Alkylated PAHs

1-Methylnaphthalene
2-Methylnaphthalene
C1-Naphthalenes
1,2-Dimethylnaphthalene
2,6-Dimethylnaphthalene
C2-Naphthalenes
2,3,5-Trimethylnaphthalene
2,3,6-Trimethylnaphthalene
C3-Naphthalenes
1,4,6,7-Tetramethylnaphthalene
C4-Naphthalenes
1-Methylphenanthrene
2-Methylphenanthrene
3-Methylphenanthrene
9/4-Methylphenanthrenes
2-Methylanthracene
C1-Phenanthrenes/Anthracenes
1,7-Dimethylphenanthrene
1,8-Dimethylphenanthrene
2,6-Dimethylphenanthrene
3,6-Dimethylphenanthrene
C2-Phenanthrenes/Anthracenes
1,2,6-Trimethylphenanthrene
C3-Phenanthrenes/Anthracenes
Retene
C4-Phenanthrenes/Anthracenes
Biphenyl
Dibenzothiophene

PAHs and alkylated PAHs determined by single-point calibration

C1-Biphenyls
C2-Biphenyls
C1-Acenaphthenes
2-Methylfluorene
C1-Fluorenes
1,7-Dimethylfluorene
C2-Fluorenes
C3-Fluorenes
2/3-Methyldibenzothiophenes
C1-Dibenzothiophene
2,4-Dimethyldibenzothiophene
C2-Dibenzothiophene
C3-Dibenzothiophene
C4-Dibenzothiophene
3-Methylfluoranthene/Benzo(a)fluorene
C1-Fluoranthenes/Pyrenes
C2-Fluoranthenes/Pyrenes
C3-Fluoranthenes/Pyrenes
C4-Fluoranthenes/Pyrenes
1-Methylchrysene
5/6-Methylchrysenes
C1-Benz(a)anthracenes/Chrysenes
5,9-Dimethylchrysene
C2-Benz(a)anthracenes/Chrysenes
C3-Benz(a)anthracenes/Chrysenes
C4-Benz(a)anthracenes/Chrysenes
7-Methylbenzo(a)pyrene
C1-Benzofluoranthenes/Benzopyrenes
C2-Benzofluoranthenes/Benzopyrenes

EXTRACTION

All samples are spiked with deuterated surrogate standards prior to extraction and extracted as per the table below. Optional extraction procedures are shown within parentheses.

Sample Extraction

Matrix	Extraction
Aqueous	No particulate - Liquid-liquid extraction with dichloromethane. Visible particulate - sample is filtered prior to extraction and the particulate fraction separately extracted by Soxhlet extraction with dichloromethane. The two extracts are then combined.(Optional: the filtrate can be added to the extraction solvent for the particulate)
Solid (sediment, soil, sludge, particles on filter paper)	Soxhlet extraction with dichloromethane (Optional: Base digestion and liquid-liquid extraction with hexane)
Solid (ash)	Soxhlet extraction with toluene
Solid (fly ash)	Sonication with hydrochloric acid and filtering. Liquid-liquid extraction of filtrate using dichloromethane, Soxhlet extraction of particulate using toluene:acetone 80:20. The two extracts are combined.
Tissue	Base digestion and liquid-liquid extraction with hexane (Optional: Soxhlet extraction with dichloromethane, this option is not recommended for samples with high lipid content)
Whole blood/serum	Liquid-liquid extraction with ethanol:hexane:saturated ammonium sulphate.
XAD-2 column and filter	XAD-2 columns and filters are usually co-extracted for multiple analyses (For example: PCB, dioxins, pesticides) and the resulting extracts are split with a portion being used for PAH analysis
Ambient air (PUF and filter)	The PUF and filter(s) are Soxhlet extracted together using dichloromethane

Stationary Source Air Samples (Stack Gas sample trains)	The filter is sonicated with dilute hydrochloride acid and filtered. Equipment rinsates are collected, filtered, dried and/or extracted depending on sampling conditions.

COLUMN CHROMATOGRAPHY CLEANUP

Extracts are routinely cleaned up using the following procedures:

- column chromatography on Silica
- gel permeation (Biobeads) column chromatography
- treatment with activated copper (except tissues)

Extracts may be cleaned up further, as necessary, using some or all of the following procedures:

- washing with base
- column chromatography on Biobeads
- column chromatography on alumina

INSTRUMENTAL ANALYSIS

Instrumental analysis is performed by low-resolution mass spectrometry (LRMS) using an RTX-5 capillary GC column. The LRMS is operated at a unit mass resolution in the electron impact (EI) ionization mode using multiple ion detection (MID) acquiring at least one characteristic ion for each target analyte and surrogate standard.

Analyte Ions Monitored, Surrogates Used and RRF Determination For PAH

TARGET ANALYTES	Quantification Ion (m/z)	Confirmation Ions (m/z)	Typical Ion Ratio (Conf./Quant.)	SURROGATE	Typical Retention Time (minutes)	RRF DETERMINED FROM
Naphthalene	128	102	0.064	d_8-Naphthalene	6.84	Naphthalene
Acenaphthylene	152	151	0.222	d_8-Acenaphthylene	10.83	Acenaphthylene
Acenaphthene	154	153	1.18	d_8-Acenaphthylene	11.33	Acenaphthene
Fluorene	166	165	1.01	d_{10}-Phenanthrene	12.63	Fluorene
Phenanthrene	178	176	0.202	d_{10}-Phenanthrene	15.04	Phenanthrene
Anthracene	178	176	0.196	d_{10}-Phenanthrene	15.15	Anthracene
Fluoranthene	202	200	0.214	d_{10}-Fluoranthene	18.06	Fluoranthene
Pyrene	202	200	0.219	d_{10}-Fluoranthene	18.60	Pyrene
Benz[a]anthracene	228	226	0.281	d_{12}-Benz[a]anthracene	21.68	Benz[a]anthracene
Chrysene[1]	228	226	0.312	d_{12}-Chrysene	21.79	Chrysene
Benzo[b]fluoranthene	252	253	0.218	d_{12}-Benzo[b]fluoranthene	25.21	Benzo[b]fluoranthene
Benzo[j,k]fluoranthenes	252	253	0.215	d_{12}-Benzo[k]fluoranthene	25.30	Benzo[k]fluoranthene
Benzo[e]pyrene	252	253	0.213	d_{12}-Benzo[a]pyrene	26.36	Benzo[e]pyrene
Benzo[a]pyrene	252	253	0.217	d_{12}-Benzo[a]pyrene	26.58	Benzo[a]pyrene
Perylene	252	253	0.212	d_{12}-Perylene	27.00	Perylene
Dibenzo[ah]anthracene[2]	278	139	0.144	d_{14}-Dibenzo[ah]anthracene	31.86	Dibenz[ah]anthracene
Indeno[1,2,3-cd]pyrene	276	138	0.179	d_{12}-Indeno[1,2,3,cd]pyrene	31.71	Indeno[1,2,3-cd]pyrene
Benzo[ghi]perylene	276	138	0.194	d_{12}-Benzo[ghi]perylene	32.53	Benzo[ghi]perylene
Biphenyl[3]	154	152	0.304	d_{10}- Biphenyl	9.81	Biphenyl
Dibenzothiophene[3]	184	152	0.073	d_{10}-Phenanthrene	14.72	Dibenzothiophene
1-Methylnaphthalene[3]	142	141	0.962	d_{10}-2-Methylnaphthalene	8.81	1-Methylnaphthalene
2-Methylnaphthalene[3]	142	141	0.930	d_{10}-2-Methylnaphthalene	8.55	2-Methylnaphthalene
1-Naphthalenes[3]	142	[4]	[4]	d_{10}-2-Methylnaphthalene	[5]	1- & 2-Methylnaphthalene
2,6-Dimethylnaphthalene[3]	156	141	0.666	d_{12}-2,6 Dimethylnaphthalene	10.17	2,6-Dimethylnaphthalene
1,2-Dimethylnaphthalene	156	141	1.26	d_{12}-2,6 Dimethylnaphthalene	10.90	1,2-Dimethylnaphthalene
C2-Naphthalenes[3]	156	[4]	[4]	d_{12}-2,6 Dimethylnaphthalene	[5]	2,6- & 1,2-Dimethylnaphthalene
2,3,5-Trimethylnaphthalene[3]	170	155	0.873	d_{12}-2,6 Dimethylnaphthalene	12.35	2,3,5- Trimethylnaphthalene
2,3,6-Trimethylnaphthalene	170	155	0.876	d_{12}-2,6 Dimethylnaphthalene	12.17	2,3,6- Trimethylnaphthalene
C3-Naphthalenes[3]	170			d_{12}-2,6 Dimethylnaphthalene	[5]	2,3,5- & 2,3,6-Trimethylnaphthalene
1,4,6,7-Tetramethylnaphthalene	184	139	0.027	d_{12}-2,6 Dimethylnaphthalene	13.89	1,4,6,7-Tetramethylnaphthalene
C4-Naphthalene		[4]	[4]	d_{12}-2,6 Dimethylnaphthalene	[5]	1,4,6,7-Tetramethylnaphthalene
2-Methylanthracene	192	191	0.531	d_{10}-Phenanthrene	16.45	2-Methylanthracene

[1] Coelutes with Triphenylene
[2] Coelutes with Dibenz[ac]anthracene
[3] These compounds are in addition to the regular suite of analytes, and are analyzed by client request only.
[4] Secondary ion confirmation procedures do not apply
[5] RRT ranges apply to alkylated PAH Totals

TARGET ANALYTES	Quantification Ion (m/z)	Confirmation Ions (m/z)	Typical Ion Ratio (Conf./Quant.)	SURROGATE	Typical Retention Time (minutes)	RRF DETERMINED FROM
3-Methylphenanthrene	192	191	0.608	d_{10}-Phenanthrene	16.27	1- & 2-Methylphenanthrene & 2-Methylanthracene
2-Methylphenanthrene	192	191	0.608	d_{10}-Phenanthrene	16.36	2-Methylphenanthrene
9/4-Methylphenanthrenes	192	191	0.634	d_{10}-Phenanthrene	16.59	1- & 2-Methylphenanthrene & 2-Methylanthracene
1-Methylphenanthrene[3]	192	191	0.634	d_{10}-Phenanthrene	16.64	1-Methylphenanthrene
C1-Phenanthrenes/Anthracenes[3]	192	[4]	[4]	d_{10}-Phenanthrene	[5]	1- & 2-Methylphenanthrene & 2-Methylanthracene
3,6-Dimethylphenanthrene[3]	206	191	0.342	d_{10}-Fluoranthrene	17.46	3,6-Dimethylphenanthrene
2,6-Dimethylphenanthrene	206	191	0.342	d_{10}-Fluoranthrene	17.54	3,6- & 1,7-Dimethyl-phenanthrenes
1,7-Dimethylphenanthrene	206	191	0.332	d_{10}-Fluoranthrene	17.89	1,7-Dimethylphenanthrene
1,8-Dimethylphenanthrene	206	191	0.332	d_{10}-Fluoranthrene	18.13	3,6- & 1,7-Dimethyl-phenanthrenes
C2-Phenanthrenes/Anthracenes[3]	206	[4]	[4]	d_{10}-Fluoranthrene	[5]	3,6- & 1,7-Dimethyl-phenanthrenes
1,2,6-Trimethylphenanthrene	220	205	0.581	d_{10}-Fluoranthrene	19.41	1,2,6-Trimethylphenanthrene
C3-Phenanthrenes/Anthracenes				d_{10}-Fluoranthrene	[5]	1,2,6-Trimethylphenanthrene
Retene[3]	234	219	1.63	d_{10}-Fluoranthene	19.53	Retene
C4-Phenanthrenes/Anthracenes	234	[4]	[4]	d_{10}-Fluoranthrene	[5]	Retene
C1-Biphenyls	168	[4]	[4]	d_{10}- Biphenyl	[5]	Biphenyl
C2-Biphenyls	182	[4]	[4]	d_{10}- Biphenyl	[5]	Biphenyl
C1-Acenaphthenes	168	[4]	[4]	d_8-Acenaphthylene	[5]	Acenaphthene
2-Methylfluorene	180	165	1.23	d_{10}-Phenanthrene	14.06	2-Methylfluorene
C1-Fluorenes	180	[4]	[4]	d_{10}-Phenanthrene	[5]	2-Methylfluorene
1,7-Dimethylfluorene	194	177	0.092	d_{10}-Phenanthrene	15.49	1,7-Dimethylfluorene
C2-Fluorenes	194	[4]	[4]	d_{10}-Phenanthrene	[5]	1,7-Dimethylfluorene
C3-Fluorenes	208	[4]	[4]	d_{10}-Phenanthrene	[5]	1,7-Dimethylfluorene
2/3-Methyldibenzothiophenes	198	197	0.738	d_{10}-Phenanthrene	16.07	2/3-Methyldibenzothiophenes
C1-Dibenzothiophenes	198	[4]	[4]	d_{10}-Phenanthrene	[5]	2/3-Methyldibenzothiophenes
2,4-Dimethyldibenzothiophene	212	197	0.514	d_{10}-Phenanthrene	17.08	2,4-Dimethyldibenzothiophene
C2-Dibenzothiophenes	212	[4]	[4]	d_{10}-Phenanthrene	[5]	2,4-Dimethyldibenzothiophene
C3-Dibenzothiophenes	226	[4]	[4]	d_{10}-Phenanthrene	[5]	2,4-Dimethyldibenzothiophene
C4-Dibenzothiophenes	240	[4]	[4]	d_{10}-Phenanthrene	[5]	2,4-Dimethyldibenzothiophene
3-Methylfluoranthene/Benzo(a)fluorene	216	215	0.880	d_{10}-Fluoranthrene	19.53	3-Methylfluoranthene
C1-Fluoranthenes/Pyrenes	216	[4]	[4]	d_{10}-Fluoranthrene	[5]	3-Methylfluoranthene
C2-Fluoranthenes/Pyrenes	230	[4]	[4]	d_{10}-Fluoranthrene	[5]	3-Methylfluoranthene
C3-Fluoranthenes/Pyrenes	244	[4]	[4]	d_{10}-Fluoranthrene	[5]	3-Methylfluoranthene
C4-Fluoranthenes/Pyrenes	258	[4]	[4]	d_{10}-Fluoranthrene	[5]	3-Methylfluoranthene
5/6-Methylchrysenes	242	[4]	[4]	d_{12}-Chrysene	23.15	6-Methylchrysene
1-Methylchrysene	242	[4]	[4]	d_{12}-Chrysene	23.32	1-Methylchrysene
C1-Benz(a)anthracenes/Chrysenes	242	[4]	[4]	d_{12}-Chrysene	[5]	1- & 6-Methylchrysenes
5,9-Dimethylchrysene	256	[4]	[4]	d_{12}-Chrysene	24.49	5,9-Dimethylchrysene

TARGET ANALYTES	Quantification Ion (m/z)	Confirmation Ions (m/z)	Typical Ion Ratio (Conf./Quant.)	SURROGATE	Typical Retention Time (minutes)	RRF DETERMINED FROM
C2-Benz(a)anthracenes/Chrysenes	256	[4]	[4]	d_{12}-Chrysene	[5]	5,9-Dimethylchrysene
C3-Benz(a)anthracenes/Chrysenes	270	[4]	[4]	d_{12}-Chrysene	[5]	5,9-Dimethylchrysene
C4-Benz(a)anthracenes/Chrysenes	284	[4]	[4]	d_{12}-Chrysene	[5]	5,9-Dimethylchrysene
7-Methylbenzo(a)pyrene	266	[4]	[4]	d_{12}-Benzo[a]pyrene	29.35	7-Methylbenzo(a)pyrene
C1-Benzofluoranthenes/Benzopyrenes	266	[4]	[4]	d_{12}-Benzo[a]pyrene	[5]	7-Methylbenzo(a)pyrene
C2-Benzofluoranthenes/Benzopyrenes	280	[4]	[4]	d_{12}-Benzo[a]pyrene	[5]	7-Methylbenzo(a)pyrene
LABELLED SURROGATE STANDARDS	**Quantification Ion (m/z)**	**Confirmation Ions (m/z)**		**RECOVERY CALCULATED AGAINST**		
d_8-Naphthalene	136	134	0.095	d_{10}-Acenaphthene	6.80	
d_{10}-2-Methylnaphthalene	152	151	0.195	d_{10}-Acenaphthene	8.47	
d_{10}-Biphenyl	164	[4]	[4]	d_{10}-Acenaphthene	9.75	
d_{12}-2,6-Dimethylnaphthalene	168	150	0.747	d_{10}-Acenaphthene	10.07	
d_8-Acenaphthylene	160	158	0.159	d_{10}-Acenaphthene	10.80	
d_{10}-Phenanthrene	188	184	0.143	d_{10}-Pyrene	14.97	
d_{10}-Fluoranthene	212	208	0.173	d_{10}-Pyrene	18.02	
d_{12}-Benz[a]anthracene	240	236	0.250	d_{10}-Pyrene	21.63	
d_{12}-Chrysene	240	236	0.278	d_{10}-Pyrene	21.73	
d_{12}-Benzo[b]fluoranthene	264	260	0.216	d_{12}-Benzo[e]pyrene	25.11	
d_{12}-Benzo[k]fluoranthene	264	260	0.208	d_{12}-Benzo[e]pyrene	25.23	
d_{12}-Benzo[a]pyrene	264	260	0.216	d_{12}-Benzo[e]pyrene	26.47	
d_{12}-Perylene	264	260	0.256	d_{12}-Benzo[e]pyrene	26.88	
d_{12}-Indeno[1,2,3,cd]pyrene	288	284	0.192	d_{12}-Benzo[e]pyrene	31.63	
d_{14}-Dibenzo[ah]anthracene	292	288	0.260	d_{12}-Benzo[e]pyrene	31.75	
d_{12}-Benzo[ghi]perylene	288	284	0.205	d_{12}-Benzo[e]pyrene	32.45	
LABELLED RECOVERY STANDARDS	**Quantification Ion (m/z)**	**Confirmation Ions (m/z)**				
d_{10}-Acenaphthene	164	160	0.464		11.24	
d_{10}-Pyrene	212	208	0.176		18.56	
d_{12}-Benzo[e]pyrene	264	260	0.269		26.25	

CALIBRATION

Initial calibration is performed using a five point calibration series of solutions that encompass the working concentration range. Initial calibration solutions contain the suite of labelled surrogate and recovery standards and authentic target PAHs listed as “PAHs and alkylated PAHs determined by multi-point calibration”. Calibration procedures use the mean RRFs determined from the initial calibration to calculate analyte concentrations. Calibration is verified at least once every 12 hours by analysis of a mid-level calibration solution.

An additional calibration solution contains the suite of labelled surrogate and recovery standards and authentic target PAHs listed as “PAHs and alkylated PAHs determined by single-point calibration”. This calibration solution is analyzed at the beginning and end of each batch (bracket) of samples and is used to establish the relative response factors. The mean RRFs determined from the single calibration solution run before and after the samples are used for quantification of sample results.

Concentration of PAHs/Alkylated PAHs Calibration Standard Solutions

TARGET ANALYTE	Level A (Sens. Std) (ng/mL)	Concentration of Calibration Standard Solutions (ng/mL)					Conc. Of Native Std (Low Level) (ng/mL)	Conc. Of Native Std (High Level) (ng/mL)
		Level B	Level C	Level D	Level E	Level F		
Acenaphthene	10	50	100	500	2000	5000	2000	20 000
Acenaphthylene	10	50	100	500	2000	5000	2000	20 000
Anthracene	10	50	100	500	2000	5000	2000	20 000
Benz[a]anthracene	10	50	100	500	2000	5000	2000	20 000
Benzo[b]fluoranthene	10	50	100	500	2000	5000	2000	20 000
Benzo[k]fluoranthene	10	50	100	500	2000	5000	2000	20 000
Benzo[ghi]perylene	10	50	100	500	2000	5000	2000	20 000
Benzo[a]pyrene	10	50	100	500	2000	5000	2000	20 000
Benzo[e]pyrene	10	50	100	500	2000	5000	2000	20 000
Biphenyl	10	50	100	500	2000	5000	2000	20 000
Chrysene	10	50	100	500	2000	5000	2000	20 000
Dibenzo[ah]anthracene	10	50	100	500	2000	5000	2000	20 000
2,6-Dimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
Fluoranthene	10	50	100	500	2000	5000	2000	20 000
Fluorene	10	50	100	500	2000	5000	2000	20 000
Indeno[1,2,3-cd]pyrene	10	50	100	500	2000	5000	2000	20 000
1-Methylnaphthalene	10	50	100	500	2000	5000	2000	20 000
2-Methylnaphthalene	10	50	100	500	2000	5000	2000	20 000
1-Methylphenanthrene	10	50	100	500	2000	5000	2000	20 000
Naphthalene	10	50	100	500	2000	5000	2000	20 000
Perylene	10	50	100	500	2000	5000	2000	20 000
Phenanthrene	10	50	100	500	2000	5000	2000	20 000
Pyrene	10	50	100	500	2000	5000	2000	20 000
2,3,5-Trimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
Dibenzothiophene	10	50	100	500	2000	5000	2000	20 000
3,6-Dimethylphenanthrene	10	50	100	500	2000	5000	2000	20 000
Retene	10	50	100	500	2000	5000	2000	20 000
2-Methylanthracene	10	50	100	500	2000	5000	2000	20 000
1,2-Dimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
2-Methylphenanthrene	10	50	100	500	2000	5000	2000	20 000
1,2,6-Trimethylphenanthrene	10	50	100	500	2000	5000	2000	20 000
2,3,6-Trimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
1,7-Dimethylphenanthrene	10	50	100	500	2000	5000	2000	20 000
1,4,6,7-Tetramethylnaphthalene	10	50	100	500	2000	5000	2000	20 000

LABELLED SURROGATE STANDARDS	Level A (Sens. Std) (ng/mL)	Concentration of Calibration Standard Solutions					Conc. Of Surrogate Std (Low Level) (ng/mL)	Conc. Of Surrogate Std (High Level) (ng/mL)
		Level B	Level C	Level D	Level E	Level F		
d_8-Naphthalene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{10}-2-Methylnaphthalene	2000	2000	2000	2000	2000	2000	2000	20 000
d_8-Acenaphthylene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{10}-Phenanthrene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{10}-Fluoranthene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Benz[a]anthracene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Chrysene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-2,6-Dimethylnaphthalene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Benzo[b]fluoranthene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Benzo[k]fluoranthene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Benzo[a]pyrene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Perylene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Indeno[1,2,3-cd]pyrene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{14}-Dibenzo[ah]anthracene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{12}-Benzo[ghi]perylene	2000	2000	2000	2000	2000	2000	2000	20 000
d_{10}-Biphenyl	2000	2000	2000	2000	2000	2000	2000	20 000
LABELLED RECOVERY STANDARDS							**Conc. Of Recovery Std (Low Level) (ng/mL)**	**Conc. Of Recovery Std (High Level) (ng/mL)**
d_{10}-Acenaphthene	2000	2000	2000	2000	2000	2000	4000	20 000
d_{10}-Pyrene	2000	2000	2000	2000	2000	2000	4000	20 000
d_{12}-Benzo[e]pyrene	2000	2000	2000	2000	2000	2000	4000	20 000

Concentrations of PAHs/Alkylated PAHs Single Point Calibration Solution

TARGET ANALYTE	Single Point Calibration Solution (ng/mL)	Conc. Of Native Std (Low Level) (ng/mL)	Conc. Of Native Std (High Level) (ng/mL)
2-Methylfluorene	2000	2000	20 000
1,7-Dimethylfluorene	2000	2000	20 000
2-Methyldibenzothiophene	2000	2000	20 000
2,4-Dimethyldibenzothiophene	2000	2000	20 000
5,9-Dimethylchrysene	2000	2000	20 000
7-Methylbenzo(a)pyrene	2000	2000	20 000
3-Methylfluoranthene	2000	2000	20 000
6-Methylchrysene	2000	2000	20 000
1-Methylchrysene	2000	2000	20 000
LABELLED SURROGATE STANDARDS		**Conc. Of Surrogate Std (Low Level) (ng/mL)**	**Conc. Of Surrogate Std (High Level) (ng/mL)**
d_8-Naphthalene	2000	2000	20 000
d_{10}-2-Methylnaphthalene	2000	2000	20 000
d_8-Acenaphthylene	2000	2000	20 000
d_{10}-Phenanthrene	2000	2000	20 000
d_{10}-Fluoranthene	2000	2000	20 000
d_{12}-Benz[a]anthracene	2000	2000	20 000
d_{12}-Chrysene	2000	2000	20 000
d_{12}-2,6-Dimethylnaphthalene	2000	2000	20 000
d_{12}-Benzo[b]fluoranthene	2000	2000	20 000
d_{12}-Benzo[k]fluoranthene	2000	2000	20 000
d_{12}-Benzo[a]pyrene	2000	2000	20 000

d_{12}-Perylene	2000	2000	20 000
d_{12}-Indeno[1,2,3-cd]pyrene	2000	2000	20 000
d_{14}-Dibenzo[ah]anthracene	2000	2000	20 000
d_{12}-Benzo[ghi]perylene	2000	2000	20 000
d_{10}-Biphenyl	2000	2000	20 000
LABELLED RECOVERY STANDARDS		**Conc. Of Surrogate Std (Low Level) (ng/mL)**	**Conc. Of Surrogate Std (High Level) (ng/mL)**
d_{10}-Acenaphthene	2000	4000	20 000
d_{10}-Pyrene	2000	4000	20 000
d_{12}-Benzo[e]pyrene	2000	4000	20 000

ANALYTE IDENTIFICATION

A chromatographic peak is identified as a target compound if the following criteria are met for the quantification and confirmation ions (where confirmation ions are available):

1. Peak responses must be at least three times the background noise level.
2. The retention time must be within three seconds of that predicted from the calibration run and the sample retention time reference (labelled compound).
3. Peak centroids for the quantification and confirmation ions must coincide within two seconds.
4. The relative ion abundance ratios must be within 20% of the opening calibration values.

QUANTIFICATION

Concentrations of target PAHs are calculated using the isotope dilution method of quantification. Compounds are quantified by comparing the area of the quantification ion to that of the corresponding deuterium-labelled standard and correcting for response factors. Response factors are determined daily using authentic PAHs. Calculations are carried out using HP EnviroQuant and Prolab MS-Extended for targeting and quantification.

$$\text{Concentration of Target (ng/g or ng/L)} = \left(\frac{\text{area of Target}}{\text{area of Surr Std}}\right) \times \left(\frac{\text{weight of Surr Std (ng)}}{\text{RRF}}\right) \times \left(\frac{1}{\text{weight of sample (g or L)}}\right)$$

where $\text{RRF} = \left(\frac{\text{area of Target}}{\text{area of Surr Std}}\right) \times \left(\frac{\text{concentration of Surr Std}}{\text{concentration of Target}}\right)$

and the Surr Std is either the surrogate or the internal standard

REPORTING LIMITS

Concentrations and detection limits for the target PAHs are reported. Typical reporting units for all data are ng/g, ng/L, or ng/sample. Concentrations for solids are reported on a dry weight basis. Concentrations in tissues (including blood and milk) are reported on a wet weight basis and/or on a lipid weight basis when requested. Concentrations in aqueous are reported on a volume basis. Concentrations in XAD-2 resin, filters and stack gas samples are reported on a per sample basis or a per volume basis. Concentrations in particulate filters are reported on a per sample basis.

The following are commonly requested reporting limits:

Sample Specific Detection Limit or Sample Detection Limit (SDL) – determined individually for every sample analysis run by converting the area equivalent of 3.0 times (2.5 times for EPA 1600 series methods) the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. The SDL accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up. Equivalent term(s): Estimated Detection Limit (EDL) from EPA method 8290.

Method Detection Limit (MDL) - determined as specified by EPA Fed. Reg. 40 CFR Part 136 Appendix B (no iteration option). The 99% confidence level MDL is determined based on analysis of a minimum of 7 replicate matrix spikes fortified at 1-10 times the estimated detection limit. MDL is determined as required based on accreditation, contract and workload requirements.

Lower Method Calibration Limit (LMCL) - determined by prorating the concentration of the lowest calibration limit for sample size and extract volume. The following equation is used. ((lowest level cal conc.) x (extract volume))/sample size. Typical extract volume for aqueous and tissue samples is 100 µL for all other matrices typical extract volume is 500 µL.

For the analysis of PAHs AXYS standard is to report sample concentrations using the SDL as the reporting limit.

QUALITY ASSURANCE/QUALITY CONTROL

All samples are analyzed in batches with the following composition:

- Batch Size - Each batch consists of up to twenty test samples and additional QC samples.
- Blanks - One procedural blank is analyzed for each batch. The procedural blank is prepared by spiking an aliquot of the surrogate standard solution into a clean matrix.
- On-going Precision and Recovery (OPR) Samples – On-going Precision and Recovery (OPR) is demonstrated by the analysis of a spiked reference matrix (SPM) analyzed with each batch. The reference sample to be analyzed is assigned to the analyst when the batch is assigned. The OPR sample is prepared by spiking an aliquot of the authentic spiking solution into an accurately weighed in-house reference matrix (known to contain low background levels of target analytes). The matrix is spiked with an aliquot of surrogate standard solution and, after an equilibration time of at least 30 minutes is extracted.
- Duplicates - Sample duplicates are analyzed (provided sufficient sample is available) for batches with 7-20 test samples, or when specified by the contract. For some matrices (XAD columns, filters, air samples) only field duplicates (if available) can be analyzed.
- Reference Samples – Certified reference materials are commercially available and are used to validate and periodically check methods. Additionally reference samples may be analyzed with a batch at the client's request.

The batch composition may vary according to batch or quality control requirements specified by a client. Each batch is carried through the complete analytical process as a unit. For sample data to be reportable the batch QC data must meet the acceptance criteria.

QC Specification Table: Authentic and Surrogate Standard Recoveries, OPR and Samples

	Typical Sample Specific* Detection Limits							
MATRIX	Solid	Aqueous	Tissue	XAD-2 Column	PUF	Filter	Procedural Blank Level (ng)	Acceptable Matrix Spike % Recovery
Analyte:	ng/g	ng/L	ng/g	ng	ng	ng		
Naphthalene	0.5	5	0.1	5	5	5	<10	70-130
Acenaphthylene	0.5	5	0.1	5	5	5	<5	70-140
Acenaphthene	0.5	5	0.1	5	5	5	<5	70-130
Fluorene	0.5	5	0.1	5	5	5	<5	60-140
Phenanthrene	0.5	5	0.1	5	5	5	<10	70-130
Anthracene	0.5	5	0.1	5	5	5	<5	70-130
Fluoranthene	0.5	5	0.1	5	5	5	<5	70-130
Pyrene	0.5	5	0.1	5	5	5	<5	70-130
Benz(a)anthracene	0.5	5	0.1	5	5	5	<5	70-130
Chrysene	0.5	5	0.1	5	5	5	<5	70-130
Benzo(b)fluoranthene	0.5	5	0.1	5	5	5	<5	70-130
Benzo(j/k)fluoranthenes	0.5	5	0.1	5	5	5	<5	70-130
Benzo(e)pyrene	0.5	5	0.1	5	5	5	<5	70-130
Benzo(a)pyrene	0.5	5	0.1	5	5	5	<5	70-130
Perylene	1.0	10	0.2	10	10	10	<5	70-130
Dibenzo(ah)anthracene	1.0	10	0.2	10	10	10	<5	70-130
Indeno(1,2,3-cd)pyrene	1.0	10	0.2	10	10	10	<5	70-130
Benzo(ghi)perylene	1.0	10	0.2	10	10	10	<5	70-130
Biphenyl	1.0	10	0.2	10	10	10	<5	70-130
Dibenzothiophene	1.0	10	0.2	10	10	10	<5	60-140
1-Methylnaphthalene	1.0	10	0.2	10	10	10	<5	70-130
2-Methylnaphthalene	1.0	10	0.2	10	10	10	<5	70-130
2,6-Dimethylnaphthalene	1.0	10	0.2	10	10	10	<10	70-130
1,2-Dimethylnaphthalene	1.0	10	0.2	10	10	10	<10	60-140
2,3,5-Trimethylnaphthalene	1.0	10	0.2	10	10	10	<10	50-150
2,3,6-Trimethylnaphthalene	1.0	10	0.2	10	10	10	<10	50-150
1,4,6,7-Tetramethyl-naphthalene	1.0	10	0.2	10	10	10	<10	50-200
2-Methylanthracene	1.0	10	0.2	10	10	10	<5	50-150
3-Methylphenanthrene	1.0	10	0.2	10	10	10	<10	N.A.
2-Methylphenanthrene	1.0	10	0.2	10	10	10	<10	50-150
9/4-Methylphenanthrenes	1.0	10	0.2	10	10	10	<10	N.A.
1-Methylphenanthrene	1.0	10	0.2	10	10	10	<10	50-150
3,6-Dimethylphenanthrene	1.0	10	0.2	10	10	10	<10	50-150
2,6-Dimethylphenanthrene	1.0	10	0.2	10	10	10	<10	N.A.
1,7-Dimethyl-phenanthrenes	1.0	10	0.2	10	10	10	<10	50-150
1,8-Dimethylphenanthrene	1.0	10	0.2	10	10	10	<10	N.A.
1,2,6-Trimethyl-phenanthrene	1.0	10	0.2	10	10	10	<10	50-150
Retene	1.0	10	0.2	10	10	10	<5	50-150
2-Methylfluorene	1.0	10	0.2	10	10	10	<5	50-150
1,7-Dimethylfluorene	1.0	10	0.2	10	10	10	<5	50-150
2/3-Methyldibenzo-thiophenes	1.0	10	0.2	10	10	10	<10	50-150
2,4-Dimethyl-dibenzothiophene	1.0	10	0.2	10	10	10	<5	50-150
3-Methylfluoranthene/ Benzo(a)fluorene	1.0	10	0.2	10	10	10	<5	50-150

5/6-Methylchrysenes	1.0	10	0.2	10	10	10	<5	50-150
1-Methylchrysene	1.0	10	0.2	10	10	10	<5	50-150
5,9-Dimethylchrysene	1.0	10	0.2	10	10	10	<5	50-150
7-Methylbenzo(a)pyrene	1.0	10	0.2	10	10	10	<5	50-150
Typical Sample Size	10 g	1 L	10 g	1 col	1 PUF	1 filter		
Typical Final Volume (µL)	500	100	100	500	500	500		

*Detection limits quoted are those routinely achieved. Lower detection limits can be achieved if required.

NOTE: QC acceptance criteria do not apply to alkylated PAH total values (e.g. C1-phenanthenes/anthracenes) as these are Tentatively Identified Compounds (TIC) of unknown accuracy.

SURROGATE STANDARD RECOVERIES:	**% RECOVERY RANGES ALL MATRICES**
d_8-naphthalene	15 – 130
d_8-acenaphthylene	20 – 130
d_{10}-phenanthrene	30 – 130
d_{10}-fluoranthene	30 – 130
d_{12}-benz[a]anthracene	30 – 130
d_{12}-chrysene	30 – 130
d_{12}-benzo[b]fluoranthene	30 – 130
d_{12}-benzo[k]fluoranthene	30 – 130
d_{12}-benzo[a]pyrene	30 – 130
d_{12}-perylene	30 – 130
d_{14}-dibenz[ah]anthracene	30 – 130
d_{12}-indeno[1,2,3-cd]pyrene	30 – 130
d_{12}-benzo[ghi]perylene	30 – 130
d_{10}-2-methylnaphthalene	20 – 130
d_{12}-2,6-dimethylnaphthalene	20 – 130
d_{10}-biphenyl	15 – 130

QC Specification Table: Instrumental Analysis, and Analyte Quantification

Parameter	Acceptance Specification
Procedural Blank	Refer to Table "QC Specification Table: Authentic and Surrogate Standard Recoveries, OPR and Samples" above, or 5 times lower than analogous analyte value detected in the samples.
Analysis Duplicate	Duplicates must fall within ±20% of the mean (applicable to concentrations >10 times the DL) These are guidelines – departures based on professional judgement allowed.
Instrument Sensitivity	S/N 3:1 for 10 pg of acenaphthene, dibenzo(a,h)anthracene.
Instrument Resolution	Calibration gas PFTBA (FC43) unit mass resolution at m/e 69/70 and 219/220, Unit mass resolution is demonstrated by the presence of a resolved peak at m/z 70 and m/e 220.
Instrument Linearity	Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs ≤20% for targets with a labelled analog present and all labelled compounds, ≤35% for targets with no labelled analog present.
Bracketing Cal	RRFs for the opening and closing calibrations over a 12 hour period must agree to within +/- 20% of the mean (ie <40 RPD between RRFs and for the opening and closing calibrations).
Continuing Cal Ver	Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within ±25% of expected values for all targets. Closing Cal Ver: Concentrations of native compounds must be within ±25% of expected values. Concentrations of labelled surrogates must be within ±25% of expected values, with any two (2) values allowed to be within ±40%
GC Resolution	Benzo[b] & [k]fluoranthene valley height must be ≤75% for equal concentrations. Phenanthrene/anthracene valley height must be ≤30% for equal concentrations.
Chromatogram Quality	Maximum peak width must be ≤15 seconds for dibenzo[ghi]perylene peak at 10% peak height.
Retention Time Window for Target Compounds	RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). A second requirement is that an authentic elute after its labelled analog.
Ion Abundance Ratios	CAL VER: Ion ratios for dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within ±35% of the mid-point of the I-CAL All other native analytes and labelled surrogates must be ±20% of the mid-point of the I-CAL Samples: Ion ratios for dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within ±35% of the 12 hour CAL (CAL VER or Bracketing) calibration standard. All other native analytes and labelled surrogates must be ±20% of the 12 hour CAL (CAL VER or Bracketing) calibration standard.

APPENDIX – SUMMARY OF MODIFICATIONS TO EPA 8270C, 8270D AND 1625B

Analysis by GC/LRMS, Key Attributes of AXYS MLA-021, EPA 8270C/D and EPA 1625B				
	MLA-021	**EPA 8270C**	**EPA 8270D**	**EPA 1625B**
MS acquisition mode	SIM[1]	Full Scan or optional SIM [1]	Full Scan or optional SIM [1]	Full Scan
Qualitative Identification Criteria	Retention time & ratio of 2 ions	Retention time & ratio of 3 [2] ions	Retention time & ratio of 3 [2] ions	Retention time & ratio of all characteristic ions
MS Ion Ratio Criteria	Within 20 % of theoretical	Within 30 % of reference spectrum	Within 30 % of reference spectrum	Within -50 % and +200 % of reference spectrum
MS Tuning Type and Check Frequency	PTFBA, daily	DFTTP [3], 12 hrs	DFTTP [3], 12 hrs	DFTTP, 8 hrs
Quantification References	Isotopically labeled standards added prior to extraction	Internal standards added just before instrumental analysis	Internal standards added just before instrumental analysis	Isotopically labeled standards added prior to extraction
Recovery correction of results	YES	NO	NO	YES
Calibration, minimum # levels	CCV Procedure: 5 levels OPTIONAL Single Point BRACKETING: 1 level	5	5	5
Initial Calibration Limit (% rsd)	20 % (35 % for targets with no labelled analog)	15 %	20 %	20 % (35 % for targets with no labelled analog)
Calibration Verification Frequency	Initially and every 12 hrs	Initially and every 12 hrs	Initially and every 12 hrs	Initially and every 8 hrs
Calibration Verification Relative Response Limit (% diff.)	< 25 % of I-CAL	< 20 % of I-CAL	< 20 % of I-CAL	Vary by compound; most stringent is acenaphthene: -20% to +25% of I-CAL
Calibration Verification IS area (% of I-CAL midpoint)	50-200 %	50-200 %	50-200 %	n.a.
Calibration verification IS RT (diff. from I-CAL midpoint)	n.a.	30 sec.	30 sec.	n.a.

Notes:

[1] SIM (Selected Ion Monitoring) is an allowable alternate technique for high sensitivity applications

[2] Based on availability, use of less ions is permitted where necessary

[3] Alternate MS tuning protocols are permitted

Appendix P

Laboratory SOPs

Axys SOP

Organochlorinated Pesticides - Axys

MLA-028

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AXYS ANALYTICAL SERVICES LTD

ANALYTICAL PROCEDURES FOR ORGANOCHLORINE PESTICIDES BY ISOTOPE DILUTION HRGC/HRMS

SCOPE

This method is for determination of organochlorine pesticides in water samples, solid (soil, sediment, biosolids etc) samples, tissue samples, blood (whole, plasma, serum) samples, milk samples, XAD-2 solid phase columns or cartridges from water or air sampling and solvent extract samples.

Samples are spiked with ^{13}C-labelled surrogate standards prior to analysis. Samples are extracted, the extracts are cleaned up by column chromatography and analyzed by high-resolution gas chromatography with high-resolution mass spectrometric detection (HRGC/HRMS).

Approved by: _____ Date: 12-MAY-2011
John Cosgrove, President and Senior Technical Director

Approved by: _____ Date: 12-MAY-2011
Shea Hewage, Director of Operations

Approved by: _____ Date: 12-MAY-2011
Dale Hoover, QA/QC Manager

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AMENDMENT PAGE

The following amendments based on management approval have been made to this document.

Page	Amendments to MLA-028 Rev. 06
7, 22, 23	Added an explanation that di-, tri- and tetrachlorobenzene recoveries may be low and that these compounds are reportable only when recoveries are judged adequate for quantification.
8	Table 2: Increased aqueous sample holding time to be 30 days.
12	Section 3.2.1: Added an example of adjusting surrogate spike amount for specific sample size, split ratio, final extract volume, etc.
22	Table 6: Added an explanation that custom QC protocols apply for non-routine targets.
23	Table 6: Deleted 13C-monochlorobenzene from table
23, 54	Table 6 and Table 8: Added specifications for $^{13}C_{12}$-PCB 159.
23, 24	Widened closing Cal Ver specifications for all labeled compounds to be ±50% of the expected values (opening and continuing Cal Vers remain at ±35%).
46	Changed Florisil elution solvent mix to be 10:90 DCM:Hexane.
47	Section 6.2.1 Added an explanation that Biobead cleanup is mandatory for all tissue matrices
48, 50	Sections 7.1.3 and 7.2.3: Added an explanation that only opening calibration verification runs are reported unless specifically requested by contract.
49, 51	Sections 7.1.4 and 7.2.4: Corrected routine GC injection volume to 1.0 µL (from 2.0 µL).
51	Section 7.2.4, table with GC/MS conditions: Corrected the injector temperature to 160°C (from 180°C).

Page	Amendments to MLA-028 Rev.05
	Updated Toxaphene terminology: Changed "total Toxaphene" to be "technical Toxaphene".
12	Section 3.2.1: Changed typical surrogate spiking volume to be 40 µL (instead of 80 µL) to accommodate for doubling concentrations of surrogates in surrogate standards.
13	Added Section 3.2.7 with instructions for standard solutions pertaining to the determination of technical Toxaphene.
14-15	Table 3: Added Toxaphene and $^{13}C_{12}$-PCB 159. Doubled concentrations of all surrogates to adjust to current practice. Corrected $^{13}C_{12}$-p,p'-DDE to be at the same level as the other surrogates.
16-18	Corrected Tables 4 and 5: Halved the nominal conc. of surrogates in Calibration Standard Solutions (reverting to MLA-028 Rev 04 conc.). Corrected $^{13}C_{12}$-p,p'-DDE to at the same level as the other surrogates.
22	Table 6: Deleted delta-HCH and 13C-delta-HCH specifications from Table 6 as this compound normally is determined in fraction E2 (in Table 7). Corrected typical SDL for technical Toxaphene to be 1 ng.
24	Corrected typo in Table 7, Instrument sensitivity (replaced "≤" by "≥").
53	Section 9.3: Added SDL estimate and definition for technical Toxaphene.
54	Table 8: Changed the surrogate for technical Toxaphene to be L-PCB-159 (instead of L-PCB-180). Entered ion masses for L-PCB-159.
57ff	Deleted Appendix A describing Toxaphene analysis by ECNI.

	Amendments to MLA-028 Rev.04
General	Doubled the default amounts of surrogate standards added.
24, 52	Corrected methoxychlor and labeled methoxychlor ion ratio specification to specify theoretical.
33	Added section 5.4.2.2: Extraction by magnetic stirring (aqueous samples)
34	Updated procedure for extraction of filtrate by magnetic stirring (in 5.4.3.2) to be the same as 5.4.2.2 above

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	Amendments to MLA-028 Rev.03
15	Table 3 – added information for 13C-PCB 153 E2 fraction recovery standard
18	Table 5 – corrected endrin aldehyde concentration
23,24	Table 6, 7 – revised RRT window determination procedure to use CAL VER and Table 9, 10 limits
53,54,55	Table 9,10- updated RT window limits from generic to compound specific values
55	Table 10 – corrected quantification and RRT reference for delta-HCH from 13C-gamma-HCH to 13C-delta-HCH
55	Table 10 –deleted 13C-endrin ketone secondary mass, specified 327.941 as single mass monitored

	Amendments to MLA-028 Rev.02
14	Table 3: Changed some nominal concentrations in authentic std solution for dichlorobenzenes, 1,2,4-trichlorobenzenes and endrin.
15	Table 3: Changed nominal concentrations/amounts added in surrogate std solution for 13C-beta-HCH, 13C-gamma-HCH and 13C-p,p'-DDE. Added 13C-p,p'-DDD and 13C-Endrin aldehyde.
16	Table 4: Changed concentrations in calibration std solutions for dichlorobenzenes and 1,2,4-trichlorobenzenes.
17	Table 4: Changed nominal concentrations in calibration std solutions for 13C-beta-HCH, 13C-gamma-HCH and 13C-p,p'-DDE. Added 13C-p,p'-DDD.
18	Table 5: Changed nominal concentrations in calibration std solutions for delta-HCH, all surrogates and the recovery standard. Added 13C-Endrin aldehyde.
23	Table 6: Added 13C-p,p'-DDD to the surrogate standard recoveries.
24	Table 7: Added 13C-Endrin aldehyde to the surrogate standard recoveries.
50	Added Section 7.3 "Lock Mass Monitoring".
53	Table 9: Separated 1,3- and 1,4-dichlorobenzene. Changed entries for Cl_6-Butadiene. Changed labeled standard for DDDs from 13C-o,p'-DDT to 13C-p,p'-DDD.
54	Table 9: Added 13C-p,p'-DDD to the labeled surrogates. Corrected m1/m2 ratios for beta-, gamma- and delta-13C-HCH from 0.77 to 0.78. Changed lock mass entries.
55	Table 10: Changed labeled standard for Endrin aldehyde from 13C-Endrin to 13C-Endrin aldehyde. Added 13C-Endrin aldehyde to the labeled surrogates. Changed lock mass entries.

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INTRODUCTION

ANALYTES OF INTEREST

This method is applicable for analysis of the following organochlorine pesticides.

Table 1. Chlorinated Pesticides

E1 Pesticides by HRGC/MS	E2 Pesticides by HRGC/MS
1,4-dichlorobenzene (1,3-Cl_2-BZ) *	Heptachlor epoxide
1,3-dichlorobenzene (1,4-Cl_2-BZ) *	alpha-Endosulphan
1,2-dichlorobenzene(1,2-Cl_2-BZ) *	delta-HCH
1,2,4-trichlorobenzene (1,2,4-Cl_3-BZ) *	Dieldrin
1,2,3-trichlorobenzene (1,2,3-Cl_3-BZ) *	Endrin
1,3,5-trichlorobenzene (1,3,5-Cl_3-BZ) *	Methoxychlor
1,2,4,5-tetrachlorobenzene (1,2,4,5-Cl_4-BZ) *	Endosulphan sulphate
1,2,3,5-tetrachlorobenzene (1,2,3,5-Cl_4-BZ) *	Endrin ketone
1,2,3,4-tetrachlorobenzene (1,2,3,4-Cl_4-BZ) *	beta-Endosulphan
Pentachlorobenzene (Cl_5-BZ)	Endrin aldehyde
Hexachlorobenzene (HCB)	
alpha-HCH	
beta-HCH	
gamma-HCH	
Heptachlor	
Aldrin	
Oxychlordane	
trans-Chlordane	
Cis-Chlordane	
o,p'-DDE	
p,p'-DDE	
trans-Nonachlor	
Cis-Nonachlor	
o,p'-DDD	
p,p'-DDD	
o,p'-DDT	
p,p'-DDT	
Mirex	
Hexachlorobutadiene (upon request)	
Octachlorostyrene (upon request)	
Technical Toxaphene (upon request)	

* Recoveries of dichlorobenzenes, trichlorobenzenes and tetrachlorobenzenes may be low due to loss through volatilization during the analytical work-up. These are 'compounds of opportunity' that may be reported when recoveries are judged adequate for quantification. Formal recovery acceptance limits have not been established.

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ANALYSIS PROCEDURES

1.0 SAMPLE STORAGE

All samples must be received and stored under the conditions presented in Table 2.

Table 2. Sample Storage, Sample Receipt and Hold Time Requirements

Matrix	Sample Size (per analysis)	Sample Container[1]	Condition Upon Receipt	Storage Conditions[2]	Sample Holding Time[3]	Extract Holding Time[3]	Preservation
Solid (Sediment/Soil/ Sludge)	10 g dry	Glass	<4°C	<-10°C	1 year	1 year	none required
Ash	5 g dry	Glass	<4°C	<-10°C	1 year	1 year	none required
Particulate Filter Paper	whole filter	Glass or foil wrapped	<4°C	<-10°C	1 year	1 year	none required
Pulp (dry)	20 g dry	Glass or foil wrapped	ambient	ambient	2 months	1 year	none required
Pulp (wet)	N/A	Glass	0-4°C	4°C	2 months	1 year	none required
Tissue	5-10 g wet	Glass or foil wrapped	<4°C	<-10°C	1 year	1 year	none required
Blood	5-20 g	Glass	<4°C	<-10°C	1 year	1 year	none required
Milk	50 g	Glass	<4°C	<-10°C	1 year	1 year	none required
Aqueous	1 litre	Brown glass	0-4°C	4°C	30 days	1 year	none required
XAD-2 Columns	One column resin particulate filter(s) wound glass filter	As is Glass Foil wrapped Foil wrapped	0-4°C 0-4°C <4°C <4°C	4°C 4°C <-10°C <-10°C	1 year 1 year 1 year 1 year	1 year 1 year 1 year 1 year	none required none required none required none required
Sample Trains (Stack Gas)	Containers A-F	Glass	0-4°C	4°C	30 days from sampling	1 year	none required
Ambient Air	PUF & Filter	Glass	<4°C	<-10°C	1 year	1 year	none required
Solvent Extract	one	Glass	<4°C	<-10°C	1 year	1 year	none required

[1] All glass containers should be organically clean; i.e., baked, solvent-rinsed or purchase 'certified' clean. All containers must be tightly sealed with screw cap lids (Teflon or foil-lined) to prevent loss of volatiles or contamination from volatiles. If samples are received in clear glass containers, they must be protected from the light.

[2] Storage temperatures quoted are nominal temperatures. Samples stored at a nominal temperature of 4°C are permitted a variance of ±2°C.

[3] These standard AXYS hold times exceed those required by some EPA methods. They apply to samples stored frozen and analyzed by this isotope dilution procedure. There is no evidence to indicate that properly stored samples are not stable for longer periods of time. Client negotiated requests for specific holding times or other method-specific holding times are adhered to.

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2.0 SAMPLE PRETREATMENT

Refer to the following standard operating procedures.

Document ID	Title
SLA-011	Compositing Samples
SLA-012	Dissection of Samples
SLA-013	Procedure for Homogenization of Solids and Tissues
SLA-014	Thawing of Samples Prior to Analysis
SLA-015	Moisture Determination

Blood Serum/Blood Plasma

Allow blood sample to thaw prior to subsampling for analysis as described in SLA-014. Homogenize by vortex mixing.

Milk

Allow milk to thaw at prior to subsampling for analysis as described in SLA-014. Homogenize the sample by shaking well.

Particulate Filter Papers

Allow the particulate filter papers to partially thaw. Fold the filter paper to fit into the soxhlet thimble for extraction.

Ambient Air (PUF and Filter)

If received in the sampling apparatus, use solvent rinsed forceps to withdraw the plug from the sampler. The associated filter is typically received in a petri dish or wrapped in foil. Use solvent rinsed forceps to handle the filter.

Pulp

Homogenize dry pulp according to standard operating procedure SLA-013. Consult with the Lab Supervisor for treatment of wet pulps.

Determine the moisture content of an accurately weighed subsample (1-2 g) of dry pulp according to standard operating procedure SLA-015.

Solids (Sediment/Soils/Ash/Sludge)

Allow the sample to thaw prior to analysis according to standard operating procedures described in SLA-014.

Homogenize the entire sample before subsampling for analysis according to procedures described in SLA-013.

Determine the moisture content on an accurately weighed subsample (1 g, depending upon sample available) according to standard operating procedure SLA-015.

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Tissue

Allow the tissue sample to thaw prior to analysis as described in SLA-014.

If the tissue sample is received as a homogenate, stir the homogenate well with a spatula prior to subsampling. Otherwise, homogenize tissue samples prior to analysis following standard operating procedures described in SLA-013.

If required, determine moisture content of an accurately weighed subsample of (1 g) according to standard operating procedures SLA-015.

XAD-2 Columns and Filters

Refer to the following standard operating procedure for details of removing the resin from the column. Filters are partially thawed prior to extraction.

Document ID	Title
SLA-043	Removing Sampling Media from Field Sampling Equipment

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3.0 MATERIALS AND REAGENTS

Refer to the following standard operating procedures.

Document ID	Title
SLA-001	Cleaning Laboratory Items
SLA-002	Glassware and Laboratory Equipment Proofs
SLA-009	Preparation of Standards
SLA_018	Solvent Rinsing of Glassware for Organic Analysis
SLA-019	Solvent Proofs
SLA-022	Use of Drying Ovens and Muffle Furnace
SLA-023	Use of Balances
SLA-041	Reagent Preparation
SLA-044	Activation of Copper Foil, Turnings, and Powder
SLA-093	Baking Anhydrous Sodium Sulphate
SQA-009	Storage and Control of Standards
SQA-003	Standard Solution Validation

3.1 Equipment List

Extraction

Separatory funnels (125 mL, 500 mL, 1000 mL)
Erlenmeyer flasks (250 mL, 500 mL, 1000 mL)
Round bottom flasks (100 mL, 250 mL, 500 mL, 1000 mL))
Beakers
Graduated Cylinders
Class A volumetric flasks, pipettes
Disposable pipettes
Disposable centrifuge tubes (15 mL)
Hamilton Syringes (5 µL, 25 µL, 50 µL, 100 µL, 250 µL, 1000 µL)
Autosampler vials (amber glass, 800 µL)
Chromatography columns (1 cm x 12 cm, 3 cm x 50 cm, 1 cm x 25 cm)
Silanized glass wool
Filter paper – Ahlstrom or equivalent
Teflon tape
Aluminum Foil
Spatula – aluminum
Disposable spoons
Rotary evaporator
Magnetic stirring plate
Millipore Filtration Apparatus
3M Empore styrene-divinylbenzene SPE Disks (SBD-XC, 47 mm)
Soxhlet apparatus (pre-cleaned) w/heating mantle
Soxhlet/Dean Stark apparatus (pre-cleaned)
Water bath capable of maintaining up to 50ºC
Balance – Top loading and analytical (2-, 3-, & 4-place)

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Glassware ovens
Drying ovens
Muffle furnace
Nitrogen source with manifold apparatus

Instruments
Hewlett Packard 6890 Series Gas Chromatograph or equivalent;
Micromass/VG Autospec Ultima mass spectrometer or equivalent;
GC Columns: DB-5 (60 m, 0.25 mm i.d., 0.10 µm film thickness)

3.2 Preparation of Standard Solutions - GC/MS Analysis

The analysis of chlorinated pesticides by high-resolution GC/MS requires the use of the surrogate, recovery, and calibration standards described below. Details of the preparation, composition and validation of concentrations of these standards are described on Standard Data Sheets.

3.2.1 Surrogate Standard

Samples are spiked with a suite of isotopically labelled surrogate standards prior to extraction procedures. The surrogate standard solution is prepared to have the nominal concentrations of surrogates presented in Table 3. An aliquot of surrogate standard solution is added to each sample prior to extraction. Typically 40 µL, equivalent to approximately 16 ng, is added to the sample. The amount of surrogate added should yield labelled concentrations in the extract approximately equal to the concentration in the calibration standards (assuming 100% recovery). The amount of surrogate added is dependent upon sample size, split ratio, final extract volume, and concentration of analytes in the sample and may be adjusted accordingly, e.g. if a 1/5 split is required, surrogates must be spiked to 5 times the routine level.

3.2.2 Recovery Standard

Samples extracts are spiked with isotopically labelled recovery standards prior to instrumental analysis. The recovery standard solutions are prepared to have the nominal concentrations of recovery standards presented in Table 3. An aliquot of recovery standard is added to the final extract just prior to instrumental analysis. The amount of recovery standard added is designed to match the amount of recovery in the calibration standards.

3.2.3 Calibration Solutions

A series of five calibration solutions containing native analytes, labelled surrogates standards, and labelled recovery standards is used to establish the initial calibration of the analytical instrument. The calibration solutions are prepared to have the nominal concentrations presented in Table 4 and Table 5. The concentration of the native analytes in the solutions varies to encompass the working range of the instrument, while the concentrations of the surrogates and recovery standards remain constant. A mid-level solution is analyzed every 12 hours, and the results must fall within the limits specified in Table 6 for E1 fraction pesticides and Table 7 for E2 fraction pesticides.

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3.2.4 Authentic Spiking Standard

The authentic spiking solution is prepared to have the nominal concentrations presented in Table 3. An aliquot of authentic spiking solution is added to an unspiked reference material (USM) to prepare a spiked reference sample as a QC sample. Typically, a 1000 µL aliquot (20 µL for aqueous samples), equivalent to 8 - 16 ng of each target analyte, is added to the matrix.

An aliquot of an authentic spiking solution containing Toxaphene is also spiked into the reference sample when this analyte is analyzed.

3.2.5 Retention Time Markers

The surrogate standard solution and calibration solutions contain a suite of isotopically labelled compounds that are used as retention time (RT) markers.

3.2.6 Solvent Blank

During the analysis of a batch of samples, a solvent blank is analyzed after the calibration solution to monitor carryover from the previous injection.

E1 Analysis: The solvent blank is prepared from toluene and contains $^{13}C_{12}$-DDT to monitor the breakdown of DDT in the injector.

E2 Analysis: The solvent blank is prepared from toluene and contains $^{13}C_{12}$-endrin to monitor the breakdown of endrin in the injector.

3.2.7 Standard Solutions for Technical Toxaphene

Separate authentic, surrogate and calibration standard solutions must be used when analysis of technical Toxaphene is requested. The authentic solution contains 10000 ng/mL of Toxaphene in hexane and the typical spiking volume is 100 µL. For water samples requiring filtration a stronger Toxaphene solution (100000 ng/mL in isooctane) is used with a typical spiking volume of 10 µL. The surrogate standard solution contains 1000 ng/mL of $^{13}C_{12}$-PCB 159 in isooctane; the typical spiking volume is 20 µL. For technical Toxaphene the same recovery standard solution and spiking volume is used as for the standard suite of chlorinated pesticides (Section 3.2.2). The bracketing calibration standard solution for technical Toxaphene contains 5000 ng/mL of Toxaphene, 100 ng/mL of the surrogate standard $^{13}C_{12}$-PCB 159 and 50 ng/mL of recovery standard $^{13}C_{12}$-PCB 138.

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Table 3. Chlorobenzenes and Pesticides - Nominal Concentrations of Authentic and Surrogate Standard Solutions (ng/mL)

Compound Name	Nominal Conc. in Authentic Std Solution (ng/mL)		Amount added to each SPM sample (ng)	Compound Name	Nominal Conc. in Authentic Std Solution (ng/mL)		Amount added to each SPM sample (ng)
	Matrix				Matrix		
	Aqueous	Other			Aqueous	Other	
1,4-dichlorobenzene	400	8	8	Dieldrin	400	8	8
1,3-dichlorobenzene	400	8	8	alpha-Endosulfan	400	8	8
1,2-dichlorobenzene	400	8	8	beta-Endosulfan	400	8	8
1,2,4-trichlorobenzene	400	8	8	Endosulfan sulphate	400	8	8
1,2,3-trichlorobenzene	400	8	8	Endrin	400	8	8
1,3,5-trichlorobenzene	400	8	8	Endrin aldehyde	400	8	8
1,2,4,5-tetrachlorobenzene	400	8	8	Endrin ketone	400	8	8
1,2,3,5-tetrachlorobenzene	400	8	8	Heptachlor epoxide	400	8	8
1,2,3,4-tetrachlorobenzene	400	8	8	Methoxychlor	400	8	8
Pentachlorobenzene	400	8	8				
Hexachlorobenzene	400	8	8				
alpha-HCH	800	16	16				
beta-HCH	800	16	16				
delta-HCH	800	16	16				
gamma-HCH	800	16	16				
Heptachlor	400	8	8				
Aldrin	800	16	16				
Octachlorostyrene	400	8	8				
Oxychlordane	800	16	16				
cis-Chlordane	800	16	16				
Trans-Chlordane	800	16	16				
o,p'-DDE	400	8	8				
p,p'-DDE	400	8	8				
cis-Nonachlor	800	16	16				
Trans-Nonachlor	800	16	16				
o,p'-DDD	400	8	8				
p,p'-DDD	400	8	8				
o,p'-DDT	400	8	8				
p,p'-DDT	400	8	8				
Mirex	400	8	8				
TCMX	400	8	8				
Technical Toxaphene	10,000	100,000	1000				

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Table 3 cont'd….

Labelled Surrogates	**Nominal Conc. in Surrogate Std Solution (ng/mL)**	**Amount added to each sample (ng)**	
$^{13}C_6$-1,4-dichlorobenzene	400	16	
$^{13}C_6$-1,2,3-trichlorobenzene	400	16	
$^{13}C_6$-1,2,3,4-tetrachlorobenzene	400	16	
$^{13}C_6$-pentachlorobenzene	400	16	
$^{13}C_6$-hexachlorobenzene	400	16	
$^{13}C_6$-beta-HCH	400	16	
$^{13}C_6$-gamma-HCH	400	16	
$^{13}C_{10}$-Heptachlor	400	16	
$^{13}C_{12}$-Aldrin	400	16	
$^{13}C_{10}$-Oxychlordane	400	16	
$^{13}C_{10}$-trans-Chlordane	400	16	
$^{13}C_{10}$-trans-Nonachlor	400	16	
$^{13}C_{10}$-cis-Nonachlor	400	16	
$^{13}C_{12}$-o,p'-DDE	400	16	
$^{13}C_{12}$-p,p'-DDE	400	16	
$^{13}C_{12}$-p,p'-DDD	400	16	
$^{13}C_{12}$-o,p'-DDT	400	16	
$^{13}C_{12}$-p,p'-DDT	400	16	
$^{13}C_{12}$-Mirex	400	16	
$^{13}C_{10}$-Heptachlor epoxide	400	16	
$^{13}C_9$-alpha-Endosulphan	400	16	
$^{13}C_6$-delta-HCH	400	16	
$^{13}C_{12}$-Dieldrin	400	16	
$^{13}C_{12}$-Endrin	400	16	
$^{13}C_{12}$-Endrin aldehyde	400	16	
$^{13}C_{12}$-Methoxychlor	400	16	
$^{13}C_9$-beta-Endosulphan	400	16	
$^{13}C_{12}$-PCB 159	1000	20	
Recovery Standards	**Nominal Conc. in Recovery Std Solution (ng/mL)**	**Amount Added to each extract (ng)**	
		E1	**E2**
$^{13}C_{12}$-PCB 52	1000	10	-
$^{13}C_{12}$-PCB 138	1000	10	-
$^{13}C_{12}$-PCB 153	1000	-	10
Extraction Standard	**Nominal Conc. In Extraction Std Solution (ng/mL)**	**Amount Added to Sample (ng)**	
TCMX[1]	1000	Project dependent	

[1] TCMX is used as an extraction standard in some circumstances (Section 9.1.3) and is monitored as an indication of extraction efficiency.

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Table 4. E1 Chlorobenzenes and Pesticides - Nominal Concentrations of Calibration Standard Solutions (ng/mL)

Compound Name	Calibration Standards					
	Level A (Instrument Spec)	Level B	Level C	Level D (Mid-Level)	Level E	Level F
1,4-dichlorobenzene	2	10	40	80	400	2000
1,3-dichlorobenzene	2	10	40	80	400	2000
1,2-dichlorobenzene	2	10	40	80	400	2000
1,2,4-trichlorobenzene	2	10	40	80	400	2000
1,2,3-trichlorobenzene	2	10	40	80	400	2000
1,3,5-trichlorobenzene	2	10	40	80	400	2000
1,2,4,5-tetrachlorobenzene	2	10	40	80	400	2000
1,2,3,5-tetrachlorobenzene	2	10	40	80	400	2000
1,2,3,4-tetrachlorobenzene	2	10	40	80	400	2000
Pentachlorobenzene	2	10	40	80	400	2000
Hexachlorobenzene	2	10	40	80	400	2000
alpha-HCH	4	20	80	160	800	4000
beta-HCH	4	20	80	160	800	4000
delta-HCH	4	20	80	160	800	4000
gamma-HCH	4	20	80	160	800	4000
Heptachlor	2	10	40	80	400	2000
Aldrin	4	20	80	160	800	4000
Octachlorostyrene	2	10	40	80	400	2000
Oxychlordane	4	20	80	160	800	4000
cis-Chlordane	4	20	80	160	800	4000
trans-Chlordane	4	20	80	160	800	4000
o,p'-DDE	2	10	40	80	400	2000
p,p'-DDE	2	10	40	80	400	2000
cis-Nonachlor	4	20	80	160	800	4000
trans-Nonachlor	4	20	80	160	800	4000
o,p'-DDD	2	10	40	80	400	2000
p,p'-DDD	2	10	40	80	400	2000
o,p'-DDT	2	10	40	80	400	2000
p,p'-DDT	2	10	40	80	400	2000
Mirex	2	10	40	80	400	2000

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Table 4 cont'd…

Labelled Surrogates	Level A (Instrument Spec)	Level B	Level C	Level D (Mid-Level)	Level E	Level F
$^{13}C_6$-1,4-dichlorobenzene	80	80	80	80	80	80
$^{13}C_6$-1,2,3-trichlorobenzene	80	80	80	80	80	80
$^{13}C_6$-1,2,3,4-tetrachlorobenzene	80	80	80	80	80	80
$^{13}C_6$-pentachlorobenzene	80	80	80	80	80	80
$^{13}C_6$-hexachlorobenzene	80	80	80	80	80	80
$^{13}C_6$-beta-HCH	80	80	80	80	80	80
$^{13}C_6$-gamma-HCH	80	80	80	80	80	80
$^{13}C_{10}$-Heptachlor	80	80	80	80	80	80
$^{13}C_{12}$-Aldrin	80	80	80	80	80	80
$^{13}C_{10}$-Oxychlordane	80	80	80	80	80	80
$^{13}C_{10}$-trans-Chlordane	80	80	80	80	80	80
$^{13}C_{12}$-o,p'-DDE	80	80	80	80	80	80
$^{13}C_{12}$-p,p'-DDE	80	80	80	80	80	80
$^{13}C_{10}$-trans-Nonachlor	80	80	80	80	80	80
$^{13}C_{10}$-cis-Nonachlor	80	80	80	80	80	80
$^{13}C_{12}$-p,p'-DDD	80	80	80	80	80	80
$^{13}C_{12}$-o,p'-DDT	80	80	80	80	80	80
$^{13}C_{12}$-p,p'-DDT	80	80	80	80	80	80
$^{13}C_{10}$-Mirex	80	80	80	80	80	80
Recovery Standards						
$^{13}C_{12}$-PCB 52	80	80	80	80	80	80
$^{13}C_{12}$-PCB 138	80	80	80	80	80	80
Extraction Standard						
TCMX	2	10	40	80	400	2000

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Table 5. E2 Pesticides - Nominal Concentrations of Calibration Solutions (ng/mL)

Compound Name	Calibration Standards					
	Level A (Instrument Spec)	Level B	Level C	Level D (Mid-Level)	Level E	Level F
delta-HCH	5	10	50	100	200	500
Heptachlor epoxide	4	8	40	80	160	400
alpha-Endosulfan	4	8	40	80	160	400
Dieldrin	4	8	40	80	160	400
Endrin	4	8	40	80	160	400
Methoxychlor	4	8	40	80	160	400
Endosulfan sulphate	4	8	40	80	160	400
Endrin ketone	4	8	40	80	160	400
beta-Endosulfan	4	8	40	80	160	400
Endrin aldehyde	4	8	40	80	160	400
Surrogates						
$^{13}C_6$-delta-HCH	80	80	80	80	80	80
$^{13}C_{12}$-Dieldrin	80	80	80	80	80	80
$^{13}C_{12}$-Endrin	80	80	80	80	80	80
$^{13}C_{12}$-Endrin aldehyde	80	80	80	80	80	80
$^{13}C_{10}$-Heptachlor epoxide	80	80	80	80	80	80
$^{13}C_{12}$-Methoxychlor	80	80	80	80	80	80
$^{13}C_9$-alpha-Endosulphan	80	80	80	80	80	80
$^{13}C_9$-beta-Endosulphan	80	80	80	80	80	80
Recovery Standard						
$^{13}C_{12}$-PCB 153	100	100	100	100	100	100

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3.3 Glassware Cleaning

All glassware used in the preparation of reagents and in the analytical procedures must be organically clean. Glassware must be washed and baked using standard operating procedures. Baked glassware must be solvent rinsed with toluene and hexane. The soxhlet apparatus, including thimble, must be or pre-cleaned by soxhleting with toluene for a minimum of 2 hours.

If baked glassware is not available, glassware must be washed and solvent rinsed following the procedures described in standard operating procedure SLA-018.

3.4 Preparation of Reagents

Activated Copper is freshly prepared according to standard operating procedure SLA-044.

Anhydrous Sodium Sulphate (Na_2SO_4, EM Science, powdered) is cleaned by baking at a minimum of 300°C as described in SLA-093.

Glass Fibre Filters (Ahlstrom, A/E glass or equivalent) are cleaned by baking overnight at a minimum of 300°C.

Glass Fibre Filter Bed is prepared and cleaned by grinding glass fibre filters in a blender and heating overnight at a minimum of 300°C. The cleaned filter bed is stored in a covered jar.

Reagent Sand (Aldrich Chemicals, white quartz, -50 +70 mesh) is proofed by lot prior to use and may be cleaned by soxhlet extraction with dichloromethane for 16 hours as necessary. The clean sand is stored in a clean glass jar.

Silanized Glass Wool is stored in a clean amber jar and is rinsed twice with toluene and twice with hexane prior to use.

Ultra Pure Water (Seastar Chemicals, contaminant free or equivalent) is used as received.

Sodium Hydroxide (NaOH, 1 M) is prepared by dissolving sodium hydroxide pellets (AR grade, 40 g) in ultra pure water (1 L). Extract the solution by shaking with dichloromethane (2 x 100 mL) followed by hexane (100 mL). Store the solution in a stoppered Erlenmeyer flask.

Solvents: All solvents used are high purity, distilled in glass solvents, either HPLC grade or pesticide residue grade. Each lot number of solvent must be checked for impurities by performing a solvent proof, prior to use. All solvent mixtures used in the analyses are made by mixing the appropriate quantities on a volume basis.

Soxhlet Thimbles: used thimbles are soaked in Contrad 70 cleaning solution and rinsed with water. Thimbles are baked overnight at a minimum of 300°C.

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3.5 Preparation of Chromatography Materials

Refer to the following Standard Operating Procedures.

Document ID	Title
SCH-001	Deactivation/Activation Procedures
SCH-002	Column Packing Procedures
SCH-003	Column Cutpoint Determination
SCH-004	Layered Silica Gel Preparation
SCH-005	Preparation of Carbon/Celite Column
SCH-006	Preparation, Use and Maintenance of Biobead Columns

Biobeads (SX-3, Bio-Rad, 200 - 400 mesh) are soaked in 1:1 dichloromethane:hexane for 24 hours as described in SCH-006.

Florisil (Fisher, 60-100 mesh) is activated by heating at 450°C for a minimum of 8 hours and deactivated with ultra pure water (typically 2.1% by weight) as described in SCH-001. The degree of activation may vary depending upon the batch of Florisil. Florisil is stored under nitrogen in a stoppered flask and allowed to equilibrate for 24 hours. The cutpoints are determined prior to use (SCH-003).

Silica Gel (Mallinckrodt, SilicAR, 60-200 mesh is heated for a minimum of 8 hours at 450°C and stored, under nitrogen, in a stoppered reagent jar as described in SCH-001.

3.6 Preparation of Chromatography Columns

3.6.1 Florisil Column

Deactivated Florisil (8 g, 2.1% deactivated) is dry packed in hexane into a glass chromatography column (1 cm x 25 cm with 250 mL reservoir) as described in SCH-002. The column is capped with a 1 cm layer of anhydrous sodium sulphate (powder) and flushed with hexane (~40 mL).

3.6.2 BioBead Column

A Biobeads (SX-3, 60 g) column is prepared and cutpoints determined as described in SCH-006. The column is cleaned with 20% methanol:dichloromethane and 1:1 dichloromethane:hexane prior to use, as described in SCH-006.

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4.0 QUALITY ASSURANCE/QUALITY CONTROL

Refer to the following Standard Operating Procedure.

Document ID	Title
SLA-016	Preparation of Quality Control (QC) Samples

All samples are analyzed in batches. The composition of a batch is detailed on a Batch List. Each batch has the following composition:

- Batch Size - Each batch consists of up to twenty test samples and additional QC samples.
- Blanks - One procedural blank is analyzed for each batch. The procedural blank is prepared by spiking an aliquot of the surrogate standard solution into a clean matrix. The clean matrices available for preparing procedural blanks are described in SLA-016. The procedural blank is extracted and analyzed using the same procedures as the test samples in the analysis batch.

  Note: For stationary source air samples, the extraction procedure for the blank (using a filter and XAD-2 resin as the matrix) starts with the acidification of the filter. The surrogate standard solution is spiked into the XAD-2 when it is in the soxhlet body.
- Duplicates – Duplicate samples are analyzed with analysis batches containing 7-20 test samples, or as required by contract. For some matrices (i.e. XAD-2 columns, particulate filters) only field duplicates can be analyzed.
- Reference Samples – The spiked reference sample (SPM) is prepared by spiking an aliquot of the authentic spiking standard solution into an accurately weighed in-house reference matrix (known to contain low background levels of target analytes). The matrix sample is spiked with an aliquot of surrogate standard solution and extracted following procedures in Section 5 of this method. The type of reference material to be analyzed is assigned to the analyst when the batch is assigned. A certified reference material, N.I.S.T. SRM 1588 Cod Oil, is commercially available and used to validate and periodically check the tissue method.

  Note: For stationary source air samples, the reference sample (a clean filter and XAD-2 resin) is spiked with an aliquot of authentic spiking standard prior to extraction. The extraction procedure starts with the acidification of the filter. The authentic standard solution is spiked into the XAD-2 when it is in the soxhlet body.

The batch composition may vary should batch or quality control requirements be specified by a client. All elements of the QA/QC program at AXYS Analytical Services are documented in the most recent version of the Quality Manual "QA/AC Policies and Procedures Manual.

The quality control limits for duplicate samples, procedural blanks, reference samples, surrogate recoveries, and detection limits are specified in the Table 6 for E1 fraction pesticides and Table 7 for E2 fraction pesticides.

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Table 6. QC Criteria for E1 Chlorinated Pesticides

Analyte	Typical Sample Specific Detection LImits					Procedural Blank Level	Acceptable Matrix Spike
	Solid	Aqueous	Tissue	Pulp	XAD-2 Column		
	ng/g	ng/L	ng/g	ng/g	ng	ng	% Recovery
Dichlorobenzenes	0.1	1.0	0.1	0.05	1.0	<1.0	***
Trichlorobenzenes	0.1	1.0	0.1	0.05	1.0	<1.0	***
Tetrachlorobenzenes	0.1	1.0	0.1	0.05	1.0	<0.5	***
Pentachlorobenzene	0.01	0.1	0.01	0.05	0.1	<0.1	70-130
Hexachlorobenzene	0.01	0.1	0.01	0.05	0.1	<0.1	70-130
alpha-HCH	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
beta-HCH	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
gamma-HCH	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
delta-HCH *	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Heptachlor	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
Aldrin	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
Oxychlordane	0.02	0.2	0.02	0.01	0.2	<0.2	70-130
trans-Chlordane	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
cis-Chlordane	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
o,p'-DDE	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
p,p'-DDE	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
trans-Nonachlor	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
cis-Nonachlor	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
o,p'-DDD	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
p,p'-DDD	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
o,p'-DDT	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
p,p'-DDT	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
Mirex	0.02	0.2	0.02	0.01	0.2	<0.1	70-130
Technical Toxaphene	0.1	1	0.1	n.a.	1	<0.5	60-150
Typical Sample Size:	10 g	1 L	10 g	20 g	1 Column		
Typical final vol., µL **	200	200	200	200	200		

* Delta-HCH normally will elute primarily in the E2 fraction and can be quantified solely from this fraction. Recoveries of delta-HCH may be reported as the sum of the E1 and E2 recoveries if significant concentrations of delta-HCH are observed in the E1 fraction.

****** Extract volumes may range from 20 µL to 200 µL. To avoid excessive loss of volatile compounds, where recovery of volatile compounds is critical, extract volumes lower than 100 µL are not recommended.

******* Recovery of dichlorobenzenes, trichlorobenzenes and tetrachlorobenzenes may be low due to loss through volatilization during the analytical work-up. These compounds may be reported only when recoveries are judged adequate for quantification. Formal recovery acceptance limits have not been established.

Note: Custom QC criteria protocols apply for non-routine targets (e.g. octachlorostyrene, hexachlorobutadiene, etc.) **and must be defined *a priori* in Project Notes.**

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SURROGATE STANDARD RECOVERIES	% RECOVERY RANGES (ALL MATRICES)
$^{13}C_6$-1,4-dichlorobenzene	[1]
$^{13}C_6$-1,2,3-trichlorobenzene	[1]
$^{13}C_6$-1,2,3,4-tetrachlorobenzene	[1]
$^{13}C_6$-Pentachlorobenzene	20-150
$^{13}C_6$-Hexachlorobenzene	20-150
$^{13}C_6$-beta-HCH	30-150
$^{13}C_6$-delta-HCH[2]	n.a.
$^{13}C_6$-gamma-HCH	30-150
$^{13}C_{10}$-Heptachlor	30-150
$^{13}C_{12}$-Aldrin	30-150
$^{13}C_{10}$-Oxychlordane	30-200
$^{13}C_{10}$-trans-Chlordane	30-200
$^{13}C_{12}$-o,p'-DDE	40-150
$^{13}C_{12}$-p,p'-DDE	40-150
$^{13}C_{10}$-trans-Nonachlor	30-150
$^{13}C_{10}$-cis-Nonachlor	30-150
$^{13}C_{12}$-p,p'-DDD	40-150
$^{13}C_{12}$-o,p'-DDT	40-150
$^{13}C_{12}$-p,p'-DDT	40-150
$^{13}C_{10}$-Mirex	30-150
$^{13}C_{12}$-PCB 159	40-130

QC Parameter	Specification
Analysis Duplicate	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL).
Procedural Blank	See Table 6 or <10% of analyte value. <0.1 ng for technical Toxaphene.
Instrument Sensitivity	S/N ≥3:1 for 2-4 pg injected for all target analytes (See Table 4). S/N ≥2:1 for 1.6 ng of technical Toxaphene.
Instrument Linearity	Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs ≤20% for targets with a labelled analog present, ≤35% for targets with no labelled analog present and all labelled compounds.
Bracketing Cal Ver	RRFs from calibration standards must agree to ±25% over a 12-hour period.
Continuing Cal Ver	Concentrations of native compounds must be within ±20% of expected values for targets with a labelled analog present, ±35% for targets with no labelled analog present. Concentrations of labelled compounds must be within ±35% of expected values, except for closing Cal Ver, where ±50% of the expected values is allowed.
Chromatogram Quality **Max Peak Width:** **Resolution**:	1. Separation between p,p'-DDD and o,p-DDT ≤20% of valley height. 2. p,p-DDT breakdown must be ≤15%.
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Retention Times	RRT windows are calculated from daily calibration verification run data using RRT references and fixed RT window brackets in seconds are specified in tables 9 and 10.
Ion Ratios	Ion ratios must fall within ±20% (±30% for $^{13}C_{10}$-Oxychlordane) of the theoretical values for positive identification of all E1 targets in the calibration standards.

[1] Recovery of dichlorobenzenes, trichlorobenzenes and tetrachlorobenzenes may be low due to loss through volatilization during the analytical work-up. These compounds may be reported only when recoveries are judged adequate for quantification. Formal recovery acceptance limits have not been established

[2] Delta-HCH normally will elute primarily in the E2 fraction and can be quantified solely from this fraction. Recoveries of ^{13}C-delta-HCH may be reported as the sum of the E1 and E2 recoveries if significant concentrations of ^{13}C-delta-HCH are observed in the E1 fraction.

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Table 7. QC Criteria for E2 Chlorinated Pesticides

Analyte:	Typical Sample Specific Detection Limits					Procedural Blank Level ng	Acceptable Matrix Spike % Recovery[2]
	Solid	Aqueous	Tissue	Pulp	XAD-2 column		
	ng/g	ng/L	ng/g	ng/g	ng		
Delta-HCH	0.05	0.5	0.05	0.05	0.5	<0.5	60-130
Heptachlor epoxide	0.05	0.5	0.05	0.05	0.5	<0.5	60-130
alpha-Endosulphan	0.05	0.5	0.05	0.05	0.5	<0.5	70-130
Dieldrin	0.05	0.5	0.05	0.05	0.5	<0.5	60-130
Endrin	0.05	0.5	0.05	0.05	0.5	<0.5	60-130
Endosulphan sulphate	0.05	0.5	0.05	0.05	0.5	<0.5	70-130
Endrin ketone	0.05	0.5	0.05	0.05	0.5	<0.5	60-130
beta-Endosulphan	0.05	0.5	0.05	0.05	0.5	<0.5	70-130
Endrin aldehyde	0.05	0.5	0.05	0.05	0.5	<0.5	50-130
Methoxychlor	0.1	1	0.1	0.1	1.0	<1	60-130
Typical Sample Size:	10 g	1 L	10 g	20 g	1 column		
Typical Final Vol, µL [1]	200	200	200	200	200		

[1] Extract volumes may range from 20 µL to 200 µL. To avoid excessive loss of volatile compounds, where recovery of volatile compounds is critical, extract volumes lower than 100 µL are not recommended.

[2] Recoveries quoted are guidelines only and vary according to matrix. Consult detailed method performance data available with method documentation for specific criteria.

SURROGATE STANDARD RECOVERIES:	**% RECOVERY RANGES ALL MATRICES**
$^{13}C_6$-delta-HCH	30-150
$^{13}C_{12}$-Dieldrin	30-150
$^{13}C_{12}$-Endrin	30-150
$^{13}C_{12}$-Endrin aldehyde	30-150
$^{13}C_{10}$-Heptachlor epoxide	30-150
$^{13}C_{12}$-Methoxychlor	30-150
$^{13}C_9$-alpha-Endosulphan	30-150
$^{13}C_9$-beta-Endosulphan	30-150

QC Parameter	Specification
Analysis Duplicate	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL).
Procedural Blank	See Table 7 or <10% of analyte value.
Instrument Sensitivity	S/N ratio ≥3:1 for 4 pg of all analytes.
Instrument Linearity	Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs ≤20% for targets with a labelled analog present, ≤35% for targets with no labelled analog present and all labelled compounds.
Bracketing Cal Ver	RRFs from calibration standards must agree to ±25% over a 12-hour period.
Continuing Cal Ver	Concentrations of native compounds must be within ±20% of expected values for targets with a labelled analog present, ±35% for targets with no labelled analog present. Concentrations of labelled compounds must be within ±35% of expected values, except for closing Cal Ver, where ±50% of the expected values is allowed.
Chromatogram Quality (GC Resolution)	^{13}C-labelled endrin breakdown must be ≤20%.
Analyte /Surrogate Ratios	Response ratio must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Retention Times	RRT windows are calculated from daily calibration verification run data using RRT references and fixed RT window brackets in seconds are specified in tables 9 and 10.
Ion Ratios	Ion ratios must fall within ±20% of the theoretical values for positive identification of all E2 targets and surrogates (with the exception of labelled methoxychlor which is ±50%) in the calibration standards (Levels C-F) and samples, and within ±50% for calibration standard Level B.

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5.0 EXTRACTION PROCEDURES

Samples are analyzed in batches. The samples to be analyzed, the batch QC samples, the name and volume of the surrogate, recovery and authentic standards required, and any additional information concerning the analysis are documented on a Batch List given to an analyst. Refer to SOP SLA-033 for details of assigning analysis batches.

The extraction systems described in this document may only be applicable to analysis of the target compounds listed in this method. If additional compounds are required to be recovered in the extract, the analyst must consider the compatibility of the extraction solvent, the surrogate standards, and the cleanup procedures with the additional analytes. Where incompatibilities exist alternative extraction systems may be required or surrogate spiking may need to be performed after extraction and splitting of the extract.

Each analyst performs the extractions according to the following written extraction procedures and completes an analysis worksheet for each sample during the sample extraction. The analyst is referred to the following Standard Operating Procedures for details of routine laboratory techniques.

Document ID	Title
SLA-004	Sample Control Procedures
SLA-005	Use and Maintenance of Rotary Evaporation Equipment
SLA-006	Nitrogen Blowdown Concentration Technique
SLA-007	Kuderna-Danish Concentration Technique
SLA-008	Preparing Extracts for Instrumental Analysis
SLA-017	Spiking Procedures
SLA-020	Gravimetric Lipid Determination by Weight of Extract
SLA-023	Use of Balances
SLA-027	Completing a Worksheet
SLA-028	Independent Gravimetric Determination of Lipid Content in Tissue
SLA-030	Micro-Lipid Determination for Human blood Analysis
SLA-033	Procedures for Making an Analysis Batch
SLA-045	Removal of Sulphur From Extracts Using Activated Copper
SLA-067	Use of Nitrogen System
SLA-072	Computer Preparation of Labels
SLA-078	Spike Witness Program
SLA-079	Agricultural Hazard Protocols for Soils
SLA-081	Labelling Protocols and Sample Extract Transfer Procedures
SLA-082	Handling of Human Biohazardous Samples
SLA-084	Preparation of Aqueous Samples for Extraction
SLA-085	Subsampling Procedures for Solids and Tissues
SLA-087	Transferring an Ampouled Standard to a Reacti-vial
SLA-092	Determination of Suspended Solids Content in Aqueous Samples
SLA-095	Use and Maintenance of the Syncore Analyst Evaporator

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The following worksheets are used to record details of the analysis

.

FWO-305 through FWO-319	Generic Worksheets

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5.1 Tissue Soxhlet Extraction

This extraction procedure is applicable to the matrix and sample size listed below.

Matrix	Sample Size
Tissue	10 g wet

Accurately weigh a homogenized tissue sample into a beaker containing anhydrous powdered sodium sulphate (75-100 g). Stir the mixture well with a spatula, and allow the mixture to dry for one hour (longer if necessary). Remix the sample with a spatula to form a free-flowing powder.

Assemble the soxhlet apparatus, including a sintered glass soxhlet thimble, and thoroughly clean by soxhleting with toluene for two hours. Discard the toluene. Rinse the apparatus with hexane.

Place a layer of clean silica or powdered anhydrous sodium sulphate into a pre-cleaned soxhlet thimble (2 g for small thimbles, 5 g for large thimbles). Quantitatively transfer the dried sample to a sintered glass soxhlet thimble. Add an aliquot(s) of the appropriate surrogate standard solutions(s) to the sample. Place the soxhlet thimble in the soxhlet apparatus. Be sure that the level of sample in the thimble is not higher than the height of the siphon arm. Add anti-bumping granules (4-5 granules) and dichloromethane (300 mL for small soxhlet, 600 mL for large soxhlet) to the soxhlet's round bottom flask. Allow the sample to reflux for 16 to 20 hours; adjust as necessary to achieve a reflux rate of a minimum of 4 cycles per hour. Allow the mixture to cool. Concentrate the extract to 1 mL. (5 mL if lipid analysis is required) by rotary evaporation (water bath <30°C).

If gravimetric lipid analysis is required, use the extract at this point, following the procedures described in SLA-020.

Add hexane (1 mL) as “keeper” to the remaining extract. Reduce the volume of the final extract to 1 mL by rotary evaporation (water bath <30°C). Add dichloromethane (1 mL) to the extract for gel permeation column cleanup.

5.1.1 Gel Permeation Cleanup

Load the extract onto a Biobead SX-3 gel permeation column with 1:1 dichloromethane:hexane and elute with 1:1 dichloromethane:hexane at 5 mL/min. Refer to the most recent Biobead cutpoint determination for the elution volume. Collect the second fraction and evaporate to 1 mL by rotary evaporation. Transfer the extract to a clean centrifuge tube with hexane rinses. Concentrate to 300 µL under a gentle stream of nitrogen and make the volume to 1 mL with hexane. The extract is ready for the column cleanup procedure (Section 6.0).

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5.2 Solids Soxhlet Extraction

This extraction procedure is applicable to the matrices and sample sizes listed below.

Matrix	Typical Sample Size
Sludge	10 g
Ash	5 g
Sediment	10 g (dry)
Pulp	20 g

Assemble the soxhlet apparatus, including the thimble, and thoroughly clean by soxhleting with toluene for two hours. Discard the toluene. Rinse the apparatus with hexane.

5.2.1 Sample Preparation

Pulp

Load a homogenized pulp sample into a pre-cleaned soxhlet thimble containing 4 g silica.

Sediment, Soil, Sludge, Ash

Accurately weigh a homogenized sample into a beaker containing anhydrous powdered sodium sulphate (75-100 g). Stir the mixture well with a spatula, and allow the mixture to dry for 30 minutes (longer if necessary). Remix sample with spatula to form a free-flowing powder.

Place a layer of clean silica or powdered anhydrous sodium sulphate into a pre-cleaned soxhlet thimble (2 g for small thimbles, 5 g for large thimbles). Quantitatively transfer the dried sample to the soxhlet thimble.

5.2.2 Soxhlet Extraction Procedure

Add an aliquot of the surrogate standard solution(s) to the sample in the soxhlet thimble. Place the soxhlet thimble with sample into the soxhlet apparatus. Be sure the level of the sample in the thimble is not higher than the siphon arm. Add anti-bumping granules (4-5 granules) and dichloromethane (300 mL for small soxhlet, 600 mL for large soxhlet) to the soxhlet's round bottom flask. Heat the sample under reflux for 16-20 hours; adjust as necessary to achieve a reflux rate of a minimum of 4 cycles per hour. Allow the mixture to cool. Concentrate the extract to 1 mL by rotary evaporation (water bath <30°C). Add activated copper to the extract to remove sulphur. Quantitatively transfer the extract to a 15 mL centrifuge tube with hexane rinses. Concentrate the extract to 300 µL under a gentle stream of nitrogen and make the volume to 1 mL with hexane. The extract is ready for the column cleanup procedure (Section 6.0).

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5.3 XAD-2 Column (Resin and Filter) Soxhlet Extraction

This procedure is applicable to the analysis of an XAD-2 water-sampling column. The analysis of a XAD-2 column usually consists of two analyses, as the filter(s) and XAD-2 resin are extracted and analyzed separately. Upon client request, the filter and resin extracts may be combined to form a single extract.

5.3.1 Sample Handling Procedures

Refer to document SLA-043 for details of sample handling procedures. If the sample consists of a large amount of XAD-2 resin or multiple filters, it may be necessary to use more than one soxhlet apparatus to extract the sample. Distribute dried XAD-2 resin (Section 5.3.2) or filters evenly amongst the required number of soxhlets. Spike the sample in multiple soxhlets with surrogate standard(s) as follows:

1. Dilute the aliquot of surrogate standard(s) in a centrifuge tube with acetone (5 mL). Ensure the solution is homogeneous by using a disposable pipette to withdraw and expel the solution several times.
2. Use a disposable pipette to distribute the surrogate solution evenly amongst the soxhlets.
3. Rinse the centrifuge tube with acetone (5 mL). Mix the rinsate in the centrifuge tube by vortex mixing. Distribute the rinsate evenly amongst the soxhlets. Repeat the rinse step once more with another 5 mL acetone.
4. Once the extraction is complete, combine the extracts

5.3.2 XAD-2 Resin – Drying Procedure

1. Place a clean large glass funnel, fitted with a large filter paper, into a beaker.
2. Quantitatively transfer the XAD-2 resin to the filter paper with ultra pure water and allow to drain.
3. If necessary, use multiple filter papers to drain all the XAD-2 resin.
4. Rinse the resin with ultra pure water and allow to drain. Discard the water.

5.3.3 XAD-2 Resin Soxhlet Extraction Procedure

1. Assemble a soxhlet apparatus. Add a small bed of glass wool (weighted down with a fritless thimble) to the bottom of the soxhlet body to prevent clogging during the reflux procedure. Thoroughly clean the apparatus by soxhleting with toluene for two hours. Discard the toluene. Rinse the apparatus with hexane.
2. Transfer the filter paper containing the XAD-2 resin to the soxhlet body or a soxhlet thimble, depending upon the amount of XAD-2 resin. Be sure that the level of XAD-2 resin is not higher than the height of the siphon arm.
3. Add the appropriate volume of dichloromethane (300 mL for small soxhlet, 600 mL for large soxhlet) and anti-bumping granules (4-5 granules) to the round bottom flask of the soxhlet apparatus.
4. Spike an aliquot of the surrogate solution into a centrifuge tube containing acetone (1 mL). Transfer the surrogate standard, along with acetone rinses of the centrifuge tube, onto the

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XAD-2 resin in the thimble prior to starting the soxhlet extraction. (Refer to Section 5.3.1 for spiking multiple soxhlets.)

5. Heat the sample under reflux for 16 -20 hours; adjust as necessary to achieve a reflux rate of a minimum of 4 cycles per hour. Allow the solution to cool. Remove water from the extract (Section 5.3.4).

EXTREMELY IMPORTANT – DO NOT CONCENTRATE THE SAMPLE BY ROTARY EVAPORATION WITHOUT A WATER REMOVAL STEP.

5.3.4 Removal of Water from XAD-2 Resin Extracts

The water removal step depends on the amount of visible water.

1. If less than 3 mL of water is visible, quantitatively transfer the entire extract to an Erlenmeyer flask.
2. If greater than 3 mL of water is visible, quantitatively transfer the extract to a separatory funnel and drain the water from the sample extract. Discard the water. Quantitatively transfer the extract to an Erlenmeyer flask.
3. Dry the extract over anhydrous powdered sodium sulphate. Return the extract to the round bottom flask with complete dichloromethane rinses. Concentrate the extract by rotary evaporation to 1 - 2 mL for extract splitting. If using a 1000 mL round bottom flask for the soxhlet extraction, transfer the extract with dichloromethane rinses to a 500 mL round bottom flask during the evaporation process. The extract is ready to be gravimetrically split according to procedures in Section 5.10. Refer to the Batch List for extract splitting instructions.

5.3.5 Filter - Dean Stark Soxhlet Extraction

This extraction procedure is applicable to glass fibre filters or filter cartridges (wound glass filters).

1. Assemble a large soxhlet apparatus, without the thimble, fit with a Dean Stark adapter and thoroughly clean by soxhleting with toluene for two hours. Discard the toluene. Rinse the apparatus with hexane.
2. Place the filters or filter cartridge directly into the pre-cleaned soxhlet body. Use a large soxhlet body to hold the filter(s); thimbles are not required. Be sure that the level of filters in the soxhlet body is not higher than the height of the siphon arm.
3. Use a 1000 mL round bottom flask for the solvent.
6. Spike the surrogate solution into a centrifuge tube containing acetone (1 mL). Transfer the surrogate standard along with acetone rinses of the centrifuge tube, onto the filter(s) in the soxhlet prior to starting the extraction. (Refer to Section 5.3.1 for spiking multiple soxhlets.)
5. Add anti-bumping granules (4-5 granules) and toluene (700 mL) to the soxhlet's round bottom flask. Fill the side arm to the top with toluene. Soxhlet extract the filter(s) or filter cartridge with until the water removal is complete (no water in the sidearm). Adjust as necessary to achieve a reflux rate of a minimum of 4 cycles per hour. When the extraction has finished, drain the water from the receiver. Monitor the amount of water collected, typically 50-150 mL should be present. Contact the Lab Supervisor if the amount of water is anomalous. Continue with the soxhlet extraction for another 8 - 12 hours. Allow the solution to cool.

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Concentrate by rotary evaporation to 1-2 mL. The extract is ready to be gravimetrically split according to procedures in Section 5.10. Refer to the Batch List for extract splitting instructions.

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5.4 Aqueous Sample Extraction

This extraction procedure is suitable for aqueous samples including drinking water, non-potable water, effluents, aqueous sludge and aqueous ash.

Matrix	Sample Size
Aqueous	1 – 4 L

This extraction procedure for aqueous samples depends on the percentage of suspended solid in the sample.

5.4.1 Sample Preparation

Aqueous samples are homogenized and subsampled by the analyst prior to extraction. An aliquot of surrogate standard solution is added to an accurately weighed sample prior to extraction. The analyst must refer to the following SOP for complete details of sample homogenization, subsampling, rinsing, surrogate spiking and filtration procedures.

SLA-084	Preparation of Aqueous Samples for Extraction

If the amount of particulate is required a suspended solids determination must be carried out prior to analysis. The determination is made according to procedures described in SLA-092.

Requirements for Filtration Procedures

The extraction procedures are dependent on the amount of particulate present in the sample:

- Samples with no visible particles are not filtered prior to extraction (Section 5.4.2, *Extraction of Samples with No Visible Solids*).
- Samples with visible particulate are filtered and extracted (Section 5.4.3, *Extraction of Samples with Visible Solids*). If a particulate weight is required, refer to the Project Notes for details on determining the weight.

NOTE: Samples with no visible particulate may also be subject to filtration prior to extraction as described in the above SOPs if indicated in the Project Notes or Batch List. Any samples that have been filtered must be extracted following the procedures described in Section 5.4.3.

5.4.2 Extraction of Samples with No Visible Solids

5.4.2.1 Extraction by Shaking in a Separatory Funnel

After homogenization, subsampling and surrogate spiking, extract the sample by adding dichloromethane (100 mL) to the separatory funnel containing the sample and shaking vigorously for two minutes. Collect the dichloromethane layer in an Erlenmeyer flask. Repeat the extraction twice more. Combine the dichloromethane layers and dry over anhydrous sodium sulphate for at least 30 minutes. Transfer the extract into a round-bottom flask with

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dichloromethane rinses. Concentrate the extract by rotary evaporation (water bath <30°C) to 1 – 2 mL. Transfer the extract to a centrifuge tube with hexane rinses. Concentrate the extract under a gentle stream of nitrogen to 300 µL. Make the volume to 1 mL with hexane. The extract is ready for the column cleanup procedure (Section 6.0).

5.4.2.2 Extraction by Magnetic Stirring

After homogenization, subsampling and surrogate spiking, add dichloromethane (300 mL) and a pre-cleaned PTFE magnetic stir bar to the sample in an erlenmeyer flask and extract by stirring the solution (with vortex) for a minimum of 30 minutes. Quantitatively transfer the solution to a separatory funnel and draw off the dichloromethane layer. Discard the aqueous layer. Dry the extract over anhydrous sodium sulphate for at least 30 minutes. Transfer the extract into a round-bottom flask with dichloromethane rinses. Concentrate the extract by rotary evaporation (water bath <30°C) to 1 – 2 mL. Transfer the extract to a centrifuge tube with hexane rinses. Concentrate the extract under a gentle stream of nitrogen to 300 µL. Make the volume to 1 mL with hexane. The extract is ready for the column cleanup procedure (Section 6.0).

5.4.3 Extraction of Samples with Visible Solids

The analyst must refer to the following SOP for complete details of sample homogenization, subsampling, rinsing, surrogate spiking and filtration procedures. An option procedure for separation of the solids from the aqueous portion is described in Section 5.4.3.1. Refer to the Batch List for instructions regarding separating the solids.

SLA-084	Preparation of Aqueous Samples for Extraction

Filtration procedures include filtering the entire sample or subsample through a Millipore filtration system containing a baked glass fibre filter paper and a glass fibre filter bed.

CAUTION: To avoid loss of volatile compounds when filtering a sample, do not draw air through the filter.

The filter and filter bed from the filtration apparatus are dried as described below:

Place the filter/filter bed/particulate in a clean beaker. Dry by mixing with anhydrous sodium sulphate (75-100 g) in the beaker.

Rinse the filtration apparatus with the appropriate dichloromethane rinses (refer to SLA-084 or SLA-086), adding the rinses to the filtrate. Extract the filtrate and particulate separately and combine as describe below.

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5.4.3.1 Optional Centrifugation Procedure for Separation of Particulate

Note: The following procedure cannot be used if the particulate weight is required.

Transfer a portion of the sample to a clean 500 mL glass jar with a clean baked 10 cm filter paper in the bottom of the jar. Spin the sample in the centrifuge tube at 1500 RPM until the solid has settled. Decant the supernatant into a separatory funnel. Repeat the procedure until the entire sample has been centrifuged, leaving the filter paper in place throughout the process. Once the entire sample has been processed, dry the particulate and filter in the jar by mixing with powdered anhydrous sodium sulphate. Extract solids as described for the particulate in Section 5.4.3.3.

Rinse the jar with ultra pure water and dichloromethane. Add rinses to the separatory funnel containing the supernatant. Extract the supernatant as described for filtrates, Section 5.4.3.2.

5.4.3.2 Filtrate

- Extract the filtrate (supernatant) by adding dichloromethane (100 mL) to the separatory funnel containing the filtrate and shaking vigorously for two minutes. Collect the dichloromethane (lower) layer in an Erlenmeyer flask. Repeat the extraction twice more. Combine the dichloromethane layers. Discard the aqueous layer.

Or Optional Procedure

- Transfer the filtrate and rinses to a clean flask. Add dichloromethane (300 mL) and a pre-cleaned PTFE magnetic stir bar to the flask, and extract by stirring the solution (with vortex) for a minimum of 30 minutes. Quantitatively transfer the solution to a separatory funnel and draw off the dichloromethane layer. Discard the aqueous layer. Dry the extract over anhydrous sodium sulphate for at least 30 minutes.

At this point, the extract may be treated in one of two ways, depending upon time constraints.

Option 1: Dry the dichloromethane extract over anhydrous sodium sulphate for a minimum of 30 minutes. Quantitatively transfer the extract with dichloromethane rinses to a round bottom flask. Use this flask for the soxhlet extraction of the particulate as described below.

Option 2: Dry the dichloromethane extract over anhydrous sodium sulphate for a minimum of 30 minutes. Quantitatively transfer the extract with dichloromethane rinses to a round bottom flask. With dichloromethane rinses, quantitatively add the concentrated particulate extract from the soxhlet procedure below to the filtrate extract. Concentrate the combined extract to 1-2 mL by rotary evaporation.

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5.4.3.3 Particulate

Place a layer of clean silica or powdered anhydrous sodium sulphate (2 g for small thimbles, 5 g for large thimbles) into a clean soxhlet thimble. Transfer the dried filter/filter bed/particulate with solvent rinses (use extraction solvent) into the thimble. Add the rinses to the soxhlet body. Place the soxhlet thimble in the soxhlet apparatus.

Option 1: Extract using use the round bottom flask containing the filtrate. Add anti-bumping granules (4-5 granules).

Option 2: Add dichloromethane (300 mL) to the soxhlet's round bottom flask. Add anti-bumping granules (4-5 granules).

Heat the sample under reflux for a minimum of 16 hours; adjust as necessary to achieve a reflux rate of at least 4 cycles per hour.

Allow the solution to cool. Concentrate the extract by rotary evaporation (water bath <30°C) to 1-2 mL. If Option 2 was chosen, combine the extracts and concentrate to 1-2 mL by rotary evaporation.

Transfer the extract to a centrifuge tube with hexane rinses. Concentrate the extract under a gentle stream of nitrogen to 300 µL. Make the volume to 1 mL with hexane. The extract is ready for the column cleanup procedure (Section 6.0).

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5.5 Samples Submitted as Extracts

This procedure is suitable for samples submitted as solvent extracts, where only extract splitting and chromatographic cleanup are required prior to instrumental analysis.

Matrix	Sample Size
Solvent Extract	One Extract

When the amount of sample is requested by the client, determine the weight of the extract as received as follows:

- Weigh the extract in the original container.
- Transfer the extract to a centrifuge tube or an Erlenmeyer flask with rinses, using the same solvent as the extract.
- Re-weigh the original container once it has air-dried.
- Record all weights on the worksheet.

1. Spike the extract with aliquots of the appropriate surrogate standards solution(s).
2. Inspect the extract for the presence of water. If less than 3 mL water, transfer extract to an Erlenmeyer flask with solvent rinses (the same solvent as sample) and dry with anhydrous powdered sodium sulphate. Transfer the extract to a clean round bottom flask with solvent rinses. Concentrate the extract to 1-2 mL by rotary evaporation in preparation for sample splitting.
3. If greater than 3 mL of water is visible, transfer the extract to a separatory funnel with solvent rinses (same solvent as sample) and separate water from the solvent. Save the solvent layer in a clean Erlenmeyer flask. Extract the water layer in a separatory funnel with two portions of the solvent. Add the solvent extracts to the original sample in the Erlenmeyer flask and discard the water. Dry the solvent layers with anhydrous powdered sodium sulphate. Transfer the solvent to a clean round bottom flask with solvent rinses and reduce volume to 1-2 mL by rotary evaporation.
4. The sample is ready to be gravimetrically split according to instructions in Section 5.10. Determine from the Batch List if the sample requires a single or multiple analysis. If multiple analysis is required, gravimetrically split the sample into equal portions to satisfy the analysis requirements and record all sample weights. If only a single analysis is required, save half of sample for backup. When splitting, always save a backup portion. Check the Batch List for detailed splitting and surrogate spiking instructions.

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5.6 Milk Extraction – Solvent Extraction Procedure

This extraction procedure is suitable for both human and cow's milk.

1. Accurately weigh a subsample of milk (50 g). Add the sample to 200 mL of 2:1 acetone:hexane in a 500 mL separatory funnel. Add aliquots of surrogate standards which have been dissolved in ~1 mL acetone. Shake the mixture for 2 min and allow the layers to separate.

2. Transfer the aqueous layer to an Erlenmeyer flask and the hexane layer to a separate Erlenmeyer. Return the aqueous layer to the separatory funnel and repeat the extraction with hexane (200 mL). Combine the hexane extracts. Discard the aqueous layer.

3. Return the hexane extracts to the separatory funnel and wash by shaking with ultra pure water (2 x 50 mL).

4. Drain the hexane extract into an Erlenmeyer flask and dry over anhydrous powdered sodium sulphate.

5. Transfer the dried extract to a 500 mL round bottom flask. If lipid analysis is required, concentrate the extract by rotary evaporation to ~5 mL, and carry out the lipid determination according to standard operating procedures.

6. Following lipid analysis, or if no lipid analysis is required, concentrate the extract to ~1 mL. Add dichloromethane (1 mL) to the extract for gel permeation column cleanup.

5.6.1 Gel Permeation Cleanup

Load the extract onto a Biobead SX-3 gel permeation column with 1:1 dichloromethane:hexane and elute with 1:1 dichloromethane:hexane at 5 mL/min. Refer to the most recent Biobead cutpoint determination for the elution volume. Collect the second fraction and evaporate to a small volume by rotary evaporation. Transfer the extract to a clean centrifuge tube with hexane rinses. Concentrate the extract to 300 µL under a gentle stream of nitrogen. Make the volume to 1 m with hexane. The extract is ready for the column cleanup procedure (Section 6.0).

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5.7 Blood Extraction Procedure

This extraction procedure is applicable to the matrix and sample size listed below.

Matrix	Typical Sample Size
Whole Blood/Serum/Plasma	5 to 20 g

Refer to the standard operating procedure SLA-082, *Handling of Human Biohazards*, for details of safety precautions when handling blood samples. Use caution when using bleach to decontaminate equipment used in the analysis of human biohazards and **avoid contact between acid and bleach.** Note that ammonium sulphate, used in the extraction below, is an acidic solution.

1. Accurately weigh a sample of serum (5 to 20 g) into a 250 mL round bottom flask. Add aliquots of surrogate standards and allow to equilibrate for 30 min.
2. Add ethanol, hexane and saturated ammonium sulphate (in the proportions described below) to the sample and shake for 30 min on the shaker table.

   ***NOTE:**

   The proportion of reagent used is critical to complete extraction of analytes. The volumes of ethanol and ammonium sulphate should be similar to the sample size and no more than one-third the volume of hexane used. The volumes of reagents used are dependent upon sample size. **For a sample of 10 g or less**, add 10 mL ethanol, 50 mL hexane and 10 mL saturated ammonium sulphate to the sample**. For sample sizes greater that 10 g**, use a ratio of sample:ethanol:saturated ammonium sulphate:hexane of 1:1:1:3, where the amount of ethanol and saturated ammonium sulphate is equal to the amount of sample, and the volume of hexane is no less than 50 mL.
3. Decant the hexane layer into a 500 mL separatory funnel.
4. Add 50 mL hexane to the aqueous layer in the round bottom flask and shake the mixture for 30 min on a shaker table. Decant the hexane into the separatory funnel containing the first hexane extraction. Discard the aqueous layer from the round-bottomed flask.
5. Backwash the hexane extract by shaking with ultra pure water (2x50 mL) to remove any residual ethanol.
6. Drain the hexane extract into a 500 mL Erlenmeyer flask and dry with anhydrous sodium sulphate.
7. Refer to the Batch List to determine whether a lipid determination is required. If so, carry out the following procedures:

   Lipid Determination: Filter the dried extract, with hexane rinses, through a baked filter paper into a round bottom flask (100 mL). Evaporate the solvent to just dryness by rotary evaporation. Add hexane (4 mL) to the residue in the round bottom flask. Using standard operating procedure SLA-030, determine the lipid content on the extract.
8. Concentrate the extract to a small volume by rotary evaporation. Transfer to a centrifuge tube with hexane rinses. Concentrate to 1 mL under a stream of nitrogen. The extract is ready for the column cleanup procedure. (Section 6.0)

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5.8 Ambient Air (PUF/Filter) Extraction Method

This method is applicable to the analysis of ambient air samples. The PUF and associated filter(s) are extracted together as one sample.

Matrix	Typical Sample Size
Air Sample	PUF + Filter(s)

5.8.1 Sample Preparation

Using clean solvent-rinsed forceps, transfer the PUF and filter(s) to a soxhlet thimble.

5.8.2 Soxhlet Extraction Procedure

Assemble the soxhlet apparatus, including the thimble, and thoroughly clean by soxhleting with toluene for two hours. Discard the toluene. Rinse the apparatus with hexane.

Place the soxhlet thimble containing the PUF and filter in a pre-cleaned soxhlet apparatus. Spike the surrogate solution onto the sample prior to starting the extraction. Add anti-bumping granules (4-5 granules) and dichloromethane (300 mL) to the soxhlet's round bottom flask Heat the sample under reflux for 16-20 hours using dichloromethane (300 mL) as the solvent. Adjust as necessary to achieve a reflux rate of at least 4 cycles per hour. Allow the extract to cool and concentrate by rotary evaporation to 5 mL. Gravimetrically split the extract, as described in Section 5.10, into two equal portions, one for the pesticide analysis and one as backup. Refer to the Batch List for extract splitting instructions.

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5.9 Stationary Source Air Samples (Stack Gas)

5.9.1 Sample Preparation

Stack gas samples are usually submitted as sample trains in several containers labelled A to F or 1 to 6. It is essential that the analyst confirm that the labels on the sample container match those on the sample log-in information prior to commencing extraction procedures.

Prior to proceeding with the sample processing, the analyst must refer to the LIMS and/or Project Notes for information regarding the solvents present in the various containers. A flow chart of the sample processing procedure is presented in Figure 1.

QC Samples

Refer to Section 4.0 for details of preparing the procedural blank and reference sample.

Glassware

Assemble the soxhlet apparatus, including the thimble, and thoroughly clean by soxhleting with toluene for two hours. Discard the toluene. Rinse the apparatus with hexane.

5.9.2 Front Half of Train

a) Container A (1)

The solvent rinses, which may include dichloromethane, toluene, and/or methanol, from the probe liner, nozzle, cyclone and front half of the filter housing are in container A. **If the rinses contain additional or different solvents, or two or more phases, consult the Supervisor for instructions.**

1. Pour the contents of container A through a Millipore filtration apparatus containing a baked filter and if needed, a glass fibre filter/filter bed. Rinse the container with dichloromethane and filter the rinses.

   CAUTION: To avoid loss of volatile compounds when filtering, DO NOT draw air through the filter. DO NOT use acetone rinses to dry the filter.
2. The filter/filter bed is ready for the acidification/sonication procedure (Section 5.9.2b). (Residual water in the filter is acceptable).
3. If methanol is not present in the filtrate, treat the filtrate as described in Step 5.
4. If methanol is present in the filtrate, transfer the filtrate to a separatory funnel with dichloromethane rinses. Make the volume of dichloromethane in the separatory funnel to 100 mL. Add ultra pure water (about equal in volume to the volume of the filtrate) to the separatory funnel. Shake the mixture gently for 10 inversions. Allow the layers to separate. If there is no phase separation, consult the Supervisor for assistance. Corrective action may include the addition of additional water or dichloromethane and another gentle shake of the mixture for 10 inversions. Draw off the organic (bottom) layer into an Erlenmeyer flask. Discard the aqueous (bottom) layer. Proceed with the dichloromethane extract as described below.

   Note: Depending upon the mix of solvent in the containers, the aqueous and organic layers may be inverted from that described above. Ensure that the organic layer is the layer retained for processing.

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5. Dry the filtrate (or filtrate extract) over powdered anhydrous sodium sulphate (Na_2SO_4) for a minimum of 30 minutes. Transfer the filtrate extract to a round bottom flask (500 mL) with dichloromethane rinses; add toluene (1 mL) as a "keeper" and concentrate to 1 mL by rotary evaporation. Use this round bottom flask for the soxhlet extraction of the XAD-2 resin (container C) and filters (Section 5.9.4).

b) Container B (2)

A particulate filter is in container B.

1. Transfer the filter to a clean, tared, piece of foil. Weigh the filter and record the weight to a minimum of 3 significant figures on the work sheet. Transfer the filter/filter bed from the processing of container A (Section 5.9.2a) and the particulate filter and all visible particulate from container B to a clean beaker. Add enough hydrochloric acid (1M, HCL) to the beaker to cover the filters and sonicate for 30 minutes. Filter the mixture through a Millipore filtration apparatus and rinse with ultra pure water until the rinsate is at the pH of ultra pure water (typically 6, check with pH paper).

   CAUTION: To avoid loss of volatile compounds when filtering, DO NOT draw air through the filter. DO NOT use acetone rinses to dry the filter.

2. Transfer the wet filters and particulate to the soxhlet thimble containing the XAD-2 resin from container C (Section 5.9.3c).
3. Combine the filtrate with the contents of container E (impinger water washes) in a separatory funnel (Section 5.9.3e).

5.9.3 Back Half of Train

c) Container C (3)

XAD-2 resin is in container C.

1. Put a layer of neutral silica or powdered anhydrous sodium sulphate (2 g for small thimbles, 5 g for large thimbles) into a pre-cleaned soxhlet thimble. Place the soxhlet thimble into a large glass funnel that is set in a beaker (400 mL). Handle the thimble with a clean piece of foil. Remove the glass wool from the top of XAD-2 trap and place into the soxhlet thimble. Rinse the XAD-2 resin from the container into the soxhlet thimble with ultra pure water. Place the glass wool from the other end of the trap on top of the resin. Allow the water to drain from the thimble.
2. Transfer the filters and particulate from containers A and B (Section 5.9.2b) to the top of the soxhlet thimble containing the XAD-2 resin. Be sure that the level of the XAD-2 and filters in the thimble is not higher than the height of the siphon arm.
3. Add an aliquot of the surrogate standard to the soxhlet thimble.
4. Discard the water rinses of the XAD-2 resin.

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d) Container D (4)

Solvent rinses, which may contain dichloromethane, toluene, and/or methanol, of the condenser, coil and back half of filter housing, are in container D. **If the rinses contain additional or different solvents, consult the Supervisor for instructions.**

1. If methanol is in the Container D rinses, combine the rinses with the filtrate from Container A, and backwash as described in Step 4 in Section 5.9.2a
2. If methanol is not present, dry the contents of container D with powdered anhydrous sodium sulphate for a minimum of 30 minutes. Transfer the extract with dichloromethane to the 500 mL round bottom flask used for the soxhlet extraction of the XAD-2 and filters (Section 5.9.4). Concentrate to 1 mL by rotary evaporation. (Add 1 mL toluene keeper to the flask if it has not been previously added.)

e) Container E (5)

Impinger contents and water rinses, or perhaps only water are in container E. **If the rinses contain ethylene glycol or solvents other than dichloromethane, toluene or methanol, consult the Supervisor for instructions.**

1. Transfer the contents of Container E to a separatory funnel. Add the aqueous filtrate from the acidification step (Section 5.9.2b) to the separatory funnel. Rinse the containers with dichloromethane and add the rinses to the separatory funnel. Extract by shaking with dichloromethane (3 x 100 mL). Combine the extracts, dry with powdered anhydrous sodium sulphate for a minimum of 30 minutes. Proceed as described below:

   i) Once the soxhlet extraction of the XAD-2 resin and filters is complete, concentrate the 80:20 toluene:acetone extract to 1 mL by rotary evaporation. Quantitatively transfer the extract from Container E with dichloromethane rinses to the round bottom flask containing the extract of the XAD-2 and filters. Concentrate the extract to 1 mL by rotary evaporation.

   OR

   ii) If time permits prior to the soxhlet extraction, quantitatively transfer the dichloromethane extract of Container E with dichloromethane rinses to the round bottom flask to be used for the soxhlet extraction of the XAD-2 resin and filters. Concentrate the extract to 1 mL by rotary evaporation. Proceed with the soxhlet extraction (Section 5.9.4)

f) Container F (6) (Final Rinses)

Solvent rinses, that may include dichloromethane, toluene, and/or methanol, of the condenser coil, back half of filter holder and impingers are in container F. The client does not always submit this container. **If the rinses contain additional or different solvents, consult the Supervisor for instructions.**

1. If methanol is in the Container F rinses, combine the rinses with the filtrate from Container A, and backwash as described in Step 4 of Section 5.9.2a.

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2. If methanol is not present, dry the contents of Container F with powdered anhydrous sodium sulphate for a minimum of 30 minutes. Transfer the extract, using dichloromethane, to the 500 mL round bottom flask used for the soxhlet extraction of the XAD-2 and filters (Section 5.9.4) and concentrate by rotary evaporation to 1 mL. (Add 1 mL toluene keeper to the flask if it has not been previously added.)

5.9.4 Soxhlet Extraction

1. Add 80:20 toluene:acetone (300 mL) and anti-bumping granules (4-5 granules) to a pre-cleaned 500 mL round bottom flask and extract the XAD-2/filters under reflux for 16-24 hours; adjust as necessary to achieve a reflux rate of 4 cycles per hour. Allow the extract to cool.
2. Remove water from the extract as follows:
    a. If less than 3 mL of water is visible, quantitatively transfer the entire extract to an Erlenmeyer flask with two acetone rinses.
    b. If greater than 3 mL of water is visible, quantitatively transfer the extract to a separatory funnel with acetone rinses. Drain the water from the sample extract. Discard the water. Quantitatively transfer the entire extract to an Erlenmeyer flask with 2 acetone rinses.
    c. Dry the extract with anhydrous powdered sodium sulphate for a minimum of 30 minutes. Return the extract to the original round bottom flask with complete toluene rinses. Refer to the Batch List for extract splitting instructions. Concentrate by rotary evaporation to 1 mL.
3. If not added prior to the soxhlet extraction, add the dichloromethane extract from Container E (Section 5.9.3e) to the concentrated XAD-2/Filter extract in the soxhlet extraction round bottom flask. Concentrate by rotary evaporation to 1 mL.
4. Elute the extract (and rinses of the round bottom flask) through a glass wool column to remove residual sodium sulphate prior to gravimetrically splitting the extract as specified on the Batch List, as described in Section 5.10.

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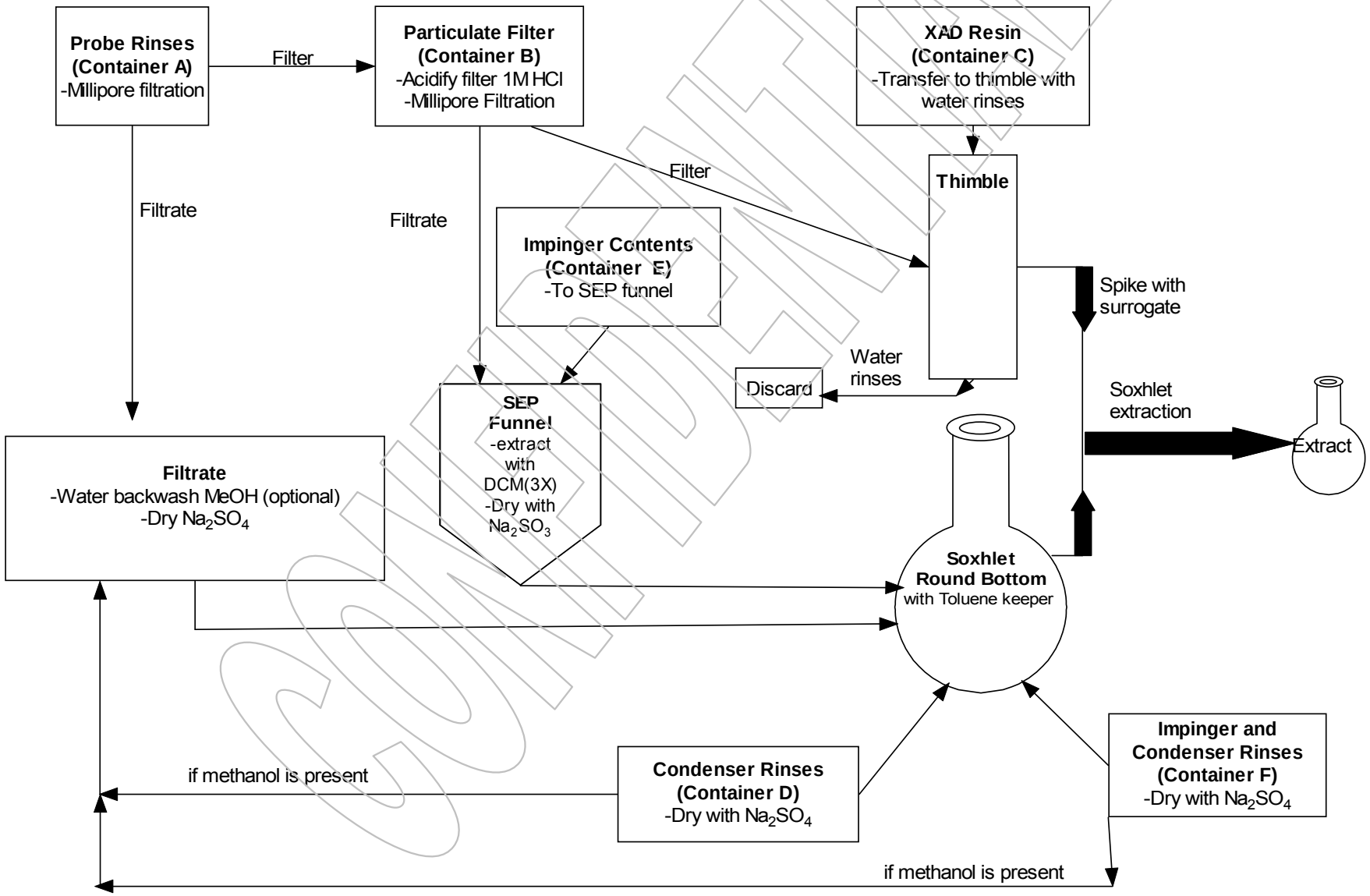
Figure 1 Processing of Sample Trains



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5.10 Extract Splitting Procedures

Gravimetrically split the extract into two portions, one for the pesticide analysis and one as backup as described below. Refer to the Batch List for extract splitting instructions. Record all weights on the worksheets.

Using a balance that weighs to three decimal places, weigh a clean, dry solvent rinsed, labelled centrifuge tube. Record the weight on the worksheet.

1. Inspect the extract for the presence of residual sodium sulphate.
    a. If present, elute the extract through a glass wool column into the pre-weighed centrifuge tube. Rinse the container with hexane and elute the rinses through the column into the centrifuge tube.
    b. If sodium sulphate is not present, transfer the extract with three hexane rinses (with vortexing of the container) to the pre-weighed centrifuge tube.

2. Mix the extract well to ensure homogeneity. Using a Pasteur pipette, draw up a portion of the extract from the bottom of the centrifuge tube. Expel the extract back into the centrifuge tube above the level of the liquid. Do this a minimum of 5 times. When mixing is complete, drain any residual extract in the pipette into the centrifuge tube. **DO NOT** rinse the pipette. Using a balance that weighs to three decimal places, weigh the centrifuge tube with extract to determine the total weight of the extract. Record the weight on the worksheet. Calculate the weight of the extract and record on the worksheet.

3. Using a clean Pasteur pipette, transfer one-portion (by weight, as specified on the Batch List) of the extract to a tared, clean, labelled glass ampoule. Record the weight of the extract. Cover the ampoule with clean foil and submit to the Sample Preparation group for sealing.

4. Reweigh the centrifuge tube, determine the weight of the remaining extract and record the weight on the worksheet. Use this portion of the extract for pesticide analysis.

5. Include on the worksheet the balance inventory number, the date of the splitting procedure, and analyst's initials.

6. Concentrate the extract by evaporation under a stream of nitrogen to 1 mL (300 µL if dichloromethane is present, 50 µL in toluene is present). Make the volume to 1 mL with hexane.

7. The extract is ready for chromatography cleanup procedures (Section 6.0).

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6.0 COLUMN CLEANUP PROCEDURES

Sample extracts are cleaned up on a Florisil column for which column cutpoints are regularly determined. The following fractions are eluted from the Florisil column.

- E1 contains non-polar and moderately polar chlorinated pesticides, chlorobenzenes, and Toxaphene.
- E2 contains the more polar chlorinated pesticides.

Some extracts require additional cleanup procedures to remove interferences. These procedures are described in Section 6.2.

6.1 Florisil Column Cleanup of E1 and E2

Note: The extract must be in hexane before loading onto the column.

Quantitatively transfer the extract and hexane rinses (3 x 1 mL) to a Florisil column (8 grams, 2.1% deactivated) Elute the column with dichloromethane:hexane (10:90, E1) and collect the eluate in a round bottom flask. Elute the column with dichloromethane (E2) and collect the eluate in a round bottom flask. Use the elution volumes determined from the Florisil cutpoint determination of the particular batch of Florisil. Typical cutpoints are as follows:

E1	10:90 dichloromethane:hexane	45 mL
E2	dichloromethane	50 mL

Concentrate each fraction to a small volume (~ 1 mL). Add activated copper to E1 extracts to remove sulphur. Transfer each extract to a centrifuge tube with hexane and concentrate the extract to 500 µL under a stream of nitrogen. Transfer each extract to an autosampler vial. Concentrate the extract to a small volume under a gentle stream of nitrogen. Rinse the centrifuge tube with hexane and add the rinse to the autosampler vial. Concentrate the extract to a small volume under a gentle stream of nitrogen. Repeat the rinse and concentration sequence twice more. Add an aliquot of the appropriate recovery standard to each extract. Adjust the volume to 200 µL with hexane. Cap the autosampler vial. The extract is ready for instrumental analysis (Section 7.1).

E1 is analyzed by HRGC/MS for some or all of the following: most chlorinated pesticides and chlorobenzenes.

E2 is analyzed by HRGC/MS for the most polar pesticides (Section 7.2).

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6.2 Additional Cleanup Procedures

Depending on the nature of the matrix or extract, an analyst may perform additional cleanup procedures prior to instrumental analysis. Once instrumental analysis has been carried out, the presence of interferences in the chromatogram may necessitate additional cleanup procedures followed by re-analysis. These are carried out upon request from a Data Interpretation Chemist or Project/QC Chemist.

6.2.1 Biobead Column (mandatory for all tissue matrices)

Uncap the autosampler vial. Transfer the extract to a centrifuge tube with enough 1:1 dichloromethane:hexane to make the volume to 2 mL. Load the extract onto a Biobead column and elute with 1:1 dichloromethane:hexane. Collect the second fraction. Refer to the most recent Biobead cutpoint for the volume of solvent to collect. Concentrate the eluate by rotary evaporation. Concentrate the extract to 1 mL by rotary evaporation and transfer to a centrifuge tube. Concentrate further under a stream of nitrogen and transfer to an autosampler vial. Adjust the volume to that specified for the fraction in Section 6.1.

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7.0 INSTRUMENTAL ANALYSIS

7.1 HR GC/MS Analysis of E1 for Pesticides and Chlorobenzenes

7.1.1 Sensitivity

The sensitivity of the instrument is verified at least weekly and after any instrument maintenance during the initial calibration by analysis of a low concentration standard solution. For 2 - 4 pg of each target analyte injected (See Table 4) the signal to noise (S/N) ratio must be greater than or equal to 3:1.

7.1.2 GC Resolution and DDT Breakdown

The GC resolution is checked daily by observing mass 235.0081 over a span of 30 seconds. The valley between p,p'-DDD and o,p-DDT must be in the centre of the span and the valley height must be <20% of the height of o,p-DDT (or the smaller peak).

The percent breakdown of DDT is checked before every batch of samples or at least every 12 hours. The breakdown is monitored by checking the breakdown of $^{13}C_{12}$-labelled DDT in the solvent blank, containing $^{13}C_{12}$-DDT. The percent breakdown is calculated as follows:

$$\% \text{ Breakdown} = 100 \times \frac{\left(\text{sum of degradation peak area } (^{13}C_{12}\text{-DDD} + {}^{13}C_{12}\text{-DDE})\right)}{\left(\text{sum of all peak areas } (^{13}C_{12}\text{-DDT} + {}^{13}C_{12}\text{-DDE} + {}^{13}C_{12}\text{-DDD})\right)}$$

GC column and/or injector servicing is performed as necessary to maintain acceptable performance.

7.1.3 Calibration

Initial calibration is performed using a series of five solutions that encompass the working concentration range of the instrument. The initial calibration solutions contain a suite of labelled surrogates, recovery standards and target compounds. The frequency of initial calibrations is specified in SIN-028. Calibration is verified at least once every 12 hours by analysis of a mid-level calibration solution, but only the opening calibration verification run prior to samples is reported unless requested otherwise by contract and specified in Project Notes. Depending on the request of the client, either continuing calibration protocols or bracketing calibration protocols are followed. Continuing calibration protocols use the mean RRF's determined from the initial calibration to calculate the analyte concentrations. Bracketing calibration procedures use mean RRFs from the analysis of the mid-level calibration solution prior to and after samples to calculate analyte concentrations. For QC specifications for the analysis of E1 pesticides, refer to Table 6.

For technical Toxaphene analysis, a single calibration solution is run every 12 hours to determine retention times and RRFs.

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7.1.4 Analysis

High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) analysis of the E1 fraction is done on a high-resolution mass spectrometer (HRMS) equipped with a high-resolution gas chromatograph (HRGC) equipped with manufacturer's software. A J&W DB-5 chromatography column (60 m, 0.25 mm i.d., 0.10 µm film thickness) is coupled directly to the HRMS source. The HRMS is operated at a static (8000) mass resolution (10% valley) in the electron ionization (EI) mode using multiple ion detection (MID) acquiring two characteristic ions for each target analyte and surrogate standard. A splitless/split injection sequence is used. The ions acquired are listed in Table 9.

A typical extract volume is 200 µL; 1.0 µL is injected. If necessary, extracts are diluted to bring all target responses within the calibration range. Typical operating conditions for the GC/MS are presented below.

GC Temperature Program		**General GC Conditions**	
Temp (°C)	50	Injector Temp (°C)	180
Hold time (min)	0.5	Injector	Split/Splitless, 2 min
Rate (C° min^{-1})	20	Carrier Gas	Helium, 200 kPa
Temp (°C)	150	Maximum Temp (°C)	320
Hold time (min)	0		
Rate (C° min^{-1})	5	**MS Conditions**	
Temp (°C)	250	Source Temp (°C)	250
Hold time (min)	0	Electron Energy (eV)	35
Rate (C° min^{-1})	50	Trap Current (µA)	500 - 900
Temp (°C)	320	Mass Resolution	8000
Hold time (min)	4	Detector Voltage (V)	340 - 400

The Instrument Chemist is referred to the Instrument Method MIN-028 E1 for further details of the instrumental analysis. When technical Toxaphene is required, the above GC program is used, and the masses for Toxaphene are added to the acquisition program (Method CL-F1-DB5-1_TP).

7.1.5 Analysis Sequence

The sequence in which a batch of samples is analyzed, after successful calibration, is as follows:

Calibration Sample
Reference Sample
Toluene Blank (containing $^{13}C_{12}$-p,p'-DDT)
Procedural Blank
Samples
Calibration Sample

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7.2 HR GC/MS Analysis of E2 for Pesticides

7.2.1 Sensitivity

The sensitivity of the GC/MS is checked at least weekly or after any instrument maintenance**.** The following sensitivity requirements must be met:

- Signal-to-noise ratios must be greater than or equal to 3:1 for 4 pg for all analytes injected.

7.2.2 Endrin Breakdown

The breakdown of $^{13}C_{12}$-labelled endrin is checked every 12 hours, prior to analysis of samples, by analyzing a solvent blank containing $^{13}C_{12}$-endrin and calculating the concentration of breakdown products (using RRFs determined for the native compounds) by applying the following formula:

$$\%Breakdown = \frac{Sum\left(^{13}C_{12}\text{-}endrin\,ketone + {}^{13}C_{12}\text{-}endrin\,aldehyde\right)}{Sum\left(^{13}C_{12}\text{-}endrin + {}^{13}C_{12}\text{-}endrin\,ketone + {}^{13}C_{12}\text{-}endrin\,aldehyde\right)} \times 100\%$$

GC column and/or injector servicing is performed as necessary for acceptable performance.

7.2.3 Calibration

Initial calibration is performed using a series of five solutions that encompass the working concentration range of the instrument. The initial calibration solutions contain a suite of labelled surrogates, recovery standards and target compounds. The frequency of initial calibrations is specified in AXYS SOP SIN-028. Calibration is verified at least once every 12 hours by analysis of a mid-level calibration solution but only the opening calibration verification run prior to samples is reported unless requested otherwise by contract and specified in Project Notes. Depending on the request of the client, either continuing calibration protocols or bracketing calibration protocols are followed. Continuing calibration protocols use the mean RRFs determined from the initial calibration to calculate the analyte concentrations. Bracketing calibration procedures use mean RRFs from the analysis of the mid-level calibration solution prior to and after samples to calculate analyte concentrations. See Table 7 for the QC specifications for E2 fraction pesticides.

7.2.4 Analysis

High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) analysis of the E2 fraction is done on a high-resolution mass spectrometer (HRMS) equipped with a high-resolution gas chromatograph (HRGC) equipped with manufacturer's chromatography software. A J&W DB-5 chromatography column (60 m, 0.25 mm i.d., 0.10 µm film thickness) is coupled directly to the HRMS source. The HRMS is operated at a static (8000) mass resolution (10% valley) in the electron ionization (EI) mode using multiple ion detection (MID) acquiring two

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characteristic ions for each target analyte and surrogate standard. A splitless/split injection sequence is used. The ions acquired are listed in Table 10.

A typical extract volume is 200 µL; 1.0 µL is injected. If necessary, extracts are diluted to bring all target responses within the calibration range.

Typical operating conditions for the GC/MS are presented below.

GC Temperature Program		**General GC Conditions**	
Temp (°C)	100	Injector Temp (°C)	160
Hold time (min)	2	Injector	Split/Splitless, 2 min
Rate 9 (C° min^{-1})	20	Carrier Gas	Helium, 200 kPa
Temp (°C)	200	Maximum Temp (°C)	320
Hold time (min)	15		
Rate (C° min^{-1})	10	**MS Conditions**	
Temp (°C)	300	Source Temp (°C)	250
Hold time (min)	5	Electron Energy (eV)	35
Rate (C° min^{-1})	-	Trap Current (µA)	500 - 900
Temp (°C)	-	Mass Resolution	8000
Hold time (min)	-	Detector Voltage (V)	340 - 400

The Instrument Chemist is referred to Instrument Method MIN-028 E2 for further details of the instrumental analysis.

7.2.5 Analysis Sequence

The sequence in which a batch of samples is analyzed, after successful calibration, is as follows:

Calibration Solution
Reference Sample
Solvent Blank (containing $^{13}C_{12}$-Endrin)
Procedural Blank
Samples
Calibration Sample

7.3 Lock Mass Monitoring

The mass spectrometer is operated in a mass-drift correction mode, using perfluorokerosene (PFK) to provide lock m/z's. The lock mass for each group of m/z's is shown in Tables 9 and 10. Each lock mass signal is monitored through the respective window and must not vary by more than 20%. Corrective actions as dilution and/or further cleanup are performed as necessary to obtain the prescribed lock mass.

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8.0 ANALYTE IDENTIFICATION

A chromatographic peak is identified as a target compound if the following criteria are met for the quantification and confirmation ions:

1. Peak responses must be at least three times the background noise level.
2. The relative retention time must be within the predicted window (Table 9, 10).
3. Peak maxima for quantification and confirmation ions must coincide within two seconds.
4. The relative ion abundance ratios must be within 20% of the theoretical, except for labelled oxychlordane which must be within 30 percent and labeled methoxychlor which should be within ±50% (the confirming ion response for L-methoxychlor is weak and the 50% specification is a guideline, ratios outside this can be accepted with professional judgment and narration explanation).

9.0 QUANTIFICATION PROCEDURES

9.1 Concentrations

Target concentrations are determined with respect to either a labelled surrogate or the internal standard as shown in Table 9 and Table 10. Mean relative response factors (RRF), determined from either a multi-level initial calibration series or a mid-level calibration standard run at the beginning and end of the samples, are used to convert raw peak areas in sample chromatograms to final concentrations as follows:

$$\underset{\text{(ng/g or ng/L)}}{\text{Concentration of Target}} = \left(\frac{\text{area of Target}}{\text{area of Qt Std}}\right) \times \left(\frac{\text{weight of Qt Std (ng)}}{\text{RRF}}\right) \times \left(\frac{1}{\text{weight of sample (g or L)}}\right)$$

where $$\text{RRF} = \left(\frac{\text{area of Target}}{\text{area of Qt Std}}\right) \times \left(\frac{\text{concentration of Qt Std}}{\text{concentration of Target}}\right)$$

and the Qt Std is either the surrogate or the internal standard

Those compounds quantified against a labelled standard added at the beginning of the analysis procedure are recovery corrected by the method of quantification. Analytes that are quantified against a recovery standard are not recovery corrected. Surrogate recoveries are determined similarly against the recovery (internal) standard and are used as general indicators of overall analytical quality.

9.2 Detection Limits

Sample specific detection limits (SDLs) are determined from the analysis data by converting the minimum detectable area to a concentration following the same procedures used to convert target peak responses to concentrations. The estimated minimum detectable area is determined as three times the height of the noise in the m/z channel of interest, converted to an area using the area height ratio of the corresponding labelled surrogate peak.

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9.3 Quantification of Technical Toxaphene

Technical Toxaphene is quantified by single solution bracketing calibration and determined by summing the responses of seven peaks and quantifying by internal standard quantification procedures. The calculations use the mean RRF determined from the bracketing calibration runs. Table 8 presents the masses monitored and the quantification references.

The sample detection limit (SDL) for technical Toxaphene is approximately 1 ng/sample for clean samples. The SDL is expressed in the terms of detection of a single Toxaphene congener (i.e. not by detection of the full technical Toxaphene pattern).

Table 8. Surrogates Used and RRF Determination for Technical Toxaphene by GC/HRMS

Compound Name	Quant. Ion m/z	Conf. Ion m/z	Quant/conf ion ratio	Ion ratio tolerance (± %)	Surrogate	RRF Determined From
Toxaphene peaks T1, T2, T3, T4,T5, T6, T7	246.9244	244.9273	0.48	20	^{13}C-PCB 159	Toxaphene peaks T1, T2, T3, T4,T5, T6, T7
Surrogate Standard						
$^{13}C_{12}$-PCB 159	299.947	301.944	0.77	20	^{13}C-PCB 138	Toxaphene peaks T1, T2, T3, T4,T5, T6, T7
Recovery Standard						
$^{13}C_{12}$-PCB 138	299.947	301.944	0.77	20		

9.4 Quantification of delta-HCH

The target analyte delta-HCH is present in both the E1 and E2 fractions. It must be quantified in both fractions and summed to determine the concentration in the extract. To quantify this analyte, the RRF of delta-HCH must be determined from calibration procedures in both analyses.

9.5 Optional High Concentration Sample Procedure

For samples with target concentrations that would exceed the working range of the method an extraction standard (tetra-chloro-m-xylene (TCMX)) is added to the sample prior to analysis instead of the labelled surrogates. The labelled surrogates are spiked to a split portion of the extract immediately after extraction and the analysis is carried through. The recovery of the extraction standard is monitored to ensure quantitative recovery from the extraction step. Final sample concentrations are adjusted to reflect the extract split factor.

9.6 Optional Low Concentration Sample Procedure

The spiking level of labelled surrogate and recovery standards may be reduced by up to a factor of 20, and the extract volume reduced accordingly to a minimum volume of 20 µL.

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Table 9. Analyte Ions Monitored, Surrogates Used, and RRF Determination for E1 Pesticides by HR GC/MS

(No entry in the "RRF Used" field designates an RRF derived from that same compound.)

Analyte Name	Quantification and Retention Time Reference	RRF Determination	Typical Retention Time	RT Win. (sec)	Acquired in Function	mass1	mass2	m1/m2 ratio	Ion Ratio Tolerance (+/- %)
1,3-Cl_2-BZ	$^{13}C_6$-1,4-Cl_2-BZ		9:05	-5,5	1	145.969	147.966	1.56	20
1,4-Cl_2-BZ	$^{13}C_6$-1,4-Cl_2-BZ		9:10	-1,3	1	145.969	147.966	1.56	20
1,2-Cl_2-BZ	$^{13}C_6$-1,4-Cl_2-BZ		9:31	-5,5	1	145.969	147.966	1.56	20
1,3,5-Cl_3-BZ	$^{13}C_6$-1,2,3-Cl_3-BZ		11:04	-5,5	1	179.93	181.927	1.03	20
1,2,4-Cl_3-BZ	$^{13}C_6$-1,2,3-Cl_3-BZ		11:47	-5,5	1	179.93	181.927	1.03	20
1,2,3-Cl_3-BZ	$^{13}C_6$-1,2,3-Cl_3-BZ		12:21	-1,3	1	179.93	181.927	1.03	20
1,2,4,5/3,5-Cl_4-BZ	$^{13}C_6$-1,2,3,4-Cl_4-BZ		14:14	-5,5	2	213.891	215.888	0.77	20
1,2,3,4-Cl_4-BZ	$^{13}C_6$-1,2,3,4-Cl_4-BZ		15:02	-1,3	2	213.891	215.888	0.77	20
Cl_5-BZ	$^{13}C_6$-Cl_5-BZ		17:27	-1,3	2	247.852	249.849	0.62	20
HCB	$^{13}C_6$-HCB		20:55	-1,3	3	283.81	285.807	1.25	20
TCMX	$^{13}C_6$-HCB		19:06	-5,5	2	241.922	243.919	0.78	20
Cl_6-Butadiene	$^{13}C_6$-1,2,3-Cl_3-BZ	1,2,3-Cl_3-BZ	12:20	-5,5	1	189.872	187.875	1.32	20
alpha-HCH	$^{13}C_6$-gamma-HCH		20:36	-5,5	3	216.915	218.912	0.77	20
beta-HCH	$^{13}C_6$-beta-HCH		21:39	-1,3	3	216.915	218.912	0.77	20
gamma-HCH	$^{13}C_6$-gamma-HCH		21:48	-1,3	3	216.915	218.912	0.77	20
delta-HCH[1]	$^{13}C_6$-delta-HCH		22:43	-1,3	3	216.915	218.912	0.77	20
Heptachlor	$^{13}C_{10}$-Heptachlor		24:25	-1,3	3	271.81	273.81	1.24	20
Aldrin	$^{13}C_{12}$-Aldrin		25:43	-1,3	3	262.857	264.854	1.55	20
Octachlorostyrene	$^{13}C_{10}$-trans-Chlordane		27:05	-5,5	3	270.844	272.841	0.62	20
Oxychlordane	$^{13}C_{10}$-Oxychlordane		27:16	-1,3	3	262.857	264.854	1.55	20
trans-Chlordane	$^{13}C_{10}$-trans-Chlordane		28:06	-1,3	4	271.81	273.807	1.24	20
cis-Chlordane	$^{13}C_{10}$-trans-Chlordane		28:41	-5,5	4	271.81	273.807	1.24	20
o,p-DDE	$^{13}C_{12}$-o,p-DDE		28:19	-1,3	4	246	247.997	1.56	20
p,p-DDE	$^{13}C_{12}$-p,p-DDE		29:29	-1,3	4	246	247.997	1.56	20
trans-Nonachlor	$^{13}C_{10}$-trans-Nonachlor		28:52	-1,3	4	271.81	273.807	1.24	20
cis-Nonachlor	$^{13}C_{10}$-cis-Nonachlor		31:12	-1,3	5	271.81	273.807	1.24	20
o,p-DDD	$^{13}C_{12}$-p,p-DDD		29:49	-5,5	5	235.008	237.005	1.56	20
p,p-DDD	$^{13}C_{12}$-p,p-DDD		31:03	-1,3	5	235.008	237.005	1.56	20
o,p-DDT	$^{13}C_{12}$-o,p-DDT		31:10	-1,3	5	235.008	237.005	1.56	20
p,p-DDT	$^{13}C_{12}$-p,p-DDT		32:24	-1,3	5	235.008	237.005	1.56	20
Mirex	$^{13}C_{10}$-Mirex		34:54	-1,3	5	269.813	271.81	0.52	20

[1] delta-HCH normally will elute primarily in the E2 fraction and can be quantified solely from this fraction. Recoveries of ^{13}C-delta-HCH may be reported as the sum of the E1 and E2 recoveries if significant concentrations of ^{13}C-delta-HCH are observed in the E1 fraction.

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Table 9 (Cont'd)

Analyte Name	Quantification and Retention Time Reference	RRF Determination	Typical Retention Time	RT Win. (sec)	Acquired in Function	mass1	mass2	m1/m2 ratio	Ion Ratio Tolerance (+/-)
$^{13}C_6$-1,4-Cl_2-BZ	$^{13}C_{12}$-PCB-52		9:10	-10,10	1	151.989	153.986	1.56	20
$^{13}C_6$-1,2,3-Cl_3-BZ	$^{13}C_{12}$-PCB-52		12:20	-10,10	1	185.95	187.947	1.03	20
$^{13}C_6$-1,2,3,4-Cl_4-BZ	$^{13}C_{12}$-PCB-52		15:02	-10,10	2	221.908	223.905	2.08	20
$^{13}C_6$-Cl_5-BZ	$^{13}C_{12}$-PCB-52		17:26	-10,10	2	255.869	257.866	1.55	20
$^{13}C_6$-HCB	$^{13}C_{12}$-PCB-52		20:55	-10,10	3	289.83	291.828	1.25	20
$^{13}C_6$-beta-HCH	$^{13}C_{12}$-PCB-52		21:38	-10,10	3	222.935	224.932	0.78	20
$^{13}C_6$-gamma-HCH	$^{13}C_{12}$-PCB-52		21:47	-10,10	3	222.935	224.932	0.78	20
$^{13}C_6$-delta-HCH	$^{13}C_{12}$-PCB-52		22:42	-10,10	3	222.935	224.932	0.78	20
$^{13}C_{10}$-Heptachlor	$^{13}C_{12}$-PCB-52		24:24	-10,10	3	276.827	278.824	1.24	20
$^{13}C_{10}$-Aldrin	$^{13}C_{12}$-PCB-52		25:41	-10,10	3	269.88	271.877	1.55	20
$^{13}C_{10}$-Oxychlordane	$^{13}C_{12}$-PCB-52		27:15	-10,10	3	269.88	271.877	1.55	30
$^{13}C_{10}$-trans-Chlordane	$^{13}C_{12}$-PCB-138		28:05	-10,10	4	276.827	278.824	1.24	20
$^{13}C_{10}$-trans-Nonachlor	$^{13}C_{12}$-PCB-138		28:51	-10,10	4	276.827	278.824	1.24	20
$^{13}C_{10}$-cis-Nonachlor	$^{13}C_{12}$-PCB-138		31:11	-10,10	5	276.827	278.824	1.24	20
$^{13}C_{12}$-o,p-DDE	$^{13}C_{12}$-PCB-138		28:18	-10,10	4	258.041	260.038	1.56	20
$^{13}C_{12}$-p,p-DDE	$^{13}C_{12}$-PCB-138		29:29	-10,10	4	258.041	260.038	1.56	20
$^{13}C_{12}$-p,p-DDD	$^{13}C_{12}$-PCB-138		31:02	-10,10	5	247.048	249.045	1.56	20
$^{13}C_{12}$-o,p-DDT	$^{13}C_{12}$-PCB-138		31:09	-10,10	5	247.048	249.045	1.56	20
$^{13}C_{12}$-p,p-DDT	$^{13}C_{12}$-PCB-138		32:23	-10,10	5	247.048	249.045	1.56	20
$^{13}C_{10}$-Mirex	$^{13}C_{12}$-PCB-138		34:53	-10,10	5	276.827	278.824	1.25	20
Recovery Standards									
$^{13}C_{12}$-PCB-52			25:07	-10,10	3	301.963	303.96	0.77	20
$^{13}C_{12}$-PCB-138			32:31	-10,10	5	299.947	301.944	0.77	20
Lock Masses									
Lock Mass					1	168.989			
Lock Mass					2, 3	230.986			
Lock Mass					4	268.982			
Lock Mass					5	292.982			

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Table 10. Analyte Ions Monitored, Surrogates Used and RRF Determination for E2 Pesticides by GC/MS

(No entry in the "RRF Used" field designates an RRF derived from that same compound.)

Analyte Name	Quantification and Retention Time Reference	RRF Determination	Typical Retention Time	RT Win. (sec)	Acquired in Function	mass1	mass2	m1/m2 ratio	Ion Ratio Tolerance (+/- %)
delta-HCH	$^{13}C_6$-delta-HCH		13:13	-1,3	1	216.915	220.909	1.63	20
Heptachlor epoxide	$^{13}C_9$-Heptachlor-Epoxide		18:31	-1,3	2	354.841	352.844	0.8	20
alpha-Endosulphan	$^{13}C_9$-alpha-endosulphan		20:59	-1,3	2	264.854	262.857	0.64	20
Dieldrin	$^{13}C_{12}$-Dieldrin		23:00	-1,3	2	264.854	262.857	0.64	20
Endrin	$^{13}C_{12}$-Endrin		24:22	-1,3	2	264.854	262.857	0.64	20
beta-Endosulphan	$^{13}C_9$-beta-Endosulphan		24:55	-1,3	2	264.854	262.857	0.64	20
Endosulphan sulphate	$^{13}C_9$-beta-Endosulphan		27:06	-5,5	2	264.854	262.857	0.64	20
Endrin aldehyde	$^{13}C_{12}$-Endrin aldehyde		25:56	-1,3	2	346.896	344.899	0.64	20
Endrin ketone	$^{13}C_{12}$-Endrin		29:00	-5,5	2	318.901	316.904	0.64	20
Methoxychlor	$^{13}C_{12}$-Methoxychlor		29:45	-1,3	3	228.111	227.107	0.17	20
Labelled Surrogates									
$^{13}C_6$-delta-HCH	$^{13}C_{12}$-PCB-153		13:12	-10,10	1	222.935	224.932	0.78	20
$^{13}C_9$-Heptachlor-Epoxide	$^{13}C_{12}$-PCB-153		18:30	-10,10	2	364.875	362.878	0.8	20
$^{13}C_9$-alpha-endosulphan	$^{13}C_{12}$-PCB-153		20:58	-10,10	2	271.877	269.88	0.64	20
$^{13}C_{12}$-Dieldrin	$^{13}C_{12}$-PCB-153		22:58	-10,10	2	271.877	269.88	0.64	20
$^{13}C_{12}$-Endrin	$^{13}C_{12}$-PCB-153		24:20	-10,10	2	271.877	269.88	0.64	20
$^{13}C_9$-beta-Endosulphan	$^{13}C_{12}$-PCB-153		24:55	-10,10	2	271.877	269.88	0.64	20
$^{13}C_{12}$-Endrin aldehyde	$^{13}C_{12}$-PCB-153		25:55	-10,10	2	358.936	356.939	0.64	20
$^{13}C_{12}$-Methoxychlor	$^{13}C_{12}$-PCB-153		29:45	-10,10	3	239.148	240.151	30	50
Recovery Standard									
$^{13}C_{12}$-PCB-153			26:16	-10,10	2	299.947	301.944	0.78	20
Lock Masses									
Lock Mass					1	218.986			
Lock Mass					2	292.982			
Lock Mass					3	230.986			
13C_{12}-Endrin ketone	breakdown check				2	327.941			

UNCONTROLLED

Appendix P

Laboratory SOPs

Axys SOP

PCB Congeners - Axys

MLA-010

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AXYS ANALYTICAL SERVICES LTD

ANALYTICAL METHOD FOR THE DETERMINATION OF:

209 PCB CONGENERS BY EPA METHOD 1668A[1] OR

EPA METHOD CBC01.2[2]

SCOPE

The analytical method described in this document determines the concentration of 209 PCB congeners in sediment, soil, sludge, tissue (including blood), aqueous samples, milk, solvent extracts, air samples and XAD-2 columns. Samples are spiked with $^{13}C_{12}$-labelled surrogate standards prior to analysis. Samples are extracted, the extracts cleaned up by column chromatography and analyzed by high-resolution gas chromatography with high-resolution mass spectrometric detection (HRGC/HRMS). The method is performed according to EPA Method 1668A, which is attached and considered to be part of this document. For PCB congener numbers 107, 108, and 109 an alternate procedure is offered to report these congeners in accordance with EPA Method 1668C specification.

This method allows for the determination of twelve PCB congeners designated as "toxic" by the World Health Organization[3].

The analysis of chlorinated pesticides, polybrominated diphenylethers, polychlorinated naphthalenes, and/or polybrominated biphenyls may also be carried out using the extraction procedures described in this document. The standards required, clean-up and instrumental analysis procedures and QA/QC specifications are described in AXYS method documents MLA-007[4], MLA-028[5], MLA-033[6,7] MLA-030[8] and MLA-026[9]. Additional details for these optional analyses are summarized in Appendix A.

The procedures documented in this method conform to EPA Method 1668A but may be modified in order to determine the concentrations of PCBs according to protocols described EPA Method CBC01.2. These modifications are described in Appendix D.

Approved by: _____ Date: 02-Jun-2011
John Cosgrove, President and Senior Technical Director

Approved by: _____ Date: 02-Jun-2011
Shea Hewage, Director of Operations

Approved by: _____ Date: 02-Jun-2011
Dale Hoover, QA Manager

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REFERENCES:

1. EPA Method 1668, Revision A - *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, with changes and corrections through to August 20, 2003.*

2. EPA Method CBC01.2 *Statement of Work (SOW) for Analysis of Chlorinated Biphenyl Congeners (CBCS),* December 2009.

3. Van den Berg et al. 1998. *Toxicity Equivalency Factors (TEF) for PCB's, PCDD's, and PCDF's for Humans and Wildlife. Environmental Health Perspective*. **106** (12): 775-792

4. AXYS Method Document MLA-007. *Analytical Method for the Determination of: Aroclors, Total PCBS, Chlorinated Pesticides, PCB Congeners, Coplanar PCBs, Toxaphene, Chlorobenzenes.*

5. AXYS Method Document MLA-028. *Organochlorine Pesticides by Isotope Dilution HRGC/HRMS.*

6. EPA Method 1614. *Brominated diphenyl ethers in water, soil, sediment, and tissue by HRGC/HRMS*

7. AXYS Method Document MLA-033. *Analytical Method for the Determination of Polybrominated Diphenylethers by EPA Method 1614*.

8. AXYS Method Document MLA-030 *Analytical Method for the Determination of Polychlorinated Naphthalenes (PCN) by High Resolution GC/MS.*

9. AXYS Method Document MLA-026. *Analytical Method for the Determination of Polybrominated Biphenyls (PBBs) by High Resolution GC/MS.*

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CHANGES FROM PREVIOUS REVISION or VERSION

The table below lists the details of the changes from revision 10 Version 01 of this document.

Page	Change Details
1, 2, 10, 105ff	Updated references to EPA method CBC01 to current CBC01.2
25	Section 3.5 "4.5% carbon/Celite": Corrected typo about instruction to mix before use.
32	Updated list of worksheets (FWO-)
50-51	Section 5.10: Harmonized blood extraction instructions with MLA-007 (and with current practice)
71	Table 6: Added column with quantification references.
107	Appendix D: Added clarification that hepta-PCBs according to EPA CBC01.2 are quantified against ^{13}C-PCB 188 and ^{13}C-PCB 189 only.
115	Appendix E – added alternate procedure for reporting PCB congener numbers 107, 108, 109 in accordance with EPA 1668C.

The table below lists the details of the changes from revision 9 of this document.

Page	Change Details
35	Section 5.2.2: Deleted requirement to add the toluene in the Dean-Stark receiver to the extract.
58	Section 5.12, point 1: Harmonized instructions for extract transfer with and without sodium sulfate. Deleted rinse instructions for PBDPE.
61	Section 6: Added three manual cleanup options. Clarified instructions for sulphur removal with activated copper. Added Figure 2 – "Flow Chart: Manual Florisil/Silica/Alumina Clean-up Column Sequence".
62	Section 6.2: Deleted sulphur removal instruction. Clarified that acid/base silica columns may be loaded using extract in any solvent.
62	Section 6.3: Clarified required extract volume (1 mL hexane). Deleted sulphur removal instruction.
63	Section 6.4: Clarified extract loading instructions and composition of rinse solvent.
64	Section 7: Added instructions of how to evaporate the extract after the final column cleanup.

The table below lists the details of the changes from revision 8 of this document.

Page	Change Details
	Introduction, section 2.0, Optional Analyses: Corrected "PCDD/F by EPA Superfund method DLM02.0" to read "PCBs by EPA method CBC01.0".
	Section 5.5.1: Allow the solution to equilibrate for at least 30 min after addition of surrogate standard solution.
	Sections 5.5.2 and 5.5.3: Added aqueous extraction option using magnetic stirring with dichloromethane.
	Section 5.9, Milk extraction: Changed surrogates to be added directly to the sample prior to the solvent instead of being added after the solvent (similarly as in MLA-007 and MLA-017). After drying with anh. sodium sulphate, added filtration through large fluted filter paper, evaporation and addition of cleanup standards. The following concentration and glass wool filtration steps omitted (similarly as in MLA-013).
	Section 5.13, SPE Disk Extraction: Deleted the SPE (solid phase extraction) procedure from this document.

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The table below lists the details of the changes from revision 7 of this document.

Page	Change Details
	General: Added references to EPA Method CBC01.0 and Appendix D to describe the analysis.
26	Section 4.1 Deleted requirement to spike field standard to OPR sample.
29	Revised the acceptance criterion for sum of PCBs in blank to 300 pg/sample. Included accepting higher concentrations if sample concentrations exceed 10x the blank.
52	Section 5.11 Correction: changed the layer to be discarded to "aqueous (top) layer"
59	Section 5.13.1 Revised procedure for the addition of surrogate standard.
65	Section 7 Revised microvialing procedure to clarify the different final extract volumes required for PCB, PCB/BDE and BDE analyses.
82	Section 10.0 Revised modification to Section 12.4.9 to include the correction of surrogate recoveries for lipid analysis.

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INTRODUCTION

1. ANALYTES OF INTEREST

This analytical method determines the concentrations of all 209 PCB congeners by high resolution GC/MS (HRGC/HRMS). PCBs are reported using the PCB numbering convention used in EPA Method 1668A; an alternate procedure for reporting PCB Congener Numbers 107, 108, 109 in accordance with EPA Method 1668C is offered.

The concentrations of some PCB congeners are reported as the sum of two or more congeners due to coelution of the congeners. The coeluting congeners are listed below.

COELUTING PCB CONGENERS
PCB 12, 13
PCB 30/18
PCB 20, 28
PCB 21, 33
PCB 26, 29
PCB 40, 41, 71
PCB 44, 47, 65
PCB 45, 51
PCB 49, 69
PCB 50, 53
PCB 59, 62, 75
PCB 61, 70, 74, 76
PCB 83, 99
PCB 85, 116, 117
PCB 86, 87, 97 108, 119, 125
PCB 88, 91
PCB 90, 101, 113
PCB 93, 95, 98, 100, 102
PCB 107, 124
PCB 110, 115
PCB 128, 166
PCB 129, 138, 160, 163
PCB 134, 143
PCB 135, 151, 154
PCB 139, 140
PCB 147, 149
PCB 156, 157[1]
PCB 153, 168
PCB 171, 173
PCB 183/185
PCB 180, 193
PCB 197/200
PCB 198, 199

[1] A second GC/MS analysis on a DB-1 column (30 m, 0.25 mm I.D., 0.25 μm film thickness) resolves the PCB 156/157 coeluting pair. This second analysis is performed upon request by the client.

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The concentrations of all other PCB congeners are reported as the concentration of individual congeners. The occasional formation of an interference during the extraction procedure and the high boiling point of the toluene may limit the quantification of PCBs 1 through 15.

A subset of congeners designated as "toxic" by the World Health Organization, can be reported with the associated toxic equivalents.

WHO TOXIC PCB CONGENERS	Congener Number
3,4,4',5-Tetrachlorobiphenyl (TeCB)	81
3,3',4,4'-TeCB	77
2,3,3',4,4'-Pentachlorobiphenyl (PeCB)	105
2,3,4,4',5-PeCB	114
2,3',4,4',5-PeCB	118
2',3,4,4',5-PeCB	123
3,3',4,4',5-PeCB	126
2,3,3',4,4',5-Hexachlorobiphenyl (HxCB)	156
2,3,3',4,4',5'-HxCB	157
2,3',4,4',5,5'-HxCB	167
3,3',4,4',5,5'-HxCB	169
2,3,3',4,4',5,5'-HpCB	189

Upon client request, any subset of the 209 PCB congeners may be reported.

2. OPTIONAL ANALYSES

The analysis of PCBs by EPA method CBC01.2 is carried out as described in this document, with the modifications described in Appendix D.

The analysis of chlorinated pesticides may be carried out concurrently with this method, using the extraction and cleanup procedures described in this document. The analyst is referred to Appendix A for details of carrying out this analysis.

The analysis of polybrominated diphenylethers is carried out using the extraction and cleanup procedures described in this method, as documented in AXYS Method Document MLA-033, *Analysis Method for the Determination of Polybrominated Diphenylethers by EPA Method 1614.*

The analysis of polybrominated biphenyls is carried out using the extraction and cleanup procedures described in this method, as documented in AXYS Method Document MLA-026,

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Analytical Method for the Determination of Polybrominated Biphenyls (PBBs) by High Resolution GC/MS.

The analysis of chloronaphthalenes is carried out using the extraction and cleanup procedures described in this method, as documented in AXYS Method Document MLA-030, *Analytical Method for the Determination of Polychlorinated Naphthalenes (PCN) by High Resolution GC/MS*.

3. CONTAMINATION AND INTERFERENCES

Contamination can come from all aspects of the analysis procedure. Care should be taken to ensure that all glassware is cleaned according to the specifications listed in Section 3.2. The Soxhlet apparatus (including thimble) must be pre-extracted with toluene for a minimum of two hours (three hours if brominated analytes are being determined) to avoid potential contamination from previous samples.

PCB congeners may be destroyed in the presence of acid and caution must be exercised to limit the exposure the sample and extract to acid.

Records of background levels within reference materials should be maintained in order to correct QC samples run within the same batch.

Further chromatographic cleanup may be carried out to resolve interferences with toxic PCB congeners. These procedures are described in Section 6.4 and Appendix B.

4. SAFETY

Refer to Section 5.0 of EPA Method 1668A for safety precautions when performing the analysis. For general safety procedures refer to SAF-001 *"Safety Manual"*. Refer to standard operating procedures SLA-079 *"Agricultural Hazard Protocols for Soils"* and SLA-082 *"Handling of Human Biohazardous Samples"* for procedures for handling of hazardous samples.

5. POLLUTION PREVENTION AND WASTE MANAGEMENT

AXYS Analytical Services Ltd. complies with all federal, provincial and municipal regulations governing waste management, including land disposal restrictions and sewage discharge regulations. AXYS' waste disposal procedures have been developed to comply with all pollution prevention regulations.

All standards are prepared in volumes consistent with volumes required by the method to minimize the disposal of standards.

Refer to AXYS standard operating procedure SAD-014 *"Sample Disposal"* for procedures for disposing of sample laboratory wastes.

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6. DEFINITIONS

Refer to AXYS document QDO-001 "QA/QC Policies and Procedures Manual" for definitions of terms used in this document.

7. METHOD PERFORMANCE

The method performance quality acceptance specifications have been verified at AXYS. Ongoing method performance is monitored by the measurement of percent surrogate recoveries in samples, percent analyte recovery in spiked matrix samples and certified reference samples, background analyte levels in procedural blanks, and relative percent difference between sample duplicates.

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ANALYSIS PROCEDURES

1. SAMPLE STORAGE AND PRESERVATION

All samples must be received and stored under the conditions presented in Table 1.

Table 1. Sample Storage, Sample Receipt and Hold Time Requirements

Matrix	Sample Size (per analysis)	Sample Container[1]	Condition upon Receipt	Storage Conditions[2]	Holding Time[3]	Extract Holding Time[4]	Preservation
Solid (Sediment/Soil/ Sludge)	10 g dry wt basis	Amber Glass	<4°C	<-10°C, dark	(1 year)	1 year	none required
Tissue	5-10 g wet	Glass or foil wrapped	<4°C	<-10°C, dark	(1 year)	1 year	none required
Blood	5-20 g	Glass	<4°C	<-10°C, dark	(1 year)	1 year	none required
Milk	50 - 150 g	Glass	<4°C	<-10°C, dark	(1 year)	1 year	none required
Aqueous (water/effluent/ wet sludge)	1 litre	Amber glass	0 – 4°C	4°C, dark	(1 year)	1 year	Add 80 mg of Na_2SO_3 if +ve for residual Cl
XAD-2 Columns	- one column - resin - particulate filter(s) - wound glass filter	-As is -Glass -Foil wrapped -Foil wrapped	0 – 4°C 0 – 4°C <4°C <4°C	4°C, dark 4ºC, dark <-10°C, dark <-10°C, dark	undefined undefined undefined undefined	undefined undefined undefined undefined	none required none required none required none required
Ambient Air	PUF & Filter(s)	Glass	<4°C	<-10°C, dark	undefined	undefined	none required
Sample Trains (Stack Gas)	Several Containers[5]	Glass	0 – 4°C	4°C	(30 days)	undefined	none required
Particulate Filter Papers	1 or more	Glass or foil wrapped	<4°C	<-10°C, dark	undefined	undefined	none required
Solvent Extract	1 Sample	Glass	<4°C	<-10°C, dark	undefined	undefined	none required

[1] All glass containers should be organically clean; i.e., baked, solvent-rinsed or purchased as certified 'clean'. All containers must be tightly sealed with screw cap lids (Teflon or foil-lined) to prevent loss of volatiles or contamination from volatiles. If samples are received in clear glass containers, they must be protected from the light. Samples for brominated analysis must be in amber glass containers.

[2] Storage temperatures quoted are nominal temperatures. Samples stored at a nominal temperature of 4ºC are permitted a variance of ±2°C.

[3] Hold times in brackets are from time of sampling. There is no evidence to indicate that properly stored samples are not stable for longer periods of time. Client requests for specific holding times or other method-specific holding times are adhered to.

[4] Holding times for extracts are from time of extraction.

[5] Refer to Section 5.11 for details of containers and contents.

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2. SAMPLE PREPARATION

Refer to the following standard operating procedures for details of laboratory techniques for sample preparation.

Document ID	Title
SLA-011	Compositing Samples
SLA-012	Dissection of Samples
SLA-013	Procedures for Homogenization of Solids and Tissues
SLA-014	Thawing Solid and Tissue Samples
SLA-015	Moisture Determination
SLA-043	Removing Sampling Media from Field Sampling Equipment
SLA-084	Preparation of Aqueous Samples for Extraction

2.1 Solids (Sediment/Soil) Samples

Allow a solid sample to thaw prior to homogenization and subsampling procedures following procedures in standard operating procedure SLA-014. Homogenize the entire sample before subsampling for analysis following standard operating procedure SLA-013.

Determine the percent moisture of an accurately weighed subsample (1 - 2 g) according to standard operating procedure SLA-015.

2.2 Tissues

Allow tissue samples to thaw prior to homogenization and subsampling procedures following procedures in standard operating procedure SLA-014. If the tissue is received as a homogenate, stir well with a spatula prior to subsampling. Otherwise, homogenize tissue samples following standard operating procedures. Samples must be extracted within 24 hours of thawing.

If required, determine the moisture content of an accurately weighed subsample (1 g) according to standard operating procedure SLA-015.

2.3 Aqueous Samples

Refer to the standard operating procedures SLA-084, *Preparation of Aqueous Samples for Extraction*, for sample preparation procedures.

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2.4 XAD-2 Columns and Filters

Refer to the following standard operating procedure SLA-043, *Removing Sampling Media from Field Sampling Equipment*, for details of removing the resin from the column. Filters are partially thawed prior to extraction.

2.5 Whole Blood/Blood Serum/Blood Plasma

Allow blood samples to thaw prior to subsampling for analysis following procedures in standard operating procedure SLA-014. Homogenize the sample by shaking well. Samples must be extracted within 24 hours of thawing.

2.6 Milk

Allow a milk sample to thaw prior to homogenization and subsampling following procedures in standard operating procedure SLA-014. Homogenize the sample by shaking well. Samples must be extracted within 24 hours of thawing.

2.7 Ambient Air (PUF and Filter)

If received in the sampling apparatus, use solvent rinsed forceps to withdraw the PUF from the sampler. The associated filter is typically received in a Petri dish or wrapped in foil. Use solvent rinsed forceps to handle the filter.

2.8 Sludge

Homogenize dry sludge according to standard operating procedure SLA-013. Consult with the Lab Supervisor for the treatment of wet sludge samples.

Determine the percent moisture of an accurately weighed subsample (1 - 2 g) of dry sludge according to standard operating procedure SLA-015.

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3. MATERIALS AND REAGENTS

Refer to the following standard operating procedures:

Document ID	Title
SLA-001	Cleaning of Laboratory Items
SLA-002	Glassware and Laboratory Equipment Proofs
SLA-009	Preparation of Standards
SLA-018	Solvent Rinsing of Glassware for Organic Analysis
SLA-019	Solvent Proofs
SLA-022	Use of Drying Ovens and Muffle Furnace
SLA-023	Use of Balances
SLA-036	Cleaning of GC/MS and GC/ECD Microvial Caps
SLA-041	Reagent Preparation
SLA-044	Activation of Copper Foil, Turnings and Powder
SLA-093	Baking of Anhydrous Sodium Sulphate
SQA-003	Standard Solution Validation
SQA-009	Storage and Control of Analytical Standards

3.1 Equipment List

Extraction

Separatory funnels (125 mL, 500 mL, 1000 mL)
Erlenmeyer flasks (250 mL, 500 mL, 1000 mL)
Round bottom flasks (100 mL, 250 mL, 500 mL, 1000 mL))
Beakers
Graduated Cylinders
Class A volumetric flasks, pipettes
Disposable pipettes
Disposable centrifuge tubes (15 mL)
Hamilton Syringes (5 µL, 25 µL, 50 µL, 100 µL, 250 µL, 1000 µL)
Autosampler vials (amber glass, 800 µL)
Chromatography columns (1 cm x 12 cm, 3 cm x 50 cm, 1 cm x 25 cm)
Silanized glass wool
Filter paper – Ahlstrom or equivalent
PTFE tape
Aluminum Foil
Spatula – aluminum
Disposable spoons
Rotary evaporator
Magnetic stirring plate, with pre-cleaned PTFE coated magnetic stirring bars
Millipore Filtration Apparatus
Soxhlet apparatus (pre-cleaned) with heating mantle

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Soxhlet/Dean-Stark apparatus (pre-cleaned)
Water bath capable of maintaining up to 50ºC
Balance – Top loading and analytical (2-, 3-, & 4-place)
Glassware ovens
Drying ovens
Muffle furnace
Nitrogen source with manifold apparatus

Instruments

Hewlett Packard 6890 Series Gas Chromatograph or equivalent;
Micromass/VG Autospec Ultima mass spectrometer or equivalent;
GC Columns: SPB-Octyl (30 m, 0.25 mm i.d., 0.25 µm film thickness)
DB-1 (30 m, 0.25 mm i.d., 0.25 µm film thickness)

3.2 Glassware

All glassware used in the preparation of reagents and in the analytical procedure must be organically clean. Glassware must be washed and baked using standard operating procedures. Baked glassware must be solvent rinsed with toluene and hexane. The Soxhlet apparatus, including thimble, must be or pre-cleaned by Soxhlet extraction with toluene for a minimum of 2 hours for PCB analyses (three hours if brominated analytes are determined).

If baked glassware is not available, glassware must be washed and water, rinsed with solvent rinsed following the procedures described in standard operating procedure SLA-018.

3.3 Preparation of Standard Solutions

The analysis of PCB congeners by EPA Method 1668A requires the use of the surrogate, cleanup, recovery (internal), authentic spike and calibration solutions described in Section 7.7 - 7.16 of EPA Method 1668A. Stock solutions are prepared from commercially available individual components. Working standards are prepared by diluting stock solutions. The Standard Data Sheets describe the details of the preparation and composition of all stock and working standard solutions used and the validated concentrations of all components.

3.3.1 Surrogate Standard Solution

Prepare the surrogate standard stock solution as described in EPA Method 1668A, Section 7.9.1. Modify the preparation of the surrogate spiking solution (Section 7.12) so that the concentration of the labelled compounds is 100 ng/mL. The volume of the aliquot used is adjusted so that the same absolute amount of standard, as described in EPA Method 1668A is added.

Prior to extraction procedures, each sample and QC sample is spiked with an aliquot of surrogate standard solution, containing a suite of $^{13}C_{12}$-labelled surrogate standards. Typically, an aliquot of 20 µL is added.

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For aqueous samples, the surrogate standard is prepared immediately prior to filtration and extraction procedures by diluting an aliquot of the stock surrogate standard (1000 ng/mL of each surrogate) in a volume of acetone, to make a solution that is 2 ng/mL of each surrogate. A 1 mL aliquot is added to each aqueous sample. Sufficient solution to spike an entire analysis batch, including QC sample, is prepared.

The amount of surrogate added is dependent upon sample size, final extract volume and concentration of analytes in the sample and may be adjusted accordingly. The Batch List indicates the name of the surrogate standard solution used and the volume added to each sample. The suite of surrogates, the nominal concentration of each surrogate in the standard solution and the amount added to each sample are presented in Table 2.

3.3.2 Cleanup Standard Solution

Prepare the cleanup standard stock solution as described in EPA Method 1668A, Section 7.9.2. Modify the preparation of the cleanup standard spiking solution (Section 7.13, EPA Method 1668A) so that the concentration of the labelled compounds is 100 ng/mL.

Just prior to chromatographic cleanup each extract is spiked with an aliquot of cleanup standard solution, containing $^{13}C_{12}$-labelled standards. Typically an aliquot of 20 µL is added. The Batch List indicates the name of the cleanup standard solution used and the volume added to each sample. The suite of standards used, the nominal concentration of each standard in the standard solution and the amount added to each sample are presented in Table 2.

3.3.3 Recovery (Internal) Standard Solution

Prepare the recovery standard stock solution as described in EPA Method 1668A, Section 7.9.3. Prepare the diluted internal (recovery) standard spiking solution as described in EPA Method 1668A, Section 7.14.

Prior to instrumental analysis, cleaned up extracts are spiked with $^{13}C_{12}$-labelled recovery (internal) standards prior to instrumental analyses. Typically, an aliquot of 5 µL of recovery standard solution is added. The Batch List indicates the name of the recovery standard solution used and the volume added to each sample. The suite of recovery standards, the nominal concentration of each standard in the solution and the amount added to each sample are presented in Table 2.

3.3.4 Calibration Solutions

A series of calibration solutions (CS-0.2 through CS-5) containing native analytes, labelled surrogate standards and labelled recovery standards are used to establish the linearity of the analytical instrument. The concentration of the native analytes in the solutions varies to encompass the working range of the instrument, while the concentration of the surrogate recovery and cleanup standards remain constant. The composition of the solutions and the nominal concentration of each component are presented in Table 3.

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CS-1 through CS-5 and CS-0.2

Prepare six calibration solutions as described in EPA Method 1668A, Section 7.10.1, at the concentrations listed in Table 5 of the EPA method. These solutions are used to establish the linearity of the GC/MS.

Calibration Solution for 209 Congeners

Prepare a calibration solution containing all 209 PCB congeners (unlabelled), the surrogate standards and the recovery standards, as described in EPA Method 1668A, Section 7.10.2, and where appropriate, the relevant field standards. This single calibration solution is used to determine the relative response factors and retention times of the PCB congeners not in the calibration solutions and is used as the calibration verification (CAL/VER) solution, analyzed at least every twelve hours to verify GC/MS performance and calibration. The nominal concentration of the unlabelled congeners in this solution is: mono-tri-CB: 25 ng/mL; tetra-hp-CB: 50 ng/mL; octa-nona-CB: 75 ng/mL.

3.3.5 Authentic Spike Solution (Precision and Recovery Standard, PAR)

Prepare the authentic spiking solution as described in EPA Method 1668A, Section 7.11. This solution is used to prepare the initial precision and recovery (IPR) samples and ongoing performance and recovery (OPR) samples. Typically an aliquot of 1 mL is added to every OPR and IPR sample. The Batch List indicates the name of the PAR standard solution used and the volume added to each sample. The composition of the solution, the nominal concentration of each component and amount added to the sample are presented in Table 2.

3.3.6 Field Surrogate Solutions

If required, a field surrogate standard solution or sampling media spiked with a field surrogate solution is provided to a client. The solution contains $^{13}C_{12}$-labelled PCBs. The Project Manager, in consultation with the client, determines the components in the solution and the appropriate concentration. The most typical field surrogates are $^{13}C_{12}$-PCB 31, $^{13}C_{12}$-PCB 95 and $^{13}C_{12}$-PCB 153. Field surrogate solutions are prepared under the direction of the Standards Chemist, according to instructions from the Project Manager.

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Table 2. Concentration of PCB Standard Solutions - HRGC/HRMS Analysis

Compound Name	Congener No (1)	Conc'n of Stock Solution (Aqueous samples)	Concentration of Standard Solution	Typical Amount Spiked into Sample
Surrogate Std Solution				
$^{13}C_{12}$-2-MoCB	1L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-4-MoCB	3L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2'-DiCB	4L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-4,4'-DiCB	15L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',6-TriCB	19L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-3,4,4'-TriCB	37L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-3,4,4',5-TeCB	81L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,3,4,4',5-PeCB*	114L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB	208L	1000 ng/mL	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB	209L	1000 ng/mL	100 ng/mL	2000 pg
Cleanup Std Solution				
$^{13}C_{12}$-2,4,4'-TriCB	28L	-	100 ng/mL	2000 pg
$^{13}C_{12}$-2,3,3',5,5'- PeCB	111L	-	100 ng/mL	2000 pg
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	-	100 ng/mL	2000 pg
Recovery Std Solution				
$^{13}C_{12}$-2,5-DiCB	9L	-	400 ng/mL	2000 pg
$^{13}C_{12}$-2,2',5,5'-TeCB	52L	-	400 ng/mL	2000 pg
$^{13}C_{12}$-2,2',4',5,5'-PeCB	101L	-	400 ng/mL	2000 pg
$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L	-	400 ng/mL	2000 pg
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L	-	400 ng/mL	2000 pg

(1) Suffix "L" designates labelled compound

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Table 2 Cont'd

Compound Name	Congener No.	Concentration of Standard Solution	Typical Amount Spiked into Sample
Authentic Spike Solution			
2-MoCB	1	1 ng/mL	1000 pg
4-MoCB	3	1 ng/mL	1000 pg
2,2'-DiCB	4	1 ng/mL	1000 pg
4,4'-DiCB	15	1 ng/mL	1000 pg
2,2',6-TriCB	19	1 ng/mL	1000 pg
2,3,5-TriCB	23	1 ng/mL	1000 pg
2',3,5-TriCB	34	1 ng/mL	1000 pg
3,4,4'-TriCB	37	1 ng/mL	1000 pg
2,2',6,6'-TeCB	54	1 ng/mL	1000 pg
3,3',4,4'-TeCB	77	1 ng/mL	1000 pg
3,4,4',5-TeCB	81	1 ng/mL	1000 pg
2,2',4,6,6'-PeCB	104	1 ng/mL	1000 pg
2,3,3',4,4'-PeCB	105	1 ng/mL	1000 pg
2,3,4,4',5-PeCB	114	1 ng/mL	1000 pg
2,3',4,4',5-PeCB	118	1 ng/mL	1000 pg
2',3,4,4',5-PeCB	123	1 ng/mL	1000 pg
3,3',4,4',5-PeCB	126	1 ng/mL	1000 pg
2,2',4,4',6,6'-HxCB	155	1 ng/mL	1000 pg
2,3,3',4,4',5-HxCB	156	1 ng/mL	1000 pg
2,3,3',4,4',5'-HxCB	157	1 ng/mL	1000 pg
2,3',4,4',5,5'-HxCB	167	1 ng/mL	1000 pg
2-3,3',4,4',5,5'-HxCB	169	1 ng/mL	1000 pg
2,2',3,3',4,4',5-HpCB	170	1 ng/mL	1000 pg
2,2',3,4,4',5,5'-HpCB	180	1 ng/mL	1000 pg
2,2',3,4,4',5,6'-HpCB	182	1 ng/mL	1000 pg
2,2',3,4',5,5',6-HpCB	187	1 ng/mL	1000 pg
2,2',3,4',5,6,6'-HpCB	188	1 ng/mL	1000 pg
2,3,3',4,4',5,5'-HpCB	189	1 ng/mL	1000 pg
2,2',3,3',5,5',6,6'-OcCB	202	1 ng/mL	1000 pg
2,3,3',4,4',5,5',6-OcCB	205	1 ng/mL	1000 pg
2,2',3,3',4,4',5,5',6-NoCB	206	1 ng/mL	1000 pg
2,2',3,3',4,5,5',6,6'-NoCB	208	1 ng/mL	1000 pg
2,2',3,3',4,4',5,5',6,6'-DeCB	209	1 ng/mL	1000 pg

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Table 3. Concentration of PCB Calibration Solutions - HRGC/HRMS Analysis

CB CONGENER	Congener No.	Solution concentration (ng/mL)					
		CS-0.2 (Hi sens)[1]	CS-1	CS-2	CS-3 (CAL/VER)	CS-4	CS-5
Native Compounds							
2-MoCB	1	0.2	1.0	5.0	50	400	2000
4-MoCB	3	0.2	1.0	5.0	50	400	2000
2,2'-DiCB	4	0.2	1.0	5.0	50	400	2000
4,4'-DiCB	15	0.2	1.0	5.0	50	400	2000
2,2',6-TriCB	19	0.2	1.0	5.0	50	400	2000
2,3,5-TriCB	23	0.2	1.0	5.0	50	400	2000
2',3,5-TriCB	34	0.2	1.0	5.0	50	400	2000
3,4,4'-TriCB	37	0.2	1.0	5.0	50	400	2000
2,2',6,6'-TeCB	54	0.2	1.0	5.0	50	400	2000
3,3',4,4'-TeCB	77	0.2	1.0	5.0	50	400	2000
3,4,4',5-TeCB	81	0.2	1.0	5.0	50	400	2000
2,2',4,6,6'-PeCB	104	0.2	1.0	5.0	50	400	2000
2,3,3',4,4'-PeCB	105	0.2	1.0	5.0	50	400	2000
2,3,4,4',5-PeCB	114	0.2	1.0	5.0	50	400	2000
2,3',4,4',5-PeCB	118	0.2	1.0	5.0	50	400	2000
2',3,4,4',5-PeCB	123	0.2	1.0	5.0	50	400	2000
3,3',4,4',5-PeCB	126	0.2	1.0	5.0	50	400	2000
2,2',4,4',6,6'-HxCB	155	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	156	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5'-HxCB	157	0.2	1.0	5.0	50	400	2000
2,3',4,4',5,5'-HxCB	167	0.2	1.0	5.0	50	400	2000
3,3',4,4',5,5'-HxCB	169	0.2	1.0	5.0	50	400	2000
2,2',3,3'4,4',5-HpCB	170	0.2	1.0	5.0	50	400	2000
2,2',3,4,4',5,5'-HpCB	180	0.2	1.0	5.0	50	400	2000
2,2',3,4,4',5,6'-HpCB	182	0.2	1.0	5.0	50	400	2000
2,2',3,4',5,5',6-HpCB	187	0.2	1.0	5.0	50	400	2000
2,2',3,4',5,6,6'-HpCB	188	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5,5'-HpCB	189	0.2	1.0	5.0	50	400	2000
2,2',3,3',5,5',6,6'-OcCB	202	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5,5',6-OcCB	205	0.2	1.0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6-NoCB	206	0.2	1.0	5.0	50	400	2000
2,2',3,3',4,5,5',6,6'-NoCB	208	0.2	1.0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6,6'-DeCB	209	0.2	1.0	5.0	50	400	2000
Surrogate Standards							
$^{13}C_{12}$-2-MoCB	1L[2]	100	100	100	100	100	100
$^{13}C_{12}$-4-MoCB	3L	100	100	100	100	100	100
$^{13}C_{12}$-2,2'-DiCB	4L	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DiCB	15L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4'-TriCB	37L	100	100	100	100	100	100

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Table 3 cont'd

CB CONGENER	Congener No.	Solution concentration (ng/mL)					
		CS-0.2 (Hi sens)[1]	CS-1	CS-2	CS-3 (CAL/VER)	CS-4	CS-5
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	100	100	100	100	100
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB	208L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	100	100	100	100	100
Cleanup Standards							
$^{13}C_{12}$-2,4,4'-TriCB	28L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	100	100	100	100	100
Recovery Standards							
$^{13}C_{12}$-2,5-DiCB	9L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',5,5'-TeCB	52L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4',5,5'-PeCB	101L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L	100	100	100	100	100	100

[1] Additional concentration used for calibration of high sensitivity HRGC/HRMS systems.
[2] Suffix "L" indicates labelled compound.

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3.4 Preparation of Reagents

Activated Copper is prepared as described in the standard operating procedure SLA-044.

Ammonium Sulphate ($(NH_4)_2SO_4$, Saturated) is prepared by dissolving ammonium sulphate (700 g) in ultra pure water (1 L). The solution is extracted by shaking twice with dichloromethane (2 x 100 L) and once with hexane (100 mL).

Anhydrous Sodium Sulphate (Na_2SO_4, granular 12-60 mesh, J.T. Baker, or demonstrated equivalent approved for use by Operations Management and QA) is cleaned by baking at a minimum of 300°C as described in SLA-093.

Glass Fibre Filters (Ahlstrom, A/E glass or equivalent) are cleaned by baking overnight at a minimum of 300°C.

Glass Fibre Filter Bed is prepared and cleaned by grinding glass fibre filters in a blender and heating overnight at a minimum of 300°C. The cleaned filter bed is stored in a covered jar.

Hydrochloric Acid (conc, Seastar Chemicals, quartz distilled) is used as received.

Hydrochloric Acid (1 M) is prepared by adding HCL (100 mL, conc,) to ultra pure water (1 L).

Potassium Hydroxide (KOH, 1M) is prepared by dissolving potassium hydroxide pellets (56 g, Fisher, certified) in ethanol (1000 mL).

Reagent Sand (Aldrich Chemicals, white quartz, -50 +70 mesh) is proofed by lot prior to use and may be cleaned by Soxhlet extraction with dichloromethane for 16 hours as necessary. The clean sand is stored in a clean glass jar

Ultra Pure Water (Seastar Chemicals (contaminant-free) or equivalent) is used as received.

Silanized Glass Wool is stored in a clean amber jar and is rinsed twice with toluene and twice with hexane prior to use.

Sodium Hydroxide (NaOH, 1 M) is prepared by dissolving sodium hydroxide pellets (AR grade, 40 g) in ultra pure water (1 L). The solution is extracted by shaking with dichloromethane (2 x 100 mL) and once with hexane (100 mL). The solution is stored in an amber jar with PTFE lined lid. Typically 3 L is prepared.

Solvents are high purity, distilled in glass solvents, either HPLC grade or pesticide residue grade. Each lot number of solvent must be checked for impurities by performing a solvent proof prior to use. All solvent mixtures used in the analyses are made by mixing the appropriate proportions of solvent on a volume:volume basis.

Soxhlet Thimbles are soaked in Contrad 70 cleaning solution, rinsed well with water and are baked overnight at a minimum of 300°C.

Sulphuric Acid (conc, Seastar Chemicals, quartz distilled) is used as received.

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3.5 Preparation of Chromatography Materials

Refer to the following standard operating procedures:

Q-Pulse ID	Title
SCH-001	Activation/Deactivation Procedures
SCH-002	Column Packing Procedures
SCH-003	Column Cutpoint Procedures
SCH-004	Layered Silica Gel Preparation
SCH-005	Carbon/Celite Column Preparation
SCH-006	Preparation, Use and Maintenance of Biobead Columns

Alumina (Fisher Basic Brockman Activity 1, 60-325 mesh) is baked for a minimum of 8 hours at 450°C and deactivated with ultra pure water (typically 1.0% w/w) as described in SCH-001. The degree of activation may vary depending upon the batch of alumina. Deactivated alumina is stored under nitrogen in a stoppered flask and allowed to equilibrate 24 hours. Cutpoints are determined prior to use (SCH-003).

Biobeads (Bio-Rad, SX-3, 200-400 mesh) are prepared by soaking the beads for 24 hours in 1:1 dichloromethane:hexane prior to column preparation as described in SCH-006.

4.5% Carbon/Celite Mixture is prepared by adding activated carbon (AX-21, Anderson Co., 4.5 g, sieved (1 mm mesh)) to Celite 545 (95.5 g) and shaking until uniform as described in SCH-005. The mixture is stored in a stoppered glass reagent bottle. The mixture must be well mixed by shaking before use. The cutpoints are determined prior to use (SCH-003).

2.1% Florisil (Supelco or US Silica, Pesticide grade, 60-100 mesh) is activated at 450°C for a minimum of 8 hours and deactivated with ultra pure water (typically 2.1% by weight) as described in SCH-001. The degree of activation may vary depending upon the batch of Florisil. Florisil is stored under nitrogen in a stoppered flask and allowed to equilibrate for 24 hours. The cutpoints are determined prior to use (SCH-003).

Silica Gel (Mallinckrodt, SilicAR 100-200 mesh) is heated for a minimum of 8 hours at 450°C and stored, under nitrogen, in a stoppered reagent jar as described in SCH-001.

28% NaOH Basic Silica is prepared by adding sodium hydroxide solution (equivalent to 28% of final weight of basic silica) to baked silica and agitating until homogeneous, as described in SCH-004. The silica is stored in a stoppered glass reagent bottle.

22% H_2SO_4 Acidic Silica is prepared by adding sulfuric acid (conc, equivalent to 22% of the final weight of acidified silica) to baked silica and agitating until homogeneous as described in SCH-004 The silica is stored in a stoppered glass reagent bottle.

44% H_2SO_4 Acidic Silica is prepared by adding sulfuric acid (conc., equivalent to 44% of final weight of acidified silica) to baked silica and agitating until homogenous, as described in

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SCH-004. The silica is stored in a stoppered glass reagent bottle.

3.6 Preparation of Chromatography Columns

3.6.1 Alumina Column

Basic alumina (6 g, 1% deactivated) is dry packed into hexane in a glass chromatography column (1 cm x 12 cm) as described in SCH-002. The column is capped with a 1 cm bed of anhydrous powdered sodium sulphate and eluted with hexane (10 mL).

3.6.2 Biobeads SX-3 Column

A Biobeads (SX-3, 60 g) column is prepared and cutpoints determined as described in SCH-006. The column is cleaned with 20% methanol:dichloromethane and 1:1 dichloromethane:hexane prior to use, as described in SCH-006.

3.6.3 4.5% Carbon/Celite Column

A carbon/Celite column is prepared by packing 4.5% carbon/Celite mixture (0.22 g) into a 9" Pasteur pipette that is fitted with a filter paper disc, as described in SCH-005. The column is pre-eluted with toluene (15 mL) and hexane (15 mL), ensuring all the toluene has been eluted from the column.

3.6.4 Florisil Column

Deactivated Florisil (8 g, 2.1% deactivated) is dry packed in hexane into a glass chromatography column (1 cm x 25 cm with 250 mL reservoir)as described in SCH-002. The column is, capped with a 1 cm layer of anhydrous sodium sulphate (powder) and flushed with hexane (~40 mL).

3.6.5 Layered Acid/Base Silica Column

A silica chromatography column (1 cm O.D. x 25 cm long) is prepared by sequentially dry-packing in hexane the following reagents, as described in SCH-004:

neutral silica (0.5 g), silica (28% NaOH, 2.0 g), neutral silica (0.5 g), silica (44% H_2SO_4, 4 g), silica (22% H_2SO_4, 2.0 g) and neutral silica (1.0 g).

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4. QUALITY ASSURANCE/QUALITY CONTROL

Refer to the following standard operating procedure:

Q-Pulse ID	Title
SLA-016	Preparation of QA/QC Samples

4.1 Quality Control Samples

All samples are analyzed in batches. The composition of a batch is detailed on a Batch List, including the method number, quality control samples and standards to use.

- Batch Size - Each batch consists of up to twenty test samples and additional QC samples.

- Blanks - One procedural blank is analyzed with each batch. The procedural blank is prepared by spiking an aliquot of the surrogate standard solution into a clean matrix. If required, an aliquot of field surrogate spiking solution is also added to the blank sample. The clean matrices available for preparing procedural blanks are described in SLA-016. The procedural blank is extracted and analyzed using the same procedures as the test samples in the analysis batch.

  Note: For stationary source air samples, the extraction procedure for the blank (using a filter and XAD-2 resin as the matrix) starts with the acidification of the filter. The surrogate standard solution is spiked into the XAD-2 when it is in the Soxhlet body.

- Initial Precision and Accuracy (IPR) is demonstrated when commencing the method or when significant changes have been made to the method. The IPR is carried out by the analysis of four spiked reference samples (prepared as described below).

- On-going Precision and Recovery (OPR) is demonstrated by the analysis of a spiked reference matrix (SPM) analyzed with each batch. The OPR sample is prepared by spiking an aliquot of the authentic spiking standard solution into an accurately weighed in-house reference matrix (known to contain low background levels of target analytes). The matrix sample is spiked with an aliquot of surrogate standard solution and extracted following procedures in Section 5 of this method. The OPR matrix to be analyzed is assigned to the analyst when the batch is assigned.

  Note: For stationary source air samples, the reference sample (a clean filter ad XAD-2 resin) is spiked with an aliquot of authentic spiking standard prior to extraction. The extraction procedure starts with the acidification of the filter. The surrogate standard solution is spiked into the XAD-2 when it is in the Soxhlet body.

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- Reference Samples – Certified reference materials are commercially available and used to validate and periodically check the methods. The type of reference material to be analyzed is assigned to the analyst when the batch is assigned.

- Duplicates - A duplicate sample is analyzed with analysis batches containing 7-20 test samples, or as required by contract, provided sufficient sample is available. For some matrices (XAD-2 columns, filters, air samples) only field duplicates (if available) can be analyzed.

4.2 QA/QC Criteria

The acceptance ranges for the recovery of target analytes in the CAL/VER solution, the IPR and the OPR samples are presented in Table 4. Elements of the QA/QC program at AXYS Analytical Services are documented in the most recent revision of QDO-001 "AXYS Analytical QA/QC Policies and Procedures Manual".

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Table 4. QC Acceptance Criteria for Chlorinated Biphenyls in CAL/VER, IPR, OPR, and Samples[1]

Congener	Cong. No.[2]	Test conc ng/mL	CAL/VER (%)		IPR (%)		OPR (%)		Labelled compound recovery in samples	
			Warning Limit	Acceptance Limit	RSD	X	Warning Limit	Acceptance Limit (%)	Warning Limit	Acceptance Limit
2-MoCB	1	50	75-125	70-130	40	60-140	70-130	50-150	-	-
4-MoCB	3	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2'-DiCB	4	50	75-125	70-130	40	60-140	70-130	50-150	-	-
4,4'-DiCB	15	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2'6-TrCB	19	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,4,4'-TrCB	37	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2'6,6'TeCB	54	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4'-TeCB	77	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,4,4',5-TeCB	81	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',4,6,6'-PeCB	104	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4'-PeCB	105	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,4,4',5-PeCB	114	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3',4,4',5-PeCB	118	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2',3,4,4',5-PeCB	123	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4',5-PeCB	126	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',4,4',6,6'-HxCB	155	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5-HxCB[3]	156	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5'-HxCB[3]	157	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3',4,4',5,5'-HxCB	167	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4',5,5'-HxCB	169	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,4',5,6,6'-HpCB	188	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5,5'-HpCB	189	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3',5,5',6,6'-OcCB	202	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5,5',6-OcCB	205	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3',4,4',5,5',6-NoCB	206	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3,'4,5,5',6,6'-NoCB	208	50	75-125	70-130	40	60-140	70-130	50-150	-	-
DeCB	209	50	75-125	70-130	40	60-140	70-130	50-150	-	-
Labelled Compounds										
$^{13}C_{12}$-2-MoCB	1L	100	65-135	50-150	50	20-135	15-140	15-140	15-130	15-150
$^{13}C_{12}$-4-MoCB	3L	100	65-135	50-150	50	20-135	15-140	15-140	15-130	15-150
$^{13}C_{12}$-2,2'-DiCB	4L	100	65-135	50-150	50	35-135	30-140	30-140	25-130	25-150
$^{13}C_{12}$-4,4'-DiCB	15L	100	65-135	50-150	50	35-135	30-140	30-140	25-130	25-150
$^{13}C_{12}$-2,2',6-TrCB	19L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-3,3',4,4'-TCB	77L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4',5-HxCB[3]	156L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB[3]	157L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150

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Congener	Cong. No.[2]	Test conc ng/mL	CAL/VER (%)		IPR (%)		OPR (%)		Labelled compound recovery in samples	
			Warning Limit	Acceptance Limit	RSD	X	Warning Limit	Acceptance Limit (%)	Warning Limit	Acceptance Limit
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB	189L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB	208L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
Cleanup Standard										
$^{13}C_{12}$-2,4,4'-TriCB	28L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135

1. QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume
2. Suffix "L" indicates labelled compound.
3. PCBs 156 and 157 are tested as the sum of two concentrations

QC Parameter	Specification
Analysis Duplicate	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL.)[1]
Procedural Blank	Analyte concentrations in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be less than 2 pg/congener/sample, and concentrations of PCB congeners 156, 157, 167 and 189 must be less than 10 pg/congener/sample. Concentrations of all other individual PCB congeners or coelutions must be less than 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be less than 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times the blank levels.
Sample Specific Detection Limit	Typical sample specific detection limits, determined from chromatographic noise, are in the range of 0.5 to 2.0 pg.
Initial Calibration	For 6-point calibration, a relative standard deviation of the RRF's ≤20% for all compounds Ion ratios for all congeners must be within ±15% of theoretical for CS 0.2. (See Section 8.1.1 for details) Minimum S:N ratio 10:1 for all calibration standards. For CS0.2, S:N ratio may be as low as 3:1 for di-PCBs and nona-PCBs.
Continuing CAL VER	Refer to Table 4 above.
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Ion Ratios	Ion ratios must fall within ±15% of the theoretical values for positive identification of all targets in the calibration standards and samples.
Sensitivity	Minimum S:N ratio 10:1 for all calibration standards. For CS0.2, S:N ratio may be as low as 3:1. for di-PCBs and nona-PCBs.

1. Duplicate criterion is a guideline; final assessment depends upon sample characteristics, overall batch QC and on-going lab performance.

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5. EXTRACTION PROCEDURES

The extraction procedures described in this section are used for the analyses of samples by EPA Method 1668A.

An analysis batch is assigned to an analyst. The samples to be analyzed, the batch QC samples, the name and volume of the surrogate, cleanup, recovery and authentic standards required, and any additional information concerning the analysis are documented on a Batch List given to an analyst. Refer to SOP SLA-033 for details of assigning analysis batches.

Each analyst performs the extraction procedure according to the following written extraction procedures and completes an analysis worksheet (refer to table of available worksheets) for each sample during the sample extraction. The analyst is referred to the following Standard Operating Procedures for details of routine laboratory techniques.

Q-Pulse ID	Title
SLA-003	Sample Receipt and Login
SLA-004	Sample Control Procedures
SLA-005	Use and Maintenance of Rotary Evaporation Equipment
SLA-006	Nitrogen Blowdown Concentration Technique
SLA-008	Preparing Extracts for Instrumental Analysis
SLA-017	Spiking Procedures
SLA-020	Gravimetric Lipid Determination by Weight of Extract
SLA-023	Use of Balances
SLA-027	Completing a Worksheet
SLA-028	Independent Gravimetric Determination of Lipid Content
SLA-030	Micro Lipid Determination for Human Blood Analysis
SLA-033	Procedures for Making an Analysis Batch
SLA-045	Removal of Sulphur From Extracts Using Activated Copper
SLA-067	Use of Nitrogen System
SLA-072	Computer Preparation of Labels
SLA-078	Spike Witness Program
SLA-079	Agricultural Hazard Protocols for Soils
SLA-081	Labelling Protocols and Sample Extract Transfer Procedures
SLA-082	Handling of Human Biohazardous Samples
SLA-084	Preparation of Aqueous Samples for Extraction
SLA-085	Subsampling Procedures for Solids and Tissues
SLA-087	Transferring an Ampouled Standard to a Reacti-vial
SLA-092	Determination of Suspended Solids Content in Aqueous Samples
SLA-095	Use and Maintenance of the Syncore Analyst Evaporator

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The following table lists the worksheets used for sample extraction and cleanup.

Number	Name
FWO-305	Sample Labeling Information
FWO-306	Sample Weight and Moisture
FWO-307	Aqueous Samples
FWO-308	Lipid Sheet
FWO-309	Standards Spiking into C
FWO-310	Sample Spiking Sheet
FWO-311	Extract Splitting
FWO-312	Cleanup Information
FWO-314	Notes
FWO-316	Suspended Solids
FWO-317	Extraction – Blood, Milk, Nonylphenols
FWO-318	Extraction – Sample Trains, Resin Acids, Multi-Residue Pesticides
FWO-319	Extraction – Ash, Acid extractable Pesticides
FWO-330	Rotovap Record Sheet
FWO-331	Dean-Stark Extraction Worksheet

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5.0.1 Extract Handling Procedures

To minimize the loss of the most volatile PCBs, sample extracts should be handled in the following manner:

a) Extracts or column eluates that are 10 mL or larger must be covered with clean aluminum foil for overnight storage at room temperature.
b) Extracts, at volumes <10 mL must be stored at 4°C (refrigerator or cooler) in centrifuge tubes that are capped and covered with foil.

Extract Evaporation Procedures

A Syncore Analyst evaporator may be used to concentrate extracts, as described in standard operating procedure SLA-095, instead of a rotary evaporator or Kuderna-Danish concentrator.

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5.1 Soxhlet Extraction of Solids

The solid Soxhlet extraction in dichloromethane, described below, allows for the determination of all 209 PCB congeners. The extraction procedure is applicable to the matrices and sample size listed below. Alternately, solids my be extracted by a Soxhlet/Dean-Stark procedure (Section 5.2)

Matrix	Sample Size
Sediments/Soil/Sludge	10 g dry weight

The size of the Soxhlet apparatus used for the extraction of sediment, soil and sludge samples is dependent upon the amount of sample used to obtain the equivalent of 10 g dry weight. Use a larger Soxhlet apparatus for sample sizes larger than 25 g wet or with greater than 60% moisture content. Adjust the amount of silica and solvent volumes accordingly.

5.1.1 Sample Preparation

Accurately weigh to a minimum of 3 significant figures, a wet sample (an amount equivalent to 10 g dry) into a beaker and add anhydrous sodium sulphate (75-100 g) to the sample. Mix well by stirring with a clean spatula, cover with clean aluminum foil and allow the mixture to dry to a free flowing powder (30 minutes minimum).

5.1.2 Soxhlet Extraction Procedure

Assemble the Soxhlet apparatus, including the thimble, and thoroughly clean by Soxhlet extraction with toluene for two hours; three hours if brominated analytes are determined. Discard the toluene. Rinse the apparatus with hexane.

Place a layer of clean silica or powdered anhydrous sodium sulphate into a pre-cleaned Soxhlet thimble (2 g for small thimbles, 5 g for large thimbles). Transfer the dried sample to the Soxhlet thimble. Add an aliquot of surrogate standard solution to the sample and allow to equilibrate for 30 minutes. Place the Soxhlet thimble with sample into the Soxhlet apparatus. Be sure the level of the sample in the thimble is not higher than the siphon arm. Add anti-bumping granules (4-5 granules) and dichloromethane (300 mL for a small Soxhlet apparatus, 600 mL for a large) to the Soxhlet apparatus' round bottom flask. Heat the sample under reflux for 16-20 hours; adjust as necessary to achieve a reflux rate of a minimum of 4 cycles per hour. Cool the solution. Add an aliquot of cleanup standard to the extract. Concentrate the extract to 1 mL by rotary evaporation. The extract is ready for chromatographic cleanup procedures (Section 6.0).

5.1.3 Biosolids

In the case of biosolid samples, an optional acid wash and gel permeation chromatographic cleanup procedure may be carried out prior to cleanup procedures. Refer to Section 5.2.3 of this method for details.

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5.2 Soxhlet/Dean-Stark Extraction of Solids

The Soxhlet/Dean-Stark extraction in toluene allows for the determination of all PCB congeners except PCB 1 through PCB 15. The occasional formation of an interference during the extraction procedure and the high boiling point of the toluene limit the quantification of these PCB congeners. The Soxhlet/Dean-Stark extraction procedure is applicable to solid samples such as sediments or soils that are >1% solid or particulate filter papers that are received wet.

Matrix	Sample Size
Sediments/Soil/Sludge	10 g dry weight.
Particulate Filter Paper	1 - several

The size of the Soxhlet apparatus used for the extraction of sediment, soil and sludge samples is dependent upon the amount of sample used to obtain the equivalent of 10 g dry weight. Use a larger Soxhlet apparatus for sample sizes larger than 25 g wet or with greater than 60% moisture content. Adjust the amounts of reagent sand, silica and solvent volumes accordingly.

Assemble the Soxhlet/Dean-Stark (SDS) apparatus, including the thimble, and thoroughly clean by Soxhlet extraction with toluene for two hours, three hours if brominated analytes are required. Discard the toluene. Rinse the apparatus with hexane.

5.2.1 Sample Preparation

Solids

Accurately weigh to a minimum of 3 significant figures, a solid sample (>1% solids), equivalent to 10 g dry, into a clean beaker. Add an aliquot of surrogate standard solution. Stir well with a clean spatula, cover with clean aluminum foil, and allow to equilibrate for 30 minutes. Add clean reagent sand (50 g) to the sample in the beaker, after equilibration with the surrogate standard solution. Mix well with a clean spatula

Add a layer of silica or powdered anhydrous sodium sulphate (2 g for small thimbles, 5 g for large thimbles) to a pre-cleaned Soxhlet thimble. Transfer the sample to the Soxhlet thimble. Rinse the beaker and spatula with the extraction solvent. Add the rinses to the Soxhlet body.

Particulate Filter Paper

Handle the wet particulate filter paper(s) with clean solvent-rinsed forceps. Fold the filter paper(s) to fit into a Soxhlet thimble for extraction. Using clean forceps place the filter(s) into a pre-cleaned Soxhlet thimble that has a layer of neutral silica or powdered anhydrous sodium sulphate (2 g for small thimbles, 5 g for large thimbles) in the bottom. Add an aliquot of surrogate standard to the sample and allow to equilibrate for 30 minutes. Refer to the Bach List for spiking and extract splitting instructions.

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5.2.2 Soxhlet/Dean-Stark Extraction Procedure

Place the thimble containing the sample in a clean SDS apparatus. Be sure that the level of sample in the thimble is not higher than the height of the siphon arm. Add anti-bumping granules (4-5 granules) and toluene (300 mL for a small Soxhlet apparatus, 600 mL for a large) to the Soxhlet apparatus' round bottom flask. Fill the Dean-Stark sidearm with toluene. Heat the sample under reflux for 16-24 hours; adjust as necessary to achieve a reflux rate of 4 cycles per hour. Drain the water from the receiver as necessary. When the extraction has finished remove the distilling flask. Drain the water from the receiver and discard any toluene left in the receiver. Allow the solution to cool. Add an aliquot of cleanup standard to the extract. Concentrate the extract to 1 mL by rotary evaporation. The extract is ready for chromatographic cleanup procedures (Section 6.0).

5.2.3 Acid Wash/Gel Permeation of Biosolids

In the case of biosolid samples, an optional acid wash and gel permeation chromatographic cleanup procedure may be carried out prior to cleanup procedures (Section 6.0 of this method). **Do not carry out the acid wash procedure if the analysis of pesticides is required.**

Acid Wash

The following precautions must be observed when carrying out the acid wash procedures.

1. Ensure the extract is dry by drying with anhydrous sodium sulphate prior to washing procedures.
2. Use only concentrated sulphuric acid for the wash.
3. Ensure the contact time with acid is less than 15 minutes per wash.

Transfer the extract, with rinses, to a 125 mL separatory funnel. Add sufficient hexane to the extract to make the volume 50 mL. Add concentrated sulphuric acid (30 mL) to the extract and gently agitate (invert 5 times). Let stand (no more than 15 minutes). If the aqueous layer is strongly coloured drain the acid and repeat the procedure with up to 3 more washes (with H_2SO_4).

Wash the extract by shaking with ultra pure water, followed by potassium hydroxide (KOH, 20%) followed by ultra pure water. Transfer the organic layer to a clean 250 mL Erlenmeyer flask and dry over anhydrous sodium sulphate (5-10 g, 10-15 minutes).

Gel Permeation Cleanup

Load the extract onto a Biobead SX-3 gel permeation column with 1:1 dichloromethane:hexane and elute with 1:1 dichloromethane:hexane at 5 mL/min. Refer to the most recent Biobead cutpoint determination for the elution volume. Typical cutpoints are as follows:

F1 0 - 140 mL
F2 140 - 300 mL

Collect the second fraction and evaporate to a small volume by rotary evaporation. The extract is ready for chromatographic cleanup procedures (Section 6.0).

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5.3 Tissue Extraction Procedure – Soxhlet

This extraction procedure is applicable to the matrix and sample size listed below.

Matrix	Sample Size
Tissue	1 - 25 g wet weight

5.3.1 Sample Preparation

Accurately weigh, to a minimum of 3 significant figures, a wet homogenized tissue sample into a beaker and add anhydrous sodium sulphate (75 g). Refer to the Batch List for the sample size. Typical sample sizes are: muscle: 10 g, liver: 5 g, fat: 1 g. Stir the mixture well with a spatula and allow the mixture to dry to a free flowing powder (30 minutes minimum).

5.3.2 Soxhlet Extraction

Assemble the Soxhlet apparatus, including a sintered glass Soxhlet thimble, and thoroughly clean by Soxhlet extrcation with toluene for two hours, three hours if brominated analytes are required. Discard the toluene. Rinse the apparatus with hexane.

Place a layer of clean silica or powdered anhydrous sodium sulphate into a pre-cleaned Soxhlet thimble (2 g for small thimbles, 5 g for large thimbles). Quantitatively transfer the dried sample to the pre-Soxhleted thimble. Add an aliquot of the surrogate standard solution to the sample in the thimble and allow to equilibrate for 30 minutes. Place the Soxhlet thimble in the Soxhlet apparatus. Be sure that the level of sample in the thimble is not higher than the height of the siphon arm. Add anti-bumping granules (4-5 granules) and dichloromethane (300 mL for a small Soxhlet apparatus, 600 mL for a large) to the Soxhlet apparatus' round bottom flask. Allow the sample to reflux for 16 to 20 hours; adjust as necessary to achieve a reflux rate of a minimum of 4 cycles per hour. Allow the mixture to cool. Add an aliquot of cleanup surrogate standard. Concentrate the extract to 1 mL (5 mL if lipid analysis is required) by rotary evaporation (water bath <30°C).

If gravimetric lipid analysis is required, use the extract at this point, following the procedures described in SLA-020. Concentrate the remaining extract to 1 mL by rotary evaporation. Add hexane (1 mL) to the extract.

If lipid analysis is not performed, add hexane (1 mL) to the extract.

5.3.3 Gel Permeation Cleanup

Load the extract onto a Biobead SX-3 gel permeation column with 1:1 dichloromethane:hexane and elute with 1:1 dichloromethane:hexane at 5 mL/min. Refer to the most recent Biobead cutpoint determination for the elution volume. Typical cutpoints are as follows:

F1	0 - 140 mL
F2	140 - 300 mL

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Discard the first fraction. Collect the second fraction and evaporate to a small volume by rotary evaporation. If the lipid content for the sample is greater than 2 g absolute (i.e. 10% of a 20 g sample), repeat the gel permeation cleanup procedure. The extract is ready for chromatographic cleanup procedures (Section 6.0).

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5.4 Tissue Extraction Procedure - Base Digestion

This extraction procedure is applicable to the matrix and sample size listed below. This method is not suitable if the analysis of pesticides is also required.

Matrix	Sample Size
Tissue	75 - 150 g wet weight.

5.4.1 Sample Preparation

Accurately weigh, to a minimum of 3 significant figures, a homogenized tissue sample into an Erlenmeyer flask (500 mL). Refer to the Batch List for sample size. Add an aliquot of surrogate standard solution to the sample and allow to equilibrate for 30 minutes. Add potassium hydroxide (KOH, 200 mL, 1M in ethanol) to the sample. Swirl, cover the flask, and **STIR SLOWLY** with a magnetic stir bar overnight. The tissue sample must be entirely dissolved. Alternatively, allow the mixture to stand overnight and stir in the morning until the tissue sample is entirely dissolved.

5.4.2 Extraction Procedure

Add ultra pure water, equal in volume to the volume of ethanolic KOH, to the Erlenmeyer flask. Stir well and transfer the ethanolic potassium hydroxide/water mixture into a separatory funnel (1000 mL). Add hexane (150 mL) to the Erlenmeyer, swirl, and then transfer the hexane to the separatory funnel. Shake the separatory funnel vigorously for 2 minutes. Allow the mixture to separate. Drain the bottom aqueous layer into the original 500 mL Erlenmeyer flask and then drain the hexane extract into a clean Erlenmeyer flask (1000 mL). Repeat the extraction of the aqueous layer twice more with hexane (2 x 150 mL). On the final extraction, draw the aqueous layer off, leaving the hexane in the separatory funnel. Add the previous hexane extracts to the separatory funnel.

Rinse the 500 mL Erlenmeyer flask used for the base digest with toluene (20 mL). Use the vortex mixer if necessary to dissolve the residue. Add the toluene to the hexane extract in the separatory funnel. Backwash the hexane extract by shaking with ultra pure water (150 mL) for 30 seconds. Discard the aqueous (lower) layer. Leave the hexane extract in the separatory funnel. Add an aliquot of PCB cleanup standard solution to the hexane extract.

Add concentrated sulphuric acid (H_2SO_4, 100 mL) to the extract and gently shake for two minutes. Let stand (no more than 15 minutes). Discard the lower acid layer. Repeat the sulphuric acid wash (100 mL, conc. H_2SO_4) until the acid layer is colourless. Backwash the extract by shaking with ultra pure water (150 mL) for 30 seconds. Discard the aqueous (lower) layer. Drain the hexane extract into the 1000 mL Erlenmeyer flask and dry over anhydrous sodium sulphate.

Transfer the dried extract to a round bottom flask (500 mL) and concentrate to approximately 1 - 2 mL by rotary evaporation.

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5.4.3 Gel Permeation Cleanup

Load the extract onto a Biobead SX-3 gel permeation column with 1:1 dichloromethane:hexane and elute with 1:1 dichloromethane:hexane at 5 mL/min. Refer to the most recent Biobead cutpoint determination for the elution volume. Typical cutpoints are as follows:

F1	0	- 140 mL
F2	140	- 300 mL

Discard the first fraction. Collect the second fraction and evaporate to a small volume by rotary evaporation. If the lipid content for the sample is greater than 2 g absolute (i.e. 10% of a 20 g sample), repeat the gel permeation cleanup procedure. The extract is ready for chromatographic cleanup procedures (Section 6.0).

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5.5 Aqueous Sample Extraction

These extraction procedures are suitable for aqueous samples including drinking water, non-potable water, effluents, aqueous sludge and aqueous ash.

Matrix	Sample Size
Aqueous	1 – 4 L

This extraction procedure for aqueous samples depends on the percentage of suspended solid in the sample. Determine the percent suspended solids on a subsample of the sample. Refer to operating procedure SLA-092 for the determination of percent solids. A typical sample size is 1 litre.

5.5.1 Sample Preparation

The surrogate standard spiking solution must be prepared prior to sample extraction. Dilute the surrogate stock solution, described in Table 2, in acetone, to make a solution that is 2 ng of each surrogate/mL. Prepare enough solution to spike all the samples in the batch as well as the QC samples. Typically, 50 µL of stock solution is dissolved in 25 mL of acetone in a volumetric flask. Mix the sample well by inverting the flask at least 10 times. A 1 mL aliquot is added to each sample, which is allowed to equilibrate for at least 30 minutes.

Prior to extraction, aqueous samples are homogenized, subsampled and spiked with an aliquot of surrogate standard solution by the analyst. The analyst must refer to the following SOPs for complete details of sample homogenization, subsampling, rinsing, surrogate spiking and filtration procedures.

SLA-084	Preparation of Aqueous Samples (Originating From A Single Bottle) for Extraction
SLA-086	Preparation of a Composite Aqueous Samples

The extraction procedures are dependent on the amount of particulate present in the sample.

- Samples with no visible particles (≤1% solids) are not filtered prior to extraction (Section 5.5.2).
- Samples with visible particulate (>1% solids) are filtered and extracted (Section 5.5.3). An optional procedure for the separation of particulate and filtrate by centrifugation may be carried out. Consult the Supervisor to determine which procedure to use.

Two technically equivalent liquid/liquid extraction procedures are described in sections 5.5.2.1/5.5.2.2 and 5.5.3.2/5.5.3.3 for aqueous samples with <1% solids and for filtrates respectively. The magnetic stirring procedure may offer some advantage in terms of cost efficiency, particularly for larger sample sizes.

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5.5.2 Extraction of Samples with <1% Solids

5.5.2.1 Extraction by Shaking in a Separatory Funnel

After homogenization, subsampling and spiking with surrogate standard, as described in SLA-084 or SLA-086, extract the sample by adding dichloromethane (100 mL or 10% of the volume of the sample) to the separatory funnel and shaking vigorously for two minutes. Collect the dichloromethane layer in an Erlenmeyer flask. Repeat the extraction twice more. Combine the dichloromethane layers and dry over anhydrous sodium sulphate for at least 30 minutes. Add an aliquot of cleanup standard solution. Transfer the extract to a Kuderna-Danish flask (500 mL) with dichloromethane. Add hexane (2 mL) and concentrate the extract to 2 mL (water bath 60°C). Alternately, transfer the extract into a round-bottom flask and concentrate to 1 mL by rotary evaporation. The extract is ready for chromatographic cleanup procedures (Section 6.0).

5.5.2.2 Extraction by Magnetic Stirring

After homogenization, subsampling and spiking with surrogate standard, as described in SLA-084 or SLA-086, add dichloromethane (300 mL) and a pre-cleaned PTFE magnetic stir bar to the sample in an erlenmeyer flask and extract by stirring the solution (with vortex) for a minimum of 30 minutes. Quantitatively transfer the solution to a separatory funnel and draw off the dichloromethane layer. Discard the aqueous layer. Dry the extract over anhydrous sodium sulphate for at least 30 minutes. Add an aliquot of cleanup standard solution. Transfer the extract to a Kuderna-Danish flask (500 mL) with dichloromethane. Add hexane (2 mL) and concentrate the extract to 2 mL (water bath 60°C). Alternately, transfer the extract into a round-bottom flask and concentrate to 1 mL by rotary evaporation. The extract is ready for chromatographic cleanup procedures (Section 6.0).

5.5.3 Extraction of Samples with >1% Solids

The analyst must refer to the following operating procedures SLA-084 or SLA-086 for complete details of sample homogenization, subsampling, rinsing, surrogate spiking and filtration procedures. The procedures are summarized below:

1. After homogenization, subsampling and spiking with surrogate standards, filter the entire sample or subsample through a Millipore filtration system containing a baked glass fibre filter paper and a glass fibre filter bed.

   CAUTION: Do not draw excess air through the filter. Do not dry the particulate with acetone rinses. The filter will be wet after filtration procedures.
2. Carefully remove the filter and filter bed from the filtration apparatus and proceed with one of the following options, as instructed on the Batch List:
   a) Dry the filter/filter bed/particulate by mixing with anhydrous sodium sulphate, load into a pre-cleaned Soxhlet thimble and place in a pre-cleaned Soxhlet apparatus. Rinse the beaker with dichloromethane. Add the rinses to the Soxhlet body.

OR

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b) Extract the wet filters by Soxhlet/Dean-Stark extraction procedures.

3. Rinse the filtration apparatus with the appropriate dichloromethane rinses (refer to SLA-084 or SLA-086), adding the rinses to the filtrate.
4. Extract the filtrate and particulate separately and combine as described in Sections 5.5.3.2/5.5.3.3 and 5.5.3.4 respectively.

5.5.3.1 Optional Centrifugation Procedure for Separation of Particulate

Note: the following procedure cannot be used if particulate weight is required.

Transfer a portion of the sample to a clean 500 mL glass jar with a clean baked 10 cm filter paper in the bottom of the jar. Spin the sample in the centrifuge at 1500 rpm until the solid has settled. Decant the supernatant into a separatory funnel (if proceeding according to Section 5.5.3.2) or an Erlenmeyer flask (if proceeding according to Section 5.5.3.3). Repeat the procedure until the entire sample has been centrifuged, leaving the filter paper in place throughout the process. Once the entire sample has been processed, dry the particulate and filter in the jar by mixing with powdered anhydrous sodium sulphate. Extract the solids as described for particulate in Section 5.5.3.4.

Rinse the jar with ultra pure water and dichloromethane. Add the rinses to the separatory funnel/Erlenmeyer flask containing the supernatant. Extract the supernatant as described for filtrates in Section 5.5.3.2 or 5.5.3.3.

5.5.3.2 Extraction of the Filtrate by Shaking in a Separatory Funnel

Quantitatively transfer the filtrate to a separatory funnel. Extract the filtrate by adding dichloromethane (100 mL or 10% the volume of sample) to the separatory funnel and shaking vigorously for two minutes. Collect the dichloromethane layer in an Erlenmeyer flask. Repeat the extraction twice more. Combine the dichloromethane layers and dry over anhydrous sodium sulphate for at least 30 minutes.

5.5.3.3 Extraction of the Filtrate by Magnetic Stirring

Quantitatively transfer the filtrate to an Erlenmeyer flask. Add dichloromethane (300 mL) and a pre-cleaned PTFE magnetic stir bar and extract by stirring the solution (with vortex) for a minimum of 30 minutes. Quantitatively transfer the solution to a separatory funnel and draw off the dichloromethane layer. Discard the aqueous layer. Dry the extract over anhydrous sodium sulphate for at least 30 minutes.

5.5.3.4 Extraction of Particulate

Assemble the Soxhlet apparatus, including the thimble, and thoroughly clean by Soxhlet extraction with toluene for two hours (3 hours if brominated analytes are required). Discard the toluene. Rinse the apparatus with hexane.

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Place a layer of silica or powdered anhydrous sodium sulphate (2 g for small thimbles, 5 g for large thimbles) into a pre-cleaned Soxhlet thimble. Transfer the dried particulate with dichloromethane rinses (use extraction solvent) to the thimble. Be sure that the level of sample in the thimble is not higher than the height of the siphon arm. Add the rinses to the thimble in the Soxhlet body. Place the Soxhlet thimble in the Soxhlet apparatus. Add anti-bumping granules (4-5 granules) and dichloromethane (300 mL for a small Soxhlet apparatus, 600 mL for a large) to the Soxhlet apparatus' round bottom flask (use the round bottom flask containing the filtrate extract if option 1 was chosen). Heat the sample under reflux for 16 - 20 hours; adjust as necessary to achieve a reflux rate of a minimum of 4 cycles per hour. Allow the solution to cool.

5.5.3.5 Combining Extracts

Combine the extract from the filtrate with the extract from the particulate, using dichloromethane rinses to transfer the extract. Add an aliquot of cleanup standard to the combined extract. Transfer the extract to a Kuderna-Danish flask (500 mL) with dichloromethane. Add hexane (2 mL) and concentrate the extract to 2 mL (water bath 60°C). Alternately, transfer the extract into a round-bottom flask and concentrate to 1 mL by rotary evaporation. The extract is ready for chromatographic cleanup procedures (Section 6.0).

Alternate Procedure for Combining Extracts

If time allows, quantitatively transfer the filtrate extract with dichloromethane rinses to a round bottom flask. Use this flask for the Soxhlet extraction of the particulate as described in Section 5.5.3.2.

5.5.4 Cleanup of Extracts From Wastewaters

Extracts from wastewater samples require a cleanup on a gel permeation column prior to the cleanup procedures described in Section 6.0.

Ensure the extract is in 1:1 dichloromethane:hexane. Load the extract onto a Biobead SX-3 gel permeation column with 1:1 dichloromethane:hexane and elute with 1:1 dichloromethane:hexane at 5 mL/min. Refer to the most recent Biobead cutpoint determination for the elution volume. Typical cutpoints are as follows:

F1	0	- 140 mL
F2	140	- 300 mL

Discard the first fraction. Collect the second fraction and evaporate to a small volume by rotary evaporation. If the lipid content for the sample is greater than 2 g absolute (i.e. 10% of a 20 g sample), repeat the gel permeation cleanup procedure. The extract is ready for chromatographic cleanup procedures (Section 6.0).

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5.6 XAD-2 Column (Resin and Filter) Extraction

This procedure is applicable to the analysis of an XAD-2 column. The analysis of a XAD-2 column usually consists of two analyses, as the filter(s) and XAD-2 resin are extracted and analyzed separately. Upon client request, the filter and resin extracts may be combined to form a single extract. If the sample is also analyzed for PCDD/F, a Soxhlet/Dean-Stark extraction of the XAD-2 resin must be carried out, as described in Section 5.6.4.

The occasional formation of an interference during the extraction procedure and the high boiling point of the toluene may limit the quantification of PCBs 1 through 15 in the filter/XAD-2 matrix.

5.6.1 Sample Handling Procedures

Refer to document SLA-043 for details of sample handling procedures. If the sample consists of a large amount of XAD-2 resin or multiple filters, it may be necessary to use more than one Soxhlet apparatus to extract the sample. Distribute the XAD-2 resin or filters evenly amongst the required number of Soxhlet apparatuses. Spike the sample in multiple Soxhlet apparatuses with surrogate standard as follows:

1. Dilute the aliquot of surrogate standard in a centrifuge tube with acetone (5 mL). Ensure the solution is homogeneous by using a disposable pipette to withdraw and expel the solution several times.
2. Use a disposable pipette to distribute the surrogate solution evenly amongst the Soxhlet apparatuses.
3. Rinse the centrifuge tube with acetone (5 mL). Mix the rinsate in the centrifuge tube by vortex mixing. Distribute the rinsate evenly amongst the Soxhlet apparatuses. Repeat the rinse step once more with another 5 mL acetone.
4. Once the extraction is complete, combine the extracts.

5.6.2 XAD-2 Resin – Drying Procedure

1. Place a clean large glass funnel, fitted with a large filter paper, into a beaker.
2. Quantitatively transfer the XAD-2 resin to the filter paper with ultra pure water and allow to drain.
3. If necessary, use multiple filter papers to drain all the XAD-2 resin.
4. Rinse the resin with ultra pure water and allow to drain. Discard the water.

5.6.3 XAD-2 Resin Soxhlet Extraction Procedure

1. Assemble a Soxhlet apparatus. Add a small bed of glass wool (weighted down with glass beads) to the bottom of the Soxhlet body to prevent clogging during the reflux procedure. Thoroughly clean the apparatus by Soxhlet extraction with toluene for two hours, three hours if brominated analytes are required. Discard the toluene. Rinse the apparatus with hexane.
2. Transfer the filter paper containing the XAD-2 resin to the Soxhlet body or a Soxhlet thimble,

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depending upon the amount of XAD-2 resin. Be sure that the level of XAD-2 resin is not higher than the height of the siphon arm.

3. Add the appropriate volume of dichloromethane (300 mL for a small Soxhlet apparatus, 600 mL for a large) and anti-bumping granules (4-5 granules) to the round bottom flask of the Soxhlet apparatus.
4. If a single analysis is required, spike an aliquot of the surrogate solution into a centrifuge tube containing acetone (1 mL). Transfer the surrogate standard, along with acetone rinses of the centrifuge tube, onto the XAD-2 resin in the thimble prior to starting the Soxhlet extraction. If multiple analyses are required, spike the surrogates after the extraction and extract splitting procedures (Section 5.12). Refer to the Batch List for spiking instructions.
5. Heat the sample under reflux for 16 -20 hours; adjust as necessary to achieve a reflux rate of a minimum of 4 cycles per hour. Allow the solution to cool. Remove water from the extract (Section 5.6.3.1).

EXTREMELY IMPORTANT – DO NOT CONCENTRATE THE SAMPLE BY ROTARY EVAPORATION WITHOUT A WATER REMOVAL STEP.

5.6.3.1 Removal of Water from XAD-2 Resin Extracts

The water removal step depends on the amount of visible water.

1. If less than 3 mL of water is visible, transfer the entire extract to an Erlenmeyer flask.
2. If greater than 3 mL of water is visible, transfer the extract to a separatory funnel and drain the water from the sample extract. Discard the water. Quantitatively transfer the extract to an Erlenmeyer flask.
3. Dry the extract over anhydrous powdered sodium sulphate. Return the extract to the round bottom flask with complete dichloromethane rinses. An aliquot of cleanup surrogate standard may be added at this point or after the extract has been split. Refer to the Batch List for spiking and extract splitting instructions. Concentrate the extract by rotary evaporation to 1 - 2 mL for extract splitting. If using a 1000 mL round bottom flask for the Soxhlet extraction, transfer the extract with dichloromethane rinses to a 500 mL round bottom flask during the evaporation process. The extract is ready to be gravimetrically split according to procedures in Section 5.12 of this method.

5.6.4 Soxhlet/Dean-Stark Extraction of XAD-2 Resin

This procedure is used only if PCDD/F analysis is required as well as PCB analysis.

1. Assemble a Soxhlet apparatus, without the thimble, and fitted with a Dean-Stark adapter. Place some clean glass wool into the bottom of the siphon arm. Clean the apparatus by Soxhlet extraction with toluene for two hours (3 hours if brominated analytes are required). Discard the toluene. Rinse the apparatus with hexane.
2. Transfer the filter paper containing the XAD-2 resin to the Soxhlet body. Be sure that the level of XAD-2 resin is not higher than the height of the siphon arm.

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3. Use a 1000 mL round bottom flask for the solvent.
4. If a single analysis is required, spike the surrogate solution into a centrifuge tube containing acetone (1 mL). Transfer the surrogate solution, along with acetone rinses of the centrifuge tube, onto the resin in the Soxhlet prior to starting the extraction. If multiple analyses are required, refer to the Batch List for spiking details.
5. Add anti-bumping granules (4-5 granules) and toluene (700 mL) to the Soxhlet apparatus' round bottom flask. Fill the sidearm to the top with toluene. Soxhlet extract the resin until the water removal is complete (no water collecting in the sidearm), adjust as necessary to achieve a reflux rate of 4 cycles per hour. When the water extraction has finished, drain the water from the receiver. Continue with the Soxhlet extraction for another 8-12 hours. Allow the solution to cool. The cleanup standard is added at this point or after the extract has been split. Refer to the Batch List for spiking and extract splitting instructions. Concentrate by rotary evaporation to 1-2 mL. The extract is ready to be gravimetrically split according to procedures in Section 5.12.

5.6.5 Filter - Soxhlet/Dean-Stark Extraction

This extraction procedure is applicable to glass fibre filters or filter cartridges (wound glass filters).

1. Assemble a large Soxhlet apparatus, without the thimble, fit with a Dean-Stark adapter and thoroughly clean by Soxhlet extraction with toluene for two hours, three hours if brominated analytes are required. Discard the toluene. Rinse the apparatus with hexane.
2. Place the filters or filter cartridge directly into the pre-cleaned Soxhlet body. Use a large Soxhlet body to hold the filter(s); thimbles are not required. Be sure that the level of filters in the Soxhlet body is not higher than the height of the siphon arm.
3. Use a 1000 mL round bottom flask for the solvent.
4. If a single analysis is required, spike the surrogate solution into a centrifuge tube containing acetone (1 mL). Transfer the surrogate standard along with acetone rinses of the centrifuge tube, onto the filter(s) in the Soxhlet apparatus prior to starting the extraction. If multiple analyses are required, refer to the Batch List for spiking details and extract splitting procedures (Section 5.12).
5. Add anti-bumping granules (4-5 granules) and toluene (700 mL) to the Soxhlet apparatus' round bottom flask. Fill the side arm to the top with toluene. Soxhlet extract the filter(s) or filter cartridge with until the water removal is complete (no water in the sidearm). Adjust as necessary to achieve a reflux rate of a minimum of 4 cycles per hour. When the extraction has finished, drain the water from the receiver. Monitor the amount of water collected, typically 50-150 mL should be present. Contact the Lab Supervisor if the amount of water is anomalous. Continue with the Soxhlet extraction for another 8 - 12 hours. Allow the solution to cool. Add the cleanup standard at this point or after the extract has been split. Refer to the Batch List for spiking and extract splitting instructions. Concentrate by rotary evaporation to 1-2 mL. The extract is ready to be gravimetrically split according to procedures in Section 5.12.

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5.7 Air Sampler (PUF/Filter) and Particulate Filter Extraction Procedure

This method is applicable to the analysis of ambient air samples consisting of polyurethane foam plug (PUF) and associated filter(s). The PUF and filter(s) are extracted together as one sample. The method is also applicable to particulate filters received dry.

Assemble the Soxhlet apparatus, including the thimble, and thoroughly clean by Soxhlet extraction with toluene for two hours, three hours if brominated analyses are required. Discard the toluene. Rinse the apparatus with hexane.

5.7.1 Sample Preparation

Particulate Filter Papers

Handle the particulate filter paper(s) with clean solvent-rinsed forceps. Fold the filter paper(s) to fit into a Soxhlet thimble for extraction. Using clean forceps place the filter(s) into a pre-cleaned Soxhlet thimble that has a layer of neutral silica or powdered anhydrous sodium sulphate (baked, 2 g for small thimbles, 5 g for large thimbles) in the bottom. Be sure that the level of the filter in the thimble is not higher than the height of the siphon arm.

PUF/Filter

Using clean solvent-rinsed forceps, transfer the PUF and filter(s) to a pre-cleaned Soxhlet thimble that has a layer of neutral silica or powdered anhydrous sodium sulphate (baked, 2 g for small thimbles, 5 g for large thimbles) in the bottom. Be sure that the level of the filter in the thimble is not higher than the height of the siphon arm.

5.7.2 Soxhlet Extraction Procedure

Place the Soxhlet thimble containing the PUF and filter(s) in a pre-cleaned Soxhlet apparatus. If a single analysis is required, spike the surrogate standard solution onto the sample prior to starting the extraction and allow to equilibrate for 30 minutes. If multiple analyses are required, refer to the Batch List for surrogate spiking instructions. Add anti-bumping granules (4-5 granules) and dichloromethane (300 mL for a small Soxhlet apparatus, 600 mL for a large) to the Soxhlet apparatus' round bottom flask. Heat the sample under reflux for 16-20 hours; adjust as necessary to achieve a reflux rate of a minimum of 4 cycles per hour. If extract is also being analyzed for PCDD/PCDF compounds, use 80:20 toluene:acetone as solvent. Allow the solution to cool. Add and aliquot of cleanup standard to the extract at this point or after the extract has been split. Refer to the Batch list for spiking instructions. Concentrate the extract to 1 - 2 mL by rotary evaporation. The extract is ready to be gravimetrically split according to procedures in Section 5.12.

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5.8 Solvent Extracts

This procedure is suitable for samples submitted as solvent extracts, where only extract splitting and chromatographic cleanup are required prior to instrumental analysis.

5.8.1 Sample Preparation

Determine the weight of the extract as received, as follows:

- Weigh the extract, to a minimum of 3 decimal places, in the original container (usually jar or ampoule).
- Transfer the extract to a centrifuge tube (if received in an ampoule) or to an Erlenmeyer flask with solvent rinses using the same solvent as in the sample.
- Reweigh the original container once it has dried.
- Record all weights on the worksheet.
- Calculate the weight of the extract.

Determine from the Batch List if the sample requires a single analysis or multiple analyses. Check the Batch List for detailed splitting and surrogate spiking instructions.

Single PCB Analysis

If only PCB congener analysis is required, add aliquots of surrogate standard solution and cleanup standard solution to the extract and allow to equilibrate for 30 minutes. Dry the extract according to procedures in Section 5.8.2.

Multiple Analyses

If multiple analyses are required, the surrogate and cleanup standards may be spiked before or after extract drying and splitting procedures. Refer to the Batch List for detailed splitting and surrogate spiking instructions. Dry the extract according to procedures in Section 5.8.2.

5.8.2 Extract Drying Procedures

Inspect the extract for the presence of water.

1. If less than 3 mL of water is visible, transfer the entire extract to an Erlenmeyer flask with solvent rinses (the same solvent as the sample).
2. If greater than 3 mL of water is visible, transfer the extract to a separatory funnel with solvent rinses (the same solvent as the sample) and drain the water from the sample extract. Discard the water. Quantitatively transfer the solvent layer to an Erlenmeyer flask.
3. Dry the extract over anhydrous powdered sodium sulphate. Quantitatively transfer the extract to a round bottom flask with solvent rinses. Concentrate the extract by rotary evaporation to 1 - 2 mL for extract splitting. Refer to the Batch List for extract splitting instructions. The extract is ready to be gravimetrically split according to procedures in Section 5.12.

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5.9 Milk Sample Extraction

This extraction procedure is suitable for both human and cow's milk.

1. Accurately weigh to a minimum of 3 significant figures, a subsample of milk (50 g). Add an aliquot of the surrogate standard solution that has been dissolved in ~1 mL acetone and allow to equilibrate for at least 30 minutes.

2. Add the sample to 200 mL of 2:1 acetone:hexane in a 500 mL separatory funnel. Shake the mixture for 2 min and allow the layers to separate.

3. Transfer the aqueous layer to an Erlenmeyer flask and the hexane layer to a separate Erlenmeyer. Return the aqueous layer to the separatory funnel and repeat the extraction with hexane (200 mL). Combine the hexane extracts. Discard the aqueous layer.

4. Return the hexane extracts to the separatory funnel and wash by shaking with ultra pure water (2 x 50 mL). Drain the hexane extract into an Erlenmeyer flask and dry over anhydrous powdered sodium sulphate.

5. Using a glass funnel lined with a large fluted filter paper, quantitatively transfer the dried extract to a pre-weighed round bottom flask and concentrate to ~5 mL by rotary evaporation. Add aliquots of the PCB cleanup standards to the extract.

6. **Lipid Determination** - Carry out the lipid analysis on the extract according to standard operating procedure SLA-020. Following lipid analysis, concentrate the remaining extract to ~1 mL. Add 1 mL dichloromethane.

7. If no lipid analysis is required, concentrate the extract to ~1 mL. Add 1 mL dichloromethane.

8. Load the extract onto a clean Biobead SX-3 column and elute with 1:1 dichloromethane:hexane. Refer to the most recent Biobead cutpoint determination for the elution volume. Discard the first fraction. Collect the second fraction. Concentrate the extract to 1 mL by rotary evaporation followed by evaporation under a gentle stream of nitrogen. The extract is ready for chromatographic cleanup procedure (Section 6.0).

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5.10 Blood Sample Extraction

This extraction procedure is applicable to the matrix and sample size listed below.

Matrix	Sample Size
Whole Blood/Serum/Plasma	5 - 20 g

Refer to the standard operating procedure SLA-082, *Handling of Human Biohazards*, for details of safety precautions when handling blood samples. Use caution when using bleach to decontaminate equipment used in the analysis of human biohazards and **avoid contact between acid and bleach.** Note that ammonium sulphate, used in the extraction below, is an acidic solution.

1. Accurately weigh a blood sample (5 to 20 g) to a minimum of 3 significant figures into a 250 mL round-bottom flask. Add an aliquot of surrogate standard, cover the flask with clean aluminum foil and allow to equilibrate for 30 minutes.

2. Add ethanol, hexane and saturated ammonium sulphate to the sample (in the proportions described below) and shake for 30 min on the shaker table. Refer to the Batch List for the volume of reagents to use.

   NOTE: The proportion of reagents used is critical to complete extraction of analytes. The minimum sample size required is 10 g and the volumes of reagents are scaled to sample size in a ratio of sample:ethanol:saturated ammonium sulphate:hexane of 1:1:1:3. An alternate procedure for sample sizes less than 10 g, using 10 mL ethanol, 50 mL hexane and 10 mL saturated ammonium may be applied on a custom basis to meet client or historical project requirements - this option requires written pre-approval of the Project Manager including confirmation that the client has been made aware of potential solvent system effects on gravimetric determination of lipids in blood matrices.

3. Decant the hexane layer into a 500 mL separatory funnel.

4. Add additional hexane (100 mL) to the aqueous layer in the round bottom flask and repeat the extraction step. Add the hexane layer to the hexane in the separatory funnel. Discard the aqueous phase.

5. Wash the hexane extracts by shaking with ultra pure water (2 x 50 mL) to remove residual ethanol. Discard the aqueous layer.

6. Transfer the hexane extract to an Erlenmeyer flask and dry over anhydrous sodium sulphate for a minimum of 30 minutes.

7. Add an aliquot of cleanup standard to the extract.

8. Refer to the Batch List to determine whether a lipid determination is required. If so, carry out the following procedures:

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Lipid Determination: Filter the dried extract, with hexane rinses, through a baked filter paper into a round bottom flask (100 mL). Evaporate the solvent to just dryness by rotary evaporation. Add hexane (4 mL) to the residue in the round bottom flask. Using standard operating procedure SLA-030, determine the lipid content on the extract.

8. Quantitatively transfer the extract with hexane rinses to a clean round bottom flask. Concentrate the extract by rotary evaporation to about 1 mL. Add dichloromethane (1 mL) to the extract.

9. Load the extract onto a Biobeads SX-3 column and elute with 1:1 dichloromethane:hexane. Refer to the most recent Biobead cutpoint determination for the elution volume. Discard the first fraction. Collect the second fraction.

10. Concentrate the extract to a small volume by rotary evaporation (water bath <30°C). Transfer to a centrifuge tube with hexane rinses. Concentrate to 1 mL under a stream of nitrogen. The extract is ready for the column cleanup procedure (Section 6.0).

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5.11 Stationary Source Air Samples (Stack Gas)

5.11.1 Sample Preparation

Stack gas samples are usually submitted as sample trains in several containers labelled A to F or 1 to 6. It is essential that the analyst confirm that the labels on the sample container match those on the sample log-in information prior to commencing extraction procedures.

Prior to proceeding with the sample processing, the analyst must refer to the LIMS and/or Project Notes for information regarding the solvents present in the various containers. A flow chart of the sample processing procedure is presented in Figure 1.

QC Samples

Refer to Section 4.1 for details of preparing the procedural blank and reference (OPR) sample.

Glassware

Assemble the Soxhlet apparatus, including the thimble, and thoroughly clean by Soxhlet extraction with toluene for two hours. If brominated analytes (PBB) are also being determined the apparatus must be extracted with toluene for a minimum of 3 hours. Discard the toluene. Rinse the apparatus with hexane.

Front Half of Train

a) Container A (1)

The solvent rinses, that may include dichloromethane, toluene, and/or methanol, from the probe liner, nozzle, cyclone and front half of the filter housing are in container A. **If the rinses contain additional or different solvents, or two or more phases, consult the Supervisor for instructions.**

1. Pour the contents of container A through a Millipore filtration apparatus containing a baked filter and if needed, a glass fibre filter/filter bed. Rinse the container with dichloromethane and filter the rinses.

   CAUTION: To avoid loss of volatile compounds when filtering, DO NOT draw air through the filter. DO NOT use acetone rinses to dry the filter.

2. The filter/filter bed is ready for the acidification/sonication procedure (Section 5.11.1b). (Residual water in the filter is acceptable).

3. If methanol is not present in the filtrate, treat the filtrate as described in Step 5.

4. If methanol is present in the filtrate, transfer the filtrate to a separatory funnel with

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dichloromethane rinses. Make the volume of dichloromethane in the separatory funnel to 100 mL. Add ultra pure water (about equal in volume to the volume of the filtrate) to the separatory funnel. Shake the mixture gently for 10 inversions. Allow the layers to separate. If there is no phase separation, consult the Supervisor for assistance. Corrective action may include the addition of additional water or dichloromethane and another gentle shake of the mixture for 10 inversions. Draw off the organic (bottom) layer into an Erlenmeyer flask. Discard the aqueous (top) layer. Proceed with the dichloromethane extract as described below.

Note: Depending upon the mix of solvent in the containers, the aqueous and organic layers may be inverted from that described above. Ensure that the organic layer is the layer retained for processing.

5. Dry the filtrate (or filtrate extract) over powdered anhydrous sodium sulphate (Na_2SO_4) for a minimum of 30 minutes. Transfer the filtrate extract to a round bottom flask (500 mL) with dichloromethane rinses; add toluene (1 mL) as a "keeper" and concentrate to 1 mL by rotary evaporation. Use this round bottom flask for the Soxhlet extraction of the XAD-2 resin (container C) and filters (Section 5.11.2).

b) Container B (2)

A particulate filter is in container B.

1. Transfer the filter to a clean, tared, piece of foil. Weigh the filter and record the weight to a minimum of 3 significant figures on the work sheet. Transfer the filter/filter bed from the processing of container A (Section 5.11.1a) and the particulate filter and all visible particulate from container B to a clean beaker. Add enough hydrochloric acid (1M, HCL) to the beaker to cover the filters and sonicate for 30 minutes. Filter the mixture through a Millipore filtration apparatus and rinse with ultra pure water until the rinsate is at the pH of ultra pure water (typically 6, check with pH paper).

   CAUTION: To avoid loss of volatile compounds when filtering, DO NOT draw air through the filter. DO NOT use acetone rinses to dry the filter.

2. Transfer the wet filters and particulate to the Soxhlet thimble containing the XAD-2 resin from container C (Section 5.11.1c).

3. Combine the filtrate with the contents of container E (impinger water washes) in a separatory funnel (Section 5.11.1e).

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Back Half of Train

c) Container C (3)

XAD-2 resin is in container C.

1. Put a layer of neutral silica or powdered anhydrous sodium sulphate (2 g for small thimbles, 5 g for large thimbles) into a pre-cleaned Soxhlet thimble. Place the Soxhlet thimble into a large glass funnel that is set in a beaker (400 mL). Handle the thimble with a clean piece of foil. Remove the glass wool from the top of XAD-2 trap and place into the Soxhlet thimble. Rinse the XAD-2 resin from the container into the Soxhlet thimble with ultra pure water. Place the glass wool from the other end of the trap on top of the resin. Allow the water to drain from the thimble.

2. Transfer the filters and particulate from containers A and B (Section 5.11.1b) to the top of the Soxhlet thimble containing the XAD-2 resin. Be sure that the level of the XAD-2 and filters in the thimble is not higher than the height of the siphon arm.

3. Add an aliquot of the surrogate standard to the Soxhlet thimble. If multiple analyses of the extract are required, refer to the Batch List for the name(s) and volume(s) of surrogate standard solutions to add.

4. Discard the water rinses of the XAD-2 resin.

d) Container D (4)

Solvent rinses, which may contain dichloromethane, toluene, and/or methanol, of the condenser, coil and back half of filter housing, are in container D. **If the rinses contain additional or different solvents, consult the Supervisor for instructions.**

1. If methanol is in the Container D rinses, combine the rinses with the filtrate from Container A, and backwash as described n Step 4 in Section 5.11.1a

2. If methanol is not present, dry the contents of container D with powdered anhydrous sodium sulphate for a minimum of 30 minutes. Transfer the extract with dichloromethane to the 500 mL round bottom flask used for the Soxhlet extraction of the XAD-2 and filters (Section 5.11.2). Concentrate to 1 mL by rotary evaporation. (Add 1 mL toluene keeper to the flask if it has not been previously added.)

e) Container E (5)

Impinger contents and water rinses, or perhaps only water are in container E. **If the rinses contain ethylene glycol or solvents other than dichloromethane, toluene or methanol, consult the Supervisor for instructions.**

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1. Transfer the contents of Container E to a separatory funnel. Add the aqueous filtrate from the acidification step (Section 511.1b) to the separatory funnel. Rinse the containers with dichloromethane and add the rinses to the separatory funnel. Extract by shaking with dichloromethane (3 x 100 mL). Combine the extracts, dry with powdered anhydrous sodium sulphate for a minimum of 30 minutes. Proceed as described below:

   i) Once the Soxhlet extraction of the XAD-2 resin and filters is complete, concentrate the 80:20 toluene:acetone extract to 1 mL by rotary evaporation. Quantitatively transfer the extract from Container E with dichloromethane rinses to the round bottom flask containing the extract of the XAD-2 and filters. Concentrate the extract to 1 mL by rotary evaporation.

   OR

   ii) If time permits prior to the Soxhlet extraction, quantitatively transfer the dichloromethane extract of Container E with dichloromethane rinses to the round bottom flask to be used for the Soxhlet extraction of the XAD-2 resin and filters. Concentrate the extract to 1 mL by rotary evaporation. Proceed with the Soxhlet extraction (Section 5.11.2)

f) Container F (6) (Final Rinses)

Solvent rinses, that may include dichloromethane, toluene, and/or methanol, of the condenser coil, back half of filter holder and impingers are in container F. The client does not always submit this container. **If the rinses contain additional or different solvents, consult the Supervisor for instructions.**

1. If methanol is in the Container F rinses, combine the rinses with the filtrate from Container A, and backwash as described in Step 4 of Section 5.11.1a.

2. If methanol is not present, dry the contents of Container F with powdered anhydrous sodium sulphate for a minimum of 30 minutes. Transfer the extract, using dichloromethane, to the 500 mL round bottom flask used for the Soxhlet extraction of the XAD-2 and filters (Section 5.11.2) and concentrate by rotary evaporation to 1 mL. (Add 1 mL toluene keeper to the flask if it has not been previously added.)

5.11.2 Soxhlet Extraction

1. Add 80:20 toluene:acetone (300 mL) and anti-bumping granules (4-5 granules) to a pre-cleaned 500 mL round bottom flask and extract the XAD-2/filters under reflux for 16-24 hours; adjust as necessary to achieve a reflux rate of 4 cycles per hour. Allow the extract to cool.

2. Remove water from the extract as follows:
   - If less than 3 mL of water is visible, quantitatively transfer the entire extract to an Erlenmeyer flask with toluene rinses.

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- If greater than 3 mL of water is visible, transfer the extract to a separatory funnel and drain the water from the sample extract. Discard the water. Quantitatively transfer the entire extract to an Erlenmeyer flask with toluene rinses.
- Dry the extract with anhydrous powdered sodium sulphate for a minimum of 30 minutes. Return the extract to the round bottom flask with complete toluene rinses. An aliquot of cleanup surrogate standard is added at this point or after the extract has been split. Refer to the Batch List for extract splitting instructions. Concentrate by rotary evaporation to 1 mL.

3. If not added prior to the Soxhlet extraction, add the dichloromethane extract from Container E (Section 5.11.1e) to the concentrated XAD-2/Filter extract in the Soxhlet extraction round bottom flask. Concentrate by rotary evaporation to 1 mL.

4. Elute the extract (and rinses of the round bottom flask) through a glass wool column to remove residual sodium sulphate prior to gravimetrically splitting the extract as specified on the Batch List, as described in Section 5.12.

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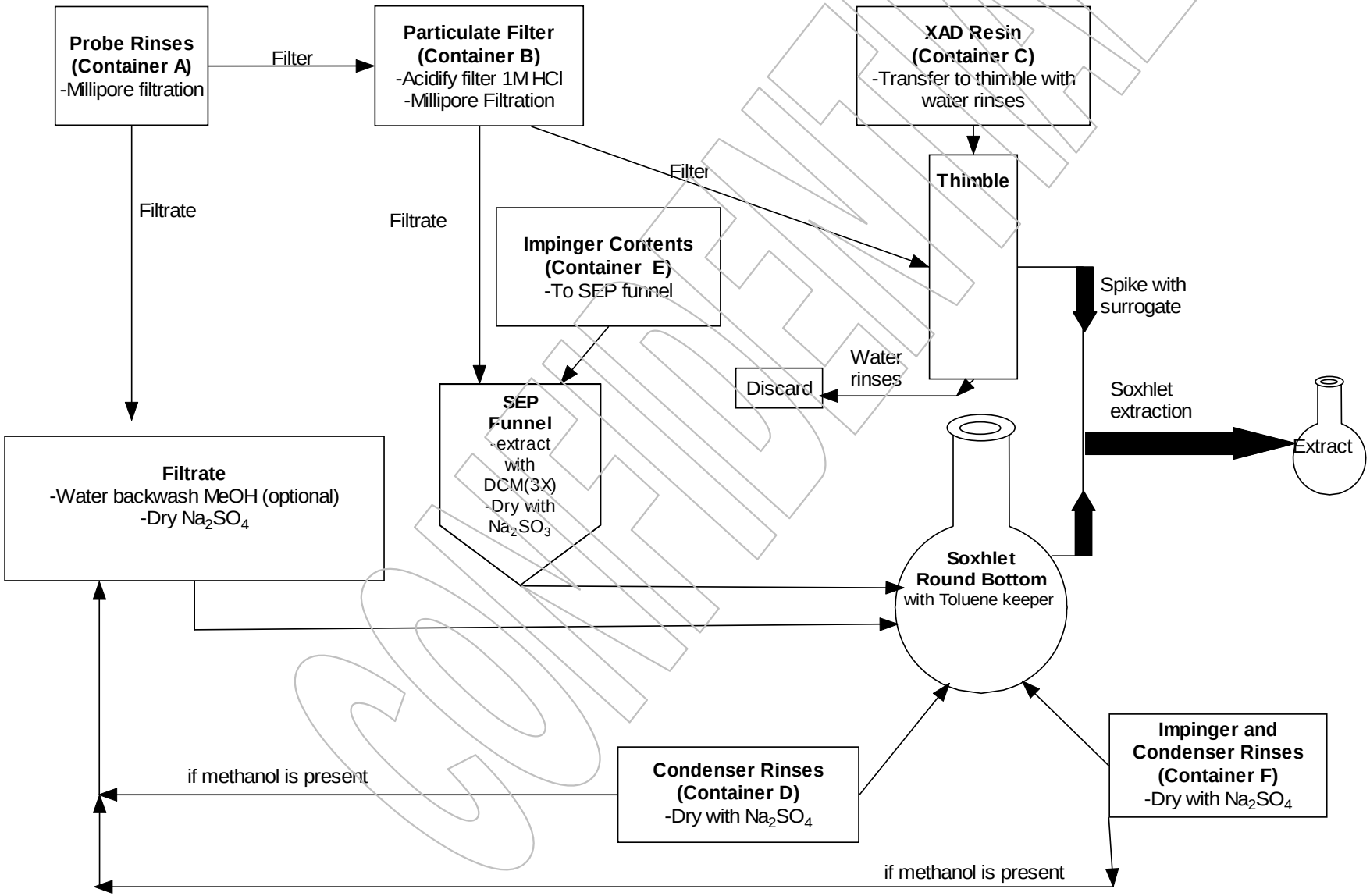
Figure 1: Processing of Sample Trains



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5.12 Extract Splitting Procedures

Gravimetrically split the extract into two portions, one for the PCB analysis and one as backup as described below. If multiple analyses are required, the extract may be split into many portions. Refer to the Batch List for extract splitting instructions. Record all weights on the worksheets.

Using a balance that weighs to three decimal places, weigh a clean, dry solvent rinsed, labelled centrifuge tube. Record the weight on the worksheet.

1. Inspect the extract for the presence of residual sodium sulphate.
   - If present, elute the extract through a glass wool column into the pre-weighed centrifuge tube. Solvent rinse the container with hexane.
   - If sodium sulphate is not present transfer the extract into the pre-weighed centrifuge tube. Solvent rinse the container with hexane.

2. Mix the extract well to ensure homogeneity. Using a Pasteur pipette, draw up a portion of the extract from the bottom of the centrifuge tube. Expel the extract back into the centrifuge tube above the level of the liquid. Do this a minimum of 5 times. When mixing is complete, drain any residual extract in the pipette into the centrifuge tube. **DO NOT** rinse the pipette. Using a balance that weighs to three decimal places, weigh the centrifuge tube with extract to determine the total weight of the extract. Record the weight on the worksheet. Calculate the weight of the extract and record on the worksheet.

3. Using a clean Pasteur pipette, transfer one portion (by weight, as specified on the Batch List) of the extract to a tared, clean, labelled glass ampoule. Record the weight of the extract. Cover the ampoule with clean foil and submit to the Sample Preparation group for sealing.

4. Reweigh the centrifuge tube, determine the weight of the remaining extract and record the weight on the worksheet. Use this portion of the extract for PCB analysis. If surrogate standard was not added prior to Soxhlet extraction, then spike the PCB portion of the extract with an aliquot of the surrogate standard. If not previously added, add an aliquot of cleanup standard to the extract. Refer to the Batch List for spiking instructions.

5. Include on the worksheet the balance inventory number, the date of the splitting procedure, and analyst's initials.

6. Concentrate the extract by evaporation under a stream of nitrogen to 1 mL.

7. If multiple analyses are required, use the procedures above to split the extract into the designated number of portions. Transfer the backup portion to a tared, clean, labelled, glass ampoule. Transfer the other portions to clean, solvent rinsed, labelled, tared centrifuge tubes if analysis is immediate or to clean, tared, glass ampoules if analysis is delayed. Record the total weight of extract, weight of centrifuge tube + extract, weight of each centrifuge tube, and weight of each portion on the worksheet. Cover the centrifuge tube portions with clean foil and

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a centrifuge tube cap and store in a refrigerator. Cover ampouled portions with foil and submit to the Sample Preparation group for ampoule sealing. Use one portion for PCB analysis.

8. The extract is ready for chromatography cleanup procedures (Section 6.0).

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6. COLUMN CLEANUP PROCEDURES

The chromatographic cleanup procedures used for the analysis of 209 PCB congeners are described in Sections 6.2 through 6.4. Optional cleanup columns described in Section 6.1 and 6.5 may be used depending upon the nature of the extract and the quality of the instrumental data. The Batch List indicates if optional columns are to be included as part of the initial extract cleanup procedures.

The nature of the extract or additional analysis requirements may necessitate using the columns in a different sequence. In this event, the analyst must ensure that the extracts are in a solvent suitable for the column.

For manual clean-up, three options for sequencing the Florisil/silica/alumina columns are permitted as shown in Figure 2 - Manual Florisil/Silica/Alumina Clean-up Column Sequence (below).

At least two tests for sulphur with activated copper must be performed (refer to SLA-045 “Removal of Sulphur from Extracts using Activated Copper”). One of these tests must be performed after the Florisil column. The test for sulphur with activated copper is ineffective in the presence of toluene. If cleanup for pesticide analysis is required refer to Appendix A for details.

In the case where polybrominated diphenylethers and/or polychlorinated naphthalenes analytes are also to be determined, along with the PCBs, the cleanup procedures may be carried out using an automated fluid management system (FMS) or using modified manual cleanup procedures. The analyst is referred to the following documents for details of FMS and manual cleanup procedures:

MLA-033	Analytical Method for the Determination of Brominated Diphenylethers (PBDE) by EPA Method 1614
MLA-030	Analytical Method for the Determination of Polychlorinated Naphthalenes (PCN)
FQA-074	Approved FMS Columns, Solvents and Programs
SLA-090	Maintenance and Use of FMS Chromatographic Cleanup Instrument

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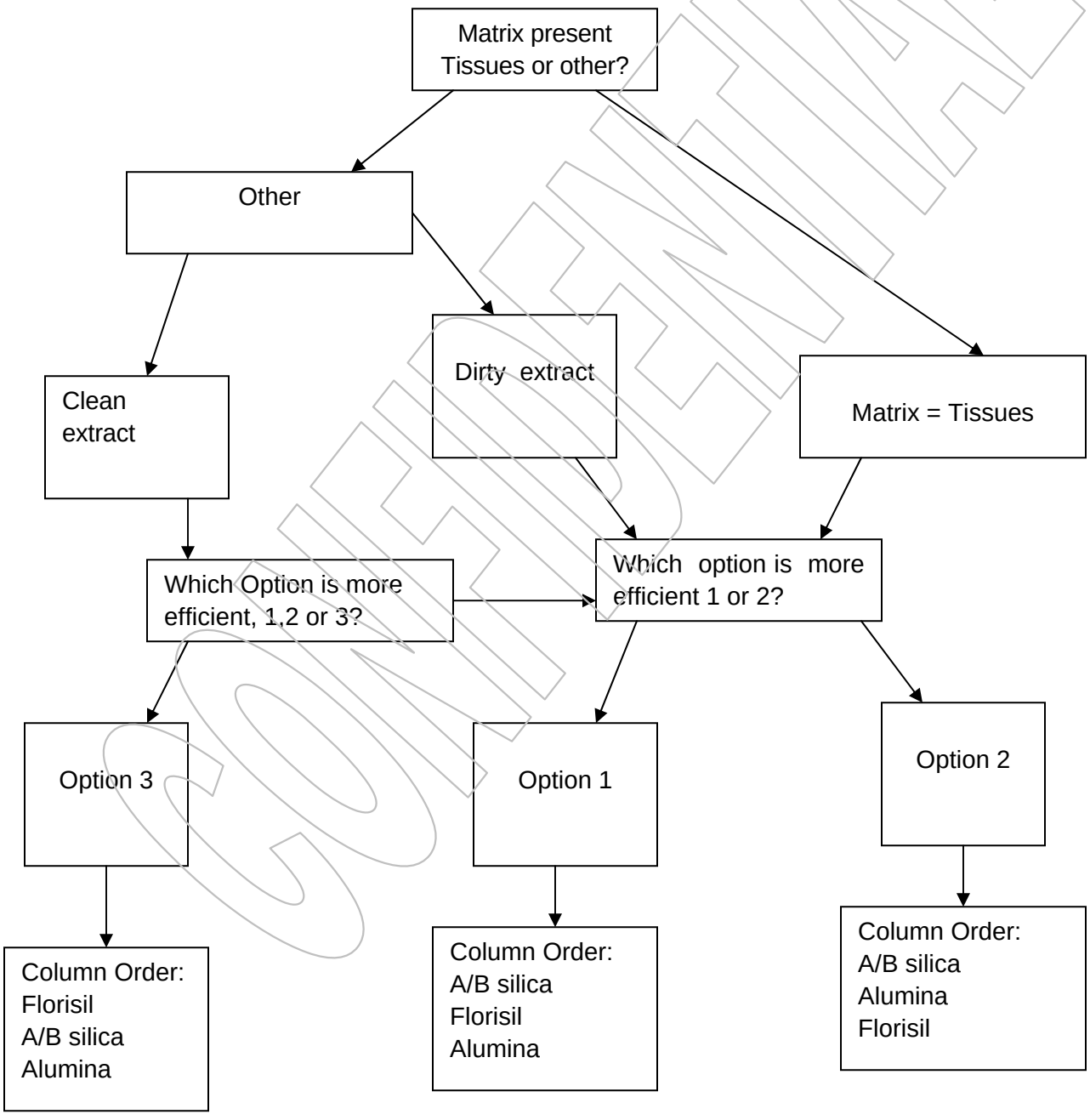
Figure 2: Flow Chart - Manual Florisil/Silica/Alumina Clean-up Column Sequence



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6.1 Optional: Gel Permeation Cleanup Column

Optional cleanup on a gel permeation column may be carried out on extracts from sediment, soil, XAD-2 column, ambient air, solvent extract and aqueous sample extracts using a Biobead column. The Biobead column may be used prior to the chromatographic sequences described in Section 6.2. The cleanup is carried out as described below.

If necessary, carry out a solvent exchange on the extract to ensure that the extract is in 1:1 dichloromethane:hexane prior to cleanup on the Biobead column. Minor amounts of other solvents (i.e. up to 1 mL of toluene) can be tolerated.

Load the extract onto a Biobead SX-3 gel permeation column (prepared as described in Section 3.6.2) with 1:1 dichloromethane:hexane and elute with 1:1 dichloromethane:hexane at 5 mL/min. Refer to the most recent Biobead cutpoint determination for the elution volumes. Typical cutpoints are as follows:

F1	0 - 140 mL
F2	140 - 300 mL

Collect the second fraction and evaporate to a small volume by rotary evaporation.

6.2 Multi-layered Acid/Base Silica Column

Extract may be loaded on to acid/base silica columns in any solvent. This column may be loaded from a round bottom flask.

Transfer the extract and hexane rinses (3 x 1-2 mL from the elution volume) to a layered acid/base silica column, prepared as described in Section 3.6.5 and elute with hexane (100 mL) at 5 mL/min. Collect the eluate in a round bottom flask and concentrate to a volume of 1 mL by rotary evaporation.

6.3 Alumina Column

The extract must be in 1 mL of hexane prior to loading onto the alumina column. Alumina columns may be loaded from a round bottom flask as long as the volume is 1 mL and the solvent is hexane. If other solvents are present in the extract a solvent exchange must be carried out as described below.

Solvent Exchange

Transfer the extract to a centrifuge tube with hexane and evaporate to 300 µL (50 µL if toluene is present) under a stream of nitrogen. Add hexane to 1 mL.

Load the extract with hexane rinses (3 x 1 mL, from the elution volume) onto an alumina column (6 g, 1% deactivated) prepared as described in Section 3.6.1. Refer to the most recent alumina cutpoint determination for the volume of solvent to use. Typical cutpoints are as follows:

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F1	hexane	15 mL
F2	1:1 dichloromethane:hexane	35 mL

Elute the column with hexane (F1) and discard the eluate. Elute the column with 1:1 dichloromethane:hexane (F2) and retain the eluate. Concentrate to 1 mL by rotary evaporation and transfer to a centrifuge tube. Concentrate under a stream of nitrogen.

6.4 Florisil Column

Florisil columns must be loaded from a centrifuge tube. The extract must be 1 mL in hexane. If other solvents are present a solvent exchange must be carried out as described in section 6.3. Load the extract (in hexane) and rinse 3 times with the E1 elution solvent (15:85 dichloromethane:hexane) on a Florisil column (8 g, 2.1% deactivated) prepared as described in Section 3.6.4. Elute the column with 15:85 dichloromethane:hexane (E1) using the volume of solvent determined from the most recent Florisil cutpoint determination. A typical cutpoint is as follows:

E1	15:85 dichloromethane:hexane	45 mL

6.5 Optional: 4.5% Carbon/Celite Column (Toxic PCB Congeners)

This column may be used as part of the initial extract cleanup where it is used just prior to the alumina column (Section 6.3). Alternately, it is may be used only after the successful HRGC/HRMS analysis of all 209 PCB congeners has been carried out.

Prepare a 4.5% carbon/Celite column as described in Section 3.6.3, (0.22 g, 4.5% carbon AX 21 on Celite, pre-eluted with 15 mL toluene, and 15 mL hexane).

Note - Watch carefully for the packing slipping in the column. Be generous with the glass wool plugs when packing columns.

Ensure the extract is in hexane (1 mL). Load the extract with hexane rinses (2 x 1 mL, taken from a 15 mL elution volume) onto the column. (A total of 3 mL of hexane should have been applied to the column). Elute the column with remaining hexane and store the eluate (E1) in a centrifuge tube that is capped and covered with clean foil.

Invert the column and elute with toluene. Refer to the most recent cutpoint determination for the elution volume. The typical elution volume is 50 - 60 mL. Collect this fraction in a 100 mL round-bottom flask. This fraction is E2. Concentrate the E2 fraction by rotary evaporation to a small volume. Transfer the extract to a clean centrifuge tube with toluene rinses and concentrate to 500 µL by evaporation under a gentle stream of nitrogen.

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7. PREPARATION FOR GC/MS ANALYSIS

After the final column concentrate the eluate to 1 mL by rotary evaporation.

If both copper tests have been done, add 1 mL of toluene to the extract in the round bottom flask before reducing on a rotovap.

If both copper tests have not been done, add 1 mL of toluene to the centrifuge tube before blow down. Transfer the extract to a centrifuge tube with hexane rinses (3 x 1 mL) and concentrate to 300 µL in a stream of nitrogen, using a flow rate that produces an obvious dip in the surface of the solvent.

Add nonane (15 µL) to a clean autosampler vial (if the extract is also being analyzed for PBDE add 15 µL of toluene rather than 15 µL of nonane). Mark the vial at the 15 µL volume. Transfer the extract to the autosampler vial and concentrate to 150 – 200 µL under a gentle stream of nitrogen. Rinse the centrifuge tube with 350 µL of hexane and add the rinse to the autosampler vial. Concentrate the extract to a 150 – 200 µL using a gentle stream of nitrogen. Make sure the volume of extract does not go below 100 µL. Rinse the centrifuge tube with 350 µL of hexane and add the rinse to the autosampler vial. Concentrate as described below:

PCB or PCB/BDE Analysis

Concentrate the extract to 15 µL. Add an aliquot of recovery standard (5 µL) to the autosampler vial. Cap the autosampler vial. Store the vials in the freezer until just prior to GC/MS analysis.

BDE Analysis

Concentrate the extract to 45 µL (15 µL for blood extracts). Add an aliquot of recovery standard (5 µL) to the autosampler vial. Cap the autosampler vial. Store the vials in the freezer until just prior to GC/MS analysis.

Refer to the following Standard Operating Procedures:

Document ID	Title
SLA-008	Preparing Extracts for Instrumental Analysis
SLA-072	Computer Preparation of Labels

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8. HRGC/HRMS ANALYSIS

Analysis by high resolution GC/MS is carried out using a Micromass Ultima high resolution mass spectrometer equipped with an HP 6890 gas chromatograph, a CTC autosampler, and an Alpha workstation running VG software. Chromatographic separation is achieved using an SPB-Octyl column (30 m, 0.25 mm I.D., 0.25 µm film thickness).

Perform the GC/MS analyses as described in Section 14 of EPA Method 1668A. Instrumental analysis details are described in the most recent revision of AXYS instrumental method MIN-010, *EPA Method 1668A - Instrument Parameters and Specifications*.

Use the calibration standard level CS-0.2 as the sensitivity standard. Analyse the solution every time an initial calibration procedure is carried out.

Table 8 of EPA Method 1668A presents the ions monitored, the ion abundance ratios, and quality control limits for all chlorination groups. The QC limits for the theoretical ratios must be satisfied for all analyses, including calibration solutions, QC samples, and test samples.

8.1 Initial Calibration

Refer to Section 10.0 of EPA Method 1668A for details of calibration procedures. Perform the initial calibration as described in Section 10.4, using the calibration solutions described on Table 3 of this method.

The initial calibration solutions establish retention times and response factors for congeners present in the calibration solutions. After analysis of the multi-level standards (CS-1 through CS-5 or CS-0.2 through CS-5 for high sensitivity option), analyze the calibration solution for 209 PCB congeners to establish the relative response factors and retention times for those PCB congeners not present in the multi-level standards solutions. The 209 congener standard need not be analyzed if only the analysis of toxic congeners is requested.

Optional Initial Calibration Procedure: A series of six calibration solutions, where the lowest concentration solution is one-half the concentration of the CS-1 solution, may be analyzed and unsmoothed data acquired and used to determine the linearity of the GC/MS. This option is used upon client request.

8.1.1 CS-0.2 Initial Calibration Criteria

An option is provided for evaluation of the CS-0.2 initial calibration results using duplicate injections performed sequentially. The CS-0.2 standard may be run twice at the beginning of the initial calibration series; the first run is quantified as a calibration run and included in the calculation of mean RRFs and the second run is quantified in concentration as a calibration verification run. Acceptability of ion ratios for the CS-0.2 standard may be based on

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evaluation of both the first and the second injections (see Figure 2). The 12-hour calibration time window always starts with the first injection of the CS-0.2 standard.

First Injection of CS-0.2 - Ion Ratio Acceptance Criteria

If the peak ion ratios for more than four congeners differ by more than 15% from theoretical or the peak ion ratio for any congener differs from theoretical by more than 35%, the instrument must be adjusted or serviced and the initial calibration sequence re-started with injection of CS-0.2.

If all ion peak ratios are within 15% of theoretical then the CS-0.2 peak ion ratio criteria have been met and a second injection of the CS-0.2 standard is not required.

If all ion peak ratios are not within 15% of theoretical for the first injection of the CS-0.2 standard but the ion peak ratios for a maximum of four congeners differ from theoretical by no more than 35% and the ion ratios for all remaining congeners are within 15% of theoretical, then further evaluation of CS 0-2 peak ion ratios may be made based on a second injection of CS-0.2.

Second Injection CS-0.2 - Ion Ratio Acceptance Criteria

If the ion peak ratios for a maximum of four congeners differ from theoretical by no more than 35%, ion ratios for all remaining congeners fall within 15% of theoretical and the ion ratio for any congener differing from theoretical by more than 15% in the first injection CS-0.2 falls within 15% of theoretical for the second injection CS-0.2 then the CS-0.2 peak ion ratio criteria have been met.

If the above conditions are not all met the instrument must be adjusted or serviced and the initial calibration sequence re-started with the first injection of CS-0.2.

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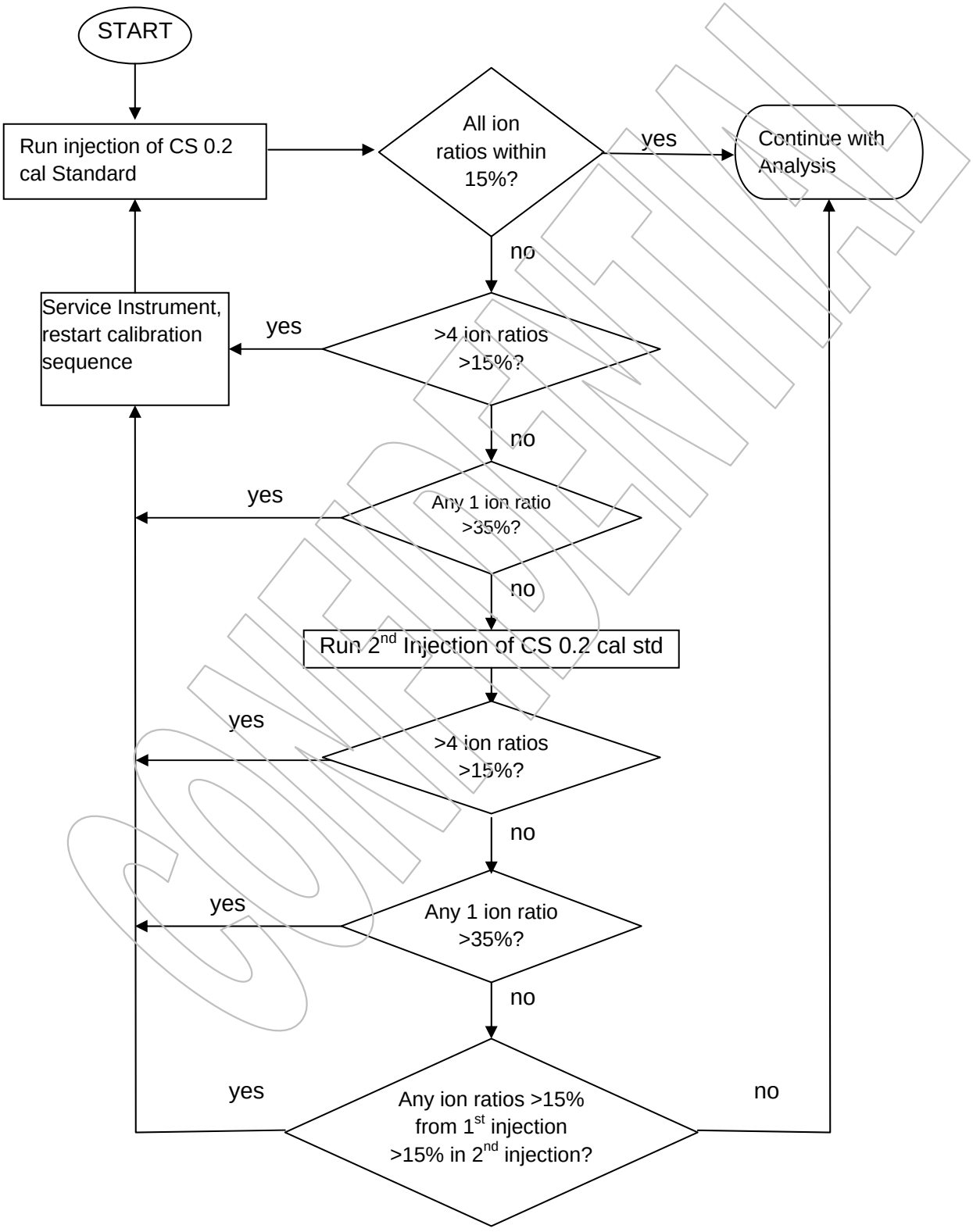
Figure 3. Procedure for Ion Ratio Criteria for CS-0.2 Initial Calibration Standard



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8.2 Calibration Verification

Every 12 hours the GC/MS system performance and calibration must be verified by the analysis of the 209 PCB congener solution. The QC criteria for the CAL/VER solution, as presented in Table 4, must be met prior to the analysis of samples. Details of the calibration verification procedures are described in the EPA Method 1668A, Section 15.0.

8.3 Analysis of Samples

Refer to Section 14.0 of EPA Method 1668A for details of instrumental analysis. Table 5 of this document summarizes the calibration and sample injection sequence.

Refer to Section 15.0 of EPA Method 1668A for details of system and laboratory performance.

Extracts may be diluted with solvent and re-injected to bring responses within linear range. Extracts may not be diluted beyond the point at which reliable isotope quantification can be performed. Routine extract dilutions should not exceed 10 times (final extract volume of 200 µL). For any extracts analyzed at a greater dilution the chromatograms from both before and after the dilution must be inspected to ensure that detector 'phantom peak' phenomenon will not, and has not, impacted the reliability of results; supervisory approval of the dilution results must be documented. Appendix C gives details on performing the check for phantom peak phenomenon. Extracts with concentrations exceeding the range for reliable isotope dilution quantification must be reanalyzed using smaller sample sizes. For very high level samples and where allowable by contract it may be permissible to respike a diluted portion of the extract with an additional aliquot of surrogate standard, reinject and correct final concentrations for dilution/respike factors and surrogate recoveries observed initially.

8.4 Resolution of Coeluting Congeners

Resolution of the PCB 156/157 co-elution is achieved by high resolution GC/MS using a Micromass Ultima high resolution mass spectrometer coupled to an HP5890 or HP6890 gas chromatograph equipped with a CTC autosampler and an Alpha workstation running VG software. Chromatographic separation is achieved using a DB-1 chromatography column (30 m, 0.25 mm id, 0.25 µm film thickness).

8.5 Interferences

Analysis of the extract on either a DB-1 or DB-5 column is useful to resolve potential interferences with PCB 169 (from PCB 190). If the data show that such interference is present, carry out a GC/MS analysis on DB-1 or DB-5 column.

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Table 5. EPA Method 1668A Instrumental Injection Sequence

TEST	Maximum Allowable Time *	Cycle
PFK Tune/Mass Res #1		Start of first cycle
CS3 run 1		
CS1, CS2, CS4, CS5		
209 Congener CS		
Instr blank		
QC Samples, Samples		
PFK Tune/Mass Res #2	PFK Tune/Mass Res #1 +12.0 hr	
CS3 run 2	CS3 run1 + 12.0 hr	Completion of first cycle
209 Congener CS		
Instr blank		
QC Samples, Samples		
PFK Tune/Mass Res #3	PFK Tune/Mass Res #2 +12.0 hr	
CS3 run 3	CS3 run2 + 12.0 hr	Completion of second cycle
Instr blank		
QC Samples, Samples		
…continue cycles or stop as below		
CS3 run 3		
PFK Tune/Mass Res #4	PFK Tune/Mass Res #3 +12.0 hr	Stop

*Time at injection

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9. QUALITATIVE AND QUANTITATIVE DETERMINATION

Refer to Section 16.0 of EPA Method 1668A for details of qualitative determination and to Section 17.0 of EPA Method 1668A for details of quantitative determination incorporating any modifications noted in Section 10 of this document and the modification below.

Peaks are assigned as target compounds on the basis of correct ion ratio within a specified retention time window. The retention time windows, around the observed retention time in the calibration standard, adjusted for any peak shifting in samples, are shown in Table 6a (for alternate reporting of PCB congener numbers 107, 108, 109 in accordance with EPA 1668C use the specific information in Table 6b, Appendix E). For Toxic/LOC/Window Defining/Labelled congeners retention time (RT) acceptance limits are determined from the mean RTs of the multi-point calibration runs; for other compounds the RT windows are determined from the single point 209 calibration standard.

9.1 Calculation of Aroclor Equivalent Concentrations from SPB-Octyl GC Column Data

Aroclor equivalent concentrations may be calculated by converting the summed concentrations of a suite of characteristic PCB congeners to concentrations using empirical factors determined from the analysis of Aroclor mixtures.

Aroclor 1016[1] = the sum of PCBs 8, 18/30, 31, 28/20 concentrations multiplied by 2.7;
Aroclor 1221 = the sum of PCBs 1, 3, 8 concentrations multiplied by 1.4;
Aroclor 1232 = the sum of PCBs 1, 3, 18/30 concentrations multiplied by 3.4;
Aroclor 1242[1] = the sum of PCBs 8, 18/30, 31, 28/20 concentrations multiplied by 3.0;
Aroclor 1248 = the sum of PCBs 44/47/65, 49/69, 66 concentrations multiplied by 6.1;
Aroclor 1254 = the sum of PCBs 86/87/97/108/119/125, 99 concentrations multiplied by 8.0;
Aroclor 1260 = the sum of PCBs 183/185, 180/193, 170 concentrations multiplied by 5.0;

Environmental samples with no clearly identified Aroclor signature are quantified as 1242/1254/1260 mixtures. Results may be reported as Aroclor 1248 instead of Aroclor 1242 and 1254 where the congener pattern clearly indicates this formulation. Other Aroclor formulations may be reported by calibration against the specific Aroclor solutions.

[1] Aroclors 1016 and 1242 may be reported as combined 1016/1242 using the 1242 factor if allowed by contract

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Table 6a. Analyte Retention Times, Surrogates Used and RRT Windows for 209 PCB's by HRGC/MS

COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
2 - MoCB	1	2051-60-7	1L		11:34:00	1L	11:34:00	1.000	-1,3	0.999	1.004
3 - MoCB	2	2051-61-8	1L/3L		13:38:00	3L	13:48:00	0.988	6	0.984	0.992
4 - MoCB	3	2051-62-9	3L		13:49:00	3L	13:48:00	1.001	-1,3	0.999	1.004
22' - DiCB	4	13029-08-8	4L		14:04:00	4L	14:03:00	1.001	-1,3	0.999	1.004
26 - DiCB	10	33146-45-1	4L/15L		14:14:00	4L	14:03:00	1.013	6	1.009	1.017
25 - DiCB	9	34883-39-1	4L/15L		16:06:00	4L	14:03:00	1.146	6	1.142	1.149
24 - DiCB	7	33284-50-3	4L/15L		16:16:00	4L	14:03:00	1.158	6	1.154	1.161
23' - DiCB	6	25569-80-6	4L/15L		16:31:00	4L	14:03:00	1.176	6	1.172	1.179
23 - DiCB	5	16605-91-7	4L/15L		16:49:00	4L	14:03:00	1.197	6	1.193	1.200
24' - DiCB	8	34883-43-7	4L/15L		16:58:00	4L	14:03:00	1.208	6	1.204	1.211
35 - DiCB	14	34883-41-5	4L/15L		18:39:00	15L	20:08:00	0.926	6	0.924	0.929
33' - DiCB	11	2050-67-1	4L/15L		19:32:00	15L	20:08:00	0.970	6	0.968	0.973
34' - DiCB	13	2974-90-5	4L/15L	12 + 13							
34 - DiCB	12	2974-92-7	4L/15L	12 + 13	19:51:00	15L	20:08:00	0.986	6	0.983	0.988
44' - DiCB	15	2050-68-2	15L		20:09:00	15L	20:08:00	1.001	-1,3	0.999	1.002
22'6 - TriCB	19	38444-73-4	19L		17:15:00	19L	17:13:00	1.002	-1,3	0.999	1.003
246 - TriCB	30	35693-92-6	19L/37L	18 + 30							
22'5 - TriCB	18	37680-65-2	19L/37L	18 + 30	19:09:00	19L	17:13:00	1.112	6	1.109	1.115
22'4 - TriCB	17	37680-66-3	19L/37L		19:36:00	19L	17:13:00	1.138	6	1.136	1.141
23'6 - TriCB	27	38444-76-7	19L/37L		19:50:00	19L	17:13:00	1.152	6	1.149	1.155
236 - TriCB	24	55702-45-9	19L/37L		19:58:00	19L	17:13:00	1.160	6	1.157	1.163
22'3 - TriCB	16	38444-78-9	19L/37L		20:05:00	19L	17:13:00	1.167	6	1.164	1.169
24'6 - TriCB	32	38444-77-8	19L/37L		20:37:00	19L	17:13:00	1.197	6	1.195	1.200
2'35 - TriCB	34	37680-68-5	19L/37L		21:56:00	19L	17:13:00	1.274	6	1.271	1.277
235 - TriCB	23	55720-44-0	19L/37L		22:06:00	19L	17:13:00	1.284	6	1.281	1.287
245 - TriCB	29	15862-07-4	19L/37L	26 + 29							
23'5 - TriCB	26	38444-81-4	19L/37L	26 + 29	22:26:00	19L	17:13:00	1.303	10	1.298	1.308
23'4 - TriCB	25	55712-37-3	19L/37L		22:40:00	37L	27:27:00	0.826	6	0.824	0.828

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COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
24'5 - TriCB	31	16606-02-3	19L/37L		22:59:00	37L	27:27:00	0.837	6	0.835	0.839
244' - TriCB	28	7012-37-5	19L/37L	20 + 28							
233' - TriCB	20	38444-84-7	19L/37L	20 + 28	23:18:00	37L	27:27:00	0.849	10	0.846	0.852
234 - TriCB	21	55702-46-0	19L/37L	21 + 33	23:30:00	37L	27:27:00	0.856	10	0.853	0.859
2'34 - TriCB	33	38444-86-9	19L/37L	21 + 33							
234' - TriCB	22	38444-85-8	19L/37L		23:57:00	37L	27:27:00	0.872	6	0.871	0.874
33'5 - TriCB	36	38444-87-0	19L/37L		25:35:00	37L	27:27:00	0.932	6	0.930	0.934
34'5 - TriCB	39	38444-88-1	19L/37L		25:58:00	37L	27:27:00	0.946	6	0.944	0.948
345 - TriCB	38	53555-66-1	19L/37L		26:33:00	37L	27:27:00	0.967	6	0.965	0.969
33'4 - TriCB	35	37680-69-6	19L/37L		27:03:00	37L	27:27:00	0.985	6	0.984	0.987
344' - TriCB	37	38444-90-5	37L		27:28:00	37L	27:27:00	1.001	-1,3	0.999	1.002
22'66' - TeCB	54	15968-05-5	54L		20:25:00	54L	20:25:00	1.000	-1,3	0.999	1.002
22'46 - TeCB	50	62796-65-0	54L/81L/77L	50 + 53	22:41:00	54L	20:25:00	1.111	10	1.107	1.115
22'56' - TeCB	53	41464-41-9	54L/81L/77L	50 + 53							
22'36 - TeCB	45	70362-45-7	54L/81L/77L	45 + 51	23:24:00	54L	20:25:00	1.146	10	1.142	1.150
22'46' - TeCB	51	68194-04-7	54L/81L/77L	45 + 51							
22'36' - TeCB	46	41464-47-5	54L/81L/77L		23:41:00	54L	20:25:00	1.160	6	1.158	1.162
22'55' - TeCB	52	35693-99-3	54L/81L/77L		25:11:00	54L	20:25:00	1.233	6	1.231	1.236
23'5'6 - TeCB	73	74338-23-1	54L/81L/77L		25:20:00	54L	20:25:00	1.241	6	1.238	1.243
22'35 - TeCB	43	70362-46-8	54L/81L/77L		25:26:00	54L	20:25:00	1.246	6	1.243	1.248
23'46 - TeCB	69	60233-24-1	54L/81L/77L	49 + 69							
22'45' - TeCB	49	41464-40-8	54L/81L/77L	49 + 69	25:40:00	54L	20:25:00	1.257	10	1.253	1.261
22'45 - TeCB	48	70362-47-9	54L/81L/77L		25:59:00	54L	20:25:00	1.273	6	1.270	1.275
2356 - TeCB	65	33284-54-7	54L/81L/77L	44 + 47 + 65							
22'44' - TeCB	47	2437-79-8	54L/81L/77L	44 + 47 + 65							
22'35' - TeCB	44	41464-39-5	54L/81L/77L	44 + 47 + 65	26:14:00	54L	20:25:00	1.285	10	1.281	1.289
2346 - TeCB	62	54230-22-7	54L/81L/77L	59 + 62 + 75							
244'6 - TeCB	75	32598-12-2	54L/81L/77L	59 + 62 + 75							
233'6 - TeCB	59	74472-33-6	54L/81L/77L	59 + 62 + 75	26:34:00	54L	20:25:00	1.301	10	1.297	1.305
22'34' - TeCB	42	36559-22-5	54L/81L/77L		26:45:00	54L	20:25:00	1.310	6	1.308	1.313
22'34 - TeCB	41	52663-59-9	54L/81L/77L	40 + 41 + 71							

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COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
23'4'6 - TeCB	71	41464-46-4	54L/81L/77L	40 + 41 + 71							
22'33' - TeCB	40	38444-93-8	54L/81L/77L	40 + 41 + 71	27:14:00	54L	20:25:00	1.334	10	1.330	1.338
234'6 - TeCB	64	52663-58-8	54L/81L/77L		27:31:00	54L	20:25:00	1.348	6	1.345	1.350
23'55' - TeCB	72	41464-42-0	54L/81L/77L		28:24:00	81L	34:31:00	0.823	6	0.821	0.824
23'45' - TeCB	68	73575-52-7	54L/81L/77L		28:42:00	81L	34:31:00	0.831	6	0.830	0.833
233'5 - TeCB	57	70424-67-8	54L/81L/77L		29:09:00	81L	34:31:00	0.845	6	0.843	0.846
233'5' - TeCB	58	41464-49-7	54L/81L/77L		29:23:00	81L	34:31:00	0.851	6	0.850	0.853
23'45 - TeCB	67	73575-53-8	54L/81L/77L		29:34:00	81L	34:31:00	0.857	6	0.855	0.858
234'5 - TeCB	63	74472-34-7	54L/81L/77L		29:50:00	81L	34:31:00	0.864	6	0.863	0.866
2345 - TeCB	61	33284-53-6	54L/81L/77L	61 + 70 + 74 + 76	30:11:00	81L	34:31:00	0.874	12	0.872	0.877
23'4'5 - TeCB	70	32598-11-1	54L/81L/77L	61 + 70 + 74 + 76							
2'345 - TeCB	76	70362-48-0	54L/81L/77L	61 + 70 + 74 + 76							
244'5 - TeCB	74	32690-93-0	54L/81L/77L	61 + 70 + 74 + 76							
23'44' - TeCB	66	32598-10-0	54L/81L/77L		30:32:00	81L	34:31:00	0.885	6	0.883	0.886
233'4 - TeCB	55	74338-24-2	54L/81L/77L		30:41:00	81L	34:31:00	0.889	6	0.887	0.890
233'4' - TeCB	56	41464-43-1	54L/81L/77L		31:13:00	81L	34:31:00	0.904	6	0.903	0.906
2344' - TeCB	60	33025-41-1	54L/81L/77L		31:27:00	81L	34:31:00	0.911	6	0.910	0.913
33'55' - TeCB	80	33284-52-5	54L/81L/77L		31:54:00	81L	34:31:00	0.924	6	0.923	0.926
33'45' - TeCB	79	41464-48-6	54L/81L/77L		33:29:00	81L	34:31:00	0.970	6	0.969	0.972
33'45 - TeCB	78	70362-49-1	54L/81L/77L		34:05:00	81L	34:31:00	0.987	6	0.986	0.989
344'5 - TeCB	81	70362-50-4	81L		34:32:00	81L	34:31:00	1.000	-1,3	1.000	1.001
33'44' - TeCB	77	32598-13-3	77L		35:08:00	77L	35:07:00	1.000	-1,3	1.000	1.001
22'466' - PeCB	104	56558-16-8	104L		26:10:00	104L	26:08:00	1.001	-1,3	0.999	1.002
22'366' - PeCB	96	73575-54-9	104L/123L/114L/ 118L/105L		26:32:00	104L	26:08:00	1.015	10	1.012	1.018
22'45'6 - PeCB	103	60145-21-3	104L/123L/114L/ 118L/105L		28:34:00	104L	26:08:00	1.093	6	1.091	1.095
22'356' - PeCB	94	73575-55-0	104L/123L/114L/ 118L/105L		28:48:00	104L	26:08:00	1.102	6	1.100	1.104
22'35'6 - PeCB	95	38379-99-6	104L/123L/114L/ 118L/105L	93 + 95 + 98 + 100 + 102							
22'44'6 - PeCB	100	39485-83-1	104L/123L/114L/ 118L/105L	93 + 95 + 98 + 100 + 102							

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COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
22'356 - PeCB	93	73575-56-1	104L/123L/114L/ 118L/105L	93 + 95 + 98 + 100 + 102	29:31:00	104L	26:08:00	1.129	20	1.123	1.136
22'456' - PeCB	102	68194-06-9	104L/123L/114L/ 118L/105L	93 + 95 + 98 + 100 + 102							
22'3'46 - PeCB	98	60233-25-2	104L/123L/114L/ 118L/105L	93 + 95 + 98 + 100 + 102							
22'346 - PeCB	88	55215-17-3	104L/123L/114L/ 118L/105L	88 + 91	30:07:00	104L	26:08:00	1.152	12	1.149	1.156
22'34'6 - PeCB	91	68194-05-8	104L/123L/114L/ 118L/105L	88 + 91							
22'33'6 - PeCB	84	52663-60-2	104L/123L/114L/ 118L/105L		30:23:00	104L	26:08:00	1.163	6	1.161	1.165
22'346' - PeCB	89	73575-57-2	104L/123L/114L/ 118L/105L		30:53:00	104L	26:08:00	1.182	6	1.180	1.184
23'45'6 - PeCB	121	56558-18-0	104L/123L/114L/ 118L/105L		31:20:00	104L	26:08:00	1.199	6	1.197	1.201
22'355' - PeCB	92	52663-61-3	104L/123L/114L/ 118L/105L		31:44:00	123L	37:12:00	0.853	6	0.852	0.854
233'5'6 - PeCB	113	68194-10-5	104L/123L/114L/ 118L/105L	90 + 101 + 113							
22'34'5 - PeCB	90	68194-07-0	104L/123L/114L/ 118L/105L	90 + 101 + 113	32:19:00	123L	37:12:00	0.869	10	0.866	0.871
22'455' - PeCB	101	37680-73-2	104L/123L/114L/ 118L/105L	90 + 101 + 113							
22'33'5 - PeCB	83	60145-20-2	104L/123L/114L/ 118L/105L	83 + 99	32:53:00	123L	37:12:00	0.884	12	0.881	0.887
22'44'5 - PeCB	99	38380-01-7	104L/123L/114L/ 118L/105L	83 + 99							
233'56 - PeCB	112	74472-36-9	104L/123L/114L/ 118L/105L		33:04:00	123L	37:12:00	0.889	6	0.888	0.890
23'44'6 - PeCB	119	56558-17-9	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 108 + 119 + 125							
233'45' - PeCB	108	70362-41-3	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 108 + 119 + 125							
22'345 - PeCB	86	55312-69-1	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 108 + 119 + 125	33:29:00	123L	37:12:00	0.900	16	0.897	0.904

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COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
22'3'45 - PeCB	97	41464-51-1	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 108 + 119 + 125							
2'3456' - PeCB	125	74472-39-2	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 108 + 119 + 125							
22'345' - PeCB	87	38380-02-8	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 108 + 119 + 125							
234'56 - PeCB	117	68194-11-6	104L/123L/114L/ 118L/105L	85 + 116 + 117							
23456 - PeCB	116	18259-05-7	104L/123L/114L/ 118L/105L	85 + 116 + 117							
22'344' - PeCB	85	65510-45-4	104L/123L/114L/ 118L/105L	85 + 116 + 117	34:12:00	123L	37:12:00	0.919	12	0.917	0.922
233'4'6 - PeCB	110	38380-03-9	104L/123L/114L/ 118L/105L	110 + 115	34:27:00	123L	37:12:00	0.926	10	0.924	0.928
2344'6 - PeCB	115	74472-38-1	104L/123L/114L/ 118L/105L	110 + 115							
22'33'4 - PeCB	82	52663-62-4	104L/123L/114L/ 118L/105L		34:43:00	123L	37:12:00	0.933	6	0.932	0.935
233'55' - PeCB	111	39635-32-0	104L/123L/114L/ 118L/105L		35:10:00	123L	37:12:00	0.945	6	0.944	0.947
23'455' - PeCB	120	68194-12-7	104L/123L/114L/ 118L/105L		35:38:00	123L	37:12:00	0.958	6	0.957	0.959
233'4'5 - PeCB	107	70424-68-9	104L/123L/114L/ 118L/105L	107 + 124	36:50:00	123L	37:12:00	0.990	10	0.988	0.992
2'3455' - PeCB	124	70424-70-3	104L/123L/114L/ 118L/105L	107 + 124							
233'46 - PeCB	109	74472-35-8	104L/123L/114L/ 118L/105L		37:05:00	123L	37:12:00	0.997	6	0.996	0.998
2'344'5 - PeCB	123	65510-44-3	123L		37:13:00	123L	37:12:00	1.000	-1,3	1.000	1.001
233'45 - PeCB	106	70424-69-0	104L/123L/114L/ 118L/105L		37:21:00	123L	37:12:00	1.004	6	1.003	1.005
23'44'5 - PeCB	118	31508-00-6	118L		37:34:00	118L	37:32:00	1.001	-1,3	1.000	1.002
2'33'45 - PeCB	122	76842-07-4	104L/123L/114L/ 118L/105L		37:55:00	118L	37:32:00	1.010	6	1.009	1.012
2344'5 - PeCB	114	74472-37-0	114L		38:07:00	114L	38:06:00	1.000	-1,3	1.000	1.001

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COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233'44' - PeCB	105	32598-14-4	105L		38:48:00	105L	38:46:00	1.001	-1,3	0.999	1.001
33'455' - PeCB	127	39635-33-1	104L/123L/114L/ 118L/105L		40:21:00	105L	38:46:00	1.041	6	1.040	1.042
33'44'5 - PeCB	126	57465-28-8	126L		42:02:00	126L	42:01:00	1.000	-1,3	1.000	1.001
22'44'66' - HxCB	155	33979-03-2	155L		32:06:00	155L	32:05:00	1.001	-1,3	0.999	1.002
22'3566' - HxCB	152	68194-09-2	155L/156L/157L/ 167L/169L		32:17:00	155L	32:05:00	1.006	6	1.005	1.008
22'34'66' - HxCB	150	68194-08-1	155L/156L/157L/ 167L/169L		32:28:00	155L	32:05:00	1.012	6	1.010	1.014
22'33'66' - HxCB	136	38411-22-2	155L/156L/157L/ 167L/169L		32:51:00	155L	32:05:00	1.024	6	1.022	1.025
22'3466' - HxCB	145	74472-40-5	155L/156L/157L/ 167L/169L		33:10:00	155L	32:05:00	1.034	6	1.032	1.035
22'34'56' - HxCB	148	74472-41-6	155L/156L/157L/ 167L/169L		34:45:00	155L	32:05:00	1.083	6	1.082	1.085
22'355'6 - HxCB	151	52663-63-5	155L/156L/157L/ 167L/169L	135 + 151 + 154							
22'33'56' - HxCB	135	52744-13-5	155L/156L/157L/ 167L/169L	135 + 151 + 154	35:29:00	155L	32:05:00	1.106	10	1.103	1.109
22'44'5'6 - HxCB	154	60145-22-4	155L/156L/157L/ 167L/169L	135 + 151 + 154							
22'345'6 - HxCB	144	68194-14-9	155L/156L/157L/ 167L/169L		35:57:00	155L	32:05:00	1.121	6	1.119	1.122
22'34'56 - HxCB	147	68194-13-8	155L/156L/157L/ 167L/169L	147 + 149	36:20:00	155L	32:05:00	1.132	10	1.130	1.135
22'34'5'6 - HxCB	149	38380-04-0	155L/156L/157L/ 167L/169L	147 + 149							
22'33'56 - HxCB	134	52704-70-8	155L/156L/157L/ 167L/169L	134 + 143	36:36:00	155L	32:05:00	1.141	10	1.138	1.143
22'3456' - HxCB	143	68194-15-0	155L/156L/157L/ 167L/169L	134 + 143							
22'344'6 - HxCB	139	56030-56-9	155L/156L/157L/ 167L/169L	139 + 140	36:58:00	155L	32:05:00	1.152	10	1.150	1.155
22'344'6' - HxCB	140	59291-64-4	155L/156L/157L/ 167L/169L	139 + 140							

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COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
22'33'46 - HxCB	131	61798-70-7	155L/156L/157L/ 167L/169L		37:11:00	155L	32:05:00	1.159	6	1.157	1.161
22'3456 - HxCB	142	41411-61-4	155L/156L/157L/ 167L/169L		37:20:00	155L	32:05:00	1.164	6	1.162	1.165
22'33'46' - HxCB	132	38380-05-1	155L/156L/157L/ 167L/169L		37:39:00	155L	32:05:00	1.174	10	1.171	1.176
22'33'55' - HxCB	133	35694-04-3	155L/156L/157L/ 167L/169L		38:11:00	155L	32:05:00	1.190	6	1.189	1.192
233'55'6 - HxCB	165	74472-46-1	155L/156L/157L/ 167L/169L		38:37:00	167L	43:57:00	0.879	6	0.878	0.880
22'34'55' - HxCB	146	51908-16-8	155L/156L/157L/ 167L/169L		38:52:00	167L	43:57:00	0.884	6	0.883	0.885
233'45'6 - HxCB	161	74472-43-8	155L/156L/157L/ 167L/169L		39:01:00	167L	43:57:00	0.888	6	0.887	0.889
22'44'55' - HxCB	153	35065-27-1	155L/156L/157L/ 167L/169L	153 + 168	39:32:00	167L	43:57:00	0.900	10	0.898	0.901
23'44'5'6 - HxCB	168	59291-65-5	155L/156L/157L/ 167L/169L	153 + 168							
22'3455' - HxCB	141	52712-04-6	155L/156L/157L/ 167L/169L		39:43:00	167L	43:57:00	0.904	6	0.903	0.905
22'33'45' - HxCB	130	52663-66-8	155L/156L/157L/ 167L/169L		40:08:00	167L	43:57:00	0.913	6	0.912	0.914
22'344'5 - HxCB	137	35694-06-5	155L/156L/157L/ 167L/169L		40:22:00	167L	43:57:00	0.918	6	0.917	0.920
233'4'5'6 - HxCB	164	74472-45-0	155L/156L/157L/ 167L/169L		40:29:00	167L	43:57:00	0.921	6	0.920	0.922
22'344'5' - HxCB	138	35065-28-2	155L/156L/157L/ 167L/169L	129 + 138 + 160 + 163							
233'4'56 - HxCB	163	74472-44-9	155L/156L/157L/ 167L/169L	129 + 138 + 160 + 163							
22'33'45 - HxCB	129	55215-18-4	155L/156L/157L/ 167L/169L	129 + 138 + 160 + 163	40:53:00	167L	43:57:00	0.930	14	0.928	0.933
233'456 - HxCB	160	41411-62-5	155L/156L/157L/ 167L/169L	129 + 138 + 160 + 163							
233'44'6 - HxCB	158	74472-42-7	155L/156L/157L/ 167L/169L		41:13:00	167L	43:57:00	0.938	6	0.937	0.939

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COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
2344'56 - HxCB	166	41411-63-6	155L/156L/157L/ 167L/169L	128 + 166							
22'33'44' - HxCB	128	38380-07-3	155L/156L/157L/ 167L/169L	128 + 166	42:08:00	167L	43:57:00	0.959	10	0.957	0.961
233'455' - HxCB	159	39635-35-3	155L/156L/157L/ 167L/169L		43:10:00	167L	43:57:00	0.982	6	0.981	0.983
233'4'55' - HxCB	162	39635-34-2	155L/156L/157L/ 167L/169L		43:28:00	167L	43:57:00	0.989	6	0.988	0.990
23'44'55' - HxCB	167	52663-72-6	167L		43:59:00	167L	43:57:00	1.001	-1,3	1.000	1.001
233'44'5 - HxCB	156	38380-08-4	156L/157L		45:11:00	156L/157L	45:10:00	1.000	6	0.999	1.001
233'44'5' - HxCB	157	69782-90-7	156L/157L	156 + 157							
33'44'55' - HxCB	169	32774-16-6	169L		48:36:00	169L	48:34:00	1.001	-1,3	1.000	1.001
22'34'566' - HpCB	188	74487-85-7	188L		38:06:00	188L	38:04:00	1.001	-1,3	1.000	1.001
22'33'566' - HpCB	179	52663-64-6	170L/180L/188L/189L		38:26:00	188L	38:04:00	1.010	6	1.008	1.011
22'344'66' - HpCB	184	74472-48-3	170L/180L/188L/189L		39:00:00	188L	38:04:00	1.025	6	1.023	1.026
22'33'466' - HpCB	176	52663-65-7	170L/180L/188L/189L		39:22:00	188L	38:04:00	1.034	6	1.033	1.035
22'34566' - HpCB	186	74472-49-4	170L/180L/188L/189L		39:50:00	188L	38:04:00	1.046	6	1.045	1.048
22'33'55'6 - HpCB	178	52663-67-9	170L/180L/188L/189L		41:17:00	188L	38:04:00	1.085	6	1.083	1.086
22'33'45'6 - HpCB	175	40186-70-7	170L/180L/188L/189L		41:57:00	188L	38:04:00	1.102	6	1.101	1.103
22'34'55'6 - HpCB	187	52663-68-0	170L/180L/188L/189L		42:15:00	188L	38:04:00	1.110	6	1.109	1.111
22'344'56' - HpCB	182	60145-23-5	170L/180L/188L/189L		42:27:00	188L	38:04:00	1.115	6	1.114	1.116
22'344'5'6 - HpCB	183	52663-69-1	170L/180L/188L/189L	183 + 185	42:56:00	188L	38:04:00	1.128	6	1.127	1.129
22'3455'6 - HpCB	185	52712-05-7	170L/180L/188L/189L	183 + 185							
22'33'456' - HpCB	174	38411-25-5	170L/180L/188L/189L		43:07:00	188L	38:04:00	1.133	6	1.131	1.134
22'33'4'56 - HpCB	177	52663-70-4	170L/180L/188L/189L		43:35:00	188L	38:04:00	1.145	6	1.144	1.146
22'344'56 - HpCB	181	74472-47-2	170L/180L/188L/189L		44:00:00	188L	38:04:00	1.156	6	1.155	1.157
22'33'44'6 - HpCB	171	52663-71-5	170L/180L/188L/189L	171 + 173	44:13:00	188L	38:04:00	1.162	10	1.159	1.164
22'33'456 - HpCB	173	68194-16-1	170L/180L/188L/189L	171 + 173							
22'33'455' - HpCB	172	52663-74-8	170L/180L/188L/189L		45:57:00	189L	51:13:00	0.897	6	0.896	0.898
233'455'6 - HpCB	192	74472-51-8	170L/180L/188L/189L		46:15:00	189L	51:13:00	0.903	6	0.902	0.904
233'4'55'6 - HpCB	193	69782-91-8	170L/180L/188L/189L	180 + 193							

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COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
22'344'55' - HpCB	180	35065-29-3	170L/180L/188L/189L	180 + 193	46:36:00	180L	46:35:00	1.000	6	0.999	1.001
233'44'5'6 - HpCB	191	74472-50-7	170L/180L/188L/189L		47:00:00	189L	51:13:00	0.918	6	0.917	0.919
22'33'44'5 - HpCB	170	35065-30-6	170L/180L/188L/189L		47:57:00	170L	47:56:00	1.000	6	0.999	1.001
233'44'56 - HpCB	190	41411-64-7	170L/180L/188L/189L		48:31:00	189L	51:13:00	0.947	6	0.946	0.948
233'44'55' - HpCB	189	39635-31-9	189L		51:14:00	189L	51:13:00	1.000	-1,3	1.000	1.001
22'33'55'66' - OcCB	202	2136-99-4	202L		43:43:00	202L	43:41:00	1.001	-1,3	1.000	1.001
22'33'45'66' - OcCB	201	40186-71-8	202L/205L		44:41:00	202L	43:41:00	1.023	10	1.021	1.025
22'344'566' - OcCB	204	74472-52-9	202L/205L		45:23:00	202L	43:41:00	1.039	6	1.038	1.040
22'33'44'66' - OcCB	197	33091-17-7	202L/205L	197 + 200	45:41:00	202L	43:41:00	1.046	6	1.045	1.047
22'33'4566' - OcCB	200	52663-73-7	202L/205L	197 + 200							
22'33'455'6 - OcCB	198	68194-17-2	202L/205L	198 + 199	48:40:00	202L	43:41:00	1.114	10	1.112	1.116
22'33'455'6' - OcCB	199	52663-75-9	202L/205L	198 + 199							
22'33'44'56' - OcCB	196	42740-50-1	202L/205L		49:23:00	205L	53:54:00	0.916	6	0.915	0.917
22'344'55'6 - OcCB	203	52663-76-0	202L/205L		49:35:00	205L	53:54:00	0.920	6	0.919	0.921
22'33'44'56 - OcCB	195	52663-78-2	202L/205L		50:59:00	205L	53:54:00	0.946	6	0.945	0.947
22'33'44'55' - OcCB	194	35694-08-7	202L/205L		53:26:00	205L	53:54:00	0.991	6	0.990	0.992
233'44'55'6 - OcCB	205	74472-53-0	205L		53:56:00	205L	53:54:00	1.001	-1,3	1.000	1.001
22'33'455'66' - NoCB	208	52663-77-1	208L		50:43:00	208L	50:42:00	1.000	-1,3	1.000	1.001
22'33'44'566' - NoCB	207	52663-79-3	208L/206L		51:42:00	208L	50:42:00	1.020	6	1.019	1.021
22'33'44'55'6 - NoCB	206	40186-72-9	206L		55:45:00	206L	55:44:00	1.000	-1,3	1.000	1.001
22'33'44'55'66' - DeCB	209	2051-24-3	209L		57:26:00	209L	57:25:00	1.000	-1,3	1.000	1.001
LABELLED COMPOUND											
13C12-2 - MoCB	**1L**		9L		11:34:00	9L	16:05:00	0.719	30	0.704	0.735
13C12-4 - MoCB	**3L**		9L		13:48:00	9L	16:05:00	0.858	30	0.842	0.874
13C12-22' - DiCB	**4L**		9L		14:03:00	9L	16:05:00	0.874	30	0.858	0.889
13C12-44' - DiCB	**15L**		9L		20:08:00	9L	16:05:00	1.252	30	1.236	1.267
13C12-22'6 - TriCB	**19L**		9L		17:13:00	9L	16:05:00	1.070	30	1.055	1.086
13C12-344' - TriCB	**37L**		52L		27:27:00	52L	25:09:00	1.091	30	1.082	1.101
13C12-22'66' - TeCB	**54L**		52L		20:25:00	52L	25:09:00	0.812	20	0.805	0.818
13C12-33'44' - TeCB	**77L**		52L		35:07:00	52L	25:09:00	1.396	20	1.390	1.403
13C12-344'5 - TeCB	**81L**		52L		34:31:00	52L	25:09:00	1.372	20	1.366	1.379

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COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
13C12-22'466' - PeCB	**104L**		101L		26:08:00	101L	32:19:00	0.809	20	0.804	0.814
13C12-233'44' - PeCB	**105L**		101L		38:46:00	101L	32:19:00	1.200	20	1.194	1.205
13C12-2344'5 - PeCB	**114L**		101L		38:06:00	101L	32:19:00	1.179	20	1.174	1.184
13C12-23'44'5 - PeCB	**118L**		101L		37:32:00	101L	32:19:00	1.161	20	1.156	1.167
13C12-2'344'5 - PeCB	**123L**		101L		37:12:00	101L	32:19:00	1.151	20	1.146	1.156
13C12-33'44'5 - PeCB	**126L**		101L		42:01:00	101L	32:19:00	1.300	20	1.295	1.305
13C12-22'44'66' - HxCB	**155L**		138L		32:05:00	138L	40:48:00	0.786	20	0.782	0.790
13C12-233'44'5 - HxCB and	**156L**		138L		45:10:00	138L	40:48:00	1.107	20	1.103	1.111
13C12-233'44'5' - HxCB	**157L**		138L								
13C12-23'44'55' - HxCB	**167L**		138L		43:57:00	138L	40:48:00	1.077	20	1.073	1.081
13C12-33'44'55' - HxCB	**169L**		138L		48:34:00	138L	40:48:00	1.190	20	1.186	1.194
13C12-22'34'566' - HpCB	**188L**		194L		38:04:00	194L	53:25:00	0.713	20	0.710	0.716
13C12-233'44'55' - HpCB	**189L**		194L		51:13:00	194L	53:25:00	0.959	20	0.956	0.962
13C12-22'33'55'66' - OcCB	**202L**		194L		43:41:00	194L	53:25:00	0.818	20	0.815	0.821
13C12-233'44'55'6 - OcCB	**205L**		194L		53:54:00	194L	53:25:00	1.009	30	1.004	1.014
13C12-22'33'44'55'6 - NoCB	**206L**		194L		55:44:00	194L	53:25:00	1.043	30	1.039	1.048
13C12-22'33'455'66' - NoCB	**208L**		194L		50:42:00	194L	53:25:00	0.949	20	0.946	0.952
13C12-22'344'55' - HpCB	**180L**		194L		46:35:00	194L	53:25:00	0.872	20	0.869	0.875
13C12-22'33'44'5 - HpCB	**170L**		194L		47:56:00	194L	53:25:00	0.897	20	0.894	0.900
13C12-22'33'44'55'66' - DeCB	**209L**		194L		57:26:00	194L	53:25:00	1.075	30	1.071	1.080
LABELLED CLEAN-UP STANDARD											
13C12-244' - TriCB	**28L**		52L		23:16:00	52L	25:09:00	0.925	20	0.918	0.932
13C12-233'55' - PeCB	**111L**		101L		35:09:00	101L	32:19:00	1.088	20	1.083	1.093
13C12-22'33'55'6 - HpCB	**178L**		138L		41:16:00	138L	40:48:00	1.011	20	1.007	1.016
LABELLED INJECTION INTERNAL STANDARD											
13C12-25 - DiCB	**9L**		138L		16:05:00	138L	40:48:00	0.394	25	0.389	0.399
13C12-22'55' - TeCB	**52L**		138L		25:09:00	138L	40:48:00	0.616	25	0.611	0.622
13C12-22'455' - PeCB	**101L**		138L		32:19:00	138L	40:48:00	0.792	25	0.787	0.797
13C12-22'344'5' - HxCB	**138L**		138L		40:48:00	138L	40:48:00	1.000	100	0.980	1.020
13C12-22'33'44'55' - OcCB	**194L**		138L		53:25:00	138L	40:48:00	1.309	25	1.304	1.314

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(1) Suffix "L" indicates labelled compound.
(2) C = co-eluting congener

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10. SUMMARY OF MODIFICATIONS TO EPA METHOD 1668A

The following sections of EPA Method 1668A have been modified as described below.

Section 4.2.1, 4.2.2: The protocol for washing reusable glassware includes a detergent wash, water rinse and baking at a minimum of 300°C for 8 hours. Immediately prior to use, glassware is solvent rinsed with toluene and hexane.

Section 4.7: The first cleanup column for tissue extracts is a gravity gel permeation column (SX-3 Biobeads). An anthropogenic isolation column 7.5.3 is not used.

Section 6.5.1: Glass wool is cleaned by rinsing twice with toluene and twice with hexane.

Section 7.12, 7.13, 9.0, 11.0: The concentration of the labelled toxics/LOC and the cleanup standard spiking solutions is 100 ng/mL and the sample spiking volume is 20 µL. The resulting final concentrations in the extracts are as specified in the method.

Section 7.14: Concentration of the labelled injection internal standard spiking solution (recovery standard) is modified so that a volume of 5 µL is added. The resulting amount of standard added to the final extract is the same as specified in the method. The solution is spiked into a 15 µL extract volume for a final extract volume of 20 µL.

Section 7.2.1: Powdered, not granular, sodium sulphate is baked at a minimum of 300°C for 8 hrs rather than at 600°C for 24 hrs.

Section 7.5.1: Silica is activated by baking at 450°C in a muffle oven for at least 8 hrs.

Section 7.5.4.1.1: Florisil is baked at 450°C in a muffle over for at least 8 hrs, then deactivated with water to 2.1% deactivation.

Section 10.3.3, 15.3.3: A S:N ratio of 3:1 for di-PCBs and nona-PCBs in CS0.2 calibration solution is acceptable.

Section 11.5.6: Unless requested by the client, the aqueous portion after filtration of aqueous samples with >1% solids is not discarded but is extracted.

Section 11.5, 11.5.2, 11.5.5, 12.3 Solid samples are dried by mixing with anhydrous sodium sulphate. The dried solid is extracted using a Soxhlet extraction apparatus. The surrogate spike is incorporated after the drying step. Equilibration time for the surrogate is 30 minutes. The extracting solvent for solids is dichloromethane.

Section 12.4, 11.8: The surrogate spike is incorporated into the sample after the drying step to eliminate the possibility of disproportional loss of volatile labelled and target compounds.

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Section 12.4.2: The precleaning of the Soxhlet apparatus is carried out using toluene instead of dichloromethane, for 2 hours.

Section 12.4.9: Lipid analysis is carried out by sub-sampling two 2 g portions of the extract from a total 30 g extract weight. The cleanup standard is spiked into the extract after Soxhlet extraction and before any lipid analysis or rotary evaporation is done. The percent surrogate recoveries are corrected for the amount of extract used for lipid analysis.

Section 12.6.1.1: Rotary evaporation is done at 30°C. Daily cleaning of the rotary evaporators include dismantling and rinsing/soaking with solvent. Proofs are run periodically but are not archived daily.

Section 12.7.4: Before Florisil or alumina cleanup procedures, a solvent exchange is done by reducing under nitrogen to 300 uL and bulking up to 1mL in hexane. If toluene is present the extract is reduced to 50 uL under nitrogen and bulked up to 1mL.

Section 12.7.7: Toluene (1 mL) is added to the eluate from the final column prior to rotary evaporation and nitrogen blow down concentration steps.

Section 13.1.1: GPC chromatography, by a gravity column, is routinely used only for tissue extracts. The GPC cleanup is optional for all other matrices.

Section 13.3.1: Routine layered silica column is as follows: 0.5 g neutral silica, 2 g 28% basic silica, 0.5 g neutral silica, 4 g 44% acidic silica, 4 g 22% acidic silica, 1 g neutral silica.

Section 13.3.4: The sample is loaded onto the column followed by 2-3 rinses of a least 1 mL, and eluted with 100mL of hexane.

Section 14.2: The volume of labelled injection internal standard (recovery standard) added to the extract is 5 µL, for a final extract volume of 20 µL. Hexane rather than nonane is used as the solvent to bring extract back to volume for re-analysis or to dilute extracts.

Section 15.3: The calibration solution containing all 209 PCB congeners is used as the CAL/VER solution.

*Section 17.*5: Extracts are diluted with hexane. The concentration of the labelled injection internal (recovery) standard is not re-adjusted to 100 pg/µL when dilutions are performed.

Section 17.0

$Conc_i$ - the concentrations of target analytes, and the labelled compound concentrations and recoveries, are calculated using the equations below. These procedures are equivalent to those described in the method but are more direct.

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$$Conc_i = \frac{A_i}{A_{si}} \times \frac{M_{si}}{RRF_{i,si}} \times \frac{1}{M_x}$$

where A_i = summed areas of the primary and secondary m/z's for the analyte peak of interest (compound *i*)

A_{si} = summed areas of the primary and secondary m/z's for the labelled surrogate peak used to quantify *i*)

M_x = mass of sample taken for analysis

M_{si} = mass of labelled surrogate (compound *si*) added to sample as calculated by the concentration of standard spiked (pg/mL) multiplied by the volume spiked (mL)

$RRF_{i,si}$ = mean relative response factor of *i* to *si* from the five-point calibration range and defined individually as:

$$\frac{A_i}{A_{si}} \times \frac{M_{si}}{M_i}$$

Calculation of Surrogate Standard Concentrations and Percent Recoveries:
Concentrations of surrogate standards are calculated using the following equation:

$$Conc_{si} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}}$$

and, the percent recoveries of the surrogate standards are calculated using the following equation:

$$\%\text{Recovery} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}} \times \frac{1}{M_{si}} \times 100$$

where A_{rs} and A_{si} are the summed peak areas (from the primary and secondary m/z channels) of recovery standard and labelled surrogate added to the sample;
M_{rs} and M_{si} are the masses of recovery standard and labelled surrogate added to the sample, and;
$RRF_{si,rs}$ is the mean relative response factor of the labelled surrogate to the recovery standard as determined by the five-point calibration range and defined individually as:

$$\frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{M_{si}}$$

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APPENDIX A

OPTIONAL ANALYSES

Chlorinated Pesticides

Polybrominated Diphenylethers

Polybrominated Biphenyls

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A OPTIONAL ANALYSES

A.1 Chlorinated Pesticides

The analysis of chlorinated pesticides may be carried out using the extraction procedures described in Section 5. The analyst is cautioned to avoid the use of concentrated H_2SO_4 during the cleanup procedures as pesticides are destroyed by strong acid.

The analyst is referred to AXYS Method Document MLA-007, *Analytical Method for the Determination of: Aroclors, Total PCBS, Chlorinated Pesticides, PCB Congeners, Coplanar PCBs, Toxaphene, Chlorobenzenes* and AXYS Method Document MLA-028, *Organochlorine Pesticides by Isotope Dilution HRGC/HRMS* for details regarding standard solutions, instrumental analysis, analyte identification and quantification procedures and QA/QC criteria for the analysis of chlorinated pesticides by LRGC/MS and HRGC/MS respectively.

Sample matrices are spiked with the appropriate surrogate for the pesticide analysis, as listed on the Batch List. The choice and quantity of surrogate and recovery standard is dependent upon the instrumental analysis (LRMS or HRMS). The final extract is cleaned up and concentrated using a modified Florisil column procedure as described below.

Florisil Cleanup Procedure

There may be no residual toluene in the extract prior cleanup on Florisil. If toluene is present, carry out a solvent exchange by transferring the extract to a clean centrifuge tube with hexane and concentrating to 50 µL under a gentle stream of nitrogen. Make to 1 mL with hexane.

Quantitatively transfer the extract and hexane rinses (3 x 1 mL from the elution volume) to a Florisil column (8 g, 2.1% deactivated) prepared as described in Section 3.6.4. Elute the column with 15:85 dichloromethane:hexane (E1) followed by dichloromethane, using the volumes of solvent determined from the most recent Florisil cutpoint determination. Typical cutpoints are as follows:

E1	15:85 dichloromethane:hexane	45 mL
E2	Dichloromethane	50 mL.

Concentrate the eluate to 1 mL by rotary evaporation Add activated copper to all E1 extracts to remove sulphur. Transfer the extract to a centrifuge tube with hexane and concentrate to 1 mL in a stream of nitrogen.

The cleaned up extract may be treated in one of two ways:

a) The extract is analyzed for pesticides by either LRGC/MS or HRGC/MS according to procedure described in either MLA-007 or MLA-028 respectively. Once the data has been accepted, the extract is subjected to further cleanup on layered acid/base silica (Section 6.2) followed by alumina (Section 6.3), prior to analysis by HRGC/MS for PCB congeners (Sections 7 through 9).

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b) The extract is split into two portions, the proportions as determined by the Project QC Chemist and documented on the Batch List. One fraction is analyzed by either LRGC/MS or HRGC/MS according to procedure described in either MLA-007 or MLA-028 respectively. The other fraction is subjected to further cleanup on layered acid/base silica (Section 6.2) followed by alumina (Section 6.3), prior to analysis by HRGC/MS for PCB congeners (Sections 7 through 9).

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A.2 Brominated Diphenylethers (PBDE)

The analysis of brominated diphenylethers may be carried out using the extraction procedure as described in Section 5. Sample matrices are spiked with the appropriate surrogate, as listed on the Batch List. The analyst is referred to the most recent version of AXYS Method Document MLA-033, *Analysis Method for the Determination of Polybrominated Diphenylethers by EPA Method 1614* for details regarding special sample handling procedures, standard solutions, chromatographic cleanup, instrumental analysis, analyte identification and quantification procedures and QA/QC criteria.

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A.3 Polybrominated Biphenyls (PBB)

The analysis of polybrominated biphenyls may be carried out using the extraction procedure as described in Section 5 and the cleanup procedures described in Section 6. Sample matrices are spiked with the PCB surrogate, which is used for the quantification of PBBs. The analyst is referred to the most recent version of AXYS Method Document MLA-026. *Analytical Method for the Determination of Polybrominated Biphenyls (PBBs) by High Resolution GC/MS* for details regarding instrumental analysis, analyte identification and quantification procedures and QA/QC criteria.

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A.4 Polychlorinated Naphthalenes (PCN)

The analysis of polychlorinated naphthalenes may be carried out using the extraction procedure as described in Section 5 of this document. Sample matrices are spiked with the appropriate surrogate, as listed on the Batch List. The analyst is referred to the most recent version of AXYS Method Document MLA-030, *Analysis Method for the Determination of Polychlorinated Naphthalenes by High Resolution GC/MS* for details regarding standard solutions, chromatographic cleanup, instrumental analysis, analyte identification and quantification procedures and QA/QC criteria.

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APPENDIX B

FRACTIONATION OF PCB CONGENERS

BY

CARBON COLUMNING

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B.1 Fractionation of Toxic PCB Congeners

Fractionation on a carbon column to remove poly-ortho-substituted PCB's as described in Section 6.5 is an option to improve the data quality for certain of the "toxic" group of PCB's. When a carbon column cleanup is required, it must be done after initial analysis on the SPB-Octyl column where the results for all 209 congeners are required.

The decision to perform carbon column cleanup is based on the degree of resolution achieved for PCB congeners 81, 123, 126 and 169 from interfering peaks arising from closely eluting poly-ortho-substituted congeners or fragment peaks from these – notably for PCB-126, due to its high toxicity. The following information is presented as a guideline on when a column carbon cleanup would be beneficial to congener resolution.

The concentrations of PCB-126 from a well-defined shouldering peak (Figure B-1) are compared before and after carbon columning in Table B-1. Table B-2 shows a comparison of results from a less-defined peak, shown in Figure B-2. Shouldering peaks with less definition than Figure B-2 should be confirmed by carbon column and reinjection on a DB-1 GC column.

Carbon column clean-up may be required to adequately resolve all toxic PCB congeners from interferences.

a) Depending upon the particular congener profile carbon column cleanup may be required due to the following chromatographic issues:

PCB 81 shoulders on a fragment peak from PCB 110/115 on the SPB-Octyl column and shoulders on a fragment peak from PCB 86 on the DB-1 column.

PCB 123 shoulders on the PCB 109 peak on both the SPB-Octyl and the DB-1 columns.

PCB 126 shoulders on a fragment peak from PCB 128/166 on the SPB-Octyl column and shoulders or may co-elute with a fragment peak from PCB 129 on the DB-1 column. Quantification of PCB 126 from the DB-1 column without prior carbon column cleanup may lead to false positive detection.

PCB 157 co-elutes with a fragment peak from PCB 202 on the DB-1 column.

PCB 169 co-elutes with a fragment peak from PCB 190/198 on the SPB-Octyl column and shoulders on a fragment peak from PCB 170 on the DB-1 column. Quantification of PCB 169 on the SPB-Octyl column without prior carbon column cleanup may lead to false positive detection. In extreme cases analysis on an SPB-Octyl following carbon column cleanup may still result in false positive detection due to co-elution with a fragment peak from any residual PCB 190/198 not removed by the carbon column.

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b) The following PCB congeners are adequately resolved on the SPB-Octyl column without the need for carbon column cleanup

PCB 77 is resolved adequately on the SPB-Octyl and the DB-1 columns

PCB 105 is resolved adequately on the SPB-Octyl column. It co-elutes with a fragment peak of PCB 132 and shoulders on a fragment peak of PCB 153 on the DB-1 column.

PCB 114 is resolved adequately on the SPB-Octyl column and the DB-1 columns

PCB 118 is resolved adequately on the SPB-Octyl column and co-elutes with PCB 106 on the DB-1 column

PCB 167 is resolved adequately on the SPB-Octyl and the DB-1 columns

PCB 189 is resolved adequately on the SPB-Octyl and the DB-1 columns.

c) The following PCB congener is adequately resolved on the DB-1 column without the need for carbon column cleanup

PCB 156 co-elutes with PCB 157 on the SPB-Octyl column and is resolved adequately on the DB-1 column

Table B-1. Comparison of PCB-126 Results Pre- and Post-Carbon Columning for a Well-defined Peak (see Figure B-1)

Compound	Pre-Carbon Octyl PB21_080 S:22	Pre-Carbon DB1 PB23_102 S:23	Post-Carbon Octyl PB2c_016 S:26
PCB-81	5.4		4.8
PCB-77	6.4		7.4
PCB-123	119		114
PCB-118	7011		7032
PCB-114	126		113
PCB-105	1903		1736
PCB-126	**24**		**29**
PCB-169	ND (8.0)	ND (1.9)	9.8

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Table B-2. Comparison of PCB-126 Results Pre- and Post-Carbon Columning for a Less-defined Peak (see Figure B-2)

Compound	Pre-Carbon Octyl	Pre-Carbon DB1	POST-Carbon Octyl
	PB21_080 S:27	PB23_102 S:25	PB2c_017b S:18
81	2.5		2.5
77	32		36
123	85		74
118	4748		4541
114	87.1		77
105	1272		1128
126	**9.4**		**11**
169	ND (4.9)	ND (.9)	2.9

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Figure B-1: Typical Chromatogram of a Well-defined Shoulder of PCB-126 on SPB-Octyl Column

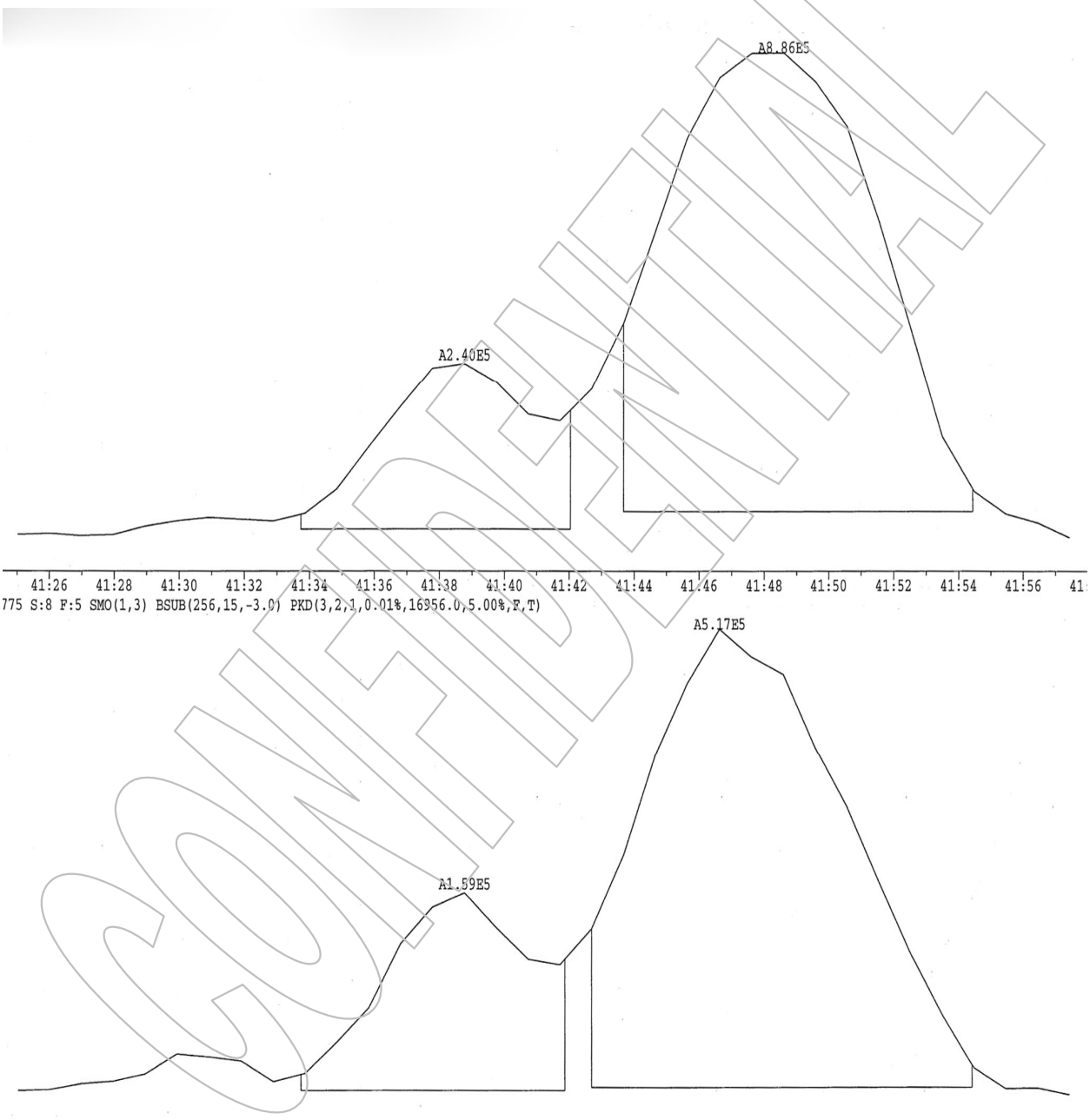

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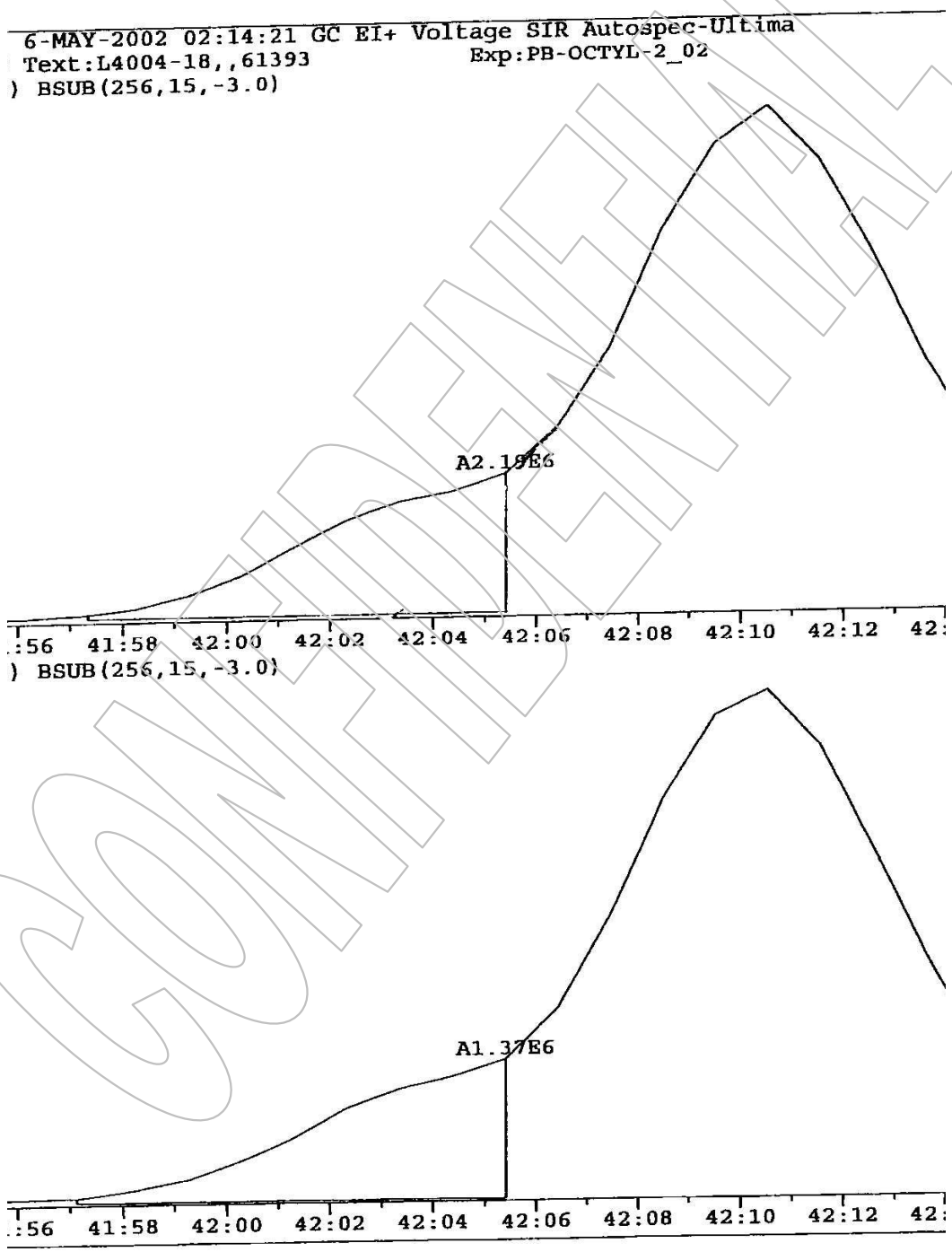
Figure B-2: Typical Chromatogram of a Less-defined Shoulder of PCB-126 on SPB-Octyl Column



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APPENDIX C

DETECTOR 'PHANTOM PEAK' PHENOMENON

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C.1 'Phantom Peak' Phenomenon

The term detector 'phantom peak' phenomenon refers to the appearance of peak response across a wide mass range resulting from high concentration impact on the MS detector, a phenomenon recognized to occur by the instrument manufacturer. While these responses are of very low relative intensity (typically less than 1/1000 of the 'true' response in the mass range of interest) at very high native to surrogate concentration ratios surrogate response may be enhanced significantly. To assess the effect of 'phantom peak' occurrence first determine the response ratio of phantom vs native congener response from a high concentration native congener for which a labelled surrogate is not present in the extract. Then, for each surrogate compound determine the potential response enhancement by multiplying the response of the associated native congener by the native:phantom ratio. Where the resulting value is greater than 1/10 of the observed surrogate response isotope dilution analysis should not be performed and re-analysis of a smaller sample (or surrogate re-spiking of the extract were allowable) are required.

Example:

The area response for PCB 153 is 2.5E9. An inspection of the chromatogram reveals a response at the mass corresponding to ^{13}C-PCB 153 of 1.2E6 yet the extract has not been spiked with ^{13}C-PCB 153. This native PCB 153: phantom response ratio is 1.2E6/2.3E9=0.0004.

The PCB 118 response is 9.8E8. The estimated phantom ^{13}C-PCB 118 response is therefore 9.8E8 x 0.0004=3.9E5. If this response is less than 1/10 of the observed ^{13}C-PCB 118 response then isotope dilution quantification of PCB 118 can proceed from these data, otherwise, re-analysis of a smaller sample is required.

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APPENDIX D

ANALYSIS OF PCBs BY EPA METHOD CBC01.2

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D. ANALYSIS OF PCB BY EPA METHOD CBC01.2

The analysis of polychlorinated biphenyls by EPA Method CBC01.2 is carried out using the procedures described in this document and according to the following additional protocols. An electronic copy of CBC01.2 is filed on the AXYS network at G:\information\Published Methods\EPA Methods\.

1. Solid samples are extracted using the Soxhlet/Dean-Stark extraction procedure, described in Section 5.2 of this document. This requirement may be waived by contract to permit Soxhlet extraction in dichloromethane (Section 5.1 of this document).
2. Carbon column isolation of PCBs 77, 126, and 169 is required if detected. This requirement may be waived by contract.
3. Hepta-PCBs are quantified against ^{13}C-PCB 188 and ^{13}C-PCB 189 only.
4. Quantification reports include the signal:noise (S:N) ratio for all analytes and standards.
5. Data reports, sample naming conventions and data flagging protocols are in accordance with the reporting requirements specified in CBC01.2, Exhibit B, Reporting and Deliverables Requirements.

Modifications:

The following modifications have been made to EPA Method CBC01.2.

1. Additional recovery (internal standard) is not added to a diluted extract.
2. The compounds typically present in the Window Defining Mixture (WDM) and in the Combined 209-Congener Standard solution are in a single solution that is analyzed as the CAL/VER solution. Analysis of the CAL/VER solution at least once every 12 hours satisfies the analysis frequency requirement for the WDM.
3. Modifications made to EPA Method 1668A, described in Section 10 of this document, are applicable.

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APPENDIX E

E. OPTIONAL REPORTING OF PCB CONGENER NUMBERS 107, 108,109 IN ACCORDANCE WITH EPA 1668C SPECIFICATION

The assignment of PCB Congener numbers 107, 108, 109 differs between EPA Methods 1668A and 1668C. When reporting these congeners in accordance with 1668C specification, the assignment criteria in Table 6a are modified as shown below in Table 6b.

Table 6b. Analyte Retention Times, Surrogates Used and RRT Windows for Optional Reporting of Congener Numbers 107,108, 109 in accordance with 1668C Specification

COMPOUND	Congener Number	CAS NO.	QUANTIFICATION REFERENCE	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
2,3,3',4,6 - PeCB	109	74472-35-8	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 109 + 119 + 125							
2,2',3,4,5 - PeCB	86	55312-69-1	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 109 + 119 + 125	33:29:00	123L	37:12:00	0.900	16	0.897	0.904
2,2',3',4,5 - PeCB	97	41464-51-1	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 109 + 119 + 125							
2',3,4,5,6' - PeCB	125	74472-39-2	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 109 + 119 + 125							
2,2',3,4,5' - PeCB	87	38380-02-8	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 109 + 119 + 125							
2,3,3',4,5' - PeCB	108	70362-41-3	104L/123L/114L/ 118L/105L	108 + 124	36:50:00	123L	37:12:00	0.990	10	0.988	0.992
2',3,4,5,5' - PeCB	124	70424-70-3	104L/123L/114L/ 118L/105L	108 + 124							
2,3,3',4',5 - PeCB	107	70424-68-9	104L/123L/114L/ 118L/105L		37:05:00	123L	37:12:00	0.997	6	0.996	0.998

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Appendix P

Laboratory SOPs

PCDDs/PCDFs

Axys SOP

MLA-017

Summary of AXYS Method MLA-017 Rev 20:

ANALYTICAL METHOD FOR THE DETERMINATION OF POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS

BY

EPA METHOD 1613B[1], EPA METHOD 8290[2]/8290A[3], ENV. CANADA EPS 1/RM/19[4] OR EPA METHOD DLM02.2[5]

AXYS Method MLA-017 describes the analysis of polychlorinated (tetra-octa) dibenzo-dioxins and dibenzofurans in solids (sediment, soil, pulp, sludge), tissues (including milk and blood), aqueous samples, XAD-2 columns, air samples, particulate filters and solvent extracts.

Target Analytes

Dioxins (PCDD)	Furans (PCDF)
2,3,7,8 Tetrachlorodibenzodioxin (TCDD)	2,3,7,8 Tetrachlorodibenzofuran (TCDF)
Total TCDD	Total TCDF
1,2,3,7,8 Pentachlorodibenzodioxin (PeCDD)	1,2,3,7,8 Pentachlorodibenzofuran (PeCDF)
Total PeCDD	2,3,4,7,8 PeCDF
	Total PeCDF
1,2,3,4,7,8 Hexachlorodibenzodioxin (HxCDD)	1,2,3,4,7,8 Hexachlorodibenzofuran (HxCDF)
1,2,3,6,7,8 HxCDD	1,2,3,6,7,8 HxCDF
1,2,3,7,8,9 HxCDD	1,2,3,7,8,9 HxCDF
Total HxCDD	2,3,4,6,7,8 HxCDF
	Total HxCDF
1,2,3,4,6,7,8 Heptachlorodibenzodioxin (HpCDD)	1,2,3,4,6,7,8 Heptachlorodibenzofuran (HpCDF)
Total HpCDD	1,2,3,4,7,8,9 HpCDF
	Total HpCDF
Octachlorodibenzodioxin (OCDD)	Octachlorodibenzofuran (OCDF)

EXTRACTION

All samples are spiked with ^{13}C-labelled surrogate standards prior to extraction and extracted as per the table below. Optional extraction procedures are shown within parentheses.

Sample Extraction

Matrix	Extraction
Aqueous	Liquid-liquid extraction with dichloromethane. (If visible particulates are present the sample is filtered prior to extraction and the particulate fraction separately extracted by Soxhlet extraction or Dean-Stark Soxhlet extraction. The two extracts are then combined.)
Solid (sediment, soil, sludge, particles on filter paper)	Soxhlet extraction with toluene:acetone 80:20. (optional: Dean-Stark Soxhlet extraction with toluene)
Solid (pulp, black liquor)	Soxhlet extraction with toluene:acetone 80:20.
Solid (ash, slag)	Sonication with hydrochloric acid and filtering. Liquid-liquid extraction of filtrate using dichloromethane, Soxhlet extraction of particulate using toluene:acetone 80:20. The two extracts are combined.
Tissue	Soxhlet extraction with dichloromethane:hexane 1:1 (optional: Base digestion and liquid-liquid extraction with hexane)
Whole blood/serum	Liquid-liquid extraction with ethanol:hexane:saturated ammonium sulphate.
Milk	Liquid-liquid extraction with acetone and hexane.
XAD-2 column and filter	XAD-2 adsorbent is dried and extracted by Soxhlet (with toluene:acetone 80:20) or Dean-Stark Soxhlet (with toluene) extraction. The filter is extracted by Dean-Stark Soxhlet extraction using toluene.
Ambient air (PUF and filter)	The PUF and filter(s) are Soxhlet extracted together using toluene:acetone 80:20.
Stationary Source Air Samples (Stack Gas sample trains)	The filter is sonicated with dilute hydrochloride acid and filtered. Equipment rinsates are collected, filtered, dried and/or extracted depending on sampling conditions.

COLUMN CHROMATOGRAPHY CLEANUP

Extracts are routinely cleaned up manually, by an automated fluid management (FMS) system, or by using a combined ("hybrid") manual and FMS cleanup procedure according to the following table:

Water Soil Sediment XAD-2 adsorbent Air samples	1) Hybrid: (M B/A wash →) M Extra-Large Layered Silver Nitrate/Acid/Base Silica Column → F Alumina → F Carbon/Celite 2) Full FMS: (M B/A wash →) F Jumbo Layered Silica Columns → F Small Layered Silica Columns → F Alumina → F Carbon/Celite 3) Manual: M Small Layered Silver Nitrate/Acid/Base Silica → M Alumina → M Copper → M Carbon/Celite (→ M Florisil)
Sludge High organic soil	1) Hybrid: (M B/A wash →) M Extra-Large Layered Silver Nitrate/Acid/Base Silica Column→ F Alumina → F Carbon/Celite 2) Full FMS: (M B/A wash →) F Jumbo Layered Silica Columns → F Small Layered Silica Columns → F Alumina → F Carbon/Celite 3) Manual: (M Biobead →) M Large Layered Silver Nitrate/Acid/Base Silica → M Alumina → M Copper → M Carbon/Celite (→ M Florisil)
Tissue Blood Milk	1) Full FMS: (M Biobead →) F Jumbo Acid Silica Column → F Small Layered Silica Columns → F Alumina → F Carbon/Celite 2) Manual: M Biobead → M Small Layered Acid/Base Silica → M Alumina → (M Copper →) M Carbon/Celite (→ M Florisil)

Notes:

Options listed as 1) in the table above are the current default options. Items in brackets are optional procedures that may be used if needed or if required by Project Managers.

M = Manual column or cleanup step

F = FMS column

An optional Biobead clean-up may be carried out for biosolid sample extracts.

INSTRUMENTAL ANALYSIS

Instrumental analysis is performed on a DB-5 capillary chromatography column coupled to a high-resolution mass spectrometer (HRMS). The HRMS is operated at a static (10000) mass resolution in the voltage selected ion-recording mode (V-SIR) using selected PFK ions as a reference for mass lock. Two masses from the molecular ion cluster are used to monitor each of the target analytes and ^{13}C-labelled surrogate standards. A second column DB-225 is used for confirmation of 2,3,7,8-TCDF identification. Five additional ions are monitored to check for interference from chlorinated diphenylethers.

Upon client request, the concentrations of PCDD/F may be determined using bracketing calibration procedures and a smaller suite of surrogate standards.

Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans

Analytes	Quantification Ion (m/z)	Confirmation Ion (m/z)	Surrogate	RRF Determined From
2,3,7,8-TCDD	320	322	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
1,3,6,8-TCDD *	320	322	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
1,3,7,9-TCDD *	320	322	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
1,2,3,7,8-PeCDD	354	356	$^{13}C_{12}$-1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	390	392	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD	390	392	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	390	392	Mean of $^{13}C_{12}$-1,2,3,6,7,8/1,2,3,4,7,8-HxCDD	1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD	424	426	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD
OCDD	458	460	$^{13}C_{12}$-OCDD	OCDD
2,3,7,8-TCDF	304	306	$^{13}C_{12}$-2,3,7,8 -TCDF	2,3,7,8-TCDF
1,2,7,8-TCDF *	304	306	$^{13}C_{12}$-2,3,7,8 -TCDF	2,3,7,8-TCDF
1,2,3,7,8-PeCDF	340	342	$^{13}C_{12}$-1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	340	342	$^{13}C_{12}$-2,3,4,7,8-PeCDF	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF	374	376	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF	374	376	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	374	376	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	374	376	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDF	408	410	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	408	410	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-HpCDF
OCDF	442	444	$^{13}C_{12}$-OCDD	OCDF
Cleanup Standard				
$^{37}Cl_4$-2,3,7,8-TCDD	328	-	$^{13}C_{12}$-1,2,3,4-TCDD	
Labelled Surrogates	**Quantification Ion (m/z)**	**Confirmation Ion (m/z)**	**Recovery Calculated Using**	
$^{13}C_{12}$-2,3,7,8-TCDD	332	334	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,7,8-PeCDD	366	368	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	402	404	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	402	404	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	436	438	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-OCDD	470	472	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-2,3,7,8 -TCDF	316	318	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,7,8-PeCDF	352	354	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-2,3,4,7,8-PeCDF	352	354	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	384	386	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	384	386	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	384	386	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	384	386	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	418	420	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	418	420	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
Recovery Stds				
$^{13}C_{12}$-1,2,3,4-TCDD	332	334		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	402	404		

*Optional isomers which may be reported upon client request.

CALIBRATION

Initial calibration is performed using a five point calibration series of solutions that encompass the working concentration range. Initial calibration solutions contain the suite of labelled surrogate and recovery standards and authentic target PCDDs/PCDFs. Calibration is verified at least once every 12 hours by analysis of a mid-level calibration solution. Calibration procedures use the mean RRFs determined from the initial calibration to calculate analyte concentrations.

Alternately clients may request initial calibration be performed using a six point calibration series of solutions if lower detection limits are required.

Concentration of PCDD/PCDF Calibration Solutions

	Concentration (ng/mL)						Authentic Standard Amount added to sample (pg)
	CS0.2	CS1	CS2	CS3	CS4	CS5	
Native Compound							
2,3,7,8-TCDD	0.1	0.5	2	10	40	200	200
2,3,7,8-TCDF	0.1	0.5	2	10	40	200	200
1,2,3,7,8-PeCDD	0.5	2.5	10	50	200	1000	1000
1,2,3,7,8-PeCDF	0.5	2.5	10	50	200	1000	1000
2,3,4,7,8-PeCDF	0.5	2.5	10	50	200	1000	1000
1,2,3,4,7,8-HxCDD	0.5	2.5	10	50	200	1000	1000
1,2,3,6,7,8-HxCDD	0.5	2.5	10	50	200	1000	1000
1,2,3,7,8,9-HXCDD	0.5	2.5	10	50	200	1000	1000
1,2,3,4,7,8-HxCDF	0.5	2.5	10	50	200	1000	1000
1,2,3,6,7,8-HxCDF	0.5	2.5	10	50	200	1000	1000
1,2,3,7,8,9-HxCDF	0.5	2.5	10	50	200	1000	1000
2,3,4,6,7,8-HxCDF	0.5	2.5	10	50	200	1000	1000
1,2,3,4,6,7,8-HpCDD	0.5	2.5	10	50	200	1000	1000
1,2,3,4,6,7,8-HpCDF	0.5	2.5	10	50	200	1000	1000
1,2,3,4,7,8,9-HpCDF	0.5	2.5	10	50	200	1000	1000
OCDD	1.0	5.0	20	100	400	2000	2000
OCDF	1.0	5.0	20	100	400	2000	2000
Surrogate Standards							**Surrogate Standard Amount added to sample (pg)**
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	100	2000
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	100	2000
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	100	2000

$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	100	2000
$^{13}C_{12}$-OCDD	200	200	200	200	200	200	4000
Cleanup Standard							
$^{37}Cl_4$-2,3,7,8-TCDD	0.1	0.5	2	10	40	200	200
Recovery Standard							
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	100	2000
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	100	2000

ANALYTE IDENTIFICATION

A chromatographic peak is identified as a target compound if the following criteria are met for the quantification and confirmation ions (where confirmation ions are available):

1. Peak responses must be at least 2.5 times the background noise level.
2. All peaks are acquired in the appropriate acquisition windows, when compared to the window standard.
3. Peak centroids for the quantification and confirmation ions must coincide within two seconds.
4. The relative ion abundance ratios must be within 15% of the expected ratio.

QUANTIFICATION

The response for any component is taken as the sum of the integrated peak areas for the two characteristic masses for that compound. Quantification is by the isotope dilution method. Target concentrations are determined with respect to labelled surrogate standards. Mean relative response factors (RRF), determined from the multi-level initial calibration series are used to convert raw peak areas in sample chromatograms to final concentrations as follows:

$$\text{Concentration of Target} = \left(\frac{\text{area of Target}}{\text{area of Qt Std}}\right) \times \left(\frac{\text{weight of Qt Std}}{\text{RRF}}\right) \times \left(\frac{1}{\text{weight of sample}}\right)$$

where $$\text{RRF} = \left(\frac{\text{area of Target}}{\text{area of Qt Std}}\right) \times \left(\frac{\text{weight of Qt Std}}{\text{weight of Target}}\right)$$

and the Qt Std is either the surrogate or the internal standard

Those compounds quantified against a labelled standard added at the beginning of the analysis procedure are recovery corrected by the method of quantification. Surrogate recoveries are determined similarly against the recovery (internal) standard and are used as general indicators of overall analytical quality.

REPORTING LIMITS

Concentrations and detection limits for the 2,3,7,8-polychlorinated dioxins and furans (tetra-octa) are reported. Typical reporting units for all data are pg/g, pg/L or pg/sample. Concentrations for solids are reported on a dry weight basis. Concentrations in tissues (including blood and milk) are reported on a wet weight basis and/or on a lipid weight basis when requested. Concentrations in aqueous samples are reported on a volume basis. Concentrations in XAD-2 resin, filters and stack gas samples are reported on a per sample basis or a per volume basis. Concentrations in particulate filters are reported on a per sample basis.

The following are commonly requested reporting limits:

Sample Specific Detection Limit or Sample Detection Limit (SDL) – determined individually for every sample analysis run by converting the area equivalent of 3.0 times (2.5 times for EPA 1600 series methods) the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. The SDL accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up. Equivalent term(s): Estimated Detection Limit (EDL) from EPA method 8290.

Method Detection Limit (MDL) - determined as specified by EPA Fed. Reg. 40 CFR Part 136 Appendix B (no iteration option). The 99% confidence level MDL is determined based on analysis of a minimum of 7 replicate matrix spikes fortified at 1-10 times the estimated detection limit. MDL is determined as required based on accreditation, contract and workload requirements.

Lower Method Calibration Limit (LMCL) - determined by prorating the concentration of the lowest calibration limit for sample size and extract volume. The following equation is used. ((lowest level cal conc.) x (extract volume))/sample size. Typical extract volume for PCDDs/PCDFs is 20 µL.

For the analysis of PCDDs/PCDFs AXYS standard is to report sample concentrations using the SDL with a minimum reporting limit of 0.5 pg absolute.

QUALITY ASSURANCE/QUALITY CONTROL

All samples are analyzed in batches with the following composition:

- Batch Size - Each batch consists of up to twenty test samples and additional QC samples.
- Blanks - One procedural blank is analyzed for each batch. The procedural blank is prepared by spiking an aliquot of the surrogate standard solution into a clean matrix.
- On-going Precision and Recovery (OPR) Samples – On-going Precision and Recovery (OPR) is demonstrated by the analysis of a spiked reference matrix (SPM) analyzed with each batch. The reference sample to be analyzed is assigned to the analyst when the batch is assigned. The OPR sample is prepared by spiking an aliquot of the authentic spiking solution into an accurately weighed in-house reference matrix (known to contain low background levels of target analytes). The matrix is spiked with an aliquot of surrogate standard solution and, after an equilibration time of at least 30 minutes is extracted.

- Duplicates - Sample duplicates are analyzed (provided sufficient sample is available) for batches with 7-20 test samples, or when specified by the contract. For some matrices (XAD columns, filters, air samples) only field duplicates (if available) can be analyzed.
- Reference Samples – Certified reference materials are commercially available and are used to validate and periodically check methods. Additionally reference samples may be analyzed with a batch at the client's request.

The batch composition may vary according to batch or quality control requirements specified by a client. Each batch is carried through the complete analytical process as a unit. For sample data to be reportable the batch QC data must meet the acceptance criteria.

QC Specification Table: Authentic and Surrogate Standard Recoveries, CAL/VER, IPR, OPR and Samples

	Test Conc. (ng/mL)	IPR		OPR (%)	I-CAL (%)	CAL/VER (%)	Labelled Compound % Rec. in Sample		
		SD (%) *	$\bar{X}$ (%)				Warning Limits	Control Limits	EPS 1/RM/19 Limits
Native Compound									
2,3,7,8-TCDD	10	28	83-129	70-130	20	78-125	-	-	-
2,3,7,8-TCDF	10	20	87-137	75-130	20	84-120	-	-	-
1,2,3,7,8-PeCDD	50	15	76-132	70-130	20	78-125	-	-	-
1,2,3,7,8-PeCDF	50	15	86-124	80-130	20	82-120	-	-	-
2,3,4,7,8-PeCDF	50	17.2	72-150	70-130	20	82-122	-	-	-
1,2,3,4,7,8-HxCDD	50	18.8	78-152	70-130	20	78-125	-	-	-
1,2,3,6,7,8-HxCDD	50	15.4	84-124	76-130	20	78-125	-	-	-
1,2,3,7,8,9-HXCDD	50	22.2	74-142	70-130	35	82-122	-	-	-
1,2,3,4,7,8-HxCDF	50	17.4	82-118	72-130	20	90-112	-	-	-
1,2,3,6,7,8-HxCDF	50	13.4	92-120	84-130	20	88-114	-	-	-
1,2,3,7,8,9-HxCDF	50	12.8	84-122	78-130	20	90-112	-	-	-
2,3,4,6,7,8-HxCDF	50	14.8	74-148	70-130	20	88-114	-	-	-
1,2,3,4,6,7,8-HpCDD	50	15.4	76-130	70-130	20	86-116	-	-	-
1,2,3,4,6,7,8-HpCDF	50	12.6	90-112	82-122	20	90-110	-	-	-
1,2,3,4,7,8,9-HpCDF	50	16.2	86-126	78-130	20	86-116	-	-	-
OCDD	100	19	89-127	78-130	20	79-125	-	-	-
OCDF	100	27	74-146	70-130	35	75-125	-	-	-
Surrogate Standards									
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	25-130	35	82-121	40-120	25-130	40-130
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	25-130	35	71-130	40-120	24-130	40-130
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	25-150	35	70-130	40-120	25-130	30-130
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	25-130	35	76-130	40-120	24-130	30-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	25-130	35	77-130	40-120	21-130	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	25-130	35	85-117	40-120	32-130	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-130	35	85-118	40-120	28-130	30-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	25-130	35	76-130	40-120	26-130	30-130
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	25-130	35	70-130	40-120	26-123	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	25-130	35	74-130	40-120	29-130	
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	37	29-136	25-130	35	73-130	40-120	28-130	

$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	26-130	35	72-130	40-120	23-130	30-130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	25-130	35	78-129	40-120	28-130	30-130
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28-141	25-130	35	77-129	40-120	26-130	
$^{13}C_{12}$-OCDD	200	47.5	20.5-138	25-130	35	70-130	25-120	17-130	30-130
Cleanup Standard									
$^{37}Cl_4$-2,3,7,8-TCDD	10	36	39-154	31-130	35	79-127	40-120	35-130	

* For comparability with EPA 1613B the precision specification for IPR is stated as %SD (=standard deviation relative to the fortification level,)

QC Specification Table: QC Samples, Instrumental Analysis, and Analyte Quantification

QC Parameter	Specification
Analysis Duplicate	Must agree to within ±20% of the mean (applicable to concentrations >10 times the DL)[1]
Procedural Blank	**Blood:** TCDD/F <0.2 pg/sample, PeCDD/F <0.5 pg/sample, HxCDD/F and HpCDD/F <1.0 pg/ sample, OCDD/F<5 pg/sample. **Other Matrices:** TCDD/F <0.5 pg/sample, PeCDD/F, HxCDD/F, HpCDD/F <1.0 pg/sample, OCDD/F <5 pg/sample. Higher levels acceptable where all sample concentrations are > 10X the blank concentrations.
Detection Limit	SDL Requirements **Blood:** Tetra-penta-CDD/F 0.2 pg/sample Hexa-octa-CDD/F 0.5 pg/sample **Other Matrices**: 1 pg/sample
Instrument Carry over and Background: **Toluene Blank**	A. 1st toluene blank following Cal Ver must have <0.6 pg TCDD and <25 pg OCDD[2]. B. 2nd toluene blank following Cal Ver must have <0.2 pg TCDD/F, <0.8 pg Pe-HpCDD/F, and <5.0 pg OCDD[2]. Blood Extract Analysis: as many toluene blanks as necessary are run to achieve an instrument blank level of <0.1 pg TCDD/F, <0.3 pg PeCDD/F, <0.5 pg HxCDD/F, <0.5 pg HpCDD/F and <3.5 pg OCDD.
Samples	<10% contribution from preceding sample (based on observed instrument carryover rate).
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Data may be taken from more than one chromatogram to get the responses in the calibrated range.
Ion Ratios	Must be within ±15% of theoretical. For 1613B applications only an alternate acceptance criteria of within ±10% of the ratio in the midpoint calibration (CS3) or calibration verification (Cal Ver), whichever is most recent., may be applied.
Sensitivity	S:N ≥10:1 for all compounds for 0.1 pg/µL (CS-0.2) plus, for bloods, S:N ≥3:1 for 0.025 pg/µL 2,3,7,8-TCDD.

[1] Duplicate criterion is a guideline; final assessment depends upon sample characteristics, overall batch QC and on-going lab performance.

[2] Instrument background specifications are calculated from spiking labelled standard into the toluene blank and expressed as pg in a 20 µL extract.

REFERENCES:

1. United States Environmental Protection Agency *Method 1613, Revision B. Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS.*
2. USEPA *Method 8290, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)* Revision 0, September 1994.
3. USEPA *Method 8290A, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)* Revision 1, January 1998.
4. Environment Canada: *Reference Method for the Determination of Polychlorinated Dibenzo-para-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Pulp and Paper Mill Effluents,* Report EPS 1/RM/19 Feb 1992.
5. USEPA Method DLM02.1, *Statement of Work (SOW) for Analysis of Chlorinated Dibenzo-p-dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs)*, January 2009.

APPENDIX A

SUMMARY OF MODIFICATIONS TO EPA METHOD 1613B

The following sections of EPA Method 1613B have been modified as described below.

Section 2.1.2

Non-aqueous liquid from multiphase samples is combined with the solid phase and extracted by Dean Stark soxhlet.

Section 7.2.1

Anhydrous sodium sulphate (Na_2SO_4) is baked overnight prior to use. There is no solvent rinse with dichloromethane.

Section 7.10

The concentration of the labelled compound spiking solution is 100 ng/mL (except for OCDD which is 200 ng/mL) and the sample spiking volume is 20 µL. The resulting concentrations in the final extracts are as specified in the method.

Section 7.11

The concentration of the clean-up standard spiking solution is 10 ng/mL and the sample spiking volume is 20 µL. The resulting concentration in the final extracts are as specified in the method.

Sections 7.13, 14.0, 15.0

An additional lower level calibration solution, 0.2 times the concentration of CS1, is prepared and may be included in the initial calibration series so that initial calibration is based on a six-point series.

Section 7.14

The concentration of the PAR spiking solutions is 0.2/1.0/2.0 ng/mL for tetra/penta, hexa, hepta, hexa/octas respectively and the spiking volume is 1 mL. The resulting final concentration in the extracts are as specified in the method.

Section 9.3.3

Table 7 (EPA 1613B) specifications for the percent recovery of surrogate standards in samples that are higher than 130% have been lowered to 130%, as presented in table ”QC Specification Table: Authentic and Surrogate Standard Recoveries, CAL/VER, IPR, OPR and Samples” of this document.

Section 11.5

Aqueous samples containing >1% visible solids are prepared and extracted using the same procedure as samples containing $\leq$1% visible solids. This involves extracting the solids by soxhlet and the filtrate by separatory funnel extraction and combining the extract from the two phases.

Section 12.0

Samples with sufficiently low moisture content are mixed with Na_2SO_4 and extracted using regular soxhlet apparatus in 80:20 toluene:acetone.

Section 12.3.1 – 12.3.5

Silica or quartz sand is not pre-extracted in the Dean Stark apparatus. Silica is baked the lab. Quartz sand is proofed prior to use. Sand is mixed with the sample in a beaker and then loaded into the soxhlet thimble.

Section 12.3.9.1.1

Sample extracts are reduced to approximately 1mL after extraction, not 5 mL.

Section 12.4

The equilibration time for the sodium sulphate drying step is sufficient to produce a dry, free-flowing powder (minimum 30 minutes). This may be less than the 12-hour minimum specified in EPA 1613B.

Section 12.5.1

Samples are spiked with cleanup standard right after extraction and before reduction; not spiked into the separatory funnels containing the extracts prior to the acid/base wash.

Section 12.5.3

Ultra-pure water is used to rinse the extract between base and acid washes, not NaCl solution.

Section 12.6.1.1

Rotary evaporator baths are maintained at 35°C. Mimic proofs are collected instead of collecting proofs each day and archiving.

Section 12.7.3

Water baths are not used with the nitrogen blowdown apparatus.

Section 12.7.4

Solvent exchange is dependent on the type of solvent present: if toluene is present the extract is reduced to 50 µL and topped up to 1 mL with hexane; if dichloromethane is present the extract is reduced to 300 µL and topped up to 1 mL with hexane.

Section 12.7.7

Sample extracts are concentrated in a microvial using nitrogen to near dryness before adding the recovery standard.

Section 13.0

Extracts may be cleaned up on silica, alumina and carbon chromatographic columns using a Fluid Management System (FMS) automated cleanup system.

Section 13.7

Gravimetric lipid analysis is carried out on two subsamples of the extract, representing 2/15ths of the extract. A correction factor is applied to the surrogate recovery standards.

Sections 14.0, 15.0, 16.0, Table 8, Table 9

M/Z channels 354/356 and 366/368 are used to confirm and quantify the native and surrogate penta-substituted dioxins, respectively; this change from the method's specification is made in the instrument method in order to avoid a persistent interference in the 356/358 and 368/370 M/Z channels. The theoretical ratio for the P5CDD M/M+2 ions is 0.61; therefore, the acceptance range is 0.52 - 0.70.

Section 14.2

Toluene instead of nonane is used to bring extracts back to volume.

Section 15.3.5

Table 6 (EPA 1613B) specifications for CAL-VER solution concentrations outside the 70-130% range have been revised to be 70-130%, as presented in table "QC Specification Table: Authentic and Surrogate Standard Recoveries, CAL/VER, IPR, OPR and Samples" of this document.

Section 15.5.3

Table 6 (EPA 1613B) specifications for OPR concentrations outside the 70-130% range have been revised to be 70-130%, as presented in table "QC Specification Table: Authentic and Surrogate Standard Recoveries, CAL/VER, IPR, OPR and Samples" of this document.

Section 17.0

Conci - the concentrations of target analytes, and the labelled compound concentrations and recoveries, are calculated using the equations below. These procedures are equivalent to those described in the method but are more direct.

$$Conc_i = \frac{A_i}{A_{si}} \times \frac{M_{si}}{RRF_{i,si}} \times \frac{1}{M_x}$$

where A_i = summed areas of the primary and secondary m/z's for the analyte peak of interest (compound i)

A_{si} = summed areas of the primary and secondary m/z's for the labelled surrogate peak used to quantify i)

M_x = mass of sample taken for analysis

M_{si} = mass of labelled surrogate (compound si) added to sample as calculated by the concentration of standard spiked (pg/mL) multiplied by the volume spiked (mL)

$RRF_{i,si}$ = mean relative response factor of i to si from the five-point calibration range and defined individually as:

$$\frac{A_i}{A_{si}} \times \frac{M_{si}}{M_i}$$

Calculation of Surrogate Standard Concentrations and Percent Recoveries:
Concentrations of surrogate standards are calculated using the following equation:

$$Conc_{si} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}}$$

and, the percent recoveries of the surrogate standards are calculated using the following equation:

$$\%Recovery = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}} \times \frac{1}{M_{si}} \times 100$$

where A_{rs} and A_{si} are the summed peak areas (from the primary and secondary m/z channels) of recovery standard and labelled surrogate added to the sample;
M_{rs} and M_{si} are the masses of recovery standard and labelled surrogate added to the sample, and;
$RRF_{si,rs}$ is the mean relative response factor of the labelled surrogate to the recovery standard as determined by the five-point calibration range and defined individually as:

$$\frac{A_{si}}{A_{rs}} \; x \; \frac{M_{rs}}{M_{si}}$$

Section 17.5

Extracts may be diluted with solvent and re-analyzed by GC/MS to bring the instrumental response to within the linear range of the instrument. Typically, no additional recovery (internal) standard is added. For very high-level samples where a smaller sample aliquot may not be representative, extracts may be diluted and respiked with labelled quantification standards and re-analyzed by GC/MS to bring the instrumental response analytes within range. Final results are recovery corrected using the mean recovery of labelled quantification standards.

APPENDIX B

SUMMARY OF MODIFICATIONS TO EPA METHOD 8290

The following modifications apply to EPA Method 8290.

1. A sample hold time of 30 days from time of sample collection is recommended. Extract hold time, stored at <-10°C, is 45 days.
2. Solid samples are dried with sodium sulphate and Soxhlet extracted using 80:20 toluene:acetone. Upon client request, optional extraction using soxhlet Dean-Stark and toluene is available.
3. The same surrogate, recovery, authentic spike and calibration solutions that are used for EPA method 1613B (described in table "Concentration of PCDD/PCDF Calibration Solutions" of this document) are used to perform EPA Method 8290.
4. The quantification is performed according to EPA Method 1613B, using an expanded suite of surrogate standards as summarized in Table "Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans" of this document. On client request ,quantification may be performed using the smaller suite of surrogate standards described in EPA 8290 (refer to table "Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans by EPA 8290" below).
5. Sample Specific Estimated Detection Limits (EDL) are reported as Sample Specific Detection Limits (SDL), calculated as described in Section "Reporting Limits" of this document.
6. Modifications made to EPA 1613B, as described in Appendix A of this document, are applicable.
7. The QC specifications in the table "QC Criteria for PCDD/F Analysis by EPA 8290" (see below) of this document are used for evaluating data.

QC Criteria for PCDD/F Analysis by EPA 8290

Initial Calibration	Native analytes: ±20% RSD for mean RRF Labelled Compounds: ±30% RSD for mean RRF
CAL-VER	Native Analytes: RRF must be ±20% of mean RRF from ICAL Labelled Compounds: RRF must be ±30% of mean RRF from ICAL
Sample Surrogate Recovery	40-135% (lower or higher recoveries for the procedural blank may be accepted based on analyst professional judgement.)
Spiked Reference Sample	In house specification: 70%-130% of the expected value for all targets except 1,2,3,7,8,9-HxCDF, which is 60%-140%. Professional judgement may be applied in consideration of overall QC data, including MS/MSD to determine acceptability.
Analysis Duplicate	Must agree to within 25% RPD
MS/MSD	Must agree to within 20% RPD

Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans by EPA 8290

Analytes	Quantification Ion (m/z)	Confirmation Ion (m/z)	Surrogate	RRF Determined From
2,3,7,8-TCDD	320	322	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
1,2,3,7,8-PeCDD	354	356	$^{13}C_{12}$-1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	390	392	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD	390	392	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	390	392	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD	424	426	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD
OCDD	458	460	$^{13}C_{12}$-OCDD	OCDD
2,3,7,8-TCDF	304	306	$^{13}C_{12}$-2,3,7,8-TCDF	2,3,7,8-TCDF
1,2,3,7,8-PeCDF	340	342	$^{13}C_{12}$-1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	340	342	$^{13}C_{12}$-1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF	374	376	$^{13}C_{12}$-1,2,3,4,7,8-HxDCF	1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF	374	376	$^{13}C_{12}$-1,2,3,4,7,8-HxDCF	1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	374	376	$^{13}C_{12}$-1,2,3,4,7,8-HxDCF	2,3,4,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	374	376	$^{13}C_{12}$-1,2,3,4,7,8-HxDCF	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDF	410	412	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	410	412	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF
OCDF	442	444	$^{13}C_{12}$-OCDD	OCDF
Labelled Surrogate Stds	**Quantification Ion (m/z)**	**Confirmation Ion (m/z)**	**Recovery Calculated Using**	
$^{13}C_{12}$-2,3,7,8-TCDF	316	318	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-2,3,7,8-TCDD	332	334	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,7,8-PeCDF	352	354	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,7,8-PeCDD	366	368	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,4,7,8-HxDCF	384	386	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	402	404	$^{13}C_{12}$-1,2,3,7, 8,9-HxCDD	
$^{13}C_{12}$-1,2,3,4,6,7,8-H$_7$CDF	418	420	$^{13}C_{12}$-1,2,3,7,8,9 -HxCDD	
$^{13}C_{12}$-1,2,3,4,6,7,8-H$_7$CDD	436	438	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-OCDD	470	472	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
Labelled Recovery Stds				
$^{13}C_{12}$-1,2,3,4-TCDD	332	334		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	402	404		

AXYS ANALYTICAL SERVICES

SEDIMENT SAMPLE ANALYSIS PLAN

for

PASSAIC RIVER MILE 10.9 SEDIMENT CHARACTERIZATION

4636 Passaic River sample analysis plan

Analysis	*Dx by EPA1613B (AXYS MLA-017) (By Dean Stark Soxhlet Extraction)*	*PCB by EPA1668A (AXYS MLA-010)*	*Pest by AXYS MLA-028*	*PAH by AXYS MLA-021*
Samples size	3g dry (Samples size modified from the routine 10g sample size to 3g sample size to maintain analysis within the instrumental linear range and reduce matrix effects)	3g dry coextracted with Pests (Samples size modified from the routine 10g sample size to 3g sample size to maintain analysis within the instrumental linear range and reduce matrix effects)	3g dry coextracted with PCBs (Samples size modified from the routine 10g sample size to 3g sample size to maintain analysis within the instrumental linear range and reduce matrix effects)	3g dry (Samples size modified from the routine 10g sample size to 3g sample size to maintain analysis within the instrumental linear range and reduce matrix effects)
Spiking	Routine spiking for aut, surr and rec.	2x overspike for aut, surr and c/up std, routine rec	2x overspike for aut, 5x overspike for surr, routine rec	5x overspike for Surrogate and authentic, 1/4 routine spike of recovery
Splitting	None required	Physical split 4/5th for PCBs (1/5ths for Pests). Further split 1/10th, 9/10th after clean up, 1/10th portion run on the instrument	Physical split 1/5th for Pests (4/5ths for PCBs)	Physical split 1/20th, 19/20th after clean up, 1/20th portion run on the instrument
Additional Clean-up	None required	None required	Manual biobead and Florisil for both fractions and a 'modified' acid wash for E1 pesticide fraction only. At least 2 Cu test are performed on the Pest portion. First Cu test to be done after biobead using Cu powder, 2nd Cu test on E1 portion on foil. If a strong rxn observed on 2nd Cu test, 3rd powder test is performed	Alumina column may be required - based on nature of PAH extract - routine PAH extract judgment to be used
Extract Final Volume	50 uL (20uL is Routine FV - 2.5 x dilution)	50 uL (20 uL is Routine FV - 2.5 x dilution)	200 uL Both fractions (routine FV)	500 uL (Routine FV)

All client samples, field duplicates and MS/MSD samples to be analyzed as noted above

Appendix P

Laboratory SOPs

VOCs

Shealy SOP

S-VO-002

SHEALY ENVIRONMENTAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

GC/MS VOLATILES ANALYSIS BASED ON EPA METHODS 8260B AND 624

PREPARED BY EPA METHODS 5030B, 5035 AND 3585

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1. SCOPE AND APPLICATION

1.1 This method is based upon SW846 8260B, and is applicable to the determination of the concentration of volatile organic compounds in solid and aqueous matrices. The modifications presented in Attachments A thru D may be followed for analysis of wastewater following Method 624. Refer to Tables I for the list of compounds applicable for this method. Additional compounds may be amenable to this method. If non-standard analytes are required, they must be validated by the procedures described in Section 13 before sample analysis.

1.2 M-xylene cannot be separated from p-xylene by the conditions specified in this method.

1.3 The practical quantitation limit (PQL) for determining an individual compound is approximately 5.0 µg/Kg (wet weight) for low level soil/sediment samples, 250 µg/kg for high level soil/sediment, 2500µg/kg for wastes (dependent of matrix), and 5.0 µg/L for aqueous samples. Some compounds have higher reporting limits. For projects requiring lower PQLs, Shealy can supply a lower calibration that will reach as low as 0.5 ug/L for most compounds. Refer to Table I for specific PQLs.

2. SUMMARY OF METHOD

2.1 Volatile compounds are purged by helium gas from aqueous and soil/sediment samples and concentrated onto a trap. The trap is then heated rapidly and all the volatile compounds are transferred into GC inlet and analyzed by GC/MS. Qualitative identification of the target compounds is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

3. DEFINITIONS

3.1 CCC (Calibration Check Compounds) – A subset of target compounds used to evaluate the calibration stability of the GC/MS system. A maximum percent deviation of the CCC's is specified for calibration acceptance.

3.2 SPCC (System Performance Check Compounds) – Target compounds designated to monitor chromatographic performance, sensitivity, and compound instability or degradation on active sites. Minimum response factors are specified for acceptable performance.

3.3 ICV (Initial Calibration Verification) / Second Source Calibration Verification – A standard prepared from a different source than the initial calibration standards. The

ICV is analyzed after the initial calibration and is used to verify the accuracy of the calibration.

3.4 CCV (Continuing Calibration Verification) – A complete set of target compounds (compounds of interest) used to evaluate the calibration stability of the GC/MS system. A maximum percent deviation of the CCV compounds is specified for calibration verification acceptance.

3.5 Batch – The batch is a set of up to 20 field samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. If there is not enough sample to analyze an MS/MSD, an LCS/LCSD should be substituted so that RPD can be calculated. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Refer to the Shealy Quality Assurance Management Plan (QAMP) for further details of the batch definition.

3.6 Method Blank – An analytical control consisting of all reagents, internal standards and surrogate standards that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

3.7 LCS (Laboratory Control Sample) – A blank spiked with the parameters of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.8 LCSD (Laboratory Control Sample Duplicate) – A second LCS that is spiked in order to determine the precision of the method. The LCSD is used if there is not enough sample to analyze an MS/MSD.

3.9 MS (Matrix Spike) – Aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.10 MSD (Matrix Spike Duplicate) – A second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method.

3.11 NCM – nonconformance memo – Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the QA Officer.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If interference is detected, it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2 The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sampling system and the concentrator must be cleaned thoroughly between samples. Whenever an unusually concentrated sample is encountered, it should be followed, if possible, by the analysis of a blank to check for cross contamination. The sample immediately following the unusually concentrated sample may also be used to check for cross-contamination.

4.5 Acetone and methylene chloride contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5. SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all Shealy associates. The following requirements must be met:

5.1.1 As stated in the Shealy Comprehensive Chemical Hygiene, Safety, and Hazard Communication Plan (P-HS-003), eye protection that satisfies ANSI Z87.1, laboratory coat, and at least latex gloves must be worn while samples, standards, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.1.2 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory.

5.1.2.1 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers should be kept closed unless transfers are being made.

5.1.2.2 All work must be stopped in the event of a known or potential compromise to the health and safety of a Shealy associate. The situation must be reported immediately to a laboratory supervisor and preferably the EH&SO (Environmental Health and Safety Officer).

6. EQUIPMENT AND SUPPLIES

6.1 Gas Chromatograph/Mass Spectrometer System – An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.2 Column – Silicon-coated fused-silica capillary columns. RTX-624 30m × 0.25mm × 1.4 μm, RTX-624 20m × 0.18mm × 1.0 μm or equivalent.

6.3 Mass Spectrometer – Capable of scanning from 35 to 300 AMU every two seconds or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-bromofluorobenzene (BFB) which meets all of the criteria in Table IV when 50 ng of the GC/MS tuning standard are injected through the GC.

6.4 GC/MS Interface – Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5 Data System – A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.6 Purge and Trap – Eclipse model 4660 purge and trap coupled to an OI 4551-A or OI model 4552(Archon) autosampler.

6.7 Syringe – 10 µL Hamilton Laboratory grade syringes or equivalent.

6.8 Carrier gas – Ultra high purity helium.

6.9 Soil sample collection kit – Two 40-ml amber VOC vials each with a magnetic stir bar and 5.0 mls of reagent water weighed to nearest 0.01 gram. One empty amber 40-ml VOC vial weighed to nearest 0.01 gram. One sealed PTFE tube containing 5.0 mls of methanol. One 2 oz glass container. Disposable plastic syringe with a barrel smaller than the neck of the soil vial. Once a sample collected in this syringe is must be immediately injected into the appropriate preservative. One syringe is needed for each sample to be collected. This is not an approved storage device.

6.10 EnCore™ sampler – (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent. Soil sample can be stored in an EnCore for up to 48 hours.

7. REAGENTS AND STANDARDS

7.1 All standards (except the gas standards) used directly out of the flame-sealed ampules are considered to be primary standards. All primary standards expire six month after the open date (or manufacturer's expiration date, whichever has the more strict criteria). After the ampule is opened, the remaining standard is stored in a Mininert. The standard must be refrigerated at ≤ -10 °C when not in use.

7.1.1 The gas standards expire one week after the open date. The standard must be refrigerated at ≤ -10 °C when not in use.

7.1.2 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift.

7.1.3 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift.

7.2 All standards that are diluted from the manufacturer's ampule before analysis are considered secondary standards. All secondary standards expire one week after their prep date (or manufacturer's expiration date, whichever has the more strict criteria). The standard must be refrigerated at ≤ -10 °C when not in use.

7.2.1 Daily working standards expire 12 hours after prep when not refrigerated and 24 hours after prep if refrigerated at 4 ± 2°C.

7.3 A minimum five-point calibration curve is prepared. The low point should be at or below the reporting limit. Refer to Table X for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low

standard must support the reporting limit and the high standard defines the upper range of the calibration.

7.4 An initial calibration verification standard (ICV) is prepared from a different source of standards used in the preparation for the initial calibration. The concentration of the ICV should be at or near the middle of the calibration range. Refer to Table XII for ICV compounds and criteria for Shealy primary standard.

7.5 An Internal Standard (IS) solution is prepared. Compounds in the IS Mix are: pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d5, 1,4- dichlorobenzene-d4.

7.5.1 Internal Standards are added to all standards and samples to result in 25-50 µg/L on-column value.

7.6 Surrogate Standard Spiking Solution – Prepared at 125 or 250 µg/mL concentration. Due to variances in autosampler loop volume, on column concentration will vary. Surrogate compounds are listed in Table IX.

7.7 GC/MS Tuning Standard: A methanol solution containing 25 µg/mL of 4-bromofluorobenzene (BFB) is prepared.

7.8 Laboratory Control Sample (LCS) Spiking Solution – Prepared at 100 µg/ml concentration. LCS compounds are listed in Table VII.

7.9 Matrix Spike Solution – Same as LCS spiking solution in 7.8 above.

7.10 Reagent Water – Shealy employs a series of in-house deionized (DI) tanks to purify the incoming water to the conductivity measurement, 0.056 µmhos/cm (corresponds to resistivity of 18 meg-ohms). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Aqueous samples are collected in three 40-ml volatile sample vials preserved with hydrochloric acid and stored at 4 ± 2°C. If 2-Chloroethyl vinyl ether or tetra ethyl lead is an analyte of interest, another set of three 40-ml volatile vials must be collected without preservative and stored at 4 ± 2°C. The compound 2-Chloroethyl vinyl ether breaks down in the presence of acid, and therefore, cannot be reported from a preserved sample.

8.2 Solid samples preserved in the field:

The following procedure must be performed with latex gloves (or equivalent).

Use the sampling kit in Section 6.9 to collect approximately 5 grams of soil sample into 2 pre-weighed 40-ml vials each containing reagent water and a stir bar. Open the methanol tube and pour the methanol into the empty 40-ml vial immediately after injecting the third 5 gram aliquot of sample. Tightly cap all the vials. In addition, solid samples are collected in a 2 oz glass container for dry weight determination. The 40-ml vials containing solid samples and reagent water should be stored in a freezer in which temperature is less than -10°C within 48 hours of collection. To avoid potential vial breakage store the vials horizontally in freezer. The solid samples preserved in methanol and those in the 2 oz container should be stored under 4 ± 2°C.

8.3 Solid Sample Collected in EnCore™ Sampler

8.3.1 Two EnCore™ Samplers should be collected for low level analysis. The samplers should be sealed immediately after collection. The samples must be preserved as follows within 48 hours of collection. Weigh two 40-ml VOC vials each containing 5.0 mls of reagent water and a magnetic stir bar to the nearest 0.01 gram. Open the sampler and carefully transfer the solid sample into the vial. Cap the vial. Re-weigh the vial. Record the weight to the nearest 0.01 g. The difference between the second and first weight is the sample weight. Record the weight in a logbook. The samples must be analyzed within 48 hours of preservation or the vials must be stored horizontally in a freezer within 48 hours of collection. Note: Care must be taken to keep vial threads clean in order to achieve a hermetic seal. Internal standard recoveries of less than 50% are typical when vial is not properly sealed.

8.3.2 An additional sample is collected for potential high level analysis in a 2 oz glass container or a third EnCore™ Sampler. Within 48 hours of collection, approximately 5 grams of the solid sample from the 2 oz jar or the contents of the sampler should be preserved in 5.0 mLs of methanol.

8.4 The maximum holding time for all samples is 14 days from collection. If 2-chloroethyl vinyl ether is an analyte of interest, the holding time is 7 days in an unpreserved vial. The compound 2-Chloroethyl vinyl ether breaks down in the presence of acid and therefore, cannot be reported from a preserved sample.

9. QUALITY CONTROL

9.1 Initial Demonstration of Capability

9.1.1 For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.1.2 For non-standard, non-regulatory analytes, an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed upon with the client.

9.2 Batch Definition – Batches are defined at the sample preparation stage. Batches should be kept together through the entire analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the Shealy QAMP for further details of the batch definition.

9.2.1 Quality Control Batch – The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank (MB). Laboratory generated QC samples (MB, LCS and MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate.

9.3 Control Limits – In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS/LCSD). These limits must be generated, at a minimum, on an annual basis. Acceptance limits are calculated by using the mean recovery ± 3 standard deviations. Refer to the LCS section below for maximum limit ranges.

9.3.1 All surrogate, LCS/D, and MS/D recoveries must be entered into the Shealy LIMS (when available) or other database so that accurate historical control limits can be generated. Surrogate and matrix spike percent recoveries will be reported for all dilutions.

9.3.2 Refer to the QAMP for further details of control limits.

9.4 Method Blank (also known as the Laboratory Reagent Blank) – A method blank is prepared and analyzed with each batch of samples. The method blank consists of organic free reagent water. Surrogates and internal standards are added and the method blank is carried through the entire analytical procedure.

9.4.1 The method blank must not contain any analyte of interest at or above the PQL (1/2 the PQL for DOD or North Carolina samples). If the method blank contains an analyte of interest at or above this limit, the method blank and associated samples must be re-analyzed with a method blank, which passes acceptance criteria. The following exceptions apply to samples other than DOD or North Carolina:

9.4.1.1 A method blank with concentrations of target compounds exceeding the limits in section 9.4.1 is acceptable in either of the following cases.

9.4.1.1.1 The concentration of the target compound in the method blank is less than 5% of the regulatory limit associated with that analyte for that sample.

9.4.1.1.2 The concentration of the target compound in the method blank is less than 5% of the sample concentration.

9.4.2 To clarify the compounds of interest that are associated with each sample the LIMS generated worksheet printout for each sample will be contained in the batch data file. This worksheet printout will list the required target compounds and the reporting limits.

9.4.3 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, sample analysis should stop immediately. Corrective action should be taken. A new method blank should be analyzed and meet the surrogate criteria before sample analysis can begin.

9.4.4 Sample results are **NOT** blank subtracted.

9.5 Laboratory Control Sample (LCS), also known as the Laboratory Fortified Blank

9.5.1 A laboratory control sample (LCS) is prepared from a source independent of the initial calibration standards and analyzed with every batch of samples. The LCS is spiked with the compounds listed in Table VII, unless specified by a client or agency. The LCS sample for low level soil (5035) must contain approximately 5 grams of Ottawa sand. The acceptable control limits for LCS/D are statistically derived. However, if the lower control limits are < 70% or the upper control limits are >130%, then the default limits of 70-130% will apply to the compounds in Table VII. The only exceptions are the * compounds found in Attachments C and D. These compounds have default control limits of 60-140% (if not statistically more stringent). Refer to attachment C for the entire list of aqueous LCS recovery limits. Refer to attachment D for the soil limits. Refer to Table VII for a list of spiked LCS compounds and their spiking concentrations. The recovery limits for each compound can be found in Attachments C and D.

9.5.2 Evaluating LCS results:

Since >90 analytes are in the LCS, it is statistically likely that a few will be outside control limits. This may not indicate that the system is out of control, therefore corrective action may not be necessary. Upper and lower marginal exceedance (ME) limits can be established to determine when corrective action is necessary. A ME is defined as being beyond the LCS control limit (3 standard deviations), but within the ME limits. ME limits are between 3 and 4

standard deviations around the mean. The volatiles LCS spiking mix contains more than 90 analytes. Up to 5 analytes may marginally exceed the control limits. If more analytes exceed the LCS control limits than is allowed, or if any "target" analyte exceeds the ME limits, the LCS fails and corrective action is necessary.

9.5.2.1 Marginal exceedances must be random. If the same analyte exceeds the LCS control limit repeatedly, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

Note: Marginal Exceedences are not allowed for SC samples. If any compounds fail to meet LCS limits, refer to actions outlined in Section 9.5.3

9.5.3 Corrective Action for LCS failure

9.5.3 If an LCS fails to meet the ME criteria for a target compound, an attempt must be made to determine the source of error and find a solution. A target compound is any compound being reported for that sample. All findings and corrective actions should be documented in the maintenance logbook. All associated samples must be reprepped and reanalyzed if the failing LCS analyte is a target compound. The corrective action applied shall be based on professional judgment in the review of other QC measures (i.e. surrogates). If analyte falls outside a second time or if there is not sufficient sample to be reanalyzed, an NCM must be filled out documenting the failure and corrective actions that were applied.

9.6 Matrix Spike (MS) and Matrix Spike Duplicate (MSD), also known as the Laboratory Fortified Matrix and Laboratory Fortified Matrix Duplicate – For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compound and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory specific historically generated limits.

9.6.1 If any individual recovery or RPD falls outside the acceptable range ≤ 30%, corrective action must occur. The initial corrective action will be to check all calculations. If the calculations are correct, check the recovery of that analyte in the Laboratory Control Sample (LCS). If the recovery of the analyte in the LCS is within limits, then matrix interference has been demonstrated and the laboratory operation may proceed. An NCM must be generated to notify the Quality Assurance Officer, project manager, and client.

9.6.2 If the recovery for any component is outside QC limits for the matrix spike/spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will include re-preparation and reanalysis of the batch. An NCM must be generated to document this occurrence.

9.6.3 Every effort is made to ensure that an MS/MSD pair is included in every batch. On the rare occasion that one is not possible (sample bottle was broken, etc.) then an LCS duplicate must be analyzed.

9.6.4 The matrix spike/spike duplicate must be analyzed at the same dilution as the parent sample (the un-spiked sample).

9.7 Surrogates

9.7.1 Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table IX.

9.7.2 If any surrogates are outside limits, an NCM must be written and the following corrective actions must take place. For high level soil samples in methanol and/or non-aqueous samples with dilutions ≥ 5x, all corrective actions are applicable with the exception of sample reanalysis.

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the sample if either of the above checks reveals a problem.
- It is only necessary to reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect. A demonstrated matrix effect must be documented on an NCM.

9.8 Shealy QC Program – Further details of QC and corrective action guidelines are presented in Section 10.4.2 of the Shealy QAMP. This section of the QAMP is used when the samples are not South Carolina compliance samples.

10. CALIBRATION AND STANDARDIZATION

10.1 Summary – The instrument is tuned for BFB, calibrated initially with a five-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table III.

10.2 All standards and samples are allowed to warm to room temperature before injecting.

10.3 All calibration standards are prepared using volumetric flasks.

10.4 Instrument Tuning – At the beginning of every twelve hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (IV) is achieved for BFB (4-Bromofluorobenzene).

10.4.1 Inject 50 ng (2 μL) of the GC/MS tuning standard (Section 7.7) into the GC/MS system. Obtain a background-subtracted mass spectrum of BFB and confirm that all the key m/z criteria in Table IV are achieved. If all criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.4.2 A purged BFB can also be used to evaluate instrument tuning. If the volume of sample purged is 5.0 mls, then BFB concentration in the aqueous solution should be 10 μg/L to result in an on-column amount of 50 ng.

10.5 Initial Calibration

10.5.1 Internal Standard Calibration Procedure – Internal standards are listed in Table VI. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.5.2 Compounds should be assigned to the IS with the closest retention time.

10.5.3 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. Additional levels can be analyzed and use the lower five for most analytes and the upper five for analytes that have poor response. Add the internal standard mixture to result in a concentration of 50 μg/L in the solution.

10.5.4 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in Section 12.5. The average RF and %RSD must meet the criteria listed in Sections 10.4.5 through 10.4.7. **The ICAL cannot be forced through zero. No sample analysis may be performed unless these criteria are met.**

10.5.5 System Performance Check Compounds (SPCCs) – The minimum average RF for volatile SPCCs is listed below. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port contamination, contamination of the front end of the analytical column, active sites in the column or chromatographic system and gas leaks or restrictions. This check must be met before analysis begins.

SPCC Compounds:	Minimum RF	Example Problem
Chloromethane	0.100	Purge flow too fast
1,1-Dichloroethane	0.100	Contaminated transfer lines in PT systems and/or active sites in trapping materials.
Bromoform	0.100	Purge flow too slow. Cold spots, active sites in the transfer lines
1,1,2,2-Tetrachloroethane	0.300	Same as 1
Chlorobenzene	0.300	Same as 1

10.5.6 Calibration Check Compounds (CCCs) – The %RSD of the response factors for each CCC in the initial calibration must be ≤ 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could affect this criterion.

10.5.6.1 CCC Compounds : 1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl Chloride

10.5.7 The average response factor is used when the %RSD of a compound is ≤ 15%.

10.5.8 For compounds that have % RSD >15% linear regression should be used. The correlation coefficient must be ≥ 0.99. The Target® software calculates the square of correlation coefficient which should be ≥ 0.99.

10.5.9 With the exception of section 10.4.10 below, it NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest of the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve.

10.5.10 A level may be removed from the calibration if the reason can be clearly documented, for example a poor purge. A minimum of five levels must remain in the calibration.

10.5.11 A level may be reanalyzed within 12 hours of the start of the calibration sequence, if no sample has been processed with the new calibration.

10.5.12 As soon as a new initial calibration curve is analyzed, all previous calibration curves are invalid whether the new calibration curve passes or not. The analysts cannot use an old curve to analyze sample.

10.5.13 If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.5.14 Quantitation is performed using average response factor from the initial curve, not the continuing calibration.

10.6 Initial Calibration Verification (Second Source Calibration Verification – A standard that is prepared from a source independent of standards of the initial calibration. The ICV contains all Target compounds and its concentration should be at or near the mid level of the initial calibration. The concentration of the ICV, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. Recovery must be within 70-130% before sample analysis to begin. The ICV must be analyzed immediately after the ICAL.

10.7 Continuing Calibration Verification (CCV), also known as the Instrument Performance Check

10.7.1 At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 50 ng injection of BFB must result in a mass spectrum for BFB which meets the criteria given in Table IV.

10.7.2 Following a successful BFB analysis, the continuing calibration verification (CCV) standard(s) are analyzed. The standards must contain all volatile analytes, including all required surrogates. A mid level calibration standard is used for the continuing calibration.

10.7.3 Continuing Calibration Verification (CCV) technical acceptance criteria:

10.7.3.1 The response factor for the SPCC compounds must meet the criteria listed in section 10.4.5.

10.7.3.2 The percent difference of the CCC compounds from the initial calibration must be ≤ 20% difference. See Section 12 for calculation. In addition, the percent difference of all other target analytes must meet the criteria in Table XIII with the following exceptions:

10.7.3.2.1 One or more CCC's may fail if the CCC is not a target analyte and all target analytes meet the 20% difference or drift criterion.

10.7.3.2.2 If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

10.7.3.2.3 To clarify the compounds of interest that are associated with each sample the LIMS generated worksheet printout for each sample will be contained in the batch data file. This worksheet printout will list the required target compounds and the reporting limits.

10.7.3.3 The internal standard response must be within 50-200% of the response in the mid-level of the initial calibration.

10.7.3.3.1 The internal standard retention times must be within ± 30 seconds of the retention times in the mid-level of the initial calibration.

10.7.4 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample injected less than 12 hours after the BFB is acceptable.)

10.7.5 In any case, the criteria for SPCC compounds must be met.

10.7.6 Corrective action for CCV failure:

10.7.6.1 Check all calculations and integrations. Inspect the GC/MS system for malfunction. Try to determine the cause of the failure. If it appears that the analytical system is in proper working order but the standard has been improperly prepared, degraded, or compromised, a new standard may be prepared and reanalyzed. If it is suspected that the instrument is unstable or malfunctioning then maintenance and/or repair must be performed before running another CCV. If the system appears to be in working order and standards are prepared correctly then a new ICAL must be analyzed before sample analysis may begin. In either case if the 2nd consecutive CCV fails to pass acceptance criteria, the analyst must perform corrective action and demonstrate that the system is stable and in proper working order with two consecutive passing CCV's or an ICAL must be analyzed before analysis of samples can begin.

11. PROCEDURE

11.1 Sample Preparation – High level soil sample preparation procedures are in Attachment B.

11.2 Sample Analysis Procedure

11.2.1 Calibrate the instrument as described in section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2 All samples must be analyzed using the same instrument conditions as the preceding continuing calibration standard.

11.2.3 The weight for soil sample in water must be determined before analysis can begin. Weigh the vial to the nearest 0.01 gram. The difference between this weight and the weight from section 6.9 is the actual sample weight.

11.2.4 The frozen soil sample must be warmed to ambient temperature before analysis can begin.

11.2.5 Add internal standard and surrogate standard to the sample to result in 25-50 μg/L concentration in the aqueous solution.

11.2.6 Load the autosampler and begin the sequence. The procedure for the samples and the standards must be the same.

11.2.7 The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in Section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.2.8 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system.

11.2.9 Target compounds identified by the data system are evaluated using the criteria listed in Section 12.1.

11.2.10 Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) may be performed if required by the client. They are evaluated using the criteria in Section 12.2.

11.3 Dilutions

11.3.1 Dilutions should be performed so that the resulting dilution factor is an integer. Dilutions may be prepared either manually or by an Archon Autosampler. The Archon may be used to prepare dilutions of 2x, 5x, 10x, 20x, 50x and 100x.

11.3.2 For aqueous, high level soil, and waste samples, if the response for any compound exceeds the working range of the GC/MS system, a dilution of the sample or extract is prepared and analyzed. An appropriate dilution should target the CCV (mid range of the ICAL). Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or its highest hits are below 25% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above the CCV (mid range of the ICAL).

11.3.3 For low level soil samples, if the response for any compound exceeds the working range of the GC/MS system, a high level soil analysis should be performed. See Attachment B-4 for details.

11.3.4 Guidance for Dilutions Due to Matrix – If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgment. For example, samples containing petroleum fuel may need to be analyzed at a higher dilution to avoid contaminating the purge-and-trap system.

11.3.5 Reporting Dilutions – The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.4 Internal standard criteria for samples:

11.4.1 If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.4.2 If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows. Refer to Section 12.3 for further evaluation of co-eluting pairs.

11.4.3 The internal standard response must be within 50 – 200% of the response in the last continuing calibration standard.

11.5 All aqueous samples must be checked for pH immediately after analysis. The pH must be taken from the parent sample in the case of a dilution. The pH verification is documented in the instrument run log. If the pH is not <2 an NCM must be completed to ensure the anomaly is communicated to the client and reported in the case narrative.

11.6 Percent Moisture – Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight.

11.7 Troubleshooting Guide

11.7.1 Instrument Maintenance – In addition to the checks listed in the instrument maintenance schedule in the Shealy QAMP, the following maintenance activities must be monitored daily and performed if necessary:

- Injection port inspection/maintenance
- Clip column
- Install new or cleaned injection port liner and gold seal
- Install new septum
- Change trap every 6 month or as necessary.
- Perform mass calibration as necessary.

11.7.2 Major Maintenance – A new calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the ion electron source, replacing the multiplier, and changing the trap to a new lot number. Refer to the manufacturer's manual for specific guidance. All maintenance must be recorded in the instrument maintenance log with the date and initials.

11.8 Procedural Variations – This Section applies to all samples except South Carolina compliance samples. One time procedural variations are allowed, only if deemed necessary in the professional judgment and supervision of a knowledgeable analyst, to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in analytical procedure must be approved by a technical director, the QA Officer, or the client, and must be fully documented (flagged and/or narrated) on the final report. The analyst must use an NCM to notify the appropriate parties and to document the variance. The project manager uses the information on the NCM to notify the client and flag/narrate the final report accordingly. A copy of the NCM is kept with the raw data and the original is filed with the final report.

11.8.1 For South Carolina compliance samples, all procedures outlined in this SOP must be followed without exception. In the event that a deviation from this SOP cannot be avoided (i.e., demonstrated and uncorrectable matrix interference, non-compatible matrix, insufficient sample amount due to client or laboratory error) it is imperative that an NCM is completed that clearly documents the anomaly. This anomaly must be communicated to the client such that corrective action activity including sample recollection can be performed. Based upon the type and severity of anomaly, the results may not be appropriate for compliance reporting. Discussions between the client, the appropriate regulatory authority, and Shealy will be necessary to resolve

certain anomalies. In any case, it is essential that any anomaly be documented on an NCM.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative identification – An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

- The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

- The relative intensities of ions must agree to within ± 30% for target analytes and ± 20% for TICs (between the standard and sample spectra). (Example: A target ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

12.1.1 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation. GC/MS analysts are trained to carefully evaluate data for compounds that have close retention times and share common ions.

12.1.1.1 If an alternate compound was selected by the analyst, the compound will be flagged with an "H" by Target®. The triple plot must be printed to document that the correct compound was selected.

12.1.1.2 If a compound fails the ratio test, the compound will be flagged with a "Q" by Target®. The triple plot must be printed to document that the correct compound was selected.

12.1.1.2.1 The following compounds may display the "Q" flag at concentrations > half the calibration range due to shared ions.

Close Eluting Compounds	
Ethylbenzene	m&p-Xylenes
o–Xylene	Styrene
Allyl chloride	Acetonitrile
Allyl chloride	Carbon disulfide
Dichlorobenzenes	Dichlorobenzenes
Vinyl acetate	Diisopropyl ether
trans-1,4-Dichloro-2-butene	1,2,3-Trichloropropane
1,2,4-Trimethylbenzene	1,3,5-Trimethylbenzene

12.2 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 type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30% and 70%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.
- Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

12.3 Calculations

12.3.1 Percent Relative Standard Deviation for Initial Calibration:

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

RF = Mean RFs from initial calibration for a compound.

SD = Standard deviation of RFs from initial calibration for a compound.

$$= \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N - 1}}$$

RF*i* = RF for each of the calibration levels.

N = Number of RF values.

12.3.2 Continuing calibration percent difference and percent drift:

$$\%Diff = \frac{RF - \overline{RF}}{\overline{RF}} \times 100$$

RF = Compound's response factor in the CCV.

$\overline{RF}$ = Compound's average response factor in the initial calibration.

$$\%Drift = \frac{\text{Calculated Conc.} - \text{Theoretical Conc.}}{\text{Theoretical Conc.}} \times 100$$

12.3.3 Concentration in the sample – The concentration of each identified analyte and surrogate in the sample is from the average RF of the initial calibration.

12.3.3.1 On-column concentration (µg/L):

$$C = \frac{A_x \times C_{is}}{A_{is} \times \overline{RF}}$$

12.4.3.2 Aqueous sample (µg/L):

Concentration = C x DF

A_x = Response for analyte, in area count of the characteristic ion.

A_{is} = Response for internal standard.

C_{is} = Concentration of internal standard.

DF = Dilution factor.

12.4.3 Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis):

$$\text{Concentration, } \mu g/kg = \frac{C \times V_0 \times DF}{W \times D}$$

V_0 = Volume of sample extract in mls.

W = Weight of sample extracted or diluted in grams.

D = (100 - % moisture in sample)/100, for a dry weight basis or 1 for a wet weight basis.

12.4.3 MS/MSD percent recovery calculation:

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

S_{SR} = Spike sample result.

S_R = Sample result.

S_A = Spike added.

12.4.4 Relative % Difference calculation for the MS/MSD:

$$RPD = \frac{MS_R - MSD_R}{½ (MS_R + MSD_R)} \times 100$$

RPD = Relative percent difference.

MS_R = Matrix spike result.

MSD_R = Matrix spike duplicate result.

12.4.5 Relative response factor calculation:

$$RF = \frac{A_x C_{is}}{\quad}$$

$A_{is}C_x$

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_x = Concentration of the compound being measured (µg/L).

C_{is} = Concentration of the specific internal standard (µg/L).

12.4.6 Calculation of TICs – The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x = Area of the total ion chromatogram for the compound being measured.

A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference.

RF = 1.

13. METHOD PERFORMANCE

13.1 Method Detection Limit – Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in Shealy QAMP.

13.1.1 Each MDL sample is prepared independently using volumetric flasks. The practice of generating one large volume of MDL sample and dividing it between the (7) MDL samples is unacceptable.

13.2 Initial Demonstration – Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests, it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be 50ug/L.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in LIMS.

13.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3 Non-standard analytes – For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

13.4 Training Qualification – The team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.5 Data Quality Objectives (DQO) – Refer to project-specific Quality Assurance plans for DQO information.

14. POLLUTION PREVENTION

14.1 Not applicable to this procedure.

15. WASTE MANAGEMENT

15.1 Waste generated in the procedure must be segregated and disposed of according to the Shealy Waste Management Plan (P-HS-001) and per the local, state, and federal regulations. The Safety Officer should be contacted, if additional information is required.

15.2 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/.MS), Method 8260B.

16.2 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Determinative Chromatographic Separations, Method 8000B.

16.3 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Purge-and-Trap For Aqueous Samples, Method 5030B.

16.4 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Method 5035, Revision 0.

16.5 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Sample Preparation For Organic Volatile Compounds, Method 5000B.

16.6 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Sample Preparation For Organic Volatile Compounds, Method 3585

16.7 Shealy Quality Assurance Management Plan (QAMP), Q-QA-001, Revision 7, July 2010.

16.8 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 3, January 2006.

17. MISCELLANEOUS

17.1 Modifications from Reference Method

17.1.1 The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.1.2 Directions for analysis of Method 624 are in Attachment B.

17.1.3 The reporting limit for total xylene is 5.0 μg/L. If m/p xylenes and o-xylene are detected at less than 5 μg/L each, but the sum is more than 5 μg/L, the total value will be reported.

17.1.4 All Department of Defense-NFESC (DoD-Navy) method requirements are found in Appendix DoD.

17.1.5 Historically the surrogate compounds have been included in the multi-point initial calibration at variable concentrations in order to evaluate the linear response as with any target analyte. However, with improvements in instrumentation and more reliance on the autosampler, an option is available depending on the project-specific data quality requirements for allowing the autosampler (or using a manual technique) to spike the initial calibration standards with surrogates in the same manner as the samples are spiked. With this option the surrogate standards in the initial calibration can be averaged to develop a response factor and an effective one point calibration with the sole purpose to measure the surrogate recovery using the same concentration for each sample analysis. For this calibration option the

surrogate linear response is less important, since multiple concentrations of surrogates are not being measured. Instead, the surrogate concentration remains constant throughout and the recovery of this known concentration can easily be attained without demonstrating if the response is linear.

APPENDIX A – TABLES

TABLE I. Shealy CAS Numbers and Reporting Limits

Analytes	CAS Number	Standard Reporting Limits				
		Trace Aqueous µg/L	Low Level Aqueous µg/L	Aqueous µg/L	Low Soil µg/kg	High Soil µg/kg
Acetone	67-64-1	N/A	N/A	20	20	1000
Acetonitrile	75-05-8	N/A	N/A	10	10	500
Acrolein	107-02-8	N/A	N/A	50	50	2500
Acrylonitrile	107-13-1	N/A	N/A	50	50	2500
Benzene	71-43-2	0.5	1	5	5	250
Benzyl chloride	100-44-7	N/A	N/A	5	5	250
Bromobenzene	108-86-1	0.5	1	5	5	250
Bromochloromethane	74-97-5	0.5	1	5	5	250
Bromodichloromethane	75-27-4	0.5	1	5	5	250
Bromoform	75-25-2	0.5	1	5	5	250
Bromomethane (Methyl bromide)	74-83-9	0.5	1	5	5	250
2-Butanone (MEK)	78-93-9	N/A	N/A	10	10	500
n-Butylbenzene	104-51-8	0.5	1	5	5	250
tert-Butylbenzene	98-06-06	0.5	1	5	5	250
sec-Butylbenzene	135-98-8	0.5	1	5	5	250
Carbon disulfide	75-15-0	0.5	1	5	5	250
Carbon tetrachloride	56-23-5	0.5	1	5	5	250
Chlorobenzene	108-90-7	0.5	1	5	5	250
2-Chloro-1,3-Butadiene (Chloroprene)	126-99-8	N/A	N/A	5	5	250
Chloroethane	75-00-3	0.5	1	5	5	250
2-Chloroethyl vinyl ether	110-75-8	N/A	N/A	10	10	500
Chloroform	75-00-3	0.5	1	5	5	250
Chloromethane (Methyl chloride)	74-87-3	0.5	1	5	5	250
3-Chloropropene (Allyl chloride)	107-05-1	N/A	N/A	10	10	500
2-Chlorotoluene	95-49-8	0.5	1	5	5	250
4-Chlorotoluene	106-43-4	0.5	1	5	5	250
Cyclohexane	110-82-7	N/A	1	5	5	250
Cyclohexanone	108-94-1	N/A	N/A	50	50	2500
Dibromochloromethane	124-48-1	0.5	1	5	5	250
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8	0.5	1	5	5	250
1,2-Dibromoethane (EDB)	106-93-4	0.5	1	5	5	250
Dibromomethane (Methylene bromide)	74-95-3	0.5	1	5	5	250
1,2-Dichlorobenzene	95-50-1	0.5	1	5	5	250
1,3-Dichlorobenzene	541-73-1	0.5	1	5	5	250
1,4-Dichlorobenzene	106-46-7	0.5	1	5	5	250

TABLE I. Shealy CAS Numbers and Reporting Limits

Analytes	CAS Number	Standard Reporting Limits				
		Trace Aqueous µg/L	Low Level Aqueous µg/L	Aqueous µg/L	Low Soil µg/kg	High Soil µg/kg
trans-1,4-Dichloro-2-butene	110-57-6	N/A	N/A	10	10	500
Dichlorodifluoromethane	75-71-8	0.5	1	5	5	250
1,1-Dichloroethane	75-34-3	0.5	1	5	5	250
1,2-Dichloroethane	107-06-2	0.5	1	5	5	250
cis-1,2-Dichloroethene	156-59-2	0.5	1	5	5	250
trans-1,2-Dichloroethene	156-60-5	0.5	1	5	5	250
1,1-Dichloroethene	75-35-4	0.5	1	5	5	250
1,3-Dichloropropane	142-28-9	0.5	1	5	5	250
2,2-Dichloropropane	594-20-7	0.5	1	5	5	250
1,1-Dichloropropene	563-58-6	0.5	1	5	5	250
cis-1,3-Dichloropropene	10061-01-5	0.5	1	5	5	250
trans-1,3-Dichloropropene	10061-02-6	0.5	1	5	5	250
1,2-Dichloropropane	78-87-5	0.5	1	5	5	250
Diisopropyl ether (IPE)	108-20-3	0.5	1	5	5	250
3,3-dimethyl-1-butanol	624-95-3	N/A	N/A	100	N/A	N/A
1,4-Dioxane	123-91-1	5	10	250	250	12,000
Ethyl acetate	141-78-6	N/A	N/A	5	5	250
Ethanol	64-17-5	N/A	N/A	100	N/A	N/A
Ethyl ether	60-29-7	0.5	1	5	5	250
Ethylbenzene	100-41-4	0.5	1	5	5	250
Ethyl methacrylate	97-63-2	N/A	N/A	5	5	250
Ethyl-tert-butyl ether	637-92-3	N/A	N/A	1.0	N/A	N/A
Hexachlorobutadiene	87-68-3	N/A	N/A	5	5	250
2-Hexanone	591-78-6	N/A	N/A	10	10	500
Isopropylbenzene	98-82-8	0.5	1	5	5	250
p-Isopropyltoluene	99-87-6	0.5	1	5	5	250
Isobutyl alcohol	78-83-1	N/A	N/A	50	50	2500
Methacrylonitrile	126-98-7	N/A	N/A	5	5	250
Methyl acetate	79-20-9	N/A	N/A	5	5	250
Methylcyclohexane	108-87-2	N/A	N/A	5	5	250
Methyl iodide (Iodomethane)	74-88-4	N/A	N/A	5	5	250
Methyl methacrylate	80-62-6	N/A	N/A	5	5	250
4-Methyl-2-Pentanone	108-10-1	N/A	N/A	10	10	500
Methyl tertiary butyl ether (MTBE)	1634-04-4	0.5	1	5	5	250
Methylene chloride	75-09-2	0.5	1	5	5	250
Naphthalene	91-20-3	0.5	1	5	5	250
n-Propylbenzene	103-65-1	0.5	1	5	5	250
Propionitrile (Ethyl cyanide)	107-12-0	NA	NA	50	50	2500
Styrene	100-42-5	0.5	1	5	5	250
Tert-amyl Alcohol	75-85-4	N/A	N/A	20	N/A	N/A

Tert-amyl-methyl ether	994-05-8	N/A	N/A	10	N/A	N/A
Tert-Butyl Alcohol	75-65-0	N/A	N/A	20	N/A	N/A
Tert-Buytl Formate	762-75-4	N/A	N/A	5.0	N/A	N/A
1,1,1,2-Tetrachloroethane	630-20-6	0.5	1	5	5	250

TABLE I. Shealy CAS Numbers and Reporting Limits

Analytes	CAS Number	Standard Reporting Limits				
		Trace Aqueous µg/L	Low Level Aqueous µg/L	Aqueous µg/L	Low Soil µg/kg	High Soil µg/kg
1,1,2,2-Tetrachloroethane	79-34-5	0.5	1	5	5	250
Tetrachloroethene	127-18-4	0.5	1	5	5	250
Tetraethyl lead	78-00-2	0.5	1	5	5	250
Tetrahydrofuran	109-99-9	NA	NA	10	10	500
Toluene	108-88-3	0.5	1	5	5	250
1,2,4-Trichlorobenzene	96-18-4	0.5	1	5	5	250
1,2,3-Trichlorobenzene	95-63-6	0.5	1	5	5	250
1,1,1-Trichloroethane	71-55-6	0.5	1	5	5	250
1,1,2-Trichloroethane	79-00-5	0.5	1	5	5	250
Trichloroethene	79-01-6	0.5	1	5	5	250
Trichlorofluoromethane	75-69-4	0.5	1	5	5	250
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	0.5	1	5	5	250
1,2,3-Trichloropropane	96-18-4	0.5	1	5	5	250
1,2,4-Trimethylbenzene	95-63-6	0.5	1	5	5	250
1,3,5-Trimethylbenzene	108-67-8	0.5	1	5	5	250
Vinyl acetate	108-05-4	0.5	1	5	5	250
Vinyl Chloride	75-01-4	0.5	1	2	10	500
Xylenes (total)	1330-20-7	0.5	1	5	5	250
m/p-Xylenes	108-38-3	0.5	1	5	5	250
o-Xylenes	95-47-6	0.5	1	5	5	250

Note: The reporting limits for non-aqueous waste samples which are prepared by waste dilution are 10x of the high soil limits.

TABLE II. Reportable Analytes for Standard Tests and TCLP

Analytes	CAS Number	Standard List	TCLP
Acetone	67-64-1	X	
Acetonitrile	75-05-8	X	
Acrolein	107-02-8	X	
Acrylonitrile	107-13-1	X	
Benzene	71-43-2	X	X
Benzyl chloride	100-44-7	X	
Bromobenzene	108-86-1	X	
Bromochloromethane	74-97-5	X	
Bromodichloromethane	75-27-4	X	
Bromoform	75-25-2	X	
Bromomethane (Methyl bromide)	74-83-9	X	
2-Butanone (MEK)	78-93-9	X	X
n-Butylbenzene	104-51-8	X	
tert-Butylbenzene	98-06-06-	X	
sec-Butylbenzene	135-98-8	X	
Carbon disulfide	75-15-0	X	
Carbon tetrachloride	56-23-5	X	X
Chlorobenzene	108-90-7	X	X
2-Chloro-1,3-Butadiene (Chloroprene)	126-99-8	X	
Chloroethane	75-00-3	X	
2-Chloroethyl vinyl ether	110-75-8	X	
Chloroform	75-00-3	X	X
Chloromethane (Methyl chloride)	74-87-3	X	
3-Chloropropene (Allyl chloride)	107-05-1	X	
2-Chlorotoluene	95-49-8	X	
4-Chlorotoluene	106-43-4	X	
Cyclohexane	110-82-7	X	
Cyclohexanone	108-94-1	X	
Dibromochloromethane	124-48-1	X	
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8	X	
1,2-Dibromoethane (EDB)	106-93-4	X	
Dibromomethane (Methylene bromide)	74-95-3	X	
1,2-Dichlorobenzene	95-50-1	X	
1,3-Dichlorobenzene	541-73-1	X	
1,4-Dichlorobenzene	106-46-7	X	
trans-1,4-Dichloro-2-butene	110-57-6	X	
Dichlorodifluoromethane	75-71-8	X	
1,1-Dichloroethane	75-34-3	X	
1,2-Dichloroethane	107-06-2	X	X
cis-1,2-Dichloroethene	156-59-2	X	

TABLE II. Reportable Analytes for Standard Tests and TCLP (continued)

Analytes	CAS Number	Shealy Standard List	TCLP
trans-1,2-Dichloroethene	156-60-5	X	
1,1-Dichloroethene	75-35-4	X	X
1,3-Dichloropropane	142-28-9	X	
2,2-Dichloropropane	594-20-7	X	
1,1-Dichloropropene	563-58-6	X	
cis-1,3-Dichloropropene	10061-01-5	X	
trans-1,3-Dichloropropene	10061-02-6	X	
1,2-Dichloropropane	78-87-5	X	
Diisopropyl ether (IPE)	108-20-3	X	
3,3-dimethyl-1-butanol	624-95-3	X	
1,4-Dioxane	123-91-1	X	
Ethyl acetate	141-78-6	X	
Ethanol	64-17-5	X	
Ethyl ether	60-29-7	X	
Ethylbenzene	100-41-4	X	
Ethyl methacrylate	97-63-2	X	
Ethyl-tert-butyl ether	637-92-3	X	
Hexachlorobutadiene	87-68-3	X	
2-Hexanone	591-78-6	X	
Isopropylbenzene	98-82-8	X	
p-Isopropyltoluene	99-87-6	X	
Isobutyl alcohol	78-83-1	X	
Methacrylonitrile	126-98-7	X	
Methyl acetate	79-20-9	X	
Methylcyclohexane	108-87-2	X	
Methyl iodide (Iodomethane)	74-88-4	X	
Methyl methacrylate	80-62-6	X	
4-Methyl-2-Pentanone	108-10-1	X	
Methyl tertiary butyl ether (MTBE)	1634-04-4	X	
Methylene chloride	75-09-2	X	
Naphthalene	91-20-3	X	
n-Propylbenzene	103-65-1	X	
Propionitrile (Ethyl cyanide)	107-12-0	X	
Styrene	100-42-5	X	
Tert-amyl Alcohol	75-85-4	X	
Tert-amyl-methyl ether	994-05-8	X	
Tert-Butyl Alcohol	75-65-0	X	
Tert-Buytl Formate	762-75-4	X	
1,1,1,2-Tetrachloroethane	630-20-6	X	
1,1,2,2-Tetrachloroethane	79-34-5	X	
Analytes	**CAS Number**	**Shealy Standard List**	**TCLP**

Tetrachloroethene	127-18-4	X	X
Tetraethyl lead	78-00-2	X	
Tetrahydrofuran	109-99-9	X	
Toluene	108-88-3	X	
1,2,4-Trichlorobenzene	96-18-4	X	
1,2,3-Trichlorobenzene	95-63-6	X	
1,1,1-Trichloroethane	71-55-6	X	

1,1,2-Trichloroethane	79-00-5	X	
Trichloroethene	79-01-6	X	X
Trichlorofluoromethane	75-69-4	X	
1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	X	
1,2,3-Trichloropropane	96-18-4	X	
1,2,4-Trimethylbenzene	95-63-6	X	
1,3,5-Trimethylbenzene	108-67-8	X	
Vinyl acetate	108-05-4	X	
Vinyl Chloride	75-01-4	X	X
Xylenes (total)	1330-20-7	X	
m/p-Xylenes	108-38-3	X	
o-Xylenes	95-47-6	X	

TABLE III. Recommended Instrumental Conditions

Mass range	35-300 amu
Scan time	≤ 1 second/scan
Initial column temperature / Hold time	45°C for 3.50 minutes
Column temperature program	10 °C/min to 100°C, 25 °C/min to 225 °C
Final column temperature / Hold time	225 °C for 3 minutes
Injector temperature	220°C
MS interface transfer line temperature	225 °C
Source temperature	According to manufacturer's specifications
Carrier gas	Helium at 0.5-1ml/min, constant flow
Trap	OI #10
Purge gas	Helium at 40ml/min
Purge time	11 min
Sample heater	50 °C soils, ambient or heated for waters
Dry purge	0 min
Desorb preheat	180°C
Desorb	200°C for 1 min
Bake	210°C for 5-7 min
Transfer line/Valve temperature	110ºC-120ºC

TABLE IV. BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
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

TABLE V. Characteristic Ions

Analyte	Primary	Secondary	Tertiary
Acetone	58	43	
Acetonitrile	40	39	
Acrolein	56	55	
Acrylonitrile	53	52	
Benzene	78		
Benzyl chloride	91		
Bromobenzene	77	156	158
Bromochloromethane	128	49	130
Bromodichloromethane	83	85	
Bromoform	173	171	
Bromomethane (Methyl bromide)	94	96	
2-Butanone (MEK)	43	72	
n-Butylbenzene	91	134	
tert-Butylbenzene	119	134	
sec-Butylbenzene	105	134	
Carbon disulfide	76		
Carbon tetrachloride	117	119	
Chlorobenzene	112	114	
2-Chloro-1,3-Butadiene (Chloroprene)	53	88	51
Chloroethane	64		
2-Chloroethyl vinyl ether	63	65	
Chloroform	83	85	
Chloromethane (Methyl chloride)	50	52	
3-Chloropropene (Allyl chloride)	76	78	
2-Chlorotoluene	91	126	
4-Chlorotoluene	91	126	
Cyclohexane	56	69	84
Cyclohexanone	55	69	98
Dibromochloromethane	129	127	
1,2-Dibromo-3-chloropropane (DBCP)	75	157	155
1,2-Dibromoethane (EDB)	107	109	
Dibromomethane (Methylene bromide)	93	174	95
1,2-Dichlorobenzene	146	148	113
1,3-Dichlorobenzene	146	148	113
1,4-Dichlorobenzene	146	148	113
trans-1,4-Dichloro-2-butene	89	53	
Dichlorodifluoromethane	85		
1,1-Dichloroethane	63	65	
1,2-Dichloroethane	62	64	98
cis-1,2-Dichloroethene	96	61	
trans-1,2-Dichloroethene	96	61	98

TABLE V. Characteristic Ions (continued)

Analyte	Primary	Secondary	Tertiary
1,1-Dichloroethene	96	61	63
1,2-Dichloropropane	63	76	
1,3-Dichloropropane	76	78	
2,2-Dichloropropane	77	79	
1,1-Dichloropropene	75	110	77
cis-1,3-Dichloropropene	75	77	
trans-1,3-Dichloropropene	75	77	
1,2-Dichloropropane	63	76	
Diisopropyl ether (IPE)	87	59	
3,3-dimethyl-1-butanol	57	69	
1,4-Dioxane	88	58	
Ethyl acetate	61		
Ethanol	45	46	
Ethyl ether	59	45	74
Ethylbenzene	106	91	
Ethyl methacrylate	69	41	
Ethyl-tert-butyl ether	59	87	
Freon 113	101	103	151
Hexachlorobutadiene	225	223	227
2-Hexanone	43	58	
Isopropylbenzene	105	120	
p-Isopropyltoluene	119	134	
Isobutyl alcohol	43	41	
Methacrylonitrile	67	41	39
Methyl acetate	43	74	
Methylcyclohexane	83	55	98
Methyl iodide (Iodomethane)	142	127	
Methyl methacrylate	41	69	
4-Methyl-2-Pentanone	43	58	
Methyl tertiary butyl ether (MTBE)	73	57	
Methylene chloride	84	49	51
Naphthalene	128		
n-Propylbenzene	91	120	
Propionitrile (Ethyl cyanide)	54	52	55
Styrene	104	51	78
Tert-amyl Alcohol	59	73	
Tert-amyl-methyl ether	87	73	
Tert-Butyl Alcohol	59	57	
Tert-Buytl Formate	59	57	
1,1,1,2-Tetrachloroethane	131	133	
1,1,2,2-Tetrachloroethane	83	85	
Analyte	**Primary**	**Secondary**	**Tertiary**

Tetrachloroethene	164	129	131
Tetraethyl lead	237		
Tetrahydrofuran	42	72	
Toluene	92	91	
1,2,4-Trichlorobenzene	180	182	145
1,2,3-Trichlorobenzene	180	182	145
1,1,1-Trichloroethane	97	99	61

1,1,2-Trichloroethane	97	83	85
Trichloroethene	130	95	97
Trichlorofluoromethane	101	103	
1,1,2-Trichloro-1,2,2-Trifluoroethane	101	103	151
1,2,3-Trichloropropane	110	97	
1,2,4-Trimethylbenzene	105	120	
1,3,5-Trimethylbenzene	105	120	
Vinyl acetate	86	43	
Vinyl Chloride	62	64	
Xylenes (total)	Summation	Summation	
m/p-Xylenes	106	91	
o-Xylenes	106	91	

TABLE VI. Characteristic Ions for Internal Standards and Surrogate Standards

Analyte	Primary	Secondary	Tertiary
Pentafluorobenzene (Internal Standard)	168		
1,2-Dichloroethane-d4 (Surrogate Standard)	65	102	
1,4-Difluorobenzene (Internal Standard)	114		
Toluene-d8 (Surrogate Standard)	98		
Chlorobenzene-d5 (Internal Standard)	117	82	119
4-Bromofluorobenzene (Surrogate Standard)	95	174	176
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	

TABLE VII. 8260B LCS/MS/MSD Compounds

LCS Compounds	Spiking Level in Extract (µg/L)
Acetone	100
Acetonitrile	100
Acrolein	500
Acrylonitrile	500
Benzene	50
Benzyl chloride	50
Bromobenzene	50
Bromochloromethane	50
Bromodichloromethane	50
Bromoform	50
Bromomethane (Methyl bromide)	50
2-Butanone (MEK)	100
n-Butylbenzene	50
tert-Butylbenzene	50
sec-Butylbenzene	50
Carbon disulfide	50
Carbon tetrachloride	50
Chlorobenzene	50
2-Chloro-1,3-Butadiene (Chloroprene)	50
Chloroethane	50
2-Chloroethyl vinyl ether	50
Chloroform	50
Chloromethane (Methyl chloride)	50
3-Chloropropene (Allyl chloride)	50
2-Chlorotoluene	50
4-Chlorotoluene	50
Cyclohexane	50
Dibromochloromethane	50
1,2-Dibromo-3-chloropropane (DBCP)	50
1,2-Dibromoethane (EDB)	50
Dibromomethane (Methylene bromide)	50
1,2-Dichlorobenzene	50
1,3-Dichlorobenzene	50
1,4-Dichlorobenzene	50
trans-1,4-Dichloro-2-butene	50
Dichlorodifluoromethane	50
1,1-Dichloroethane	50
1,2-Dichloroethane	50

TABLE VII. 8260B LCS/MS/MSD Compounds (continued)

LCS Compounds	Spiking Level in Extract (µg/L)
cis-1,2-Dichloroethene	50
trans-1,2-Dichloroethene	50
1,1-Dichloroethene	50
1,3-Dichloropropane	50
2,2-Dichloropropane	50
1,1-Dichloropropene	50
cis-1,3-Dichloropropene	50
trans-1,3-Dichloropropene	50
1,2-Dichloropropane	50
Diisopropyl ether (IPE)	50
3,3-dimethyl-1-butanol	1000
1,4-Dioxane	500
Ethylbenzene	50
Ethanol	5000
Ethyl ether	50
Ethyl methacrylate	50
Ethyl-tert-butyl ether	5.0
Hexachlorobutadiene	50
2-Hexanone	100
Isopropylbenzene	50
p-Isopropyltoluene	50
Isobutyl alcohol	500
Methacrylonitrile	50
Methyl acetate	50
Methylcyclohexane	50
Methyl iodide (Iodomethane)	50
Methyl methacrylate	50
4-Methyl-2-Pentanone	100
Methyl tertiary butyl ether (MTBE)	50
Methylene chloride	50
Naphthalene	50
n-Propylbenzene	50
Propionitrile (Ethyl cyanide)	500
Styrene	50
Tert-amyl Alcohol	1000
Tert-amyl-methyl ether	50
Tert-Butyl Alcohol	1000
Tert-Buytl Formate	250
1,1,1,2-Tetrachloroethane	50
1,1,2,2-Tetrachloroethane	50
Tetrachloroethene	50
LCS Compounds	**Spiking Level in Extract** (µg/L)
Tetrahydrofuran	50

Toluene	50
1,2,4-Trichlorobenzene	50

1,2,3-Trichlorobenzene	50
1,1,1-Trichloroethane	50
1,1,2-Trichloroethane	50
Trichloroethene	50
Trichlorofluoromethane	50
1,2,3-Trichloropropane	50
1,2,4-Trimethylbenzene	50
1,3,5-Trimethylbenzene	50
Vinyl acetate	50
Vinyl Chloride	50
Xylenes (total)	100
m/p-Xylenes	50
o-Xylenes	50

TABLE VIII. TCLP LCS/MS/MSD Compounds

LCS Compounds	Spiking Level in Sample

	(µg/L)
Benzene	50
2-Butanone (MEK)	100
Carbon tetrachloride	50
Chlorobenzene	50
Chloroform	50
1,2-Dichloroethane	50
1,1-Dichloroethene	50
Tetrachloroethene	50
Trichloroethene	50
Vinyl chloride	50

Recovery limits for the LCS and for matrix spikes are generated from historical data. Refer to Attachments C and D for recovery limits.

TABLE IX. 8260C Surrogate Compounds

Surrogate Compounds	Spiking Level in extract (µg/L or µg/kg)
1,2-Dichloroethane-d4	50
Toluene-d8	50
4-Bromofluorobenzene	50

Recovery limits for the LCS and for matrix spikes are generated from historical data. Refer to LIMS for recovery limits.

TABLE X. Calibration Levels, Aqueous (µg/L) and Solid (µg/kg), Regular Level

Aqueous Analyte	Level 1	Level 2	Level 3	Level 4	Level 5

Acetone	10	40	100	200	800
Acetonitrile	10	40	100	200	800
Acrolein	5	20	50	100	400
Acrylonitrile	5	20	50	100	400
Benzene	5	20	50	100	400
Benzyl chloride	5	20	50	100	400
Bromobenzene	5	20	50	100	400
Bromochloromethane	5	20	50	100	400
Bromodichloromethane	5	20	50	100	400
Bromoform	5	20	50	100	400
Bromomethane (Methyl bromide)	5	20	50	100	400
2-Butanone (MEK)	10	40	100	200	800
n-Butylbenzene	5	20	50	100	400
tert-Butylbenzene	5	20	50	100	400
sec-Butylbenzene	5	20	50	100	400
Carbon disulfide	5	20	50	100	400
Carbon tetrachloride	5	20	50	100	400
Chlorobenzene	5	20	50	100	400
2-Chloro-1,3-Butadiene (Chloroprene)	5	20	50	100	400
Chloroethane	5	20	50	100	400
2-Chloroethyl vinyl ether	10	40	100	200	800
Chloroform	5	20	50	100	400
Chloromethane (Methyl chloride)	5	20	50	100	400
3-Chloropropene (Allyl chloride)	5	20	50	100	400
2-Chlorotoluene	5	20	50	100	400
4-Chlorotoluene	5	20	50	100	400
Cyclohexane	5	20	50	100	400
Dibromochloromethane	5	20	50	100	400
1,2-Dibromo-3-chloropropane (DBCP)	5	20	50	100	400
1,2-Dibromoethane (EDB)	5	20	50	100	400
Dibromomethane (Methylene bromide)	5	20	50	100	400
1,2-Dichlorobenzene	5	20	50	100	400
1,3-Dichlorobenzene	5	20	50	100	400
1,4-Dichlorobenzene	5	20	50	100	400
trans-1,4-Dichloro-2-butene	5	20	50	100	400
Dichlorodifluoromethane	5	20	50	100	400

TABLE X. Calibration Levels, Aqueous (µg/L) and Solid (µg/kg), Regular Level (cont)

Aqueous Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
1,1-Dichloroethane	5	20	50	100	400
1,2-Dichloroethane	5	20	50	100	400
cis-1,2-Dichloroethene	5	20	50	100	400
trans-1,2-Dichloroethene	5	20	50	100	400
1,1-Dichloroethene	5	20	50	100	400
1,3-Dichloropropane	5	20	50	100	400
2,2-Dichloropropane	5	20	50	100	400
1,1-Dichloropropene	5	20	50	100	400
cis-1,3-Dichloropropene	5	20	50	100	400
trans-1,3-Dichloropropene	5	20	50	100	400
1,2-Dichloropropane	5	20	50	100	400
Diisopropyl ether (IPE)	5	20	50	100	400
3,3-dimethyl-1-butanol	20	100	400	1000	2000
1,4-Dioxane	50	200	500	1000	4000
Ethanol	50	100	500	2000	10000
Ethylbenzene	5	20	50	100	400
Ethyl methacrylate	5	20	50	100	400
Ethyl-tert-butyl ether	5	20	50	100	400
Hexachlorobutadiene	5	20	50	100	400
2-Hexanone	10	40	100	200	800
Isopropylbenzene	5	20	50	100	400
p-Isopropyltoluene	5	20	50	100	400
Isobutyl alcohol	5	20	50	100	400
Methacrylonitrile	5	20	50	100	400
Methyl acetate	5	20	50	100	400
Methylcyclohexane	5	20	50	100	400
Methyl iodide (Iodomethane)	5	20	50	100	400
Methyl methacrylate	5	20	50	100	400
4-Methyl-2-Pentanone	10	40	100	200	800
Methyl tertiary butyl ether (MTBE)	5	20	50	100	400
Methylene chloride	5	20	50	100	400
Naphthalene	5	20	50	100	400
n-Propylbenzene	5	20	50	100	400
Propionitrile (Ethyl cyanide)	5	20	50	100	400
Styrene	5	20	50	100	400
Tert-amyl Alcohol	20	100	400	1000	2000
Tert-amyl-methyl ether	5	20	50	100	400
Tert-Butyl Alcohol	20	100	400	1000	2000
Tert-Buytl Formate	5	25	100	400	1000
1,1,1,2-Tetrachloroethane	5	20	50	100	400
Aqueous Analyte	**Level 1**	**Level 2**	**Level 3**	**Level 4**	**Level 5**

1,1,2,2-Tetrachloroethane	5	20	50	100	400
Tetrachloroethene	5	20	50	100	400
Toluene	5	20	50	100	400
1,2,4-Trichlorobenzene	5	20	50	100	400
1,2,3-Trichlorobenzene	5	20	50	100	400
1,1,1-Trichloroethane	5	20	50	100	400

1,1,2-Trichloroethane	5	20	50	100	400
Trichloroethene	5	20	50	100	400
Trichlorofluoromethane	5	20	50	100	400
1,2,3-Trichloropropane	5	20	50	100	400
1,2,4-Trimethylbenzene	5	20	50	100	400
1,3,5-Trimethylbenzene	5	20	50	100	400
Vinyl acetate	5	20	50	100	400
Vinyl Chloride	5	20	50	100	400
Xylenes (total)	20	80	200	400	1600
m/p-Xylenes	10	40	100	200	800
o-Xylenes	10	40	100	200	800

TABLE XI. Low Level Calibration Levels, Aqueous (µg/L)

Low Level Aqueous Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Acetone	1	2	10	40	100	200	800
Acetonitrile	5	10	50	200	500	1000	4000
Acrolein	5	10	50	200	500	1000	4000
Acrylonitrile	1	2	10	40	100	200	800
Benzene	0.5	1	5	20	50	100	400
Benzyl chloride	0.5	1	5	20	50	100	400
Bromobenzene	0.5	1	5	20	50	100	400
Bromochloromethane	0.5	1	5	20	50	100	400
Bromodichloromethane	0.5	1	5	20	50	100	400
Bromoform	0.5	1	5	20	50	100	400
Bromomethane (Methyl bromide)	0.5	1	5	20	50	100	400
2-Butanone (MEK)	1	2	10	40	100	200	800
n-Butylbenzene	0.5	1	5	20	50	100	400
tert-Butylbenzene	0.5	1	5	20	50	100	400
sec-Butylbenzene	0.5	1	5	20	50	100	400
Carbon disulfide	0.5	1	5	20	50	100	400
Carbon tetrachloride	0.5	1	5	20	50	100	400
Chlorobenzene	0.5	1	5	20	50	100	400
2-Chloro-1,3-Butadiene (Chloroprene)	0.5	1	5	20	50	100	400
Chloroethane	0.5	1	5	20	50	100	400
2-Chloroethyl vinyl ether	0.5	1	5	20	50	100	400
Chloroform	0.5	1	5	20	50	100	400
Chloromethane (Methyl chloride)	0.5	1	5	20	50	100	400
3-Chloropropene (Allyl chloride)	0.5	1	5	20	50	100	400
2-Chlorotoluene	0.5	1	5	20	50	100	400
4-Chlorotoluene	0.5	1	5	20	50	100	400
Cyclohexane	0.5	1	5	20	50	100	400
Dibromochloromethane	0.5	1	5	20	50	100	400
1,2-Dibromo-3-chloropropane (DBCP)	0.5	1	5	20	50	100	400
1,2-Dibromoethane (EDB)	0.5	1	5	20	50	100	400
Dibromomethane (Methylene bromide)	0.5	1	5	20	50	100	400
1,2-Dichlorobenzene	0.5	1	5	20	50	100	400
1,3-Dichlorobenzene	0.5	1	5	20	50	100	400
1,4-Dichlorobenzene	0.5	1	5	20	50	100	400

TABLE XI. Low Level Calibration Levels, Aqueous (µg/L) (continued)

Low Level Aqueous Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
trans-1,4-Dichloro-2-butene	0.5	1	5	20	50	100	400
Dichlorodifluoromethane	0.5	1	5	20	50	100	400
1,1-Dichloroethane	0.5	1	5	20	50	100	400
1,2-Dichloroethane	0.5	1	5	20	50	100	400
cis-1,2-Dichloroethene	0.5	1	5	20	50	100	400
trans-1,2-Dichloroethene	0.5	1	5	20	50	100	400
1,1-Dichloroethene	0.5	1	5	20	50	100	400
1,3-Dichloropropane	0.5	1	5	20	50	100	400
2,2-Dichloropropane	0.5	1	5	20	50	100	400
1,1-Dichloropropene	0.5	1	5	20	50	100	400
cis-1,3-Dichloropropene	0.5	1	5	20	50	100	400
trans-1,3-Dichloropropene	0.5	1	5	20	50	100	400
1,2-Dichloropropane	0.5	1	5	20	50	100	400
Diisopropyl ether (IPE)	0.5	1	5	20	50	100	400
3,3-dimethyl-1-butanol	10	20	100	400	1000	2000	8000
1,4-Dioxane	5	10	50	200	500	1000	4000
Ethanol	50	100	500	2000	5000	10000	40000
Ethylbenzene	0.5	1	5	20	50	100	400
Ethyl methacrylate	0.5	1	5	20	50	100	400
Ethyl-tert-butyl ether	0.5	1	5	20	50	100	400
Hexachlorobutadiene	0.5	1	5	20	50	100	400
2-Hexanone	1	2	10	40	100	200	800
Isopropylbenzene	0.5	1	5	20	50	100	400
p-Isopropyltoluene	0.5	1	5	20	50	100	400
Isobutyl alcohol	5	10	50	200	500	1000	4000
Methacrylonitrile	0.5	1	5	20	50	100	400
Methyl acetate	0.5	1	5	20	50	100	400
Methylcyclohexane	0.5	1	5	20	50	100	400
Methyl iodide (Iodomethane)	0.5	1	5	20	50	100	400
Methyl methacrylate	0.5	1	5	20	50	100	400
4-Methyl-2-Pentanone	1	2	10	40	100	200	800
Methyl tertiary butyl ether (MTBE)	0.5	1	5	20	50	100	400
Methylene chloride	0.5	1	5	20	50	100	400
Naphthalene	0.5	1	5	20	50	100	400
n-Propylbenzene	0.5	1	5	20	50	100	400
Propionitrile (Ethyl cyanide)	5	10	50	200	500	1000	4000
Styrene	0.5	1	5	20	50	100	400
Tert-amyl Alcohol	10	20	100	400	1000	2000	8000
Tert-amyl-methyl ether	0.5	1	5	20	50	100	400
Tert-Butyl Alcohol	10	20	100	400	1000	2000	8000
Low Level Aqueous Analyte	**Level 1**	**Level 2**	**Level 3**	**Level 4**	**Level 5**	**Level 6**	**Level 7**

Tert-Buytl Formate	2.5	5.0	25	100	250	500	2000
1,1,1,2-Tetrachloroethane	0.5	1	5	20	50	100	400
1,1,2,2-Tetrachloroethane	0.5	1	5	20	50	100	400
Tetrachloroethene	0.5	1	5	20	50	100	400

Toluene	0.5	1	5	20	50	100	400
1,2,4-Trichlorobenzene	0.5	1	5	20	50	100	400
1,2,3-Trichlorobenzene	0.5	1	5	20	50	100	400
1,1,1-Trichloroethane	0.5	1	5	20	50	100	400
1,1,2-Trichloroethane	0.5	1	5	20	50	100	400
Trichloroethene	0.5	1	5	20	50	100	400
Trichlorofluoromethane	0.5	1	5	20	50	100	400
1,2,3-Trichloropropane	0.5	1	5	20	50	100	400
1,2,4-Trimethylbenzene	0.5	1	5	20	50	100	400
1,3,5-Trimethylbenzene	0.5	1	5	20	50	100	400
Vinyl acetate	0.5	1	5	20	50	100	400
Vinyl Chloride	0.5	1	5	20	50	100	400
Xylenes (total)	1	2	10	40	100	200	800
m/p-Xylenes	0.5	1	5	20	50	100	400
o-Xylenes	0.5	1	5	20	50	100	400

TABLE XII. ICV Acceptance Criteria for Shealy Primary Standard

Analyte	%Difference or %Drift
Acetone	± 25
Acetonitrile	± 25
Acrolein	± 25
Acrylonitrile	± 25
Benzene	± 25
Benzyl chloride	± 25
Bromobenzene	± 25
Bromochloromethane	± 25
Bromodichloromethane	± 25
Bromoform	± 25
Bromomethane (Methyl bromide)	± 25
2-Butanone (MEK)	± 25
n-Butylbenzene	± 25
tert-Butylbenzene	± 25
sec-Butylbenzene	± 25
Carbon disulfide	± 25
Carbon tetrachloride	± 25
Chlorobenzene	± 25
2-Chloro-1,3-Butadiene (Chloroprene)	± 25
Chloroethane	± 25
2-Chloroethyl vinyl ether	± 25
Chloroform	± 25
Chloromethane (Methyl chloride)	± 25
3-Chloropropene (Allyl chloride)	± 25
2-Chlorotoluene	± 25
4-Chlorotoluene	± 25
Cyclohexane	± 25
Dibromochloromethane	± 25
1,2-Dibromo-3-chloropropane (DBCP)	± 25
1,2-Dibromoethane (EDB)	± 25
Dibromomethane (Methylene bromide)	± 25
1,2-Dichlorobenzene	± 25
1,3-Dichlorobenzene	± 25
1,4-Dichlorobenzene	± 25
trans-1,4-Dichloro-2-butene	± 25
Dichlorodifluoromethane	± 25
1,1-Dichloroethane	± 25
1,2-Dichloroethane	± 25

TABLE XII. ICV Acceptance Criteria for Shealy Primary Standard (continued)

Analyte	%Difference or %Drift
cis-1,2-Dichloroethene	± 25
trans-1,2-Dichloroethene	± 25
1,1-Dichloroethene	± 25
1,3-Dichloropropane	± 25
2,2-Dichloropropane	± 25
1,1-Dichloropropene	± 25
cis-1,3-Dichloropropene	± 25
trans-1,3-Dichloropropene	± 25
1,2-Dichloropropane	± 25
Diisopropyl ether (IPE)	± 25
3,3-dimethyl-1-butanol	± 25
1,4-Dioxane	± 25
Ethanol	± 25
Ethylbenzene	± 25
Ethyl methacrylate	± 25
Ethyl-tert-butyl ether	± 25
Hexachlorobutadiene	± 25
2-Hexanone	± 25
Isopropylbenzene	± 25
p-Isopropyltoluene	± 25
Isobutyl alcohol	± 25
Methacrylonitrile	± 25
Methyl acetate	± 25
Methylcyclohexane	± 25
Methyl iodide (Iodomethane)	± 25
Methyl methacrylate	± 25
4-Methyl-2-Pentanone	± 25
Methyl tertiary butyl ether (MTBE)	± 25
Methylene chloride	± 25
Naphthalene	± 25
n-Propylbenzene	± 25
Propionitrile (Ethyl cyanide)	± 25
Styrene	± 25
Tert-amyl Alcohol	± 25
Tert-amyl-methyl ether	± 25
Tert-Butyl Alcohol	± 25
Tert-Butyl Formate	± 25
1,1,1,2-Tetrachloroethane	± 25
1,1,2,2-Tetrachloroethane	± 25
Tetrachloroethene	± 25
Analyte	%Difference or %Drift

Toluene	± 25
1,2,4-Trichlorobenzene	± 25
1,2,3-Trichlorobenzene	± 25
1,1,1-Trichloroethane	± 25
1,1,2-Trichloroethane	± 25
Trichloroethene	± 25
Trichlorofluoromethane	± 25

1,2,3-Trichloropropane	± 25
1,2,4-Trimethylbenzene	± 25
1,3,5-Trimethylbenzene	± 25
Vinyl acetate	± 25
Vinyl Chloride	± 25
Xylenes (total)	± 25
m/p-Xylenes	± 25
o-Xylenes	± 25

Table XIII. CCV Acceptance Criteria for Shealy Primary Standard

Analyte	%Difference or %Drift
Acetone	40
Acetonitrile	30
Acrolein	40
Acrylonitrile	40
Benzene	20
Benzyl chloride	30
Bromobenzene	30
Bromochloromethane	30
Bromodichloromethane	30
Bromoform	30
Bromomethane (Methyl bromide)	30
2-Butanone (MEK)	30
n-Butylbenzene	30
tert-Butylbenzene	30
sec-Butylbenzene	30
Carbon disulfide	30
Carbon tetrachloride	30
Chlorobenzene	20
2-Chloro-1,3-Butadiene (Chloroprene)	30
Chloroethane	30
2-Chloroethyl vinyl ether	30
Chloroform	20
Chloromethane (Methyl chloride)	30
3-Chloropropene (Allyl chloride)	30
2-Chlorotoluene	30
4-Chlorotoluene	30
Cyclohexane	30
Cyclohexanone	40
Dibromochloromethane	30
1,2-Dibromo-3-chloropropane (DBCP)	30
1,2-Dibromoethane (EDB)	30
Dibromomethane (Methylene bromide)	30
1,2-Dichlorobenzene	30
1,3-Dichlorobenzene	30
1,4-Dichlorobenzene	30
trans-1,4-Dichloro-2-butene	30
Dichlorodifluoromethane	40
1,1-Dichloroethane	20
1,2-Dichloroethane	20
cis-1,2-Dichloroethene	20
trans-1,2-Dichloroethene	20

Analyte	%Difference or %Drift
1,1-Dichloroethene	20
1,3-Dichloropropane	30
2,2-Dichloropropane	40
1,1-Dichloropropene	30
cis-1,3-Dichloropropene	30
trans-1,3-Dichloropropene	30
1,2-Dichloropropane	20
Diisopropyl ether (IPE)	30
3,3-dimethyl-1-butanol	30
1,4-Dioxane	40
Ethanol	40
Ethylbenzene	20
Ethyl methacrylate	30
Ethyl-tert-butyl ether	30
Hexachlorobutadiene	30
2-Hexanone	40
Isopropylbenzene	30
p-Isopropyltoluene	30
Isobutyl alcohol	30
Methacrylonitrile	30
Methyl acetate	30
Methylcyclohexane	30
Methyl iodide (Iodomethane)	30
Methyl methacrylate	30
4-Methyl-2-Pentanone	40
Methyl tertiary butyl ether (MTBE)	30
Methylene chloride	30
Naphthalene	40
n-Propylbenzene	30
Propionitrile (Ethyl cyanide)	30
Styrene	30
Tert-amyl Alcohol	40
Tert-amyl-methyl ether	40
Tert-Butyl Alcohol	40
Tert-Buytl Formate	40
1,1,1,2-Tetrachloroethane	30
1,1,2,2-Tetrachloroethane	30
Tetrachloroethene	30
Toluene	20
1,2,4-Trichlorobenzene	30
1,2,3-Trichlorobenzene	30
1,1,1-Trichloroethane	20
Analyte	**%Difference or %Drift**
1,1,2-Trichloroethane	20

Trichloroethene	20
Trichlorofluoromethane	30
1,2,3-Trichloropropane	30
1,2,4-Trimethylbenzene	30

1,3,5-Trimethylbenzene	30
Vinyl acetate	30
Vinyl Chloride	20
Xylenes (total)	30
m/p-Xylenes	30
o-Xylenes	30

ATTACHMENTS

MODIFICATIONS REQUIRED FOR ANALYSIS OF WASTEWATER FOLLOWING METHOD 624

ATTATCHMENT A: REQUIREMENTS FOR METHOD 624

1. Method 624 is required for demonstration of compliance with NPDES wastewater discharge permits. The standard analyte list and reporting limits are listed in Table A-1.

2. This method can be applied only to aqueous matrices. If 2-chloroethyl vinyl ether is an analyte of interest the sample should be collected in unpreserved 40 ml VOC vials and analyzed within 7 days of collection.

3. The tune period for this method is defined as 12 hours. The tuning criteria is the same as for method 8260B(Table-VI).

4. Initial calibration curve requirements:

   4.1 The initial calibration curve for this method requires at least three levels.

   4.2 Target® compounds must have RSD ≤ 35%.

   4.3 If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds.

5. Continuing calibration verification (CCV)

   5.1 A continuing calibration verification standard at 20µg/L should be analyzed at the start of every 20 samples. The acceptance criteria for CCV is listed in table A-2.

   5.2 If the responses for all parameters of interests fall within the designated ranges, analysis of actual samples can begin. If any individual response falls outside the range, repeat the test only for those parameters that failed to meet the calibration acceptance criteria. If the response for a parameter does not fall within the range in this second test, a new calibration curve or RF must be prepared for that parameter.

   5.3 The analyst may chose to proceed with the analysis of sample and report only those parameters that meet the acceptance criteria.

6. Matrix Spike and LCS requirements: A full analyte spike is required for method 624. The spiking levels are given in Table A-3. For every batch, one LCS and one MS are required. Each compound of interest must have an acceptable recovery in either the LCS or MS.

   Acceptance criteria are listed in Table A-2.

7. Qualitative identification

   7.1 The retention time must fall within ±30 seconds of the retention time of the authentic compound.

7.2 The relative intensities of ions should agree to within ± 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30% and 70%.)

TABLE A-1. Shealy Method 624 Standard Reporting List and Reporting Limits

Analytes	CAS Number	Aqueous (µg/L)
Acetone	67-64-1	20
Benzene	71-43-2	5
Bromodichloromethane	75-27-4	5
Bromoform	75-25-2	5
Bromomethane (Methyl bromide)	74-83-9	5
Carbon tetrachloride	56-23-5	5
Chlorobenzene	108-90-7	5
Chloroethane	75-00-3	5
2-Chloroethyl vinyl ether	110-75-8	10
Chloroform	67-66-3	5
Chloromethane (Methyl chloride)	74-87-3	5
Cis-1,2-Dichloroethene	156-59-2	5
Cis-1,3-Dichloropropene	10061-01-5	5
Dibromochloromethane	124-48-1	5
1,2-Dichlorobenzene	95-50-1	5
1,3-Dichlorobenzene	541-73-1	5
1,4-Dichlorobenzene	106-46-7	5
1,1-Dichloroethane	75-34-3	5
1,2-Dichloroethane	107-06-2	5
1,1-Dichloroethene	75-35-4	5
1,2-Dichloropropane	78-87-5	5
1,4-Dioxane	123-91-1	250
Ethylbenzene	100-41-4	5
Methylene chloride	75-09-2	5
1,1,2,2-Tetrachloroethane	79-34-5	5
Tetrachloroethene	127-18-4	5
Toluene	108-88-3	5
trans-1,2-Dichloroethene	156-60-5	5
Trans-1,3-Dichloropropene	10061-02-6	5
1,1,1-Trichloroethane	71-55-6	5
1,1,2-Trichloroethane	79-00-5	5
Trichloroethene	79-01-6	5
Trichlorofluoromethane	75-69-4	5
1,2,4-Trimethylbenzene	95-63-6	5
Vinyl Chloride	75-01-4	2
Xylenes (total)	1330-20-7	5

Table A-2. Method 624 Calibration and QC Acceptance Criteria [1]

Analytes	Standard Conc (µg/L)	%Recovery Range for Ccal [2]	Limit [3] for s (µg/L)	Range [4] For $\bar{X}$ (µg/L)	%Recovery Range for LCS and MS
Benzene	20	60.4-136.0	6.9	15.2-26.0	37-151
Bromodichloromethane	20	65.5-134.5	6.4	10.1-28.0	35-155
Bromoform	20	71.0-129.0	5.4	11.4-31.1	45-169
Bromomethane (Methyl bromide)	20	14.0-186.0	17.9	D-41.2	D-242
Carbon tetrachloride	20	73.0-127.0	5.2	17.2-23.5	70-140
Chlorobenzene	20	66.0-134.0	6.3	16.4-27.4	37-160
Chloroethane	20	38.0-162.0	11.4	8.4-40.4	14-230
2-Chloroethyl vinyl ether	40	D [1]-224.0	25.9	D-101.0 [5]	D-305
Chloroform	20	67.5-132.5	6.1	13.7-24.2	51-138
Chloromethane (Methyl chloride)	20	D-204.0	19.8	D-45.9	D-273
Cis-1,2-Dichloroethene	20	N/A	N/A	N/A	N/A
Cis-1,3-Dichloropropene	20	24.0-176.0	15.8	1.0-39.0	D-227
Dibromochloromethane	20	67.5-132.5	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	20	63.0-137.0	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	20	73.0-127.0	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	20	63.0-137.0	7.1	11.8-34.7	18-190
1,1-Dichloroethane	20	72.5-127.5	5.1	14.2-28.5	59-155
1,2-Dichloroethane	20	68.0-132.0	6.0	14.3-27.4	49-155
1,1-Dichloroethene	20	50.5-149.5	9.1	3.7-42.3	D-234
1,2-Dichloropropane	20	34.0-166.0	13.8	3.8-36.2	D-210
1,4-Dioxane	1000	N/A	N/A	N/A	N/A
Ethylbenzene	20	59.0-141.0	7.5	17.4-26.7	37-162
Methylene chloride	20	60.5-139.5	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	20	60.5-139.5	7.4	13.5-27.2	46-157
Tetrachloroethene	20	73.5-126.5	5.0	17.0-26.6	64-148
Toluene	20	74.5-125.5	4.8	16.6-26.7	47-150
trans-1,2-Dichloroethene	20	69.5-130.5	5.7	13.6-28.5	54-156
Trans-1,3-Dichloropropene	20	24.0-176.0	10.4	7.6-32.4	17-183
1,1,1-Trichloroethane	20	75.0-125.0	4.6	13.7-30.1	52-162
1,1,2-Trichloroethane	20	71.0-129.0	5.5	14.3-27.1	52-150
Trichloroethene	20	66.5-133.5	6.6	18.6-27.6	71-157
Trichlorofluoromethane	20	48.0-152.0	10.0	8.9-31.5	17-181
1,2,4-Trimethylbenzene	20	N/A	N/A	N/A	N/A
Vinyl Chloride	20	4.0-196	20.0	D-43.5	D-251
Xylenes	40	N/A	N/A	N/A	N/A

1. Based on Table 5 of EPA Method 624. D = Detected; result must be greater than zero.

For compounds without acceptance criteria, the criteria for method 8260B should followed.

2. Converted to %recovery from Range for Q in Table 5 of Method 624 by dividing the upper and lower concentration limits with standard concentration, 20µg/L.
3. Standard deviation of four recovery measurements.
4. Average recovery of four recovery measurements.
5. The concentration of 2-Chloroethyl vinyl ether in the Shealy mix is 40µg/L. The upper limit is increased proportionally.

TABLE A-3. Method 624 LCS and MS Compounds and Spike Concentrations

LCS Compounds	Spiking Level in Extract (µg/L)
Benzene	20
Bromodichloromethane	20
Bromoform	20
Bromomethane (Methyl bromide)	20
Carbon tetrachloride	20
Chlorobenzene	20
Chloroethane	40
2-Chloroethyl vinyl ether	20
Chloroform	20
Chloromethane (Methyl chloride)	20
Cis-1,3-Dichloropropene	20
Dibromochloromethane	20
1,2-Dichlorobenzene	20
1,3-Dichlorobenzene	20
1,4-Dichlorobenzene	20
1,1-Dichloroethane	20
1,2-Dichloroethane	20
1,1-Dichloroethene	20
1,2-Dichloropropane	20
Ethylbenzene	20
Methylene chloride	20
1,1,2,2-Tetrachloroethane	20
Tetrachloroethene	20
Toluene	20
trans-1,2-Dichloroethene	20
Trans-1,3-Dichloropropene	20
1,1,1-Trichloroethane	20
1,1,2-Trichloroethane	20
Trichloroethene	20
Trichlorofluoromethane	20
Vinyl Chloride	20

ATTACHMENT B: BATCH QC REQUIREMENT SUMMARY

B-1. This attachment is added to clarify batch QC requirements.

B-2. General Principle

If two different types of analyses, i.e. 624 and 8260B; soil preserved in sodium bisulfate and soil in reagent water, are combined in the same analytical sequence, separate QC checks must be performed for each type, which include CCV, MB, LCS, MS and MSD.

B-3. Method 624 QC Requirements

1. 12-hour tune window.
2. Up to 20 samples in a batch.
3. CCV at 20 µg/L, meets criteria for Target® compounds (Table A-2).
4. Method blank.
5. Full list LCS (Table A-3) at 20 µg/L, including gaseous compounds, meets the recovery criteria for Target® compounds.(Table A-2)
6. If 8260B analyses are performed in the same sequence, one CCV, one method blank and one LCS can be analyzed and evaluated for both methods for up to 20 samples. The CCV should be prepared at 20 µg/L.
7. One MS per batch at 20 µg/L. (separate MS/MSD for 8260B)
8. Surrogate acceptance limits are 70-130%.

B-4. 5035/8260B High Level Sample

I. Preparation Procedure

1. If samples are not field preserved with methanol, approximately 5 grams of soil should be preserved with 5.0 mls of methanol within 48 hours of sample collection.
2. Add 5 uls of 2500 ug/ml surrogate standards.
3. Shake manually or vortex for approximately 2 minutes.
4. Allow the solvent and solid to separate.
5. Add 1.0 ml (or lesser amount if dilution is required) of the extract into a 50 ml volumetric flask containing approximately 40 mls of reagent water. Fill to the mark and slowly invert 3 times.
6. Add internal standard.
7. Transfer to 40 ml VOC vial preserved with HCl.
8. The sample is ready for analysis.

II. QC Requirements and Preparation:

1. An extraction batch is created for up to 20 samples when surrogate addition is complete.
2. A batch should contain a method blank (MB)
3. The MB contains 5.0 mls of methanol.

4. Add 5.0 uls of 2500 ug/ml surrogate standards to the MB
5. Follow step 3 through 8 in the preceding section to prepare sample for analysis.
6. Samples can be added to the extraction batch within 24 hours of the initiation of the batch.

III. Corrective Actions

1. Analyst should establish surrogate recovery acceptance criteria for high level soil samples with at least 20 data points. The criteria is updated annually. The range is $\overline{X} \pm 3 * s$, in which $\overline{X}$ is the average recovery of all data points, s is the standard deviation of all data points.
2. If the extraction blank and sample fail to meet the surrogate recovery acceptance criteria, they should be reanalyzed.

B-5. Non-aqueous VOC Sample (soluble in methanol)

I. Prep Procedure

1. If sample's solubility in methanol is low, refer to the procedure for 5035B High Level Sample Prep Procedure. (section B-3)
2. Weigh approximately 1.0 gram of the sample into a 40-ml vial, add methanol to bring the final volume to 10 ml.
3. Mix the sample thoroughly by inverting the vial at least 3 times.
4. Add 1.0 ml (or lesser amount if dilution is required) of the waste dilution into a 50 ml volumetric flask containing approximately 40 mls of reagent water. Fill to the mark and slowly invert 3 times.
5. Add surrogate and internal standard.
6. Transfer to 40 ml VOC vial preserved with HCl.
7. The sample is ready for analysis.

II. QC Requirement

1. A batch contains up to 20 samples.
2. A method blank with 10 mls of methanol should be prepared.
3. Sample can be added to the batch within 24 hours of the initiation of the batch.

B-6. TCLP VOC

I. QC Requirement

1. A leachate blank is analyzed with each leaching batch.
2. A matrix spike containing all the TCLP compounds (Table X) is analyzed for each leaching batch.
3. A reagent water LCS containing all the TCLP compounds (Table X) is analyzed for each analytical batch in addition to the regular batch LCS for 8260B or 624.

ATTACHMENT C: AQUEOUS LCS RECOVERY LIMITS

Aqueous LCS/D Analyte	Lower % Recovery Limit	Upper % Recovery Limit
Acetone	70	130
Acetonitrile	*60	*140
Acrolein	*60	*140
Acrylonitrile	70	130
Benzene	70	130
Benzyl chloride	*60	*140
Bromobenzene	70	130
Bromochloromethane	70	130
Bromodichloromethane	70	130
Bromoform	70	130
Bromomethane (Methyl bromide)	70	130
2-Butanone (MEK)	70	130
n-Butylbenzene	70	130
tert-Butylbenzene	70	130
sec-Butylbenzene	70	130
Carbon disulfide	70	130
Carbon tetrachloride	70	130
Chlorobenzene	70	130
2-Chloro-1,3-Butadiene (Chloroprene)	70	130
Chloroethane	70	130
2-Chloroethyl vinyl ether	70	130
Chloroform	70	130
Chloromethane (Methyl chloride)	*60	*140
3-Chloropropene (Allyl chloride)	70	130
2-Chlorotoluene	70	130
4-Chlorotoluene	70	130
Cyclohexane	70	130
Dibromochloromethane	70	130
1,2-Dibromo-3-chloropropane (DBCP)	70	130
1,2-Dibromoethane (EDB)	70	130
Dibromomethane (Methylene bromide)	70	130
1,2-Dichlorobenzene	70	130
1,3-Dichlorobenzene	70	130
1,4-Dichlorobenzene	70	130
trans-1,4-Dichloro-2-butene	70	130
Dichlorodifluoromethane	*60	*140
1,1-Dichloroethane	70	130
1,2-Dichloroethane	70	130
cis-1,2-Dichloroethene	70	130
trans-1,2-Dichloroethene	70	130
1,1-Dichloroethene	70	130

ATTACHMENT C: AQUEOUS LCS RECOVERY LIMITS (continued)

Aqueous LCS/D Analyte	Lower % Recovery Limit	Upper % Recovery Limit
1,3-Dichloropropane	70	130
2,2-Dichloropropane	70	130
1,1-Dichloropropene	70	130
cis-1,3-Dichloropropene	70	130
trans-1,3-Dichloropropene	70	130
1,2-Dichloropropane	70	130
Diisopropyl ether (IPE)	70	130
1,4-Dioxane	*60	*140
Ethylbenzene	70	130
Ethyl methacrylate	70	130
Hexachlorobutadiene	*60	*140
2-Hexanone	70	130
Isopropylbenzene	70	130
p-Isopropyltoluene	70	130
Isobutyl alcohol	*60	*140
Methacrylonitrile	70	130
Methyl acetate	70	130
Methylcyclohexane	70	130
Methyl iodide (Iodomethane)	70	130
Methyl methacrylate	70	130
4-Methyl-2-Pentanone	70	130
Methyl tertiary butyl ether (MTBE)	70	130
Methylene chloride	70	130
Naphthalene	70	130
n-Propylbenzene	70	130
Propionitrile (Ethyl cyanide)	70	130
Styrene	70	130
1,1,1,2-Tetrachloroethane	70	130
1,1,2,2-Tetrachloroethane	70	130
Tetrachloroethene	70	130
Toluene	70	130
1,2,4-Trichlorobenzene	70	130
1,2,3-Trichlorobenzene	70	130
1,1,1-Trichloroethane	70	130
1,1,2-Trichloroethane	70	130
Trichloroethene	70	130
Trichlorofluoromethane	70	130
1,2,3-Trichloropropane	70	130
1,2,4-Trimethylbenzene	70	130
1,3,5-Trimethylbenzene	70	130
Vinyl acetate	*60	*140

ATTACHMENT C: AQUEOUS LCS RECOVERY LIMITS (continued)

Aqueous LCS/D Analyte	Lower % Recovery Limit	Upper % Recovery Limit
Vinyl Chloride	70	130
Xylenes (total)	70	130
m/p-Xylenes	70	130
o-Xylenes	70	130

ATTACHMENT D: SOLID LCS RECOVERY LIMITS

Solid LCS/D Analyte	Lower % Recovery Limit	Upper % Recovery Limit
Acetone	70	130
Acetonitrile	*60	*140
Acrolein	*60	*140
Acrylonitrile	*60	*140
Benzene	70	130
Benzyl chloride	70	130
Bromobenzene	70	130
Bromochloromethane	70	130
Bromodichloromethane	70	130
Bromoform	70	130
Bromomethane (Methyl bromide)	70	130
2-Butanone (MEK)	70	130
n-Butylbenzene	70	130
tert-Butylbenzene	70	130
sec-Butylbenzene	70	130
Carbon disulfide	70	130
Carbon tetrachloride	70	130
Chlorobenzene	70	130
2-Chloro-1,3-Butadiene (Chloroprene)	70	130
Chloroethane	70	130
Chloroform	70	130
Chloromethane (Methyl chloride)	*60	*140
3-Chloropropene (Allyl chloride)	*60	*140
2-Chlorotoluene	70	130
4-Chlorotoluene	70	130
Dibromochloromethane	70	130
1,2-Dibromo-3-chloropropane (DBCP)	70	130
1,2-Dibromoethane (EDB)	70	130
Dibromomethane (Methylene bromide)	70	130
1,2-Dichlorobenzene	70	130
1,3-Dichlorobenzene	70	130
1,4-Dichlorobenzene	70	130
trans-1,4-Dichloro-2-butene	70	130
Dichlorodifluoromethane	*60	*140
1,1-Dichloroethane	70	130
1,2-Dichloroethane	70	130
cis-1,2-Dichloroethene	70	130
trans-1,2-Dichloroethene	70	130
1,1-Dichloroethene	70	130
1,3-Dichloropropane	70	130
2,2-Dichloropropane	70	130

ATTACHMENT D: SOLID LCS RECOVERY LIMITS(continued)

Solid LCS/D Analyte	Lower % Recovery Limit	Upper % Recovery Limit
1,1-Dichloropropene	70	130
cis-1,3-Dichloropropene	70	130
trans-1,3-Dichloropropene	70	130
1,2-Dichloropropane	70	130
Diisopropyl ether (IPE)	70	130
1,4-Dioxane	*60	*140
Ethyl ether	70	130
Ethylbenzene	70	130
Ethyl methacrylate	70	130
Hexachlorobutadiene	70	130
2-Hexanone	70	130
Isopropylbenzene	70	130
p-Isopropyltoluene	70	130
Isobutyl alcohol	*60	*140
Methacrylonitrile	70	130
Methyl iodide (Iodomethane)	70	130
Methyl methacrylate	70	130
4-Methyl-2-Pentanone	70	130
Methyl tertiary butyl ether (MTBE)	70	130
Methylene chloride	70	130
Naphthalene	70	130
n-Propylbenzene	70	130
Propionitrile (Ethyl cyanide)	70	130
Styrene	70	130
1,1,1,2-Tetrachloroethane	70	130
1,1,2,2-Tetrachloroethane	70	130
Tetrachloroethene	70	130
Toluene	70	130
1,2,4-Trichlorobenzene	70	130
1,2,3-Trichlorobenzene	70	130
1,1,1-Trichloroethane	70	130
1,1,2-Trichloroethane	70	130
Trichloroethene	70	130
Trichlorofluoromethane	70	130
1,2,3-Trichloropropane	70	130
1,2,4-Trimethylbenzene	70	130
1,2,3-Trichloropropane	70	130
1,2,4-Trimethylbenzene	70	130
1,3,5-Trimethylbenzene	70	130
Vinyl acetate	70	130

ATTACHMENT D: SOLID LCS RECOVERY LIMITS(continued)

Solid LCS/D Analyte	Lower % Recovery Limit	Upper % Recovery Limit
Vinyl Chloride	70	130
Xylenes (total)	70	130
m/p-Xylenes	70	130
o-Xylene	70	130

* These compounds cannot exceed 60-140% recovery. All others cannot exceed 70-130%.

APPENDIX DoD

APPENDIX DoD: QSM Requirements

Sections found in this appendix replace and/or supplement the existing sections of the SOP. These requirements must be met when analyzing samples for the Department of Defense-NFESC (Navy) as stipulated in the DOD Quality Systems Manual (version 3, January 2006).

10.7.7 Calibration Check Compounds (CCCs) – The %RSD of the response factors for each CCC in the initial calibration must be ≤ 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could affect this criterion.

10.7.7.1 CCC Compounds : 1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl Chloride

10.7.8 The average response factor is used when the %RSD of a compound is ≤ 15%.

10.7.9 For compounds that have % RSD >15% linear regression should be used. The correlation coefficient must be ≥0.995. The Target® software calculates the square of correlation coefficient which should be ≥0.99.

10.5.1 Lower Order of Quantitation (LOQ) Verification – This is an analysis of a QC sample containing the analytes of interest in each matrix 1-2 times the claimed LOQ

10.5.1.1 A successful analysis is one where the recovery of each analyte is within the established test method acceptance criteria or client data quality objectives for accuracy.

10.5.1.2 This single analysis is not required if the bias and precision of the measurement system is evaluated at the LOQ.

10.5.1.3 The LOQ must not be set any lower than the low-level calibration standard fro multi-point calibration or no lower than a low-level calibration check sample for single level calibration.

TABLE DoD-I. Volatile Organic Compounds and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	High Soil µg/kg
Acetone	67-64-1	20	1000
Benzene	71-43-2	5	250
Bromobenzene	108-86-1	5	250
Bromochloromethane	74-97-5	5	250
Bromodichloromethane	75-27-4	5	250
Bromoform	75-25-2	5	250
Bromomethane (Methyl bromide)	74-83-9	5	250
2-Butanone (MEK)	78-93-9	10	500
n-Butylbenzene	104-51-8	5	250
tert-Butylbenzene	98-06-06-	5	250
sec-Butylbenzene	135-98-8	5	250
Carbon disulfide	75-15-0	5	250
Carbon tetrachloride	56-23-5	5	250
Chlorobenzene	108-90-7	5	250
Chloroethane	75-00-3	5	250
Chloroform	75-00-3	5	250
Chloromethane (Methyl chloride)	74-87-3	5	250
3-Chloropropene (Allyl chloride)	107-05-1	10	500
2-Chlorotoluene	95-49-8	5	250
4-Chlorotoluene	106-43-4	5	250
Dibromochloromethane	124-48-1	5	250
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8	5	250
1,2-Dibromoethane (EDB)	106-93-4	5	250
Dibromomethane (Methylene bromide)	74-95-3	5	250
1,2-Dichlorobenzene	95-50-1	5	250
1,3-Dichlorobenzene	541-73-1	5	250
1,4-Dichlorobenzene	106-46-7	5	250
trans-1,4-Dichloro-2-butene	110-57-6	10	500
Dichlorodifluoromethane	75-71-8	5	250
1,1-Dichloroethane	75-34-3	5	250
1,2-Dichloroethane	107-06-2	5	250
cis-1,2-Dichloroethene	156-59-2	5	250
trans-1,2-Dichloroethene	156-60-5	5	250
1,1-Dichloroethene	75-35-4	5	250
1,3-Dichloropropane	142-28-9	5	250
2,2-Dichloropropane	594-20-7	5	250
1,1-Dichloropropene	563-58-6	5	250
cis-1,3-Dichloropropene	10061-01-5	5	250
trans-1,3-Dichloropropene	10061-02-6	5	250
1,2-Dichloropropane	78-87-5	5	250

TABLE DoD-I. Volatile Organic Compounds and Standard Reporting Limits

Analyte	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	High Soil µg/kg
Ethylbenzene	100-41-4	5	250
Ethyl methacrylate	97-63-2	5	250
Hexachlorobutadiene	87-68-3	5	250
2-Hexanone	591-78-6	10	500
Isopropylbenzene	98-82-8	5	250
p-Isopropyltoluene	99-87-6	5	250
4-Methyl-2-Pentanone	108-10-1	10	500
Methyl tertiary butyl ether (MTBE)	1634-04-4	5	250
Methylene chloride	75-09-2	5	250
Naphthalene	91-20-3	5	250
n-Propylbenzene	103-65-1	5	250
Styrene	100-42-5	5	250
1,1,1,2-Tetrachloroethane	630-20-6	5	250
1,1,2,2-Tetrachloroethane	79-34-5	5	250
Tetrachloroethene	127-18-4	5	250
Toluene	108-88-3	5	250
1,2,4-Trichlorobenzene	96-18-4	5	250
1,2,3-Trichlorobenzene	95-63-6	5	250
1,1,1-Trichloroethane	71-55-6	5	250
1,1,2-Trichloroethane	79-00-5	5	250
Trichloroethene	79-01-6	5	250
Trichlorofluoromethane	75-69-4	5	250
1,2,3-Trichloropropane	96-18-4	5	250
1,2,4-Trimethylbenzene	95-63-6	5	250
1,3,5-Trimethylbenzene	108-67-8	5	250
Vinyl Chloride	75-01-4	2	500
Xylenes (total)	1330-20-7	5	250
m/p-Xylenes	108-38-3	5	250
o-Xylenes	95-47-6	5	250

TABLE DoD-II. Volatile Organic Surrogate Compounds and Control Limits

Surrogate Compounds	Concentration in Standard (µg/L or mg/kg)	Aqueous Control Limits		Solid Control Limits	
		Lower	Upper	Lower	Upper
1,2-Dichloroethane-d4	50	70	120	n/a	n/a
4-Bromofluorobenzene	50	75	120	85	120
Toluene-d8	50	85	120	85	115

TABLE DoD-III. Aqueous LCS/MS Control Limits for Volatile Organic Compounds

Analyte	Aqueous Control Limits			
	Lower	Upper	Lower ME	Upper ME
Acetone	40	140	20	160
Benzene	80	120	75	130
Bromobenzene	75	125	70	130
Bromochloromethane	65	130	55	140
Bromodichloromethane	75	120	70	130
Bromoform	70	130	60	140
Bromomethane (Methyl bromide)	30	145	10	165
2-Butanone (MEK)	30	150	10	170
n-Butylbenzene	70	135	55	150
tert-Butylbenzene	70	130	60	140
sec-Butylbenzene	70	125	65	135
Carbon disulfide	35	160	15	185
Carbon tetrachloride	65	140	55	150
Chlorobenzene	80	120	75	130
Chloroethane	60	135	50	145
Chloroform	65	135	50	150
Chloromethane (Methyl chloride)	40	125	25	140
2-Chlorotoluene	75	125	65	135
4-Chlorotoluene	75	130	65	135
Dibromochloromethane	60	135	45	145
1,2-Dibromo-3-chloropropane (DBCP)	50	130	35	145
1,2-Dibromoethane (EDB)	80	120	75	125
Dibromomethane (Methylene bromide)	75	125	65	135
1,2-Dichlorobenzene	70	120	60	130
1,3-Dichlorobenzene	75	125	65	130
1,4-Dichlorobenzene	75	125	65	130
Dichlorodifluoromethane	30	155	40	175
1,1-Dichloroethane	70	135	60	145
1,2-Dichloroethane	70	130	60	140
cis-1,2-Dichloroethene	70	125	60	135
trans-1,2-Dichloroethene	60	140	45	150
1,1-Dichloroethene	70	130	55	140
1,3-Dichloropropane	75	125	65	135
2,2-Dichloropropane	70	135	60	150
1,1-Dichloropropene	75	130	65	140
cis-1,3-Dichloropropene	70	130	60	140
trans-1,3-Dichloropropene	55	140	40	155
Ethylbenzene	75	140	65	135
Hexachlorobutadiene	50	120	35	160

TABLE DoD-III. Aqueous LCS/MS Control Limits for Volatile Organic Compounds (continued)

Analyte	Aqueous Control Limits			
	Lower	Upper	Lower ME	Upper ME
2-Hexanone	55	130	45	140
Isopropylbenzene	75	125	65	135
p-Isopropyltoluene	75	130	65	140
4-Methyl-2-Pentanone	60	135	45	145
Methyl tertiary butyl ether (MTBE)	65	125	55	135
Methylene chloride	55	140	40	155
Naphthalene	55	140	40	150
n-Propylbenzene	70	130	65	140
Styrene	65	135	55	145
1,1,1,2-Tetrachloroethane	80	130	75	135
1,1,2,2-Tetrachloroethane	65	130	55	140
Tetrachloroethene	45	150	25	165
Toluene	75	120	70	130
1,2,4-Trichlorobenzene	65	135	55	145
1,2,3-Trichlorobenzene	55	140	45	155
1,1,1-Trichloroethane	65	130	55	145
1,1,2-Trichloroethane	75	125	65	135
Trichloroethene	70	125	60	135
Trichlorofluoromethane	60	145	45	160
1,2,3-Trichloropropane	75	125	65	130
1,2,4-Trimethylbenzene	75	130	65	140
1,3,5-Trimethylbenzene	75	130	65	140
Vinyl Chloride	50	145	35	165
Xylenes (total)	Analyzed and reported as m/p xylene and o-xylene			
m/p-Xylenes	75	130	65	135
o-Xylenes	80	120	75	130

TABLE DoD-IV. Solid LCS/MS Control Limits for Volatile Organic Compounds

Analyte	Solid Control Limits

	Lower	Upper	Lower ME	Upper ME
Acetone	20	160	10	180
Benzene	75	125	32	135
Bromobenzene	65	120	22	130
Bromochloromethane	70	125	30	135
Bromodichloromethane	70	130	30	135
Bromoform	55	135	45	150
Bromomethane (Methyl bromide)	30	160	10	180
2-Butanone (MEK)	30	160	10	180
n-Butylbenzene	65	140	50	150
tert-Butylbenzene	65	130	55	145
sec-Butylbenzene	65	130	50	145
Carbon disulfide	45	160	30	180
Carbon tetrachloride	65	135	55	145
Chlorobenzene	75	125	65	130
Chloroethane	40	155	20	175
Chloroform	70	125	65	135
Chloromethane (Methyl chloride)	50	130	40	140
2-Chlorotoluene	70	130	60	140
4-Chlorotoluene	75	125	65	135
Dibromochloromethane	65	130	55	140
1,2-Dibromo-3-chloropropane (DBCP)	40	135	25	150
1,2-Dibromoethane (EDB)	70	125	60	135
Dibromomethane (Methylene bromide)	75	130	65	135
1,2-Dichlorobenzene	75	120	65	125
1,3-Dichlorobenzene	70	125	65	135
1,4-Dichlorobenzene	70	125	65	135
Dichlorodifluoromethane	35	135	15	155
1,1-Dichloroethane	75	125	65	135
1,2-Dichloroethane	70	135	60	145
cis-1,2-Dichloroethene	65	125	55	135
trans-1,2-Dichloroethene	65	135	55	145
1,1-Dichloroethene	65	135	55	150
1,3-Dichloropropane	75	125	70	130
2,2-Dichloropropane	65	135	55	145
1,1-Dichloropropene	70	135	60	145
cis-1,3-Dichloropropene	70	125	65	135
trans-1,3-Dichloropropene	65	125	55	140
Ethylbenzene	75	125	65	135
Hexachlorobutadiene	55	140	40	155

TABLE DoD-IV. Solid LCS/MS Control Limits for Volatile Organic Compounds (continued)

Analyte	Solid Control Limits			
	Lower	Upper	Lower ME	Upper ME
2-Hexanone	45	145	30	160
Isopropylbenzene	75	130	70	140
p-Isopropyltoluene	75	135	65	140
4-Methyl-2-Pentanone	45	145	30	165
Methylene chloride	55	140	40	155
Naphthalene	40	125	25	140
n-Propylbenzene	65	135	50	145
Styrene	75	125	65	135
1,1,1,2-Tetrachloroethane	75	125	65	135
1,1,2,2-Tetrachloroethane	55	130	40	145
Tetrachloroethene	65	140	55	150
Toluene	70	125	60	135
1,2,4-Trichlorobenzene	65	130	55	140
1,2,3-Trichlorobenzene	60	135	50	145
1,1,1-Trichloroethane	70	135	55	145
1,1,2-Trichloroethane	60	125	50	140
Trichloroethene	75	125	70	130
Trichlorofluoromethane	25	185	10	215
1,2,3-Trichloropropane	65	130	50	140
1,2,4-Trimethylbenzene	65	135	55	145
1,3,5-Trimethylbenzene	65	135	55	145
Vinyl Chloride	60	125	45	140
Xylenes (total)	Analyzed and reported as m/p xylene and o-xylene			
m/p-Xylenes	80	125	70	135
o-Xylenes	75	125	70	135

TABLE DoD-V. Characteristic Ions for Volatile Organic Compounds

Analyte	Primary	Secondary	Tertiary

Acetone	58	43	
Benzene	78		
Bromobenzene	77	156	158
Bromochloromethane	128	49	130
Bromodichloromethane	83	85	
Bromoform	173	171	
Bromomethane (Methyl bromide)	94	96	
2-Butanone (MEK)	43	72	
n-Butylbenzene	91	134	
tert-Butylbenzene	119	134	
sec-Butylbenzene	105	134	
Carbon disulfide	76		
Carbon tetrachloride	117	119	
Chlorobenzene	112	114	
Chloroethane	64		
Chloroform	83	85	
Chloromethane (Methyl chloride)	50	52	
2-Chlorotoluene	91	126	
4-Chlorotoluene	91	126	
Cyclohexane	56	69	84
Cyclohexanone	55	69	98
Dibromochloromethane	129	127	
1,2-Dibromo-3-chloropropane (DBCP)	75	157	155
1,2-Dibromoethane (EDB)	107	109	
Dibromomethane (Methylene bromide)	93	174	95
1,2-Dichlorobenzene	146	148	113
1,3-Dichlorobenzene	146	148	113
1,4-Dichlorobenzene	146	148	113
Dichlorodifluoromethane	85		
1,1-Dichloroethane	63	65	
1,2-Dichloroethane	62	64	98
cis-1,2-Dichloroethene	96	61	
trans-1,2-Dichloroethene	96	61	98
1,1-Dichloroethene	96	61	63
1,3-Dichloropropane	76	78	
2,2-Dichloropropane	77	79	
1,1-Dichloropropene	75	110	77
cis-1,3-Dichloropropene	75	77	
trans-1,3-Dichloropropene	75	77	

TABLE DoD-V. Characteristic Ions for Volatile Organic Compounds

Analyte	Primary	Secondary	Tertiary

1,2-Dichloropropane	63	76	
Ethylbenzene	106	91	
Hexachlorobutadiene	225	223	227
2-Hexanone	43	58	
Isopropylbenzene	105	120	
p-Isopropyltoluene	119	134	
4-Methyl-2-Pentanone	43	58	
Methyl tertiary butyl ether (MTBE)	73	57	
Methylene chloride	84	49	51
Naphthalene	128		
n-Propylbenzene	91	120	
Styrene	104	51	78
1,1,1,2-Tetrachloroethane	131	133	
1,1,2,2-Tetrachloroethane	83	85	
Tetrachloroethene	164	129	131
Toluene	92	91	
1,2,4-Trichlorobenzene	180	182	145
1,2,3-Trichlorobenzene	180	182	145
1,1,1-Trichloroethane	97	99	61
1,1,2-Trichloroethane	97	83	85
Trichloroethene	130	95	97
Trichlorofluoromethane	101	103	
1,2,3-Trichloropropane	110	97	
1,2,4-Trimethylbenzene	105	120	
1,3,5-Trimethylbenzene	105	120	
Vinyl Chloride	62	64	
Xylenes (total)	Summation	Summation	
m/p-Xylenes	106	91	
o-Xylenes	106	91	
Pentafluorobenzene (Internal Standard)	168		
1,2-Dichloroethane-d4 (Surrogate Standard)	65	102	
1,4-Difluorobenzene (Internal Standard)	114		
Toluene-d8 (Surrogate Standard)	98		
Chlorobenzene-d5 (Internal Standard)	117	82	119
4-Bromofluorobenzene (Surrogate Standard)	95	174	176
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	

ATTACHMENT E

18.0 1,4-Dioxane by Selected Ion Monitoring

1,4-Dioxane may be detected at concentrations below what is possible by typical full scan electron impact mass spectroscopy by utilizing Selected Ion Monitoring (SIM). Primary and secondary ions are selected for quantitative and monitoring purposes. A heated purge is used to enhance the purge efficiency for 1,4-Dioxane and the associated internal standard (IS) 1,4-Dioxane-d8. An appropriate surrogate is selected to monitor recovery efficiency for the analyses. IS 1,4-Dioxane-d8 is added to each calibration standard, sample and QC sample at 100 ug/L. The surrogate is added to each sample and QC sample at 50 ug/L with a recovery limit of 40-170%. The table below outlines the calibration standard concentrations for 1,4-Dioxane and associated surrogate.

Aqueous Analyte	**Level 1**	**Level 2**	**Level 3**	**Level 4**	**Level 5**	**Level 6**
1,4-Dioxane	3	10	25	50	100	150
1,2-Dichloroethane-d4 (surr)	3	10	25	50	100	150

The following table lists the ions selected for monitoring for each analyte of interest:

Analyte	**Primary Ion**	**Secondary Ion**
1,4-Dioxane	88	58
1,2-Dichloroethane-d4 (surr)	65	102
1,4-Dioxane-d8 (IS)	96	n/a

Appendix P

Laboratory SOPs

SVOCs

Shealy SOP

S-EX-017 (Preparation)

S-SV-021 (Analysis)

SHEALY ENVIRONMENTAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

ULTRASONIC EXTRACTION
METHOD 3550 B/C

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1. SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes for analyses by methods 8015, FL-PRO, 8081, 8270, and 8082. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of less than or equal to 20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of greater than 20 mg/kg) is much simpler and therefore faster.

1.3 Ultrasonic extraction is not as rigorous as other extraction methods for soils/solids. Therefore, it is critical that the method (including the manufacturer's instructions) be followed explicitly in order to achieve the maximum extraction efficiency.

1.4 EPA has not validated Method 3550 for the extraction of organophosphorus compounds from solid matrices. There are concerns that the ultrasonic energy may lead to the breakdown of some organophosphorus compounds. As a result, this extraction technique should not be used for organophosphorus compounds.

2. SUMMARY OF METHOD

2.1 Low concentration method – A minimum of 30 g of sample is mixed with 30-60 g of anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using ultrasonic extraction. The extract is separated from the sample by filtration and concentrated using Turbo Vap® technique. The extract is ready for analysis after concentration.

2.2 Medium/high concentration method – A minimum of 1 g of sample is mixed with 2 g of anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using ultrasonic extraction. A portion of the extract is removed for analysis.

3. DEFINITIONS

3.1 Refer to the QAMP for the definition of terms used in this SOP.

4. 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 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 organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse. All items should be hand-rinsed very carefully to avoid this problem.

4.3 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. To help avoid interference, glassware must be cleaned in the following order and no steps can be omitted. Wash with warm soapy water. Rinse with warm tap water. Rinse with reagent water. Rinse with acetone.

- Note: Beakers and Turbo Vap® concentrator tubes should be dried at 350 ±10°C for 2 hours instead of being rinsed with acetone. **All glassware used for Pest/PCB extraction and concentration must be dried, no exceptions.**

- Note: Acetone rinsed glassware that is stored in laboratory cabinets should be rinsed with acetone at time of use.

4.4 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.

5. SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all Shealy personnel.

5.2 As stated in the Shealy Comprehensive Chemical Hygiene, Safety, and Hazard Communication Plan (P-HS-003), eye protection that satisfies ANSI Z87.1, laboratory coat, and at least latex or nitrile gloves must be worn while samples, standards, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3 The health and safety hazards of many of the chemicals used in the procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazard is known:

5.3.1 The following material is classified as a **carcinogen**:
Methylene chloride

5.3.2 The following materials are known to be **flammable**:
n-hexane, acetone, methylene chloride

5.3.3 The following materials are known to be **irritants**:
n-hexane, acetone, methylene chloride

5.4 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 Any accidents and spills greater than 50 ml must be reported to the lab supervisor, team leader, or safety officer.

5.6 Discard chipped or broken glassware to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.7 All work must be stopped in the event of a known or potential compromise to the health and safety of Shealy personnel. The situation must be reported immediately to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1 Apparatus for grinding dry waste samples.

6.2 Ultrasonic preparation – A horn-type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

6.2.1 SONICATOR® Model 3000 ULTRASONIC Liquid PROCESSOR by MISONIX- This device is an ultrasonic disruptor that has 1500 V rms (max). The SONICATOR® has a dual horn apparatus, which accommodates two 3/4” diameter extenders for simultaneous sample extraction for the low concentration method or a 1/8” tapered microtip probe that attaches to a 1/2” tapped horn for the medium/high concentration method.

6.2.2 SONABOX™ Acoustic Enclosure (Heat Systems – Ultrasonics, Inc., Model 432B or equivalent) – Recommended for use with the above ultrasonic disruptor. The SONABOX™ aids in the reduction of cavitation noise levels. The Sonabox Acoustic Enclosure reduces noise levels down to safe, comfortable levels.

6.2.3 As an alternative to the SONICATOR® PROGRAMMABLE ULTRASONIC PROCESSOR, an A.S.E. ® 200 ACCELERATED SOLVENT EXTRACTOR

can be used. This device is an automated system for extracting organic compounds from a variety of solid and semisolid samples.

6.3 Pasteur glass pipets – 2 mL, disposable.

6.4 Pipeting bulb – 1 mL.

6.5 Beakers – 600, 400, 250, 150 mL.

6.6 Glass powder funnel.

6.7 Filter paper – Whatman No. 41 or equivalent.

6.8 Turbo Vap® II (Zymark Model ZW 8001 or equivalent) – Capable of maintaining temperature range of 45 ± 2°C at 0.4 – 0.6 psi +- 0.1 on either end.

6.9 Turbo Vap® concentrator tubes – 200 mL capacity.

6.10 Balance – Top loading, capable of accurately weighing to the nearest 0.1 g.

6.11 Vials – 12 mL and 2 mL with Teflon (PTFE)-lined screw caps or crimp tops.

6.12 Spatula – Stainless steel, PTFE, or disposable wooden.

6.13 Syringe – 1 mL, gas-tight.

6.14 Graduated cylinder – 100 mL.

7. REAGENTS AND STANDARDS

- **Note: All standards and reagents dilutions are made using volumetric glassware unless otherwise noted.**

- **Note: All stored reagents and standards are labeled with the following information:**

    1. **Name of standard or solution**
    2. **Concentration**
    3. **Analyst's initials**
    4. **Prep date**
    5. **Expiration date**
    6. **Tracking number**
    7. **Warning label of any hazards and/or precautions for use**

7.1 Reagent Water – Shealy employs a series of in-house deionizing (DI) tanks to purify the incoming water to the conductivity measurement, 0.056 μmhos/cm (corresponds

to resistivity of 18 meg-ohms). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2 Reagent grade chemicals shall be used in all tests. Other grades may be used, provided that the reagent is demonstrated to be of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass or Teflon to prevent the leaching of contaminants from plastic containers.

7.3 Extraction solvents – Samples should be extracted using a solvent system that gives the optimum, reproducible recovery of the analytes of interest from the sample matrix. All solvents must be pesticide quality or equivalent.

Category	Determinative Method	Extraction Solvent (s) (v/v)
BNA	8270	1:1 Methylene Chloride/Acetone
TPH-DRO	8015	Methylene Chloride
FL-PRO	FL-PRO	Methylene Chloride
Pesticide	8081	1:1 Methylene Chloride/Acetone
PCB	8082	1:1 Methylene Chloride/Acetone

7.3.1 Other solvent systems may be employed, provided that the analyst can demonstrate adequate performance for the analytes of interest in the sample matrix.

7.4 Exchange/ Rinsing Solvents– All solvents must be pesticide quality or equivalent.

Category	Determinative Method	Extraction Solvent (s) (v/v)	Exchange Solvent	Rinsing Solvent
BNA	8270	1:1 Methylene Chloride/Acetone	N/A	Methylene Chloride
TPH-DRO	8015	Methylene Chloride	N/A	Methylene Chloride
FL-PRO	FL-PRO	Methylene Chloride	N/A	Methylene Chloride
Pesticide	8081	1:1 Methylene Chloride/Acetone	Hexane	Hexane
PCB	8082	1:1 Methylene Chloride/Acetone	Hexane	Hexane

7.5 Stock standard solutions – Commercially available. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration

date is provided, the stock solutions may be used for up to two years and must be replaced sooner if verification from an independent source indicates a problem.

7.6 Spike and surrogate solutions – Refer to Table II for appropriate concentration of spiking and surrogate solutions used for different determinative methods. These solutions may be used for up to 6 months and must be replaced sooner if there is a recovery problem.

- **Note: All standards prepared for surrogate, LCS, and matrix spiking solutions must be analyzed by GC or GC/MS prior to use for sample extraction.**

7.7 See Table III, IV, V, VI, and VII for lists of specific compounds and each compound's concentration in spike and surrogate solutions for different methods.

7.8 The standard solutions in Section 7.9, if made in large quantity (>250 mL) at one time, are stored in 500 mL amber glass containers with PTFE lined caps. The analyst must mark the meniscus line on the container to monitor the evaporation of solvents. Before using the solution, pour part of it into a 40 mL amber glass container with PTFE lined cap. Use the solution in the smaller container to spike the samples. Re-mark the meniscus line on the larger container. If significant solvent loss is observed, the standard must be discarded and new solution must be prepared.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples must be stored at 4±2°C from the time of receipt until extraction.

8.2 Samples have a 14 days holding time prior to being extracted. After extraction, extracts must be analyzed within 40 days.

9. QUALITY CONTROL

9.1 Initial Demonstration of Capability and MDL:

9.1.1 The initial demonstration of capability (IDOC) and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.2 Extraction Batch – A group of up to 20 samples that are of the same matrix and are processed together within 24 hours using the same procedures and reagents. The batch must contain a method blank (MB), a laboratory control sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD) pair. If there is not enough sample volume to perform an MS/MSD, a laboratory control sample duplicate (LCSD) must be performed to generate precision data. If the clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3 Sample Count – Laboratory generated QC samples (MB, LCS, and MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

9.4 Method Blank (MB) – One method blank must be processed with each batch. The method blank consists of anhydrous sodium sulfate containing all reagents specific to the method that is carried through the same extraction procedure as samples. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated concentration of compounds or false positive data. Acceptance criteria of method blanks and corrective actions are contained within the individual analytical method SOP.

9.4.1 Method blank is prepared by taking a minimum of 30 g of anhydrous sodium sulfate through the procedure described in Section 11.

9.5 Laboratory Control Sample (LCS) – One solid LCS must be processed with each batch. The LCS should contain known amount of all compounds of interest and must be carried through the entire extraction procedure. The LCS is used to monitor the accuracy of the extraction process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Acceptance criteria of LCS and corrective actions are contained within the individual analytical method SOP.

9.5.1 LCS is prepared by spiking a minimum of 30 g of anhydrous sodium sulfate with 1.0 mL of appropriate spike solution (see Table II). The LCS is then processed as described in Section 11.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentration of all compounds of interest has been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in addition to MS/MSD. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. **Samples identified as field blanks cannot be used for MS/MSD analysis**. Acceptance criteria of MS/MSD and corrective actions are contained within the individual analytical method SOP.

9.6.1 If MS/MSD are not possible due to limited sample quantity, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.6.2 The matrix spike sample is prepared by spiking a minimum of 30 g of sample with 1.0 mL of appropriate spike solution (see Table II). The MS/MSD are then processed as described in Section 11.

10. CALIBRATION AND STANDARDIZATION

10.1 The balance calibration is checked at the beginning of each day using a certified weight set and recorded in a logbook.

10.2 The SONICATOR® Model 3000 must be programmed prior to use:

10.2.1 Turn POWER SWITCH to **ON** position. The power switch is located on the back of the unit.

10.2.2 Programming the Proper Tip: Once the unit has been turned on, a prompt for the proper tip will appear. The following question will appear on the display: **Are you using a MicroTip(Y/N)**? The answer to this question sets up proper operating parameters for the horn that will be used. If using a MicroTip horn, answer "**YES**" to this question. If using any other type of horn, answer "**NO**".

10.2.3 Program Mode or Continuous Operation: Next, the display will have two options for operation: Press **PROG** to Program Timer and **PULSAR**, or Press Start for Continuous Operation. Pressing **START** will cause the unit to go into a Continuous mode of operation with the Power setting at 0.0. No processing will occur until the Power Select Knob is turned clockwise to a value greater than 0.0. This mode allows the operator to start processing quickly without going to any programmed memory setups.

To program a setup or access a previously programmed memory setup, press the **PROG** key on the keypad.

10.2.4 Programming Mode:

1. Process Time Programming- The "Process Time" is the total processing time desired. When running the Program, processing will continue until the Elapsed Time equals the programmed Process Time. Note that Elapsed Time is only counted when the horn is "**ON**", therefore, only "**ON-Time**" is counted. Pressing **CLEAR** at any time will zero the Process Time value. Setting the value to 00.00.00 (hr:min:sec) will allow the unit to run continuously with no automatic shutdown. **When finished keying the desired value, 00.01.30, press ENTER.**

2. Pulse-ON Time Programming- After entering the desired Process Time, the next screen prompts for the **Pulse-ON** time. If processing continuously, (no pulsing), enter 00:00:0 (min:sec:tenths) for the Pulse-**ON** time and press **ENTER**. By entering zero the Pulse-OFF time prompt will be skipped. **The Pulse-ON time used for this method 3550B) is 00.01.0. Press ENTER after keying this value.**

3. Pulse-OFF Time Programming- After entering the desired Pulse-ON time, the next prompt will be for the Pulse-OFF time. **The desired Pulse-OFF time is 00.01.0 (min:sec:tenths).**

4. Setting Initial Output Level (Knob Setting) - After programming the **ON/OFF** times, the following prompt will be to select an initial Power setting. Key-in a value from **0.0** to **10.0** (in 0.5 increments only), then press ENTER. This will be the knob setting when START is pressed to begin processing. If initial output level is set at 0.0, when START is pressed to begin processing, no processing will occur until the knob is turned clockwise to a value greater than 0.0. **All samples should be sonicated at the setting of 10.0.**

5. Temperature Monitoring - NOT APPLICABLE. Press **NO** to this prompt to return to the program screen. No further programming information is required.

11. PROCEDURE

- Note: To achieve the maximum extraction efficiency, the following should be employed:

  - The horn must be properly maintained, including tuning according to the manufacturer's instructions prior to use, and inspection of the horn tip for excessive wear. The sonicators are currently on auto tune.

  - The samples must be properly prepared by thorough mixing with sodium sulfate so that it forms a free-flowing powder prior to the addition of the solvent.

  - Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. The analyst must observe such mixing at some point during the extraction process.

- Sample handling: (See S-QA-010 – Sub Sampling SOP for sub-sampling instructions before weighting up a sample)

11.1 Extraction method for samples expected to contain low concentrations of organics and pesticides (less than or equal to 20 mg/kg):

11.1.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

11.1.1.1 Weigh a minimum of 30.0 of sample into a beaker. Do not target a specific weight. Record the weight to the nearest 0.1 g. If samples are to be extracted and analyzed by FL-PRO, 25.0-25.9 g aliquot of samples should be used.

11.1.1.2 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 30-60 g of anhydrous sodium sulfate, using a spatula. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.

11.1.1.3 Add 1.0 mL of the surrogate spiking solution to all samples, including the MB, LCS, LCSD, and MS/MSD.

11.1.1.4 For the LCS, LCSD and the MS/MSD, add 1.0 mL of the matrix spiking solution.

11.1.1.5 Record the chemical ID's and expiration dates of the surrogate and matrix spiking solutions and volumes used on the batch sheet. These chemical ID's will be entered into LIMS during batch promotion.

11.1.1.6 Immediately after adding the surrogate spiking solution and matrix spiking solution, if applicable, to a sample, add 100 mL of the appropriate extraction solvent or solvent mixture.

- Record the chemical IDs of solvent(s) used for extraction for subsequent entry into LIMS.

11.1.2 Obtain two additional clean beakers. Weigh at least 60 grams of anhydrous sodium sulfate into each beaker. Add 100 mL of the solvent or solvent mixture to the beakers. These beakers will be sonicated between each sample pair for at least one minute, and then the horn should be wiped down. This process will be defined as the decontamination procedure.

11.1.3 Place the bottom surface of the tip of the 3/4" disrupter horn about 1/2" below the surface of the solvent, but above the sediment layer.

- Note: Be sure the horn is properly tuned according to the manufacturer's instructions.

11.1.4 With the power output control knob set at 10 (full power), press the **START** key to run the preset program. The sample will be extracted ultrasonically for 3 minutes. (Output control knob at 10 (full power), mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time)). Do not use microtip probe when this program is in operation.

11.1.5 Allow sample to settle; then filter extract through Whatman No.41 filter paper or glass wool filled with 10-20 g of sodium sulfate (pre-moistened with solvent) placed in a glass powder funnel that is resting on a clean 200

mL concentrator tube. After sample transfer, rinse the filter paper or glass wool with 5-10 mL solvent.

11.1.6 Repeat the extraction (steps 11.1.3 - 11.1.5) two more times with two additional 100 mL portions of solvent.

11.1.6.1 After the second extraction, filter the solvent extract and combine with the first solvent extract, then concentrate the extract to approximately 80 mL using the nitrogen blow down technique. See step 11.2.

11.1.6.2 After the final extraction, filter the entire sample (solvent extract and solid portions), collect and add the filtrate to the partially concentrated solvent extract and concentrate the extract to the desired volume using the nitrogen blow down technique.

11.1.6.3 The decontamination procedure should be employed at this point, before another sample pair is sonicated.

11.2 Nitrogen blow-down technique with TurboVap® II:

11.2.1 Place the tube in the Turbo Vap® that is preheated to 40°C for Methylene Chloride extracts, 45°C for Methylene Chloride-Acetone extracts and 65°C for Hexane extracts. Initial recommended pressure set at 6 psi of nitrogen and this may vary by +/- 1.0. Final recommended pressure set at 18 psi and this may vary by +/- 1.0

11.2.1.1 Make sure initial pressure is set before lowering lid and beginning concentration. Increased pressure can result in splashing of sample extracts and cross contamination.

11.2.1.2 As sample/solvent volume decreases, the analyst must periodically check to ensure the pressure is adequate to generate the vortex shearing effect. Pressure should be increased incrementally throughout the concentrating process to maintain vortex effect as sample extract volume decreases.

Refer to 11.2.1.3 if solvent exchange is required, go to step 11.2.1.4 if no solvent exchange is needed.

11.2.1.3 If exchange solvent is needed, concentrate the extract to approximately 10 mL, add 100 mL of the appropriate exchange solvent (see Section 7.4), mix well assuring that the exchange solvent has mixed in the tip of the concentrator tube, and continue with the concentration process.

11.2.1.4 The extract must not be allowed to become dry because compounds of interest may be lost. When the volume of the solvent is reduced below 0.5 mL, semivolatile analytes may be reduced or lost.

11.2.1.5 Concentrate the extract to approximately 1 mL below the desired final volume specified in Table I, using a gentle stream of nitrogen.

11.2.2 Qualitatively transfer the concentrated extract to an appropriately labeled and calibrated 12 mL vial with a PTFE-lined screw cap by using a 2 mL disposable Pasteur pipet. The vial label should include the following information: method (BNA, PAH, FL-PRO, Herb, Pest/PCB, etc.), prep batch number and sample ID. Alternatively, the extract could be qualitatively transferred to a Class A volumetric flask and brought up to volume with appropriate solvent. The extract then can be transferred to the aforementioned 12 mL vial.

11.2.2.1 After vialing the concentrated extract, rinse the concentrator tube with small portions of the same solvent used to rinse the concentrator tube during the concentration process. Add the rinsate to the vial. Bring the concentrated extract to final volume as specified in Table I with that same solvent.

11.2.3 The extract may now be analyzed for the target analytes using the appropriate determinative method. If a cleanup procedure is required, proceed to 11.4. If the extract is not going to be analyzed immediately, it should be stored at 4 ± 2^0C.

11.3 Extraction method for samples expected to contain high concentrations of organics (greater than 20 mg/kg):

11.3.1 Transfer approximately 1.0 ± 0.1 g (record weight to the nearest 0.1 g) of sample to a 20 or 40 mL vial. Wipe the mouth of the vial with a tissue (Kimwipe) to remove any sample material. Cap the vial before proceeding with the next sample to avoid any cross contamination.

11.3.2 Add 2 g of anhydrous sodium sulfate to each sample vial and mix well. The blank, LCS, and LCSD (if applicable) should be 2g of anhydrous sodium sulfate.

11.3.3 Add 1.0 mL of the surrogate spiking solution to all samples, including the MB, LCS, LCSD (if applicable), and MS/MSD.

11.3.4 For the LCS, LCSD (if applicable), and sample selected for the MS/MSD, add 1.0 mL of the matrix spiking solution.

11.3.5 Immediately add make-up volume of the appropriate solvent or solvent mixture (refer to Section 7.4) that is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8 inch tapered MicroTip ultrasonic probe for 2 minutes at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%.

11.3.6 Filter the sample extract through filter paper and collect the extract in a 40 mL glass vial. The vial label should include the follow information: method (BNA, PAH, FL-PRO, Herb, Pest/PCB, etc.), prep batch number and sample ID. The entire 10 mL of extraction solvent cannot be recovered from the sample. Therefore, the analyst should collect a volume appropriate for the sensitivity of the determinative method. For instance, for methods that do not require that the extract be concentrated further, the extract may be collected in a scintillation vial or other sealable container. For extracts that will require further concentration, it is advisable to collect a standard volume for all such samples in order to simplify the calculation of the final results. For instance, collect 5.0 mL of extract in a clean concentrator tube. This volume represents exactly half of the total volume of the original sample extract. As necessary, account for the "loss" of half of the extract in the final volume (e.g., 0.5 mL vs. 1.0 mL) to compensate for the loss.

11.3.7 The extract is ready for analysis, depending on the extent of interfering co-extractives.

11.3.8 If analysis of the extract will not be performed immediately, the extract should be stored in at 4 ± 2^0C. If cleanup required proceed to 11.4.

11.4 (See SOP S-SV-013 Cleanup SOP for complete cleanup instructions.)

11.4.1 Sulfuric Acid Cleanup: This method is used for rigorous cleanup of sample extracts prior to analysis of Aroclors. This method is used to provide accuracy in quantitation of Aroclors by eliminating elevated baselines or overly complex chromatograms. **Sulfuric Acid cleanup is mandatory for all PCB extracts including the corresponding QC samples.**

11.4.2 Silica Gel Cleanup - **Silica gel cleanup is mandatory for FL-PRO analysis**.

11.5 Procedural Variations – This Section applies to all samples except South Carolina compliance samples. One time procedural variations are allowed, only if deemed necessary in the professional judgment and supervision of a knowledgeable analyst, to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in analytical procedure must be approved by a technical director, the QA Officer, or the client, and must be fully documented (flagged and/or narrated) on the final report. The analyst must use an NCM to notify the appropriate parties and to document the variance. The project manager uses the information on

the NCM to notify the client and flag/narrate the final report accordingly. A copy of the NCM is kept with the raw data and the original is filed with the final report.

11.5.1 For South Carolina compliance samples, all procedures outlined in this SOP must be followed without exception. In the event that a deviation from this SOP cannot be avoided (i.e., demonstrated and uncorrectable matrix interference, non-compatible matrix, insufficient sample amount due to client or laboratory error) it is imperative that an NCM is completed that clearly documents the anomaly. This anomaly must be communicated to the client such that corrective action activity including sample recollection can be performed. Based upon the type and severity of anomaly, the results may not be appropriate for compliance reporting. Discussions between the client, the appropriate regulatory authority, and Shealy will be necessary to resolve certain anomalies. In any case, it is essential that any anomaly be documented on an NCM.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Not applicable.

13. METHOD PERFORMANCE

13.1 Method performance is determined by the analysis of MS and MSD samples as well as method blanks and laboratory control samples. The MS/MSD and LCS must fall within the percent recovery limits and the method blank must meet the criteria specified in determinative SOP.

13.2 Initial Demonstration - Each laboratory must make an initial demonstration of capability for each individual method. This requires analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The QC check may also be obtained from an outside source. (For certain tests more than one set of QC checks samples may be necessary in order to demonstrate capability for the full analyte list.)

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.3.2 Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs.

13.3 Training Qualification - The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience to perform this procedure.

14. POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1 Waste generated in the procedure must be disposed of according to the Shealy Waste Management Plan (P-HS-001) and per the local, state, and federal regulations. The Safety Officer should be contacted, if additional information is required.

15.2 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1 SW-846, Test Method for Evaluating Solid Waste, Third Edition – Ultrasonic Extraction, Method 3550 B/C, Revision 3, February 2007.

16.2 FLDEP, Method for Determination of Petroleum Range Organics – FL-PRO.

16.3 Shealy Quality Assurance Management Plan (QAMP), Q-QA-001.

16.4 Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.1, April 2009.

17. MISCELLANEOUS

17.1 All glassware, **new or used**, in this procedure must be washed with detergent, rinsed with tap water, then with reagent water, and then with acetone. Acetone rinsed glassware that is stored in laboratory cabinets should be rinsed with acetone at the time of use. Note: Beakers and Turbo Vap® concentrator tubes should be dried at 350 ± 10°C for 2 hours instead of being rinsed with acetone. **All glassware used for Pest/PCB extraction and concentration must be dried, no exceptions.**

- Note: The used hexane must be collected and stored in a sealed container in the liquid room to be disposed of properly.

Figure 1. Extraction of Sample with Low Concentration of Organics and Pesticides

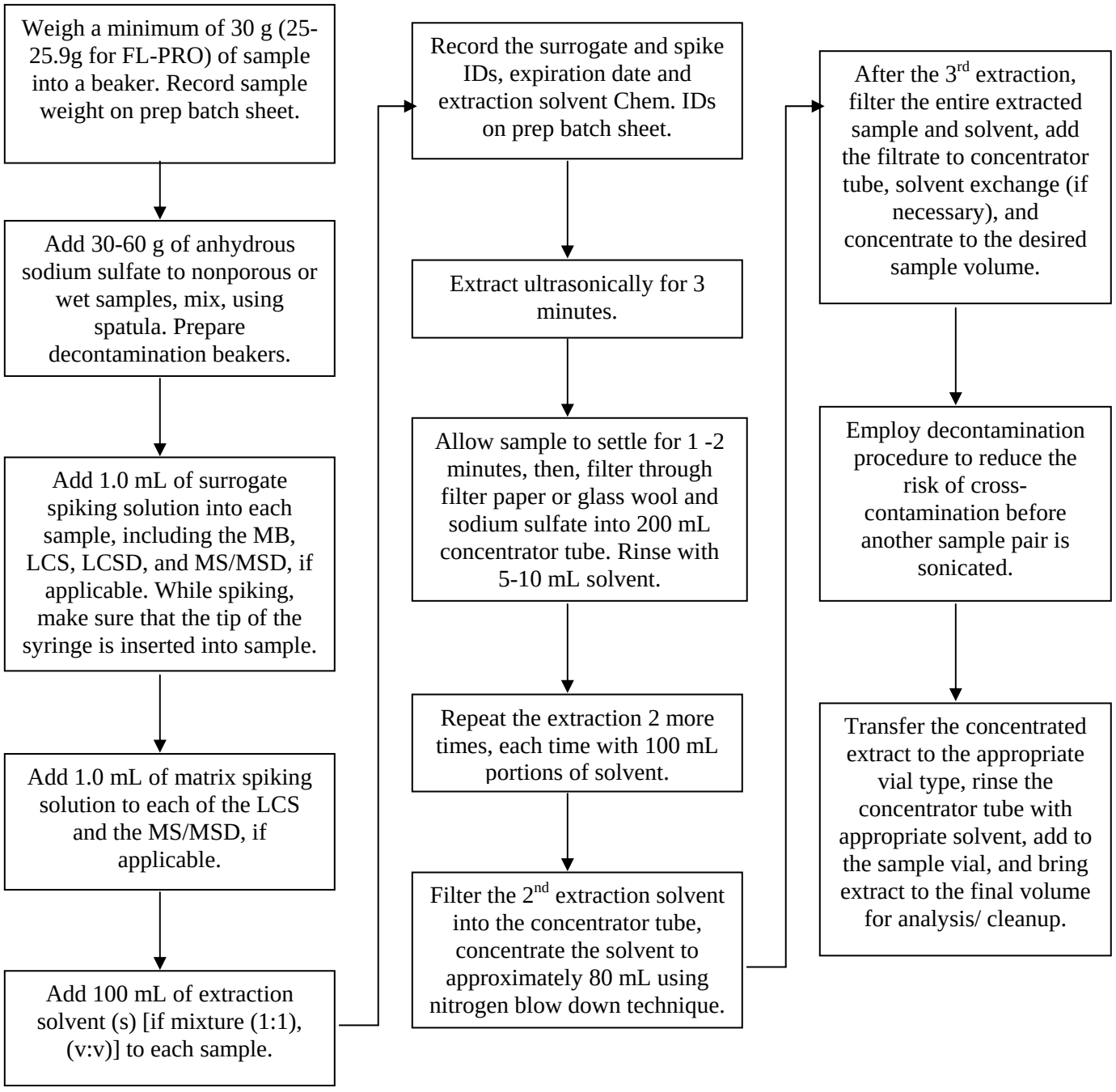


Figure 2. Nitrogen Blow down Technique

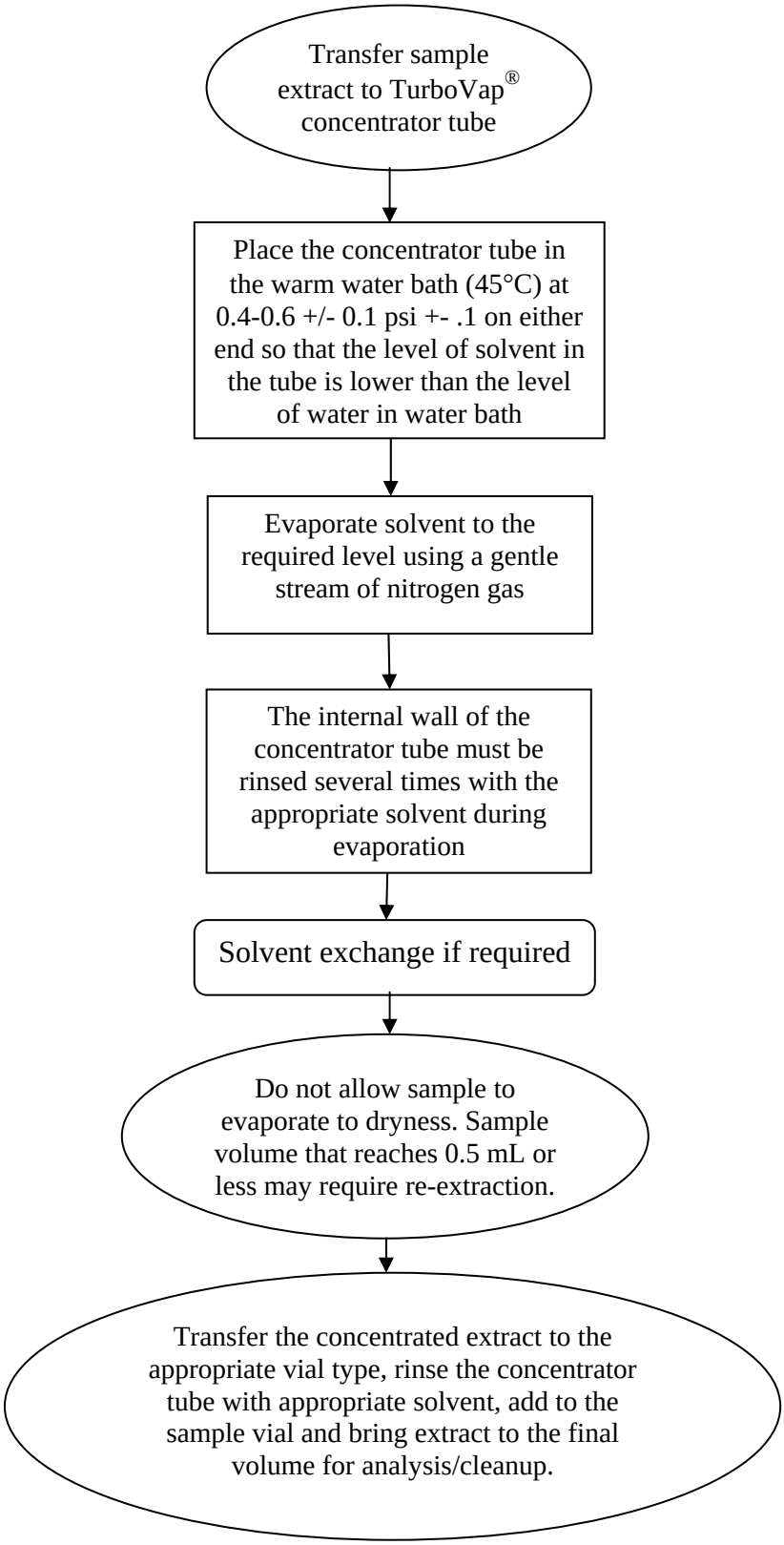
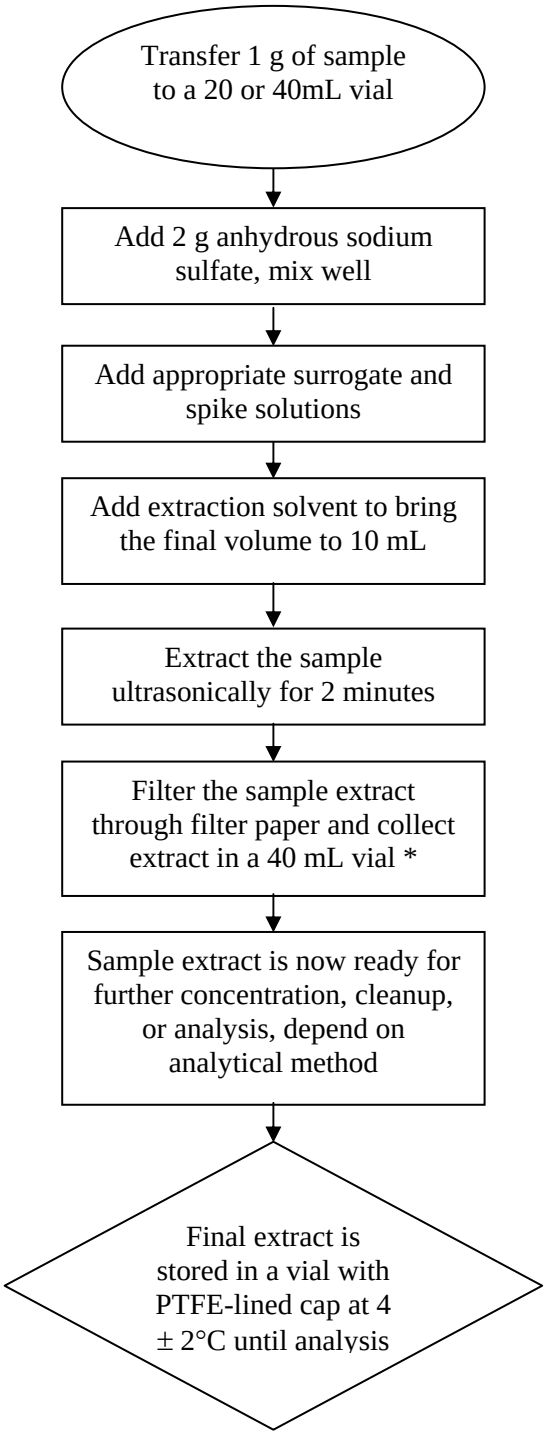


Figure 3. Extraction of Sample with High Concentration of Organics and Pesticides



APPENDIX A

TABLES

Table I. Ultrasonic Extraction Conditions and Cleanup Procedured for Various Determinative Methods

Category	Method	Extraction Solvent (s) (v/v)	Exchange Solvent	Final Extract Volume (mL)	Cleanup Procedure	Volume of Extract Required for Cleanup (mL)	Volume of Extract after Cleanup (mL)
BNA	8270	1:1 Methylene Chloride/Acetone	N/A	5.0	N/A	N/A	N/A
TPH-DRO	8015	Methylene Chloride	N/A	5.0	N/A	N/A	N/A
FL-PRO	FL-PRO	Methylene Chloride	N/A	2.0	Silica Gel	2.0	2.0
Pesticide	8081	1:1 Methylene Chloride/Acetone	Hexane	5.0	Florisil Cartridge (optional)	1.0	1.0
PCB	8082	1:1 Methylene Chloride/Acetone	Hexane	5.0	Sulfuric Acid	5.0	5.0

Table II. Surrogate and Spike Solutions for Various Determinative Methods

Method			Concen-tration (µg/mL)	Stock Solution (µg/mL)	Volume of Stock (µg/mL)	Dilute to (mL)	Foot Notes (#)
8081	Spike		0.1	20	0.05	10	# 1
	Surrogate		2.5	200	1.25	100	
8015	Spike		2,500	20,000	1.25	10	
	Surrogate		250	10,000	2.5	100	
FL-PRO	Spike		5,100	17,000	3.0	10	
	Surrogate		100 (OTP)	10,000 (OTP)	0.25	25	
			600 (C_{39})	3,000 (C_{39})	5.0		
8082	Spike		2.5	1,000	0.125	50	# 5
	AR1221		5.0	1000	0.25	50	
	Surrogate		2.5	200	1.25	100	
8270	8270 Spike	# 5	100	1,000	1.00	10	# 4
		# 6	200	2,000	1.00	10	# 4
	Surrogate		100	4,000	2.5	100	
Low-level 8270	8270 Spike	# 5	20	1,000	0.2	10	# 4
		# 6	40	2,000	0.2	10	# 4
	Surrogate		20	4,000	0.5	100	

* These standards are combined in the same flask and diluted to 100 mL to yield a concentration of 100 µg/mL for each of the compounds.

1. ALL compounds are at the above stated concentration with the following exception:
   Compounds 5X the stated concentration:
   4,4'-DDD, 4,4'-DDT, Endofulfan II, Endosulfan sulfate, Endrin.

2. ALL compounds are at the above stated concentration with the following exception:
   Compounds 2X the stated concentration:
   Toxaphene.

3. ALL compounds are at the above stated concentration with the following exception:
   Compounds 100X the stated concentration:
   MCPA, MCPP.

4. All compounds are at the above stated concentration with the following exceptions,
   compounds at 2x the stated concentration: benzoic acid,
   butyl benzyl phthalate, 2-nitroaniline

2-nitrophenol, 2,4-dintrotoulene, 2,6-dintrotoulene, 3-nitroaniline
, 4-nitroaniline
Compounds at 5x the stated concentration: hexachlorocyclopentadiene,
pentachlorophenol
2-methyl-4,6-dinitrophenol, 4-nitrophenol, 2,4-dinitrophenol

5. Aroclor spikes will be rotated through the following list at the concentrations stated in the table: Aroclor 1221, Aroclor 1232, Aroclor 1242, Aroclor 1248, Aroclor 1254, and Aroclor 1016/1260. The next Aroclor in the list will be prepared each time a new standard is made. Each Aroclor must be used within a two year period to meet NELAC and DOD requirements.

Table III. Spike and Surrogate Compounds for Test Method 625/8270

Spike Compound (for 8270/ 625)	Concentration (µg/mL)	Concentration for Low Level Analysis (µg/mL)	Amount added (mL)
1-Chloronaphthalene	100	20	1.0
1,2,4-Trichlorobenzene	100	20	1.0
1,2-Dichlorobenzene	100	20	1.0
1,3-Dichlorobenzene	100	20	1.0
1,4-Dichlorobenzene	100	20	1.0
2,2'-oxybis(1-chloropropane)*	100	20	1.0
2,4,5-Trichlorophenol	100	20	1.0
2,4,6-Trichlorophenol	100	20	1.0
2,4-Dichlorophenol	100	20	1.0
2,4-Dimethylphenol	100	20	1.0
2,4-Dinitrophenol	200	40	1.0
2,4-Dinitrotoluene	200	40	1.0
2,6-Dinitrotoluene	200	40	1.0
2-Chloronaphthalene	100	20	1.0
2-Chlorophenol	100	20	1.0
2-Methylnaphthalene	100	20	1.0
2-Methylphenol	100	20	1.0
2-Nitroaniline	100	20	1.0
2-Nitrophenol	200	40	1.0
3,3'-Dichlorobenzidine	200	40	1.0
3,3'-Dimethylbenzidine	200	40	1.0
3-Nitroaniline	100	20	1.0
3-Methaphenol	100	20	1.0
4,6-Dinitro-2-methylphenol	500	100	1.0
4-Bromophenyl phenyl ether	100	20	1.0
4-Chloro-3-methylphenol	100	20	1.0
4-Chloroaniline	100	20	1.0
4-Chlorophenyl phenyl ether	100	20	1.0
4-Methylphenol	100	20	1.0
4-Nitroaniline	100	20	1.0
4-Nitrophenol	500	100	1.0
Acenaphthene	100	20	1.0
Acetophenone	100	20	1.0
Acenaphthylene	100	20	1.0
Anthracene	100	20	1.0
Atrazine	100	20	1.0
Azobenzene	100	20	1.0
Benzaldehyde	100	20	1.0

Table III. Spike and Surrogate Compounds for Test Method 625/8270 continued…

Spike Compound (for 8270/ 625)	Concentration (µg/mL)	Concentration for Low Level Analysis (µg/mL)	Amount added (mL)
Benzidine	200	40	1.0
Benzyl alcohol	100	20	1.0
Benzo(a)anthracene	100	20	1.0
Benzo(a)pyrene	100	20	1.0
Benzo(b)fluoranthene	100	20	1.0
Benzo(g,h,i)perylene	100	20	1.0
Benzoic Acid	200	40	1.0
Biphenyl	100	20	1.0
Benzo(k)fluoranthene	100	20	1.0
Bis(2-chloroethoxy)methane	100	20	1.0
Bis(2-chloroethyl)ether	100	20	1.0
Bis(2-ethylhexyl)phthalate	100	20	1.0
Butyl benzyl phthalate	200	40	1.0
Carbazole	100	20	1.0
Chrysene	100	20	1.0
n-Decane (C10)	100	20	1.0
DEET	100	20	1.0
Dibenz(a,h)anthracene	100	20	1.0
Dibenzofuran	100	20	1.0
Diethylphthalate	100	20	1.0
Dimethylphthalate	100	20	1.0
Di-n-butyl phthalate	100	20	1.0
Di-n-octyl phthalate	100	20	1.0
epsilon-Caprolactam	100	20	1.0
Fluoranthene	100	20	1.0
Fluorene	100	20	1.0
Hexachlorobenzene	100	20	1.0
Hexachloro-1,3-butadiene	100	20	1.0
Hexachlorocyclopentadiene	500	100	1.0
Hexachloroethane	100	20	1.0
Indeno(1,2,3-cd)pyrene	100	20	1.0
Isophorone	100	20	1.0
Naphthalene	100	20	1.0
Nitrobenzene	100	20	1.0
N-Nitroso-di-n-propylamine	100	20	1.0
N-Nitrosodimethylamine	100	20	1.0
N-Nitrosodiphenylamine	100	20	1.0
n-Octadecane (C18)	100	20	1.0

Table III. Spike and Surrogate Compounds for Test Method 625/8270 continued…

Spike Compound (for 8270/ 625)	Concentration (µg/mL)	Concentration for Low Level Analysis (µg/mL)	Amount added (mL)
Pentachlorophenol	500	100	1.0
Piperonyl butoxide	200	40	1.0
Phenanthrene	100	20	1.0
Phenol	200	20	1.0
Pyrene	100	20	1.0
Pyridine	100	20	1.0
Surrogate Compound			
2,4,6-Tribromophenol	100	20	1.0
2-Fluorobiphenyl	100	20	1.0
2-Fluorophenol	100	20	1.0
Nitrobenzene-d5	100	20	1.0
Phenol-d5	100	20	1.0
Terphenyl-d14	100	20	1.0

* 2,2'-oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl) ether.

Table IV. Spike and Surrogate Compounds for Test Method 8015

Spike Compound	Concentration (µg/mL)	Amount Added (mL)
Diesel Range Hydrocarbon	2500 (sum of 10 compounds in Diesel Range, 250 each)	1.0
Surrogate Compound		
OTP	250	1.0

Table V. Spike and Surrogate Compounds for Test Method FL-PRO

Spike Compound	Concentration (µg/mL)	Amount Added (mL)
Petroleum Hydrocarbon (C_8-C_{40} even)	5,100	1.0
Surrogate Compound		
OTP	100	1.0
Nonatriacontane (C_{39})	600	1.0

Table VI. Spike and Surrogate Compounds for Test Method 8081

Spike Compound	Concentration (µg/mL)	Amount Added (mL)
4,4'-DDD	0.5	1.0
4,4'-DDE	0.5	1.0
4,4'-DDT	0.5	1.0
Aldrin	0.5	1.0
alpha-BHC	0.5	1.0
beta-BHC	0.5	1.0
delta-BHC	0.5	1.0
alpha-Chlordane	0.5	1.0
gamma-Chlordane	0.5	1.0
Dieldrin	0.5	1.0
Endosulfan I	0.5	1.0
Endosulfan II	0.5	1.0
Endosulfan sulfate	0.5	1.0
Endrin	0.5	1.0
Endrin Aldehyde	0.5	1.0
Endrin Ketone	0.5	1.0
gamma-BHC (Lindane)	0.5	1.0
Heptachlor	0.5	1.0
Heptachlor Epoxide	0.5	1.0
Methoxychlor	0.5	1.0
Surrogate Compound		
2,4,5,6-Tetrachloro-m-xylene	2.5	1.0
Decachlorobiphenyl	2.5	1.0

Table VII. Spike and Surrogate Compounds for Test Method 8082

Spike Compound	Concentration (µg/mL)	Amount Added (mL)
Aroclor 1016/1260	2.5	1.0
Aroclor 1221	5.0	1.0
Aroclor 1232	2.5	1.0
Aroclor 1242	2.5	1.0
Aroclor 1248	2.5	1.0
Aroclor 1254	2.5	1.0
Surrogate Compound		
2,4,5,6-Tetrachloro-m-xylene	2.5	1.0
Decachlorobiphenyl	2.5	1.0

APPENDIX DoD
TABLES

DoD Table I. Spike and Surrogate Compounds for Test Method 8081*

Spike Compound	Concentration (µg/mL)	Amount Added (mL)
4,4'-DDD	0.5	1.0
4,4'-DDE	0.5	1.0
4,4'-DDT	0.5	1.0
Aldrin	0.5	1.0
alpha-BHC	0.5	1.0
alpha-Chlordane	0.5	1.0
beta-BHC	0.5	1.0
gamma-Chlordane	0.5	1.0
delta-BHC	0.5	1.0
Dieldrin	0.5	1.0
Endosulfan I	0.5	1.0
Endosulfan II	0.5	1.0
Endosulfan sulfate	0.5	1.0
Endrin	0.5	1.0
Endrin Aldehyde	0.5	1.0
Endrin Ketone	0.5	1.0
gamma-BHC (Lindane)	0.5	1.0
Heptachlor	0.5	1.0
Heptachlor Epoxide	0.5	1.0
Methoxychlor	0.5	1.0
Surrogate Compound		
2,4,5,6-Tetrachloro-m-xylene	2.5	1.0
Decachlorobiphenyl	2.5	1.0

***** For DOD all target analytes must be spiked in the LCS, MS, and MSD. Target analytes are identified by the client on a project-specific basis.

DoD Table II. Spike and Surrogate Compounds for Test Method 8082

Spike Compound	Concentration (µg/mL)	Amount Added (mL)
Aroclor 1016/1260	2.5	1.0
Aroclor 1221	5.0	1.0
Aroclor 1232	2.5	1.0
Aroclor 1242	2.5	1.0
Aroclor 1248	2.5	1.0
Aroclor 1254	2.5	1.0
Surrogate Compound		
2,4,5,6-Tetrachloro-m-xylene	2.5	1.0
Decachlorobiphenyl	2.5	1.0

DoD Table III. Spike and Surrogate Compounds for Test Method 8270

Spike Compound (for 8270)	Concentration (µg/mL)	Amount added (mL)
1,2,4-Trichlorobenzene	100	1.0
1,2-Dichlorobenzene	100	1.0
1,2-Diphenylhydrazine	100	1.0
1,3-Dichlorobenzene	100	1.0
1,4-Dichlorobenzene	100	1.0
2,2'-oxybis(1-chloropropane)*	100	1.0
2,4,5-Trichlorophenol	100	1.0
2,4,6-Trichlorophenol	100	1.0
2,4-Dichlorophenol	100	1.0
2,6-Dichlorophenol	100	1.0
2,4-Dimethylphenol	100	1.0
2,4-Dinitrophenol	200	1.0
2,4-Dinitrotoluene	200	1.0
2,6-Dinitrotoluene	200	1.0
2-Chloronaphthalene	100	1.0
2-Chlorophenol	100	1.0
2-Methylnaphthalene	100	1.0
2-Methylphenol	100	1.0
2-Nitroaniline	100	1.0
2-Nitrophenol	200	1.0
3,3'-Dichlorobenzidine	200	1.0
3-Nitroaniline	100	1.0
3-Methaphenol	100	1.0
4,6-Dinitro-2-methylphenol	500	1.0
4-Bromophenyl phenyl ether	100	1.0
4-Chloro-3-methylphenol	100	1.0
4-Chloroaniline	100	1.0
4-Chlorophenyl phenyl ether	100	1.0
4-Methylphenol	100	1.0
4-Nitroaniline	100	1.0
4-Nitrophenol	500	1.0
Acenaphthene	100	1.0
Acetophenone	100	1.0
Acenaphthylene	100	1.0
Anthracene	100	1.0
Benzidine	200	1.0
Benzyl Alcohol	100	1.0

DoD Table III. Spike and Surrogate Compounds for Test Method 8270 continued…

Spike Compound (for 8270)	Concentration (µg/mL)	Amount added (mL)

Benzo(a)anthracene	100	1.0
Benzo(a)pyrene	100	1.0
Benzo(b)fluoranthene	100	1.0
Benzo(g,h,i)perylene	100	1.0
Benzoic Acid	200	1.0
Benzo(k)fluoranthene	100	1.0
Bis(2-chloroethoxy)methane	100	1.0
Bis(2-chloroethyl)ether	100	1.0
Bis(2-ethylhexyl)phthalate	100	1.0
Butyl benzyl phthalate	200	1.0
Carbazole	100	1.0
Chrysene	100	1.0
Dibenz(a,h)anthracene	100	1.0
Dibenzofuran	100	1.0
Diethylphthalate	100	1.0
Dimethylphthalate	100	1.0
Di-n-butyl phthalate	100	1.0
Di-n-octyl phthalate	100	1.0
Fluoranthene	100	1.0
Fluorene	100	1.0
Hexachlorobenzene	100	1.0
Hexachloro-1,3-butadiene	100	1.0
Hexachlorocyclopentadiene	500	1.0
Hexachloroethane	100	1.0
Indeno(1,2,3-cd)pyrene	100	1.0
Isophorone	100	1.0
Naphthalene	100	1.0
Nitrobenzene	100	1.0
N-Nitroso-di-n-propylamine	100	1.0
N-Nitrosodimethylamine	100	1.0
N-Nitrosodiphenylamine	100	1.0
N-Nitrosopyrrolidine	100	1.0
Pentachlorophenol	500	1.0
Piperonyl butoxide	200	1.0
Phenanthrene	100	1.0
Phenol	200	1.0
Pyrene	100	1.0

DoD Table III. Spike and Surrogate Compounds for Test Method 8270 continued…

Surrogate Compound	Concentration (µg/mL)	Amount added (mL)
2,4,6-Tribromophenol	100	1.0

2-Fluorobiphenyl	100	1.0
2-Fluorophenol	100	1.0
Nitrobenzene-d5	100	1.0
Phenol-d5	100	1.0
Terphenyl-d14	100	1.0

SHEALY ENVIRONMENTAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

GC/MS ANALYSIS BASED ON EPA METHOD 8270D

PREPARED BY EPA METHODS 3520C, 3550C AND 3580A

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SCOPE AND APPLICATION

1.1 This method is based upon SW846 8270D, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. Direct injection of a sample may be used in limited applications. Refer to Tables I, II, III-A, and III-B for the list of Shealy compounds and Table DoD-I for Navy compounds applicable for this method. Additional compounds may be amenable to this method. If non-standard analytes are required, they must be validated by the procedures described in Section 13 before sample analysis may begin.

1.2 The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.

- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.

- Pentachlorophenol, α,α-Dimethylphenethylamine, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 2,4-dinitrophenol, 4-chloro-3-methyphenol, P-phenylenediamine, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

- Hexachlorophene is not amenable to analysis by this method.

- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method.

1.3 The standard reporting limit (SRL) of this method for determining an individual compound is approximately 0.33 mg/Kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent of matrix and method of preparation), and 5 µg/L for groundwater samples. Some compounds have higher reporting limits. Refer to Tables I and II for specific PQLs. Reporting limits will be proportionately higher for sample extracts that require dilution.

SUMMARY OF METHOD

2.1 Aqueous samples are extracted with methylene chloride using continuous liquid/liquid extraction. Solid samples are extracted with methylene chloride/acetone using sonication. Waste dilution is used for samples that are miscible with solvent. The extract is dried, concentrated to a volume of 1, 2, or 5 mL, and analyzed by GC/MS. Extraction procedures are detailed in Methods 3520C and 3550C. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

DEFINITIONS

3.1 Batch – The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a laboratory control sample (LCS), and a method blank (MB). In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Batches are defined at the sample preparation stage. Preparation batches should be kept together through the entire analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the Shealy Quality Assurance Management Plan (QAMP) for further details of the batch definition.

3.2 Relative Response Factor (RRF) – A measure of the relative mass spectral response of an analyte compared to its internal standard. RRFs are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

3.3 Method Blank – A quality control sample consisting of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

3.4 LCS (Laboratory Control Sample) – A blank spiked with the parameters of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.5 MS (Matrix Spike) – Aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.6 MSD (Matrix Spike Duplicate) – A second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method.

3.7 ICV (Initial Calibration Verification) / Second Source Calibration Verification – A standard that is prepared from a different source than the initial calibration standards. The ICV is analyzed after the initial calibration and is used to verify the accuracy of the calibration.

3.8 CCV (Continuing Calibration Verification) – A standard prepared from the same parent standard as the initial calibration. The CCV is used to verify that the instrument response is reliable, and has not changed significantly from the initial calibration curve being used.

3.9 The definitions of any additional terms used in this SOP may be found in the Shealy Quality Assurance Management Plan (QAMP).

INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control Section. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If interference is detected, it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2 The use of high purity reagents, solvents, and gases helps to minimize interference problems. Refer to P-QA-006 Solvent Purity Check policy for the procedure for testing the purity of solvents used for extraction.

4.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples.

4.5 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all Shealy associates. The following requirements must be met:

5.2 As stated in the Shealy Comprehensive Chemical Hygiene, Safety, and Hazard Communication Plan (P-HS-003), eye protection that satisfies ANSI Z87.1, laboratory coat, and at least latex gloves must be worn while samples, standards, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.3.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Methylene chloride, benzo(a)anthracene, benzidine, 3,3'-Dichlorobenzidine, n-nitrosodimethylamine, dibenzo(a,h)anthracene, and benzo(a)pyrene. Primary standards should be purchased in solution. If neat materials must be obtained, they shall be handled in a hood.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers should be kept closed unless transfers are being made.

5.5 All work must be stopped in the event of a known or potential compromise to the health and safety of a Shealy associate. The situation must be reported immediately to a laboratory supervisor.

EQUIPMENT AND SUPPLIES

6.1 Gas Chromatograph/Mass Spectrometer System – An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.1.1 System One
HP6890 GC/5973 MSD

6.1.2 System Two
HP6890 GC/5975N MSD

6.1.3 System Three
HP6890N GC/5975N MSD

6.2 Column – 30 m × 0.25 mm I.D. (or 0.20 mm I.D.) 0.5-µm film thickness silicon-coated fused-silica capillary column (Agilent DB-5MS or equivalent). Alternate

columns [Agilent DB-5.625MS (20 m × 0.18 mm ID × 0.36-µm film thickness)] are acceptable if they provide acceptable performance.

6.3 Mass Spectrometer – Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table V when 50 ng of the GC/MS tuning standard is injected through the GC.

6.4 GC/MS Interface – Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5 Data System – A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.6 Syringe – 10 µL or 5 µL Hamilton Laboratory grade syringes or equivalent.

6.7 Carrier gas – Ultra high purity helium.

REAGENTS AND STANDARDS

7.1 A minimum five-point calibration curve is prepared. The low point should be at or below the reporting limit. Refer to Tables X-A and X-B for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2 An initial calibration standard (ICV) is prepared from a source independent of the source of standards prepared for the initial calibration. The concentration of the ICV should be at or near the middle of the calibration range. Refer to Table XI for ICV compounds and criteria for Shealy primary standard and Table DoD-VII for Navy ICV compounds and criteria.

7.3 Continuing calibration verification (CCV) is a standard prepared from the same source as the standards for the initial calibration. The CCV is the verification of the initial calibration that is required during the course of analysis at periodic intervals. Refer to Tables XII-A, and XII-B for the list of CCV compounds and acceptance

criteria. Navy CCV compound list and acceptance criteria are found in Table DoD-VIII.

7.4 An Internal Standard solution is prepared. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1, 4-dichlorobenzene-d5, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.2.1 Internal Standards are added to all standards and extracts to results in 40 ng injected onto the column. For example, if the volume of an extract used were 1 ml, 10 µL of a 4000 µg/mL internal standard solution would be added for a 1 µL injection.

7.3 Surrogate Standard Spiking Solution – Prepare as indicated in the preparative methods. All standards prepared for surrogate, LCS, and matrix spiking solutions must be analyzed by GC/MS prior to use for sample extraction. See appropriate preparation SOP. Surrogate compounds are listed in Table IX. Navy surrogate compounds and control limits listed in Table DoD-II.

7.4 GC/MS Tuning Standard: A methylene chloride solution containing 25 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT, should also be included in the Tuning Standard at 25 µg/mL.

7.5 Laboratory Control Spiking Solution – Prepare as indicated in the preparative methods. All standards prepared for surrogate, LCS, and matrix spiking solutions must be analyzed by GC/MS prior to use for sample extraction. See appropriate preparation SOP. LCS compounds and levels are listed in Tables VII and VIII. Navy specific LCS/MS compounds and control limits are found in Table DoD-III for aqueous samples and DoD-IV for solid samples.

7.6 Matrix Spike Solution – Prepare as indicated in the preparative methods. See preparation SOP. The matrix spike compounds and levels are the same as the LCS compounds.

7.7 The standards listed in 7.1 to 7.6 should be refrigerated at ≤ 10 °C when not in use. Refrigeration at –10°C to –20°C may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once every six months. The calibration verification standard must be prepared every week.

SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Aqueous samples are collected in two 1-liter amber glass containers. Solid samples are collected in a 4 oz glass container. Samples are stored at 4 ± 2°C.

8.2 Aqueous samples are extracted within 7 days of collection. Solid samples are extracted within 14 days of collection. The extracts should be analyzed within 40 days of extraction.

QUALITY CONTROL

9.1 Initial Demonstration of Capability

9.1.1 For the standard analyte list, the initial demonstration and method detection limit (MDL) studies (performed yearly) described in the Shealy QAMP must be acceptable before analysis of samples may begin.

9.1.2 For non-standard, non-regulatory analytes, an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration suggested is the analysis of an extracted standard at the reporting limit and a five point calibration curve.

9.2 Batch Definition – Batches are defined at the sample preparation stage. Batches should be kept together through the entire analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the QAMP for further details of the batch definition.

9.2.1 Quality Control Batch – The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch should contain a matrix spike/spike duplicate (MS/MSD), a laboratory control sample (LCS), and a method blank (MB). Laboratory generated QC samples (MB, LCS and MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count but cannot be used for matrix spikes. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and a sample duplicate.

9.3 Control Limits – **In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS/LCSD).** These limits must be determined annually. The recovery limits are mean recovery ± 3 standard deviations. Control limits for compliance with the Department of Defense Quality Systems Manual can be found in Appendix DoD.

9.3.1 All surrogate, LCS/D, and MS/D recoveries must be entered into Shealy LIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions not greater than five.

9.3.2 Refer to the QAMP for further details of control limits.

9.4 Method Blank (Laboratory Reagent Blank) – One method blank must be processed with each preparation and/or analytical batch. The method blank consists of a similar matrix to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results. The method blank is to contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

9.4.1 The method blank must not contain any analyte of interest at or above the PQL. If the method blank contains an analyte of interest at or above the PQL, then the method blank and associated samples must be reanalyzed. If the method blank contamination is confirmed, the entire batch must be re-prepared and reanalyzed. The following exceptions apply:

9.4.1.1 If the method blank contains analytes of interest at or above the PQL, then:

9.4.1.1.1 The method blank concentration must be less than 5% of the regulatory limit associated with that analyte for that sample. If not, re-prep and reanalyze all samples which do not fall within this criterion.

9.4.1.1.2 The method blank contamination must be < 5% of the sample concentration. If not, re-prep and reanalyze all samples which do not fall within this criterion.

9.4.2 To clarify the compounds of interest that are associated with each sample the LIMS generated worksheet printout for each sample will be contained in the batch data file. This worksheet printout will list the required target compounds and the reporting limits.

9.4.3 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, sample analysis should stop immediately. Corrective action should be taken. The method blank should be reanalyzed if the analyst feels that the failure could be attributed to instrument problems. If the analyst feels that the failure is due to a poor extraction, entire batch must be sent for re-extraction.

9.5 Instrument Blank – Instruments must be evaluated for contamination during each 12-hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. Surrogate

standards may be added to the instrument blank for additional quality control. The instrument blank is evaluated in the same way as the method blank.

9.6 Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD) – Analyze an LCS for each batch of samples. If an MS/MSD pair is not performed, an LCS/LCSD pair must be performed. The LCS and LCSD are prepared in the same manner. Both the LCS and LCSD should contain a full analyte spike of the analytes of interest, and must contain the same analytes as the matrix spike. **The LCS/D is of a different source than the ICAL**. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will be the re-preparation and reanalysis of the batch.

9.6.1 LCS compounds are included in Table VII with appropriate spike concentrations.

9.6.2 Some clients require a full analyte spike list for the LCS. The added compounds must be statistically evaluated to determine if the in-house recovery limits are achievable and realistic.

9.7 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are the same as the LCS/D. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory specific generated limits.

9.7.1 If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check all calculations. If the calculations are correct, check the recovery of that analyte in the Laboratory Control Sample (LCS). If the recovery of the analyte in the LCS is within limits, then matrix interference has been demonstrated and the laboratory operation may proceed.

9.7.2 If the recovery for any component is outside QC limits for the matrix spike/spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will include re-preparation and reanalysis of the batch. An NCM must be generated to document this occurrence.

9.7.3 Every effort is made to ensure that an MS/MSD pair is included in every batch. On the rare occasion that one is not possible (sample bottle was broken, etc.) then an LCSD (duplicate) must be analyzed.

9.7.4 The matrix spike/spike duplicate must be analyzed at the same dilution as the most concentrated reportable analysis as the parent sample (the un-spiked sample).

9.8 Surrogates

9.8.1 Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the percent recovery falls within the required limits. Surrogate compounds must be spiked at either 100 or 150 ng on-column, depending on the surrogate. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table IX. Refer to Table DoD-II for Navy specific surrogate concentrations and acceptance criteria.

9.8.2 If any surrogate is outside the acceptance limits, an NCM must be written and the following corrective actions must take place (except for dilutions ≥ 5 x).

- Check all calculations for error.
- Ensure that instrument performance is acceptable. If the system is demonstrated to be out of control, all steps taken to return the system to control must be fully documented as part of the corrective action.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveals a problem.
- If the above corrective actions have taken place and the result is a surrogate that is outside of the limits, re-extract and reanalyze the sample. If the re-extract is outside of limits, flag the data as "Estimated Concentration" due to demonstrated matrix effect.
- It is only necessary to re-extract/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.9 Nonconformance and Corrective Action – Any deviations from QC procedures must be documented as an NCM, with applicable cause and corrective action approved by the QA Manager.

9.10 Quality Assurance Summaries – Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.11 Shealy QC Program – Further details of QC and corrective action guidelines are presented in the Shealy QAMP. Refer to this document if the samples are from a state other than South Carolina, or if the samples are for non-regulatory reporting. If samples are being analyzed for the Department of Defense, refer to the DoD Quality Systems Manual for additional information.

CALIBRATION AND STANDARDIZATION

10.1 Summary – The instrument is tuned for DFTPP, calibrated and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table V.

10.2 All standards and extracts are allowed to warm to room temperature before injecting.

10.3 Instrument Tuning – At the beginning of every twelve hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (Table V) are achieved for DFTPP (decafluorotriphenylphosphine).

10.3.1 Inject 50 ng of the GC/MS tuning standard (Section 7.4) into the GC/MS system. The mass spectrum of DFTPP must be acquired in the following manner: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the beginning of the elution of DFTPP. Do not subtract part of the DFTPP peak.. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. Any maintenance or adjustments to the instrument and the acceptable standard file name must be documented to show that the system has returned to control. The performance criteria in Table V must be achieved before any samples, blanks, or standards are analyzed.

10.3.2 The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. Benzidine and pentachlorophenol should not exhibit excessive tailing. The tailing factor for benzidine and for pentachlorophenol should be ≤ 2

10.3.3 If DDT is an analyte of interest, it must be included in the tuning standard, and it breakdown must be $\leq 20\%$. Refer to Section 12 for the appropriate calculations.

10.4 Initial Calibration

10.4.1 Internal Standard Calibration Procedure – Internal standards are listed in Table VI-A. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.4.2 Compounds should be assigned to the IS with the closest retention time.

10.4.3 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor response. Add the internal standard mixture to result in 40 ng on column or 20 ng on column if a 0.5ul injection is used. (For example, if the volume of the calibration standard used is 1 mL, add 10 µL of the 4000 µg/mL internal standard solution for a 1µL injection). The concentrations of all analytes are listed in Tables X-A and X-B.

10.4.4 Several sub-lists are used to encompass all target compounds listed in this SOP. The compounds in each sub-list match the compounds in each mix. A single sub-list can be recalibrated at any time without recalibrating the entire method list. If a sub-list is recalibrated, all compounds within that mix must be calibrated for all levels of the curve (all levels that apply to each particular compound). A calibration history must be generated from Target to trace when each sub-list has been recalibrated.

10.4.5 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in Sections 12.5.1 and 12.5.3. **The ICAL cannot be forced through zero. No sample analysis may be performed unless these criteria are met.**

10.4.6 The Mean Relative Response Factor must be calculated for all compounds using the equation in 12.5.1. Calculate the Percent Relative Standard Deviation (%RSD) of the RRF values for the initial calibration using the equation in 12.5.3. If the % RSD of any analyte in the initial calibration is ≤ 20%, then average response factor may be used for quantitation. For those analytes with a %RSD >20%, a linear curve fit may be used. The correlation coefficient must be ≥ 0.995. The Target data system measures the square of the correlation coefficient, which must be ≥ 0.990.

10.4.7 Up to 10% of the compounds in the initial calibration are allowed to fail the criteria in section 10.4.6. Any data generated by the use of the RRF from a calibration that does not meet the above criteria must be qualified as estimated and used for screening data only. In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit.

10.4.7.1 For any regulatory compliance samples, all target project compounds must meet the initial calibration criteria in section 10.4.6.

10.4.8 Demonstration of sensitivity: For compounds that require a linear fit, the low point of the ICAL must be reprocessed against the ICAL it is a pat of.

Treat the low point as an unknown sample and recalculate the concentrations. The low point concentrations for compounds using a linear fit should be 70-130% of the true value. Compounds that do not meet this criteria should be considered out of control and corrective action must b taken such as re-defining the lower limit of quantitation and/or reporting those "out of control" compounds as estimated values when the concentration is near the low point when the data quality requirements of a project dictate such a need.

10.4.9 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) for alternative curve fits, the system is considered too reactive and corrective action must be taken and the initial calibration re-analyzed.

10.4.10 The relative response factor (RRF) at each calibration concentration for each semivolatile target compound must be greater than or equal to the compound's minimum acceptable relative response factor listed in Table VI.

10.4.11 If time remains in the 12-hour period initiated by the DFTPP injection, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.12 Quantitation is performed using the calibration curve or average response factor from the initial curve, not the continuing calibration.

10.5 Initial Calibration Verification (Second Source Calibration Verification) - A standard that is prepared from a source independent of standards for the initial calibration. The ICV contains all TCL compounds and its concentration should be at or near the mid level of the initial calibration. The concentration of the ICV, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. For most compounds, the recovery should be between 70-130%. Any compounds failing to meet the 70-130% recovery will be documented with an NCM. These compounds will not be reported for any samples analyzed under this ICV until another passing ICAL and ICV are processed. The ICV must be analyzed after the ICAL and before sample analysis can begin.

10.6 Continuing Calibration Verification (Instrument Performance Check) –

10.6.1 At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 50 ng or less injection of DFTPP must result in a mass spectrum which meets the criteria given in Table V. The tailing factors for benzidine and pentachlorophenol should meet criteria described in Section 10.3.2. If the analytical sequence contains only base fraction or acid fraction samples, only the tailing factor for benzidine need to be evaluated for base fraction sample, or pentachlorophenol for acid fraction.

10.6.2 Following a successful DFTPP analysis, the continuing calibration verification (CCV) standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A continuing calibration standard is analyzed for each sub-list at or near the mid-point of the curve. These concentrations are varied weekly to verify the ICAL.

10.6.3 The following criteria must be met for the continuing calibration to be acceptable:

10.6.3.1 Each of the analytes in the calibration verification standard must meet the minimum response factors as noted in Table 4. This is the same check that is applied during the initial calibration.

10.6.3.2 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.

10.6.3.3 Calculate the percent drift or percent difference of the response factors for each target analyte using the equations in 12.5.4. The percent drift or percent difference should be less than or equal to 20% for each target analyte.

10.6.3.4 Up to 10% of the compounds in the continuing calibration are allowed to fail the criteria in section 10.6.3.3. Any data generated by the use of the RRF from a calibration that does not meet the above criteria must be qualified as estimated and used for screening data only. In order to report non-detects, it must be demonstrated that there is adequate sensitivity to detect the failed compounds at the applicable lower quantitation limit. In addition, if there are DoD samples to be analyzed, the percent difference or drift of all required analytes must within the limits set in Tables XII-A, B, and Table DoD-VIII (Navy). For any regulatory compliance samples, all target project compounds must meet the continuing calibration validation criteria in section 10.6.3.3.

10.6.3.4.1 Any analyte that is not a target compound is not required to pass the above criteria.

10.6.3.4.2 To clarify the compounds of interest that are associated with each sample, the LIMS generated worksheet printout for each sample will be contained in the batch data file. This worksheet printout will list the required target compounds and the reporting limits.

10.6.3.5 The internal standard response must be within 50-200% of the response in the mid-level of the initial calibration.

10.6.3.5.1 The internal standard retention times must be ± 30 seconds of the retention times in the mid-level of the initial calibration.

10.6.4 Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the DFTPP have passed.

PROCEDURE

11.1 Sample Preparation – See SOP S-EX-003, Continuous Liquid-Liquid Extraction, and S-EX-005, Ultrasonic Extraction, for appropriate preparation method.

11.2 Sample Analysis Procedure

11.2.1 Calibrate the instrument as described in Section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2 All samples must be analyzed using the same instrument conditions as the preceding continuing calibration standard.

11.2.3 Add internal standard to the extract to result in 40 ng injected on column (for example, 10 µL internal standard solution in 1 mL of extract for a 1 µL injection). Mix thoroughly before injection into the instrument.

11.2.4 Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.

11.2.5 The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in Section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.2.6 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system.

11.2.7 Target compounds identified by the data system are evaluated using the criteria listed in Section 12.1.

11.2.8 Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TICs) may be performed if requested by the client. They are evaluated using the criteria in Section 12.5.2.

11.3 Dilutions – If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range, or close to the CCV concentration. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.3.1 Guidance for Dilutions Due to Matrix – If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgment. For example, samples containing organic acids or are too viscous to allow proper injection into the inlet, may need to be analyzed at a higher dilution to avoid destroying the column or damaging the injection syringe.

11.3.2 Reporting Dilutions – The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.4 Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at 4 ± 2°C, protected from light in Teflon-lined screw cap vials.

11.5 Internal standard criteria for samples:

11.5.1 If the retention time for any internal standard changes by more than ± 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.5.2 If the retention time of any internal standard in any sample varies by more than ± 0.1 minute from the preceding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

11.5.3 The internal standard response must be within 50 – 200% of the response in the last continuing calibration standard.

11.6 Percent Moisture – Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP S-IN-023 for determination of percent moisture.

11.7 Troubleshooting Guide

11.7.1 Daily Instrument Maintenance – In addition to the checks listed in the instrument maintenance schedule in the Shealy QAMP, the following daily maintenance should be performed:

- Clip column as necessary.
- Install new or cleaned injection port liner as necessary.
- Install new septum as necessary.
- Perform mass calibration as necessary.

11.7.2 Major Maintenance – A new calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the ion volume or repeller, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

All maintenance performed must be recorded in the instrument maintenance log with each entry dated and initialed by the analyst that is performing the maintenance.

11.8 Procedural Variations – This Section applies to all samples except South Carolina compliance samples. One time procedural variations are allowed, only if deemed necessary in the professional judgment and supervision of a knowledgeable analyst, to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in analytical procedure must be approved by a technical director, the QA Officer, or the client, and must be fully documented (flagged and/or narrated) on the final report. The analyst must use an NCM to notify the appropriate parties and to document the variance. The project manager uses the information on

the NCM to notify the client and flag/narrate the final report accordingly. A copy of the NCM is kept with the raw data and the original is filed with the final report.

11.8.1 For South Carolina compliance samples, all procedures outlined in this SOP must be followed without exception. In the event that a deviation from this SOP cannot be avoided (i.e., demonstrated and uncorrectable matrix interference, non-compatible matrix, insufficient sample amount due to client or laboratory error) it is imperative that an NCM is completed that clearly documents the anomaly. This anomaly must be communicated to the client such that corrective action activity including sample recollection can be performed. Based upon the type and severity of anomaly, the results may not be appropriate for compliance reporting. Discussions between the client, the appropriate regulatory authority, and Shealy will be necessary to resolve certain anomalies. In any case, it is essential that any anomaly be documented on an NCM.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative identification – An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The retention time window position is established for each analyte and surrogate once per ICAL. The position shall be set using the mid-point standard of the initial calibration curve.

- The RRT of each target analyte in each calibration standard must be within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same twelve hour time period as the sample.

- The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

- The relative intensities of ions should agree to within ± 30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

12.1.1 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.1.1.1 If an alternate compound was selected by the analyst, the compound will be flagged with an "H" by Target®.

12.1.1.2 If a compound fails the ration test, the compound will be flagged with a "Q" by Target®.

12.2 Mass chromatogram searches – Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 10-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte, a mass chromatogram search is made.

- Hexachlorophene – Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes after chrysene-d12. If peaks for both ions coincide then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.

12.3 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 type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

- The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30% and 70%.)

- Molecular ions present in the reference spectrum should be present in the sample spectrum.

- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of co-eluting compounds.

- Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of

background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

- Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

12.4 Anyone evaluating data is trained to know how to handle isomers with identical mass spectra and close elution times. These include:

Chloronaphthalenes
Dichlorobenzenes
Methylphenols, benzyl alcohol
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Extra precautions concerning these compounds are to more closely scrutinize retention time vs. the calibration standard and also to check that all isomers have distinct retention times.

A second category of problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol
α,α-Dimethylphenethylamine
p-Phenylenediamine

Manually checking the integrations would be appropriate for these compounds. All manual integration chromatograms must be printed and must include the reason for the integration, the date the integration was performed, and the initials of the analyst performing the manual integration. This information should be included in the final data package.

12.5 Calculations

12.5.1 Relative response factor calculation:

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

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_x = Concentration of the compound being measured (µg/L).

C_{is} = Concentration of the specific internal standard (µg/L).

12.5.2 Calculation of TICs – The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x = Area of the total ion chromatogram for the compound being measured.

A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference.

RF = 1.

12.5.3 Percent Relative Standard Deviation for Initial Calibration:

$$\%RSD = \frac{SD}{\overline{RF}} x100$$

$\overline{RF}$ = Mean of RFs from initial calibration for a compound.

SD = Standard deviation of RFs from initial calibration for a compound.

$$= \sqrt{\sum_{i=1}^{N} \frac{(RFi - \overline{RF})^2}{N - 1}}$$

Rf *i* = RF for each of the calibration levels.

N = Number of RF values.

12.5.4 Continuing calibration percent difference and percent drift:

$$\%Diff = \frac{RF - \overline{RF}}{\overline{RF}} x100$$

RF = Compound's response factor in the CCV.

$\overline{RF}$ = Compound's average response factor in the initial calibration.

$$\% \text{ Drift} = \frac{\text{Calculated Conc.} - \text{Theoretical Conc.}}{\text{Theoretical Conc.}} \text{ x } 100$$

12.5.5 Concentration in the extract – The concentration of each identified analyte and surrogate in the extract is calculated from the linear curve fitted to the initial calibration points, or from the average RF of the initial calibration.

12.5.5.1 Average response factor – If the %RSD of the response factors in the initial calibration is ≤ 20%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is}\,\overline{RF}}$$

12.5.5.2 Linear fit:

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

C_{ex} = Concentration in extract, µg/mL.

R_x = Response for analyte.

R_{is} = Response for internal standard.

C_{is} = Concentration of internal standard.

A = Intercept.

B = Slope.

12.5.6 The concentration in the sample is then calculated:

12.5.6.1 Aqueous calculation:

$$\text{Concentration, } \mu g/L = \frac{C_{ex}V_t}{V_o}$$

V_t = Volume of total extract, µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1 mL extract will mean V_t = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, V_t = 2,000 µL.) .

V_o = Volume of water extracted (mL).

12.5.6.2 Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis:

$$\text{Concentration, } g/kg = \frac{C_{ex}V_t}{W_sD}$$

W_s = Weight of sample extracted or diluted in grams.

D = (100 - % moisture in sample)/100, for a dry weight basis or 1 for a wet weight basis.

12.5.7 MS/MSD percent recovery calculation:

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

S_{SR} = Spike sample result.

S_R = Sample result.

S_A = Spike added.

12.5.8 Relative % Difference calculation for the MS/MSD:

$$RPD = \frac{MS_R - MSD_R}{½ (MS_R + MSD_R)} \times 100$$

RPD = Relative percent difference.

MS_R = Matrix spike result.

MSD_R = Matrix spike duplicate result.

METHOD PERFORMANCE

13.1 Method Detection Limit – The laboratory must generate a valid method detection limit for each analyte of interest on an annual basis or when there has been a major system change. These changes would include new instrumentation, change in prep volume, or injection volume. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in Shealy QAMP.

13.2 Initial Demonstration – Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests, it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be 100ug/L.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in Table XIV.

13.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3 Non-standard analytes – For non-standard analytes, an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the

minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

13.4 Training Qualification – The team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.5 Data Quality Objectives (DQO) – Refer to project-specific Quality Assurance plans for DQO information.

POLLUTION PREVENTION

14.1 Not applicable to this procedure.

WASTE MANAGEMENT

15.1 Waste generated in the procedure must be segregated and disposed of according to the Shealy Waste Management Plan and per the local, state, and federal regulations. The Safety Officer should be contacted, if additional information is required.

15.2 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

REFERENCES

16.1 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry GC/MS, Method 8270D and 8000B.

16.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996, Section 3520C, and 3550C.

16.3 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Sample Preparation for Organic Volatile Compounds, Method 3580A

16.4 J.W. Eichelberger, L.E. Harris, and W.L. Budde, “Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry”, Analytical Chemistry, 47, 995 (1975).

16.5 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 3, January 2006.

16.6 Shealy Quality Assurance Management Plan (QAMP), Q-QA-001, Revision 4, July 16, 2008

MISCELLANEOUS

17.1 Modifications from Reference Method:

17.1.1 The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.1.2 Directions for analysis of PAH only samples are in Attachment B.

17.1.3 Department of Defense method requirements are in Appendix DoD.

APPENDIX A – TABLES

TABLE I. Shealy Primary Standards* and Standard Reporting Limits

Analyte	CAS number	Limits Aqueous µg/L	Low Soil/Sediment µg/kg
1-Chloronaphthalene	90-13-1	5	330
1,2,4-Trichlorobenzene	120-82-1	5	330
1,2-Dichlorobenzene	95-50-1	5	330
1,3-Dichlorobenzene	541-73-1	5	330
1,4-Dichlorobenzene	106-46-7	5	330
2,2'-oxybis(1-chloropropane)**	108-60-1	5	330
2,4,5-Trichlorophenol	95-95-4	5	330
2,4,6-Trichlorophenol	88-06-2	5	330
2,4-Dichlorophenol	120-83-2	5	330
2,4-Dimethylphenol	105-67-9	5	330
2,4-Dinitrophenol	51-28-5	25	830
2,4-Dinitrotoluene	121-14-2	10	330
2,6-Dinitrotoluene	606-20-2	10	330
2-Chloronaphthalene	91-58-7	5	330
2-Chlorophenol	95-57-8	5	330
2-Methylnaphthalene	91-57-6	5	330
2-Methylphenol	95-48-7	5	330
2-Nitroaniline	88-74-4	10	330
2-Nitrophenol	88-75-5	10	330
3,3'-Dichlorobenzidine	91-94-1	5	330
3,3'-Dimethylbenzidine	119-93-7	5	330
3-Nitroaniline	99-09-2	10	330
4,6-Dinitro-2-methylphenol	534-52-1	25	830
4-Bromophenyl phenyl ether	101-55-3	5	330
4-Chloro-3-methylphenol	59-50-7	5	330
4-Chloroaniline	106-47-8	5	330
4-Chlorophenyl phenyl ether	7005-72-3	5	330
3 & 4-Methylphenol	106-44-5	10	330
4-Nitroaniline	100-01-6	10	330
4-Nitrophenol	100-02-7	25	830
Acenaphthene	83-32-9	5	330
Acenaphthylene	208-96-8	5	330
Anthracene	120-12-7	5	330
Azobenzene	103-33-3	5	330
Benzidine	92-87-5	5	330

Benzoic Acid	65-85-0	10	330
Benzo(a)anthracene	56-55-3	5	330

TABLE I. Shealy Primary Standards* and Standard Reporting Limits (continued)

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Benzo(a)pyrene	50-32-8	5	330
Benzo(b)fluoranthene	205-99-2	5	330
Benzo(g,h,i)perylene	191-24-2	5	330
Benzo(k)fluoranthene	207-08-9	5	330
Bis(2-Chloroethoxy)methane	111-91-1	5	330
Bis(2-chloroethyl)ether	111-44-4	5	330
Bis(2-ethylhexyl)phthalate	117-81-7	5	330
Butyl benzyl phthalate	85-68-7	10	330
Carbazole	86-74-8	5	330
Chrysene	218-01-9	5	330
DEET	134-62-3	5	330
Dibenz(a,h)anthracene	53-70-3	5	330
Dibenzofuran	132-64-9	5	330
Diethylphthalate	84-66-2	5	330
Dimethyl phthalate	131-11-3	5	330
Di-n-butyl phthalate	84-74-2	5	330
Di-n-octylphthalate	117-84-0	5	330
Fluoranthene	206-44-0	5	330
Fluorene	86-73-7	5	330
Hexachlorobenzene	118-74-1	5	330
Hexachlorobutadiene	87-68-3	5	330
Hexachlorocyclopentadiene	77-47-4	25	830
Hexachloroethane	67-72-1	5	330
Indeno(1,2,3-cd)pyrene	193-39-5	5	330
Isophorone	78-59-1	5	330
Naphthalene	91-20-3	5	330
Nitrobenzene	98-95-3	5	330
N-Nitroso-di-n-propylamine	621-64-7	5	330
N-Nitrosodimethylamine	62-75-9	5	330
N-Nitrosodiphenylamine	86-30-6	5	330
Pentachlorophenol	87-86-5	25	830
Phenanthrene	85-01-8	5	330
Phenol	108-95-2	5	330
Piperonyl butoxide	51-03-6	10	330
Pyrene	129-00-0	5	330
Pyridine	110-86-1	5	330

*The Shealy primary standard is the standard normally used at Shealy. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.

**2,2'-oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether.

TABLE II. Shealy Appendix IX Standard* and Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
1,2,4,5-Tetrachlorobenzene	95-94-3	5	33
1,3,5-Trinitrobenzene	99-35-4	25	830
1,3-Dinitrobenzene	99-65-0	25	830
1,4-Dioxane	123-41-1	5	33
1,4-Naphthoquinone	130-15-4	10	67
1-Chloronaphthalene	90-13-1	5	330
1-Methylnaphthalene	90-12-0	5	33
1-Naphthylamine	134-32-7	5	33
2,3,4,6-Tetrachlorophenol	58-90-2	10	67
2,6-Dichlorophenol	87-65-0	5	33
2-Acetylaminofluorene	53-96-3	25	67
2-Naphthylamine	91-59-8	5	33
2-Picoline	109-06-8	5	33
3,3'-Dimethylbenzidine	119-93-7	25	830
3-Methylchloanthrene	56-49-5	10	67
4-Aminobiphenyl	62-67-1	10	67
4-Nitroquinoline-1-oxide	56-57-5	25	170
5-Nitro-o-toluidine	99-55-8	10	67
7,12-Dimethylbenz(a)anthracene	57-97-6	5	33
a,a-Dimethyl-phenethylamine	122-09-8	50	67
Acetophenone	98-86-2	5	33
Aniline	62-53-3	5	33
Aramite	140-57-8	25	170
Atrazine	1912-24-9	5	33
Azobenzene****	103-33-3	5	330
Benzaldhyde	100-52-7	5	33
Benzidine	92-87-5	25	830
Benzoic Acid	65-85-0	50	1700
Benzyl alcohol	100-51-6	5	33
Caprolactam	105-60-2	5	33
Chlorobenzilate	510-15-6	10	67
Diallate***	2303-16-4	10	67
Diallate-isomer1	2303-16-4	10	67
Diallate-isomer2	2303-16-4	10	67
Dichlorofenthion	97-17-6	5	33
Dimethoate**	60-51-5	10	67

Dinoseb	88-85-7	5	33
Disulfoton**	298-04-4	5	33
Ethyl methanesulfonate	62-50-0	5	33
Ethyl Parathion	56-38-2	25	170
Famphur***	52-85-7	25	830

TABLE II. Shealy Appendix IX Standard* and Standard Reporting Limits (continued)

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Hexachloroproprene	1888-71-7	10	33
Isodrin***	465-73-6	5	33
Isosafrole	120-58-1	5	33
m-Dinitrobenzene	99-65-0	10	67
Methapyrilene	91-80-5	25	830
Methyl methanesulfonate	66-27-3	5	33
Methyl parathion**	298-00-0	25	170
N-Decane	124-18-5	5	33
N,N-Diethyl-m-toluamide (DEET)	134-62-3	10	330
N-Nitrosodiethylamine	55-18-5	5	33
N-Nitrosodimethylamine	62-75-9	5	330
N-Nitroso-di-n-butylamine	924-16-3	5	33
N-Nitrosomethylethylamine	10595-95-6	5	33
N-Nitrosomorpholine	59-89-2	5	33
N-Nitrosopiperidine	100-75-4	5	33
N-Nitrosopyrrolidine	930-55-2	5	33
octa-Decane	593-45-3	5	33
o,o-Diethyl-o-pyrazinyl ester	297-97-2	5	33
o,o,o-Triethyl-Phosphorothioate**	126-68-1	5	33
o-Toluidine	95-53-4	5	33
p-(Dimethylamino)azobenzene	60-11-7	5	33
Parathion**	56-38-2	25	830
p-Chlorobenzilate***	510-15-6	10	330
Pentachlorobenzene	608-93-5	5	33
Pentachloroethane	76-01-7	5	33
Pentachloronitrobenzene	82-68-8	25	67
Phenacetin	62-44-2	5	33
Phorate**	298-02-2	5	33
p-Phenylenediamine	106-50-3	50	170
Piperonyl butoxide (PIP)	51-03-6	25	830
Pronamide	23950-58-5	10	67
Pyridine	110-86-1	5	33
Safrole	94-59-7	5	33

Sulfotepp**	3689-24-5	10	33
Sym-Trinitrobenzene	99-35-4	10	67
Thionazin**	297-97-2	5	330

*The Appendix IX standard contains additional analytes required for the Appendix IX list.
The Shealy primary standard must also be analyzed to include the entire Appendix IX list.

** May also be analyzed by method 8141A, which can achieve lower reporting limits.

*** May also be analyzed by method 8081A, which can achieve lower reporting limits.

****Azobenzene is formed by decomposition of 1,2-diphenylhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

TABLE III-A. Reportable Analytes for Shealy Standard Tests, Primary Standard

Analytes	CAS Number	Shealy Standard List	TCLP	TCL	Appendix IX
1,2,4-Trichlorobenzene	120-82-1	X		X	X
1,2-Dichlorobenzene	95-50-1	X		X	X
1,3-Dichlorobenzene	541-73-1	X		X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X
2,2'-oxybis(1-chloropropane)*	108-60-1	X		X	X
2,4,5-Trichlorophenol	95-95-4	X	X	X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X
2,4-Dichlorophenol	120-83-2	X		X	X
2,4-Dimethylphenol	105-67-9	X		X	X
2,4-Dinitrophenol	51-28-5	X		X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X		X	X
2-Chloronaphthalene	91-58-7	X		X	X
2-Chlorophenol	95-57-8	X		X	X
2-Methylnaphthalene	91-57-6	X		X	X
2-Methylphenol	95-48-7	X	X	X	X
2-Nitroaniline	88-74-4	X		X	X
2-Nitrophenol	88-75-5	X		X	X
3,3'-Dichlorobenzidine	91-94-1	X		X	X
3-Nitroaniline	99-09-2	X		X	X
4,6-Dinitro-2-methylphenol	534-52-1	X		X	X
4-Bromophenyl phenyl ether	101-55-3	X		X	X
4-Chloro-3-methylphenol	59-50-7	X		X	X
4-Chloroaniline	106-47-8	X		X	X
4-Chlorophenyl phenyl ether	7005-72-3	X		X	X
4 & 3-Methylphenol	106-44-5	X	X	X	X
4-Nitroaniline	100-01-6	X		X	X
4-Nitrophenol	100-02-7	X		X	X

Acenaphthene	83-32-9	X		X	X
Acenaphthylene	208-96-8	X		X	X
Anthracene	120-12-7	X		X	X
Benzo(a)anthracene	56-55-3	X		X	X

TABLE III-A. Reportable Analytes for Shealy Standard Tests, Primary Standard (continued)

Analytes	CAS Number	Shealy Standard List	TCLP	TCL	Appendix IX
Benzo(a)pyrene	50-32-8	X		X	X
Benzo(b)fluoranthene	205-99-2	X		X	X
Benzo(g,h,i)perylene	191-24-2	X		X	X
Benzo(k)fluoranthene	207-08-9	X		X	X
Bis(2-Chloroethoxy)methane	111-91-1	X		X	X
Bis(2-chloroethyl)ether	111-44-4	X		X	X
Bis(2-ethylhexyl)phthalate	117-81-7	X		X	X
Butyl benzyl phthalate	85-68-7	X		X	X
Carbazole	86-74-8	X		X	
Chrysene	218-01-9	X		X	X
Dibenz(a,h)anthracene	53-70-3	X		X	X
Dibenzofuran	132-64-9	X		X	X
Diethylphthalate	84-66-2	X		X	X
Dimethyl phthalate	131-11-3	X		X	X
Di-n-butyl phthalate	84-74-2	X		X	X
Di-n-octylphthalate	117-84-0	X		X	X
Fluoranthene	206-44-0	X		X	X
Fluorene	86-73-7	X		X	X
Hexachlorobenzene	118-74-1	X	X	X	X
Hexachlorobutadiene	87-68-3	X	X	X	X
Hexachlorocyclopentadiene	77-47-4	X		X	X
Hexachloroethane	67-72-1	X	X	X	X
Indeno(1,2,3-cd)pyrene	193-39-5	X		X	X
Isophorone	78-59-1	X		X	X
Naphthalene	91-20-3	X		X	X
Nitrobenzene	98-95-3	X	X	X	X
N-Nitroso-di-n-propylamine	621-64-7	X		X	X
N-Nitrosodiphenylamine	86-30-6	X		X	X
Pentachlorophenol	87-86-5	X	X	X	X
Phenanthrene	85-01-8	X		X	X
Phenol	108-95-2	X		X	X
Pyrene	129-00-0	X		X	X

*2,2-oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether.

TABLE III-B. Reportable Analytes for Shealy Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	Shealy Standard List	TCLP	TCL	Appendix IX
1,2,4,5-Tetrachlorobenzene	95-94-3				X
1,3,5-Trinitrobenzene	99-35-4				X
1,3-Dinitrobenzene	99-65-0				X
1,4-Naphthoquinone	130-15-4				X
1-Chloronaphthalene	90-13-1				
1-Naphthylamine	134-32-7				X
2,3,4,6-Tetrachlorophenol	58-90-2				X
2,6-Dichlorophenol	87-65-0				X
2-Acetylaminofluorene	53-96-3				X
2-Naphthylamine	91-59-8				X
2-Picoline	109-06-8				X
3,3'-Dimethylbenzidine	119-93-7				X
3-Methylchloanthrene	56-49-5				X
4-Aminobiphenyl	62-67-1				X
4-Nitroquinoline-1-oxide	56-57-5				X
5-Nitro-o-toluidine	99-55-8				X
7,12-Dimethylbenz(a)anthracene	57-97-6				X
a,a-Dimethyl-phenethylamine	122-09-8				X
Acetophenone	98-86-2				X
Aniline	62-53-3				X
Aramite	140-57-8				X
Azobenzene	103-33-3				
Benzidine	92-87-5				
Benzoic acid	65-85-0				
Benzyl alcohol	100-51-6				X
Diallate	2303-16-4				X
Dichlorofenthion	97-17-6				
Dimethoate*	60-51-5				X
Diphenylamine****	122-39-4				X
Disulfoton*	298-04-4				X
Ethyl methanesulfonate	62-50-0				X
Famphur*	52-85-7				X
Hexachlorophene***	70-30-4				X

Hexachloroproprene	1888-71-7				X
Isodrin**	465-73-6				X
Isosafrole	120-58-1				X
Methapyrilene	91-80-5				X
Methyl methanesulfonate	66-27-3				X
Methyl parathion*	298-00-0				X

TABLE III-B. Reportable Analytes for Shealy Standard Tests, Appendix IX Standard (continued)

Semivolatiles	CAS Number	Shealy Standard List	TCLP	TCL	Appendix IX
N,N-Diethyl-m-toluamide (DEET)	134-62-3				
N-Nitrosodiethylamine	55-18-5				X
N-Nitrosodimethylamine	62-75-9				X
N-Nitroso-di-n-butylamine	924-16-3				X
N-Nitrosomethylethylamine	10595-95-6				X
N-Nitrosomorpholine	59-89-2				X
N-Nitrosopiperidine	100-75-4				X
N-Nitrosopyrrolidine	930-55-2				X
o,o,o-Triethyl-Phosphorothioate*	126-68-1				X
o-Toluidine	95-53-4				X
p-(Dimethylamino)azobenzene	60-11-7				X
Parathion*	56-38-2				X
p-Chlorobenzilate**	510-15-6				X
Pentachlorobenzene	608-93-5				X
Pentachloroethane	76-01-7				X
Pentachloronitrobenzene	82-68-8				X
Phenacetin	62-44-2				X
Phorate*	298-02-2				X
p-Phenylenediamine	106-50-3				X
Piperonyl butoxide (PIP)	51-03-6				
Pronamide	23950-58-5				X
Pyridine	110-86-1		X		X
Safrole	94-59-7				X
Sulfotepp*	3689-24-5				X
Thionazin*	297-97-2				X

*May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

**May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits.

***Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram. (See Section 12.2).

****Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore, these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

TABLE IV. Recommended Instrument Conditions

Mass range	35-500 amu
Scan time	≤ 1 second/scan
Initial column temperature / Hold time	40°C for 3 minutes
Column temperature program	40 – 110 °C at 20 °C/min, 6 °C/min to 130, 18 °C/min to 310
Final column temperature / Hold time	310 °C for 5 minutes (or until at least one minute after benzo(g,h,i)perylene has eluted)
Injector temperature	250 – 300 °C
Transfer line temperature	250 – 300 °C
Source temperature	According to manufacturer's specifications
Injector	Grob-type, split / splitless
Sample volume	0.5, 1, or 2 µl
Carrier gas	Helium at 30 cm/sec

TABLE V. DFTPP Key Ions and Ion Abundance Criteria

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% mass 443
442	Base Peak or > 50% of mass 198
443	15 – 24% of mass 442

TABLE VI – Minimum RRF Acceptance Criteria for Initial and Continuing Calibration

Analyte	Minimum RRF	Analyte	Minimum RRF
Benzaldehyde	0.01	Diethylphthalate	0.01
Phenol	0.800	Fluorene	0.900
bis-(2-Chloroethyl)ether	0.700	4-Chlorophenyl-phenylether	0.400
2-Chlorophenol	0.800	4-Nitroaniline	0.01
2-Methylphenol	0.700	4,6-Dinitro-2-methylphenol	0.01
2,2'-oxybis(1-Chloropropane)	0.01	N-Nitrosodiphenylamine	0.01
Acetophenone	0.01	1,2,4,5- Tetrachlorobenzene	0.01
4-Methylphenol	0.600	4-Bromophenyl-phenylether	0.100
N-Nitroso-di-n-propylamine	0.500	Hexachlorobenzene	0.100
Hexachloroethane	0.300	Atrazine	0.01
Nitrobenzene	0.200	Pentachlorophenol	0.050
Isophorone	0.400	Phenanthrene	0.700
2-Nitrophenol	0.100	Anthracene	0.700
2,4-Dimethylphenol	0.200	Di-n-butylphthalate	0.01
bis(2-Chloroethoxy)methane	0.300	Fluoranthene	0.600
2,4-Dichlorophenol	0.200	Pyrene	0.600
Naphthalene	0.700	Butylbenzylphthalate	0.01
4-Chloroaniline	0.01	3,3'-Dichlorobenzidine	0.01
Hexachlorobutadiene	0.01	Benzo(a)anthracene	0.800
Caprolactam	0.01	Chrysene	0.700
4-Chloro-3-methylphenol	0.200	bis(2-Ethylhexyl)phthalate	0.01
2-Methylnaphthalene	0.400	Di-n-octylphthalate	0.01
Hexachlorocyclopentadiene	0.01	Benzo(b)fluoranthene	0.700
2,4,6-Trichlorophenol	0.200	Benzo(k)fluoranthene	0.700
2,4,5-Trichlorophenol	0.200	Benzo(a)pyrene	0.700
1,1'-Biphenyl	0.01	Indeno(1,2,3-cd)pyrene	0.500
2-Chloronaphthalene	0.800	Dibenzo(ah)anthracene	0.400
2-Nitroaniline	0.01	Benzo(g,h,i)perylene	0.500
Dimethylphthalate	0.01	4-Nitroaniline	0.01
2,6-Dinitrotoluene	0.200	4,6-Dinitro-2-methylphenol	0.01
Acenaphthylene	0.900	N-Nitrosodiphenylamine	0.01
3-Nitroaniline	0.01	1,2,4,5- Tetrachlorobenzene	0.01
Acenaphthene	0.900	4-Bromophenyl-phenylether	0.100
2,4-Dinitrophenol	0.01	Hexachlorobenzene	0.100
4-Nitrophenol	0.01	Atrazine	0.01
Dibenzofuran	0.800		
2,4-Dinitrotoluene	0.200		

TABLE VI-A. Characteristic Ions for Shealy Primary Standard

Analyte	Primary	Secondary	Tertiary
1,2,4-Trichlorobenzene	180	182	145
1,2-Dichlorobenzene	146	148	111
1,3-Dichlorobenzene	146	148	111
1,4-Dichlorobenzene	146	148	111
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	115
1-Methylnaphthalene	142	141	115
2,2'-oxybis(1-chloropropane)*	45	77	79
2,4,5-Trichlorophenol	196	132	97
2,4,6-Tribromophenol (Surrogate Standard)	330	332	62
2,4,6-Trichlorophenol	196	198	200
2,4-Dichlorophenol	162	164	98
2,4-Dimethylphenol	122	107	121
2,4-Dinitrophenol	184	154	63
2,4-Dinitrotoluene	165	63	182
2,6-Dinitrotoluene	165	89	121
2-Chloronaphthalene	162	164	127
2-Chlorophenol	128	130	64
2-Fluorobiphenyl (Surrogate Standard)	172	171	N/A
2-Fluorophenol (Surrogate Standard)	112	64	92
2-Methylnaphthalene	142	141	115
2-Methylphenol	108	107	77
2-Nitroaniline	138	65	92
2-Nitrophenol	139	65	109
3,3'-Dichlorobenzidine	252	254	N/A
3-Nitroaniline	138	65	92
4,6-Dinitro-2-methylphenol	198	121	105
4-Bromophenylphenylether	248	250	141
4-Chloro-3-methylphenol	107	142	144
4-Chloroaniline	127	65	129
4-Chlorophenylphenylether	204	206	141
4 & 3-Methylphenol	108	107	77
4-Nitroaniline	138	65	92
4-Nitrophenol	109	65	81
Acenaphthene	153	152	154
Acenaphthene-d10 (Internal Standard)	164	162	160
Acenaphthylene	152	151	153
Anthracene	178	176	179
Atrazine	200	173	215
Benzaldehyde	77	105	106

TABLE VI-A. Characteristic Ions for Shealy Primary Standard (continued)

Analyte	Primary	Secondary	Tertiary
Benzo(a)anthracene	228	229	226
Benzo(a)pyrene	252	253	125
Benzo(b)fluoranthene	252	253	125
Benzo(g,h,i)perylene	276	138	277
Benzo(k)fluoranthene	252	253	125
Bis(2-chloroethoxy)methane	93	63	95
Bis(2-Chloroethyl)ether	93	63	95
Bis(2-ethylhexyl)phthalate	149	167	279
Butylbenzylphthalate	149	91	206
Caprolactam	113	55	56
Carbazole	167	139	N/A
Chrysene	228	226	229
Chrysene-d12 (Internal Standard)	240	236	120
Dibenz(a,h)anthracene	278	279	139
Dibenzofuran	168	139	84
Diethylphthalate	149	177	150
Dimethylphthalate	163	164	194
Di-n-Butylphthalate	149	150	104
Di-n-octylphthalate	149	150	N/A
Fluoranthene	202	101	100
Fluorene	166	165	167
Hexachlorobenzene	284	142	249
Hexachlorobutadiene	225	223	227
Hexachlorocyclopentadiene	237	272	235
Hexachloroethane	117	201	199
Indeno(1,2,3-cd)pyrene	276	N/A	N/A
Isophorone	82	138	95
Naphthalene	128	129	102
Naphthalene-d8 (Internal Standard)	136	N/A	N/A
Nitrobenzene	77	123	51
Nitrobenzene-d5 (Surrogate Standard)	82	54	128
N-Decane	52	71	99
N-Nitrosodimethylamine	74	42	44
N-Nitroso-di-n-propylamine	70	42	130
N-Nitrosodiphenylamine	169	168	167
Octa-Decane	57	85	127
Pentachlorophenol	266	264	268
Perylene-d12 (Internal Standard)	264	260	265

TABLE VI-A. Characteristic Ions for Shealy Primary Standard (continued)

Analyte	Primary	Secondary	Tertiary
Phenanthrene	178	176	179
Phenanthrene-d10 (Internal Standard)	188	N/A	N/A
Phenol	94	66	65
Phenol-d5 (Surrogate Standard)	99	71	N/A
Pyrene	202	101	100
Terphenyl-d14 (Surrogate Standard)	244	122	N/A

* 2,2'-oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

TABLE VI-B. Characteristic Ions for Shealy Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
1,2,4,5-Tetrachlorobenzene	216	179	107
1,3,5-Trinitrobenzene	74	75	213
1,3-Dinitrobenzene	168	76	50
1,4-Naphthoquinone	158	102	76
1-Chloronaphthalene	162	127	164
1-Naphthylamine	143	115	89
2,3,4,6-Tetrachlorophenol	232	131	166
2,6-Dichlorophenol	162	164	98
2-Acetylaminofluorene	181	223	152
2-Naphthylamine	143	115	89
2-Picoline	93	66	78
3,3'-Dimethylbenzidine	212	N/A	N/A
3-Methylchloanthrene	268	252	126
4-Aminobiphenyl	169	168	115
4-Nitroquinoline-1-oxide	190	89	160
5-Nitro-o-toluidine	152	106	N/A
7,12-Dimethylbenz(a)anthracene	256	241	120
a,a-Dimethyl-phenethylamine	58	134	N/A
Acetophenone	105	77	120
Aniline	66	93	65
Aramite 1	185	191	319
Aramite 2	185	191	319
Azobenzene	77	182	51
Benzoic acid	105	122	77
Benzyl alcohol	79	108	51
Diallate	86	70	234
Dichlorofenthion	223	279	97
Dimethoate	87	93	125
Disulfoton	88	89	97
Ethyl methanesulfonate	79	109	97
Famphur	218	125	93
Hexachloropropene	213	141	117
Isodrin	193	263	147
Isosafrole 1	131	162	104
Isosafrole 2	131	162	104
Methapyrilene	58	97	191
Methyl methanesulfonate	80	79	65

TABLE VI-B. Characteristic Ions for Shealy Appendix IX Standard (continued)

Analyte	Primary	Secondary	Tertiary
Methyl parathion	109	125	263
N,N-Diethyl-m-toluamide (DEET)	119	190	91
N-Nitrosodiethylamine	102	44	56
N-Nitrosodimethylamine	74	42	44
N-Nitroso-di-n-butylamine	84	57	116
N-Nitrosomethylethylamine	88	42	43
N-Nitrosomorpholine	56	116	86
N-Nitrosopiperidine	42	55	114
N-Nitrosopyrrolidine	100	41	69
o,o,o-Triehtyl-phosphorothioate	198	121	97
o-Toluidine	106	107	77
p-(Dimethylamino)azobenzene	120	225	77
Parathion	97	291	109
p-Chlorobenzilate	251	139	111
Pentachlorobenzene	250	215	108
Pentachloroethane	167	117	83
Pentachloronitrobenzene	237	142	295
Phenacetin	108	137	179
Phorate	121	75	260
p-Phenylenediamine	108	80	52
Piperonyl butoxide	176	177	149
Pronamide	173	255	145
Pyridine	79	52	50
Safrole	162	104	131
Sulfotepp	322	202	97
Thionazin	107	96	248

TABLE VII. Method 8270D LCS Spiking Compounds and Concentrations

LCS Compounds	Concentration in Spiking Standard (µg/mL)
1-Chloronaphthalene	100
1,2-Dichlorobenzene	100
1,3-Dichlorobenzene	100
1,4-Dichlorobenzene	100
1,2,4-Trichlorobenzene	100
2-Chloronaphthalene	100
2-Chlorophenol	100
2-Methylphenol (o-cresol)	100
2-Methylnaphthalene	100
2-Nitroaniline	200
2-Nitrophenol	200
2,4-Dichlorophenol	100
2,4-Dimethylphenol	100
2,4-Dinitrophenol	500
2,4-Dinitrotoluene	200
2,6-Dinitrotoluene	200
2,4,5-Trichlorophenol	100
2,4,6-Trichlorophenol	100
3-Methylphenol (m-cresol)	100
3-Nitroaniline	200
3,3'-Dichlorobenzidine	100
3,3'-Dimethylbenzidine (o-tolidine)	100
4-Bromophenyl phenyl ether	100
4-Chloroaniline	100
4-Chlorophenyl phenyl ether	100
4-Methylphenol (p-cresol)	100
4-Nitroaniline	200
4-Nitrophenol	500
4-Chloro-3-methylphenol	100
4,6-Dinitro-2-methylphenol (Dinitro-o-cresol)	500
Acenaphthene	100
Acenaphthalene	100
Anthracene	100
Azobenzene	100
Benz(a)anthracene	100
Benzidine	100
Benzo(a)pyrene	100
Benzo(b)fluoranthene	100

TABLE VII. Method 8270D LCS Spiking Compounds and Concentrations (continued)

LCS Compounds	Concentration in Spiking Standard (µg/mL)
Benzo(g,h,i)perylene	100
Benzoic Acid	200
Benzo(k)fluoranthene	100
Benzyl butyl phthalate	100
Bis(2-chloroethoxy)methane	100
Bis(2-chloroethyl)ether	100
Bis(2-chloroisopropyl)ether	100
Bis(2-ethylhexyl)phthalate	100
Carbazole	100
Chrysene	100
Dibenz(a,h)anthracene	100
Dibenzofuran	100
DEET	100
Diethylphthalate	100
Dimethylphthalate	100
Di-n-butylphthalate	100
Di-n-octylphthalate	100
Fluoranthene	100
Fluorene	100
Hexachlorobenzene	100
Hexachlorobutadiene	100
Hexachlorocyclopentadiene	500
Hexachloroethane	100
Ideno(1,2,3-cd)pyrene	100
Isophorone	100
Naphthalene	100
Nitrobenzene	100
N-Nitrosodimethylamine	100
N-Nitroso-di-n-propylamine	100
N-Nitrosodiphenylamine	100
Pentachlorophenol	500
Phenanthrene	100
Phenol	100
Piperonyl butoxide	200
Pyrene	100
Pyridine	100

Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA department.

TABLE VIII. TCLP BNA LCS Compounds and Concentrations

LCS Compounds	Concentration in Spiking Standard (µg/mL)
1,4-Dichlorobenzene	100
2,4,5-Trichlorophenol	100
2,4,6-Trichlorophenol	100
2,4-Dinitrotoluene	100
2-Methylphenol	100
3-Methylphenol	100
4-Methylphenol	100
Hexachlorobenzene	100
Hexachlorobutadiene	100
Hexachloroethane	100
Nitrobenzene	100
Pentachlorophenol	100
Pyridine	100

TABLE IX. Method 8270D Surrogate Compounds and Concentrations

Surrogate Compounds	Concentration in Standard (µg/mL)
2,4,6-Tribromophenol	100
2-Fluorobiphenyl	100
2-Fluorophenol	100
Nitrobenzene-d5	100
Phenol-d5/-d6	100
Terphenyl-d14	100

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

TABLE X-A. Possible Calibration Levels (not all are required), Primary Standard, µg/mL

Analyte 1 ul injection	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9
1,2,4-Trichlorobenzene	1	2	5	10	20	25	30	40	50
1,2-Dichlorobenzene	1	2	5	10	20	25	30	40	50
1,3-Dichlorobenzene	1	2	5	10	20	25	30	40	50
1,4-Dichlorobenzene	1	2	5	10	20	25	30	40	50
2,2'-oxybis(1-chloropropane)*	1	2	5	10	20	25	30	40	50
2,4,5-Trichlorophenol	1	2	5	10	20	25	30	40	50
2,4,6-Trichlorophenol	1	2	5	10	20	25	30	40	50
2,4-Dichlorophenol	1	2	5	10	20	25	30	40	50
2,4-Dimethylphenol	1	2	5	10	20	25	30	40	50
2,4-Dinitrophenol	2	4	10	20	40	50	60	80	100
2,4-Dinitrotoluene	2	4	10	20	40	50	60	80	100
2,6-Dinitrotoluene	2	4	10	20	40	50	60	80	100
2-Chloronaphthalene	1	2	5	10	20	25	30	40	50
2-Chlorophenol	1	2	5	10	20	25	30	40	50
2-Methylnaphthalene	1	2	5	10	20	25	30	40	50
2-Methylphenol	1	2	5	10	20	25	30	40	50
2-Nitroaniline	1	2	5	10	20	25	30	40	50
2-Nitrophenol	2	4	10	20	40	50	60	80	100
3,3'-Dichlorobenzidine	5	20	25	50	100	125	150	200	250
3-Nitroaniline	1	2	5	10	20	25	30	40	50
4,6-Dinitro-2-methylphenol	5	20	25	50	100	125	150	200	250
4-Bromophenyl phenyl ether	1	2	5	10	20	25	30	40	50
4-Chloro-3-methylphenol	1	2	5	10	20	25	30	40	50
4-Chloroaniline	1	2	5	10	20	25	30	40	50
4-Chlorophenyl phenyl ether	1	2	5	10	20	25	30	40	50
4-Methylphenol	1	2	5	10	20	25	30	40	50
4-Nitroaniline	1	2	5	10	20	25	30	40	50
4-Nitrophenol	5	20	25	50	100	125	150	200	250
Acenaphthene	1	2	5	10	20	25	30	40	50
Acenaphthylene	1	2	5	10	20	25	30	40	50
Anthracene	1	2	5	10	20	25	30	40	50
Benzo(a)anthracene	1	2	5	10	20	25	30	40	50
Benzo(a)pyrene	1	2	5	10	20	25	30	40	50
Benzo(b)fluoranthene	1	2	5	10	20	25	30	40	50
Benzo(g,h,i)perylene	1	2	5	10	20	25	30	40	50
Benzo(k)fluoranthene	1	2	5	10	20	25	30	40	50

TABLE X-A. Possible Calibration Levels (not all are required), Primary Standard, µg/mL (continued)

Analyte 1 ul injection	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9
Bis(2-chloroethoxy)methane	1	2	5	10	20	25	30	40	50
Bis(2-chloroethyl)ether	1	2	5	10	20	25	30	40	50
Bis(2-ethylhexyl)phthalate	1	2	5	10	20	25	30	40	50
Butyl benzyl phthalate	2	4	10	20	40	50	60	80	100
Carbazole	1	2	5	10	20	25	30	40	50
Chrysene	1	2	5	10	20	25	30	40	50
Dibenz(a,h)anthracene	1	2	5	10	20	25	30	40	50
Dibenzofuran	1	2	5	10	20	25	30	40	50
Diethylphthalate	1	2	5	10	20	25	30	40	50
Dimethyl phthalate	1	2	5	10	20	25	30	40	50
Di-n-butyl phthalate	1	2	5	10	20	25	30	40	50
Di-n-octylphthalate	1	2	5	10	20	25	30	40	50
Fluoranthene	1	2	5	10	20	25	30	40	50
Fluorene	1	2	5	10	20	25	30	40	50
Hexachlorobenzene	1	2	5	10	20	25	30	40	50
Hexachlorobutadiene	1	2	5	10	20	25	30	40	50
Hexachlorocyclopentadiene	5	20	25	50	100	125	150	200	250
Hexachloroethane	1	2	5	10	20	25	30	40	50
Indeno(1,2,3-cd)pyrene	1	2	5	10	20	25	30	40	50
Isophorone	1	2	5	10	20	25	30	40	50
Naphthalene	1	2	5	10	20	25	30	40	50
Nitrobenzene	1	2	5	10	20	25	30	40	50
N-Nitroso-di-n-propylamine	1	2	5	10	20	25	30	40	50
N-Nitrosodiphenylamine	1	2	5	10	20	25	30	40	50
Pentachlorophenol	5	20	25	50	100	125	150	200	250
Phenanthrene	1	2	5	10	20	25	30	40	50
Phenol	1	2	5	10	20	25	30	40	50
Pyrene	1	2	5	10	20	25	30	40	50

* 2,2'-oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether.

TABLE X-B. Possible Calibration Levels (not all are required), Appendix IX Standard, µg/mL

Semivolatiles 1 ul injection	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9
1,2,4,5-Tetrachlorobenzene	1	2	5	10	20	25	30	40	50
1,3,5-Trinitrobenzene	5	20	25	50	100	125	150	200	250
1,3-Dinitrobenzene	5	20	25	50	100	125	150	200	250
1,4-Naphthoquinone	2	4	10	20	40	50	60	80	100
1-Chloronaphthalene	1	2	5	10	20	25	30	40	50
1-Naphthylamine	1	2	5	10	20	25	30	40	50
2,3,4,6-Tetrachlorophenol	2	4	10	20	40	50	60	80	100
2,6-Dichlorophenol	1	2	5	10	20	25	30	40	50
2-Acetylaminofluorene	5	20	25	50	100	125	150	200	250
2-Naphthylamine	1	2	5	10	20	25	30	40	50
2-Picoline	1	2	5	10	20	25	30	40	50
3,3'-Dimethylbenzidine	5	20	25	50	100	125	150	200	250
3-Methylcholanthrene	2	4	10	20	40	50	60	80	100
4-Aminobiphenyl	2	4	10	20	40	50	60	80	100
4-Nitroquinoline-1-oxide	5	20	25	50	100	125	150	200	250
5-Nitro-o-toluidine	2	4	10	20	40	50	60	80	100
7,12-Dimethylbenz(a)anthracene	1	2	5	10	20	25	30	40	50
a,a-Dimethyl-phenethylamine	2	4	10	20	40	50	60	80	100
Acetophenone	1	2	5	10	20	25	30	40	50
Aniline	1	2	5	10	20	25	30	40	50
Aramite	5	20	25	50	100	125	150	200	250
Azobenzene*	1	2	5	10	20	25	30	40	50
Benzidine	5	20	25	50	100	125	150	200	250
Benzoic acid	2	4	10	20	40	50	60	80	100
Benzyl alcohol	1	2	5	10	20	25	30	40	50
Diallate	2	4	10	20	40	50	60	80	100
Dichlorofenthion	1	2	5	10	20	25	30	40	50
Dimethoate	2	4	10	20	40	50	60	80	100
Disulfoton	1	2	5	10	20	25	30	40	50
Ethyl methanesulfonate	1	2	5	10	20	25	30	40	50
Famphur	5	20	25	50	100	125	150	200	250
Hexachloropropene	2	4	10	20	40	50	60	80	100
Isodrin	1	2	5	10	20	25	30	40	50
Isosafrole 1+2	1	2	5	10	20	25	30	40	50
Methapyrilene	1	2	5	10	20	25	30	40	50
Methyl methanesulfonate	1	2	5	10	20	25	30	40	50
Methyl parathion	5	20	25	50	100	125	150	200	250

TABLE X-B. Possible Calibration Levels (not all are required), Appendix IX Standard, µg/mL (continued)

Semivolatiles 1 ul injection	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8	Level 9
N,N-Diethyl-m-toluamide (DEET)	1	2	5	10	20	25	30	40	50
N-Nitrosodiethylamine	1	2	5	10	20	25	30	40	50
N-Nitrosodimethylamine	1	2	5	10	20	25	30	40	50
N-Nitroso-di-n-butylamine	1	2	5	10	20	25	30	40	50
N-Nitrosomethylethylamine	1	2	5	10	20	25	30	40	50
N-Nitrosomorpholine	1	2	5	10	20	25	30	40	50
N-Nitrosopiperidine	1	2	5	10	20	25	30	40	50
N-Nitrosopyrrolidine	1	2	5	10	20	25	30	40	50
o,o,o-Triethyl-phosphorothioate	1	2	5	10	20	25	30	40	50
o-Toluidine	1	2	5	10	20	25	30	40	50
p-(Dimethylamino)azobenzene	1	2	5	10	20	25	30	40	50
Parathion	5	20	25	50	100	125	150	200	250
p-Chlorobenzilate	2	4	10	20	40	50	60	80	100
Pentachlorobenzene	1	2	5	10	20	25	30	40	50
Pentachloroethane	1	2	5	10	20	25	30	40	50
Pentacloronitrobenzene	5	20	25	50	100	125	150	200	250
Phenacetin	1	2	5	10	20	25	30	40	50
Phorate	1	2	5	10	20	25	30	40	50
p-Phenylenediamine	10	20	50	100	200	250	300	400	500
Piperonyl butoxide (PIP)	1	2	5	10	20	25	30	40	50
Pronamide	2	4	10	20	40	50	60	80	100
Pyridine	1	2	5	10	20	25	30	40	50
Safrole	1	2	5	10	20	25	30	40	50
Sulfotepp	1	2	5	10	20	25	30	40	50
Thionazin	1	2	5	10	20	25	30	40	50

*Azobenzene is formed by decomposition of 1,2-diphenylhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

TABLE XI. ICV Acceptance Criteria for Shealy Primary Standard

Analyte	% Difference or % Drift
1-Chloronaphthalene	± 30
1,2-Dichlorobenzene	± 30
1,3-Dichlorobenzene	± 30
1,4-Dichlorobenzene	± 30
1,2,4-Trichlorobenzene	± 30
2-Chloronaphthalene	± 30
2-Chlorophenol	± 30
2-Methylphenol (o-cresol)	± 30
2-Methylnaphthalene	± 30
2-Nitroaniline	± 30
2-Nitrophenol	± 30
2,4-Dichlorophenol	± 30
2,4-Dimethylphenol	± 30
2,4-Dinitrophenol	± 30
2,4-Dinitrotoluene	± 30
2,6-Dinitrotoluene	± 30
2,4,5-Trichlorophenol	± 30
2,4,6-Trichlorophenol	± 30
3-Methylphenol (m-cresol)	± 30
3-Nitroaniline	± 30
3,3'-Dichlorobenzidine	± 30
3,3'-Dimethylbenzidine (o-tolidine)	± 30
4-Bromophenyl phenyl ether	± 30
4-Chloroaniline	± 30
4-Chlorophenyl phenyl ether	± 30
4-Methylphenol (p-cresol)	± 30
4-Nitroaniline	± 30
4-Nitrophenol	± 30
4-Chloro-3-methylphenol	± 30
4,6-Dinitro-2-methylphenol (Dinitro-o-cresol)	± 30
Acenaphthene	± 30
Acenaphthylene	± 30
Anthracene	± 30
Azobenzene	± 30
Benz(a)anthracene	± 30
Benzidine	± 30
Benzo(a)pyrene	± 30
Benzo(b)fluoranthene	± 30
Benzo(g,h,i)perylene	± 30

TABLE XI. ICV Acceptance Criteria for Shealy Primary Standard (continued)

Analyte	% Difference or % Drift
Benzoic Acid	± 30
Benzo(k)fluoranthene	± 30
Benzyl butyl phthalate	± 30
Bis(2-chloroethoxy)methane	± 30
Bis(2-chloroethyl)ether	± 30
Bis(2-chloroisopropyl)ether	± 30
Bis(2-ethylhexyl)phthalate	± 30
Carbazole	± 30
Chrysene	± 30
Dibenz(a,h)anthracene	± 30
Dibenzofuran	± 30
DEET	± 30
Diethylphthalate	± 30
Dimethylphthalate	± 30
Di-n-butylphthalate	± 30
Di-n-octylphthalate	± 30
Fluoranthene	± 30
Fluorene	± 30
Hexachlorobenzene	± 30
Hexachlorobutadiene	± 30
Hexachlorocyclopentadiene	± 30
Hexachloroethane	± 30
Indeno(1,2,3-cd)pyrene	± 30
Isophorone	± 30
Naphthalene	± 30
Nitrobenzene	± 30
N-Nitrosodimethylamine	± 30
N-Nitroso-di-n-propylamine	± 30
N-Nitrosodiphenylamine	± 30
Pentachlorophenol	± 30
Phenanthrene	± 30
Phenol	± 30
Piperonyl butoxide	± 30
Pyrene	± 30
Pyridine	± 30

TABLE XII-A. CCV Acceptance Criteria for Shealy Primary Standard

Analyte	% Difference or % Drift
1,2,4-Trichlorobenzene	20

1,2-Dichlorobenzene	20
1,3-Dichlorobenzene	20
1,4-Dichlorobenzene	20
2,2'-oxybis(1-chloropropane)	20
2,4,5-Trichlorophenol	20
2,4,6-Trichlorophenol	20
2,4-Dichlorophenol	20
2,4-Dimethylphenol	20
2,4-Dinitrophenol	20
2,4-Dinitrotoluene	20
2,6-Dinitrotoluene	20
2-Chloronaphthalene	20
2-Chlorophenol	20
2-Methylnaphthalene	20
2-Methylphenol	20
2-Nitroaniline	20
2-Nitrophenol	20
3,3'-Dichlorobenzidine	20
3-Nitroaniline	20
4,6-Dinitro-2-methylphenol	20
4-Bromophenylphenylether	20
4-Chloro-3-methylphenol	20
4-Chloroaniline	20
4-Chlorophenylphenylether	20
4 & 3-Methylphenol	20
4-Nitroaniline	20
4-Nitrophenol	20
Acenaphthene	20
Acenaphthylene	20
Anthracene	20
Benzo(a)anthracene	20
Benzo(a)pyrene	20
Benzo(b)fluoranthene	20

TABLE XII-A. CCV Acceptance Criteria for Shealy Primary Standard (continued)

Analyte	%Difference or %Drift
Benzo(g,h,i)perylene	20

Benzo(k)fluoranthene	20
Bis(2-chloroethoxy)methane	20
Bis(2-Chloroethyl)ether	20
Bis(2-ethylhexyl)phthalate	20
Butylbenzylphthalate	20
Carbazole	20
Chrysene	20
Dibenz(a,h)anthracene	20
Dibenzofuran	20
Diethylphthalate	20
Dimethylphthalate	20
Di-n-Butylphthalate	20
Di-n-octylphthalate	20
Fluoranthene	20
Fluorene	20
Hexachlorobenzene	20
Hexachlorobutadiene	20
Hexachlorocyclopentadiene	20
Hexachloroethane	20
Indeno(1,2,3-cd)pyrene	20
Isophorone	20
Naphthalene	20
Nitrobenzene	20
N-nitrosodimethylamine	20
N-Nitroso-di-n-propylamine	20
N-Nitrosodiphenylamine	20
Pentachlorophenol	20
Phenanthrene	20
Phenol	20
Pyrene	20

TABLE XII-B. CCV Acceptance Criteria for Shealy Appendix IX Standard

Analyte	%Difference or %Drift
1,2,4,5-Tetrachlorobenzene	20

1,3,5-Trinitrobenzene	20
1,3-Dinitrobenzene	20
1,4-Naphthoquinone	20
1-Chloronaphthalene	20
1-Naphthylamine	20
2,3,4,6-Tetrachlorophenol	20
2,6-Dichlorophenol	20
2-Acetylaminofluorene	20
2-Naphthylamine	20
2-Picoline	20
3,3'-Dimethylbenzidine	20
3-Methylchloanthrene	20
4-Aminobiphenyl	20
4-Nitroquinoline-1-oxide	20
5-Nitro-o-toluidine	20
7,12-Dimethylbenz(a)anthracene	20
a,a-Dimethyl-phenethylamine	20
Acetophenone	20
Aniline	20
Aramite 1	20
Aramite 2	20
Azobenzene	20
Benzoic acid	20
Benzyl alcohol	20
Diallate	20
Dichlorofenthion	20
Dimethoate	20
Disulfoton	20
Ethyl methanesulfonate	20
Famphur	20
Hexachloropropene	20
Isodrin	20
Isosafrole 1	20
Isosafrole 2	20
Methapyrilene	20
Methyl methanesulfonate	20

TABLE XII-B. CCV Acceptance Criteria for Shealy Appendix IX Standard (continued)

Analyte	%Difference or %Drift
Methyl parathion	20
N,N-Diethyl-m-toluamide (DEET)	20
N-Nitrosodiethylamine	20
N-Nitrosodimethylamine	20

N-Nitroso-di-n-butylamine	20
N-Nitrosomethylethylamine	20
N-Nitrosomorpholine	20
N-Nitrosopiperidine	20
N-Nitrosopyrrolidine	20
o,o,o-Triehtyl-phosphorothioate	20
o-Toluidine	20
p-(Dimethylamino)azobenzene	20
Parathion	20
p-Chlorobenzilate	20
Pentachlorobenzene	20
Pentachloroethane	20
Pentachloronitrobenzene	20
Phenacetin	20
Phorate	20
p-Phenylenediamine	20
Piperonyl butoxide	20
Pronamide	20
Pyridine	20
Safrole	20
Sulfotepp	20
Thionazin	20

TABLE XIII. Initial Demonstration Recovery and Precision Limits

Compound	Spiking Concentration (µg/L)	Limit for Relative Standard Deviation	Limit for Average Recovery (%)
1,2,4-Trichlorobenzene	100	40	30-130

1,2-Dichlorobenzene	100	40	30-130
1,3-Dichlorobenzene	100	40	30-130
1,4-Dichlorobenzene	100	40	30-130
2,4,6-Trichlorophenol	100	40	30-130
2,4-Dichlorophenol	100	40	30-130
2,4-Dimethylphenol	100	40	30-130
2,4-Dinitrophenol	100	40	30-130
2,4-Dinitrotoluene	100	40	30-130
2,6-Dinitrotoluene	100	40	30-130
2-Chloronaphthalene	100	40	30-130
2-Chlorophenol	100	40	30-130
2-Methyl-4,6-dinitrophenol	100	40	30-130
2-Nitrophenol	100	40	30-130
3,3'Dichlorobenzidine	100	40	30-130
4-Bromophenyl phenyl ether	100	40	30-130
4-Chloro-3-methylphenol	100	40	30-130
4-Chlorophenyl phenyl ether	100	40	30-130
4-Nitrophenol	100	40	30-130
Acenaphthene	100	40	30-130
Acenaphthylene	100	40	30-130
Anthracene	100	40	30-130
Benz(a)anthracene	100	40	30-130
Benzo(a)pyrene	100	40	30-130
Benzo(b)fluoranthene	100	40	30-130
Benzo(g,h,i)perylene	100	40	30-130
Benzo(k)fluoranthene	100	40	30-130
Benzylbutyl phthalate	100	40	30-130
Bis(2-chloroethoxy)methane	100	40	30-130
Bis(2-chloroethyl)ether	100	40	30-130
Bis(2-chloroisopropyl)ether	100	40	30-130
Bis(2-ethylhexyl)phthalate	100	40	30-130
Chrysene	100	40	30-130
Dibenzo(a,h)anthracene	100	40	30-130
Diethyl phthalate	100	40	30-130

TABLE XIII. Initial Demonstration Recovery and Precision Limits (continued.)

Compound	Spiking Concentration (µg/L)	Limit for Relative Standard Deviation	Limit for Average Recovery (%)
Dimethyl phthalate	100	40	30-130

Di-n-butyl phthalate	100	40	30-130
Di-n-octylphthalate	100	40	30-130
Fluoranthene	100	40	30-130
Fluorene	100	40	30-130
Hexachlorobenzene	100	40	30-130
Hexachlorobutadiene	100	40	30-130
Hexachloroethane	100	40	30-130
Indeno(1,2,3-cd)pyrene	100	40	30-130
Isophorone	100	40	30-130
Naphthalene	100	40	30-130
Nitrobenzene	100	40	30-130
N-Nitroso-di-n-propylamine	100	40	30-130
Pentachlorophenol	100	40	30-130
Phenanthrene	100	40	30-130
Phenol	100	40	30-130
Pyrene	100	40	30-130

ATTACHMENT A

MODIFICATIONS REQUIRED FOR ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) ONLY SAMPLES BY 8270D

❖ REQUIREMENTS FOR PAH ONLY ANALYSIS

1. The tailing factors for benzidine and pentachlorophenol need not be evaluated.

2. Calibration standards should include all the PAH compounds (Table B-1) plus the base neutral surrogates and internal standard compounds.

3. Initial calibration: All compounds %RSD ≤ 20%, or a linear curve with a correlation coefficient ≥ 0.995 may be used. The Target data system measures the square of the correlation coefficient, which must be ≥ 0.990.

4. Continuing calibration verification

   - The percent difference or drift of all analytes other than the SPCC compounds must within the limits set in Table XIV-A.

Table A-1. Shealy Standard Reporting List and Reporting Limits, PAH Compounds Only

		Standard Reporting Limits

PAH Analytes	CAS Number	Aqueous µg/L	Low Soil/Sediment µg/kg
Acenaphthene	83-32-9	5	330
Acenaphthylene	208-96-8	5	330
Anthracene	120-12-7	5	330
Benzo(a)anthracene	56-55-3	5	330
Benzo(a)pyrene	50-32-8	5	330
Benzo(b)fluoranthene	205-99-2	5	330
Benzo(g,h,i)perylene	191-24-2	5	330
Benzo(k)fluoranthene	207-08-9	5	330
Chrysene	218-01-9	5	330
Dibenz(a,h)anthracene	53-70-3	5	330
Fluoranthene	206-44-0	5	330
Fluorene	86-73-7	5	330
Indeno(1,2,3-cd)pyrene	193-39-5	5	330
Naphthalene	91-20-3	5	330
Phenanthrene	85-01-8	5	330
Pyrene	129-00-0	5	330

APPENDIX NC

APPENDIX – North Carolina Requirements

Sections found in this appendix replace and/or supplement the existing sections of the SOP. These requirements must be met when analyzing samples for the Department of Defense-NFESC (Navy) as stipulated in the DOD Quality Systems Manual (Version 3, January 2006).

9.0 QUALITY CONTROL

9.4 Method Blank Acceptance Criteria – replaces Section 9.4 and 9.4 sub-sections.

9.4 Method Blank (MB) – One method blank must be processed with each preparation and/or analytical batch. The method blank consists of a similar matrix to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results. The method blank is to contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

9.4.1 For a method blank to be acceptable for use with the accompanying samples, the concentration of analytes detected in the blank must be ≤ one-half (1/2) the practical quantitation limit (PQL) or project specific reporting limits.

9.4.1.1 The acceptance criterion for common laboratory contaminants is that no analytes should exceed the PQL.

9.4.2 If the MB does not meet the criteria above, the source of the contamination shall be investigated and measures taken to minimize or eliminate the problem. The affected samples shall be reprocessed or data shall be appropriately qualified. All steps taken to return the system to control must be fully documented.

9.4.3 If reanalysis is not possible due to limited sample volume or holding time, the samples associated with the contaminated blank must be evaluated as to the best corrective action for the samples (e.g., reprocessing or data qualifying codes). In all cases the corrective action(s) must result in the completion of an NCM.

APPENDIX DoD

APPENDIX – DoD QSM Requirements

Sections found in this appendix replace and/or supplement the existing sections of the SOP. These requirements must be met when analyzing samples for the Department of Defense-NFESC (Navy) as stipulated in the DOD Quality Systems Manual (Version 3, January 2006).

10.0 QUALITY CONTROL

9.5 Method Blank Acceptance Criteria – replaces Section 9.4 and 9.4 sub-sections.

9.4 Method Blank (MB) – One method blank must be processed with each preparation and/or analytical batch. The method blank consists of a similar matrix to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results. The method blank is to contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

9.4.1 For a method blank to be acceptable for use with the accompanying samples, the concentration of analytes detected in the blank should be ≤ one-half (1/2) the practical quantitation limit (PQL) or project specific reporting limits.

9.4.1.1 The acceptance criterion for common laboratory contaminants is that no analytes should exceed the PQL.

9.4.2 If the MB does not meet the criteria above, the source of the contamination shall be investigated and measures taken to minimize or eliminate the problem. The affected samples shall be reprocessed or data shall be appropriately qualified. All steps taken to return the system to control must be fully documented.

9.4.3 If reanalysis is not possible due to limited sample volume or holding time, the samples associated with the contaminated blank must be evaluated as to the best corrective action for the samples (e.g., reprocessing or data qualifying codes). In all cases, the corrective action(s) must result in the completion of an NCM.

9.12 Analysis Carryover Study – The analysis carryover study must be performed on an annual basis per technology per model. The study will also need to be repeated after any changes have been made (e.g. instrument conditions) that could effect the carryover. The carryover study demonstrates the concentration at which a target or non-target analyte may be detected without contaminating the subsequent sample(s). A carryover verification standard (CVS) is analyzed at the same concentration as the highest point in the initial calibration and will be followed immediately by an instrument blank. The maximum carryover criteria are as follows:

9.12.1 The resultant carryover must be ≤ ½ the applicable PQL.

9.12.2 If a sample is nondetect after being analyzed immediately after a sample with high concentrations of target and/or non-target compound(s), the sample results may be reported.

Additional studies may be performed to identify how many blanks are required in the contiguous sequence to achieve the ≤ ½ PQL criteria. These studies must be fully documented and readily available for analysts.

10.5.1 Lower Order of Quantitation (LOQ) Verification – This is an analysis of a QC sample containing the analytes of interest in each matrix 1-2 times the claimed LOQ

10.5.1.1 A successful analysis is one where the recovery of each analyte is within the established test method acceptance criteria or client data quality objectives for accuracy.

10.5.1.2 This single analysis is not required if the bias and precision of the measurement system is evaluated at the LOQ.

10.5.1.3 The LOQ must not be set any lower than the low-level calibration standard for multi-point calibration or no lower than a low-level calibration check sample for single level calibration.

TABLE DoD-I. Semi-volatile Organic Target Compounds and Standard Reporting Limits

		Standard Reporting Limits

Analytes	CAS Number	Aqueous µg/L	Low Soil/Sediment µg/kg
1,2,4-Trichlorobenzene	120-82-1	5.0	330
1,2-Dichlorobenzene	95-50-1	5.0	330
1,2-Diphenylhydrazine	122-66-7	5.0	330
1,3-Dichlorobenzene	541-73-1	5.0	330
1,4-Dichlorobenzene	106-46-7	5.0	330
2,2'-oxybis(1-chloropropane)**	108-60-1	5.0	330
2,4,5-Trichlorophenol	95-95-4	5.0	330
2,4,6-Trichlorophenol	88-06-2	5.0	330
2,4-Dichlorophenol	120-83-2	5.0	330
2,6-Dichorophenol	87-65-0	5.0	330
2,4-Dimethylphenol	105-67-9	5.0	330
2,4-Dinitrophenol	51-28-5	25	830
2,4-Dinitrotoluene	121-14-2	10.0	330
2,6-Dinitrotoluene	606-20-2	10.0	330
2-Chloronaphthalene	91-58-7	5.0	330
2-Chlorophenol	95-57-8	5.0	330
2-Methylnaphthalene	91-57-6	5.0	330
2-Methylphenol	95-48-7	5.0	330
2-Nitroaniline	88-74-4	10.0	330
2-Nitrophenol	88-75-5	10.0	330
3,3'-Dichlorobenzidine	91-94-1	25	830
3-Nitroaniline	99-09-2	10.0	330
4,6-Dinitro-2-methylphenol	534-52-1	25	830
4-Bromophenyl phenyl ether	101-55-3	5.0	330
4-Chloro-3-methylphenol	59-50-7	5.0	330
4-Chlorophenyl phenyl ether	7005-72-3	5.0	330
3 & 4-Methylphenol	106-44-5	10.0	670
4-Nitroaniline	100-01-6	10.0	330
4-Nitrophenol	100-02-7	25	830
Acenaphthene	83-32-9	5.0	330
Acenaphthylene	208-96-8	5.0	330
Anthracene	120-12-7	5.0	330
Benzidine	92-87-5	25	830
Benzoic Acid	65-85-0	250	8,300
Benzo(a)anthracene	56-55-3	5.0	330
Benzo(a)pyrene	50-32-8	5.0	330
Benzo(b)fluoranthene	205-99-2	5.0	330
Benzo(g,h,i)perylene	191-24-2	5.0	330

TABLE DoD-I. Semi-volatile Organic Target Compounds and Standard Reporting Limits (continued)

		Standard Reporting Limits

Analytes	CAS Number	Aqueous µg/L	Low Soil/Sediment µg/kg
Benzo(k)fluoranthene	207-08-9	5.0	330
Benzyl Alcohol	100-51-6	5.0	330
Bis(2-Chloroethoxy)methane	111-91-1	5.0	330
Bis(2-chloroethyl)ether	111-44-4	5.0	330
Bis(2-ethylhexyl)phthalate	117-81-7	5.0	330
Butyl benzyl phthalate	85-68-7	10.0	330
Carbazole	86-74-8	5.0	330
Chrysene	218-01-9	5.0	330
Dibenz(a,h)anthracene	53-70-3	5.0	330
Dibenzofuran	132-64-9	5.0	330
Diethylphthalate	84-66-2	5.0	330
Dimethyl phthalate	131-11-3	5.0	330
Di-n-butyl phthalate	84-74-2	5.0	330
Di-n-octylphthalate	117-84-0	5.0	330
Fluoranthene	206-44-0	5.0	330
Fluorene	86-73-7	5.0	330
Hexachlorobenzene	118-74-1	5.0	330
Hexachlorobutadiene	87-68-3	5.0	330
Hexachloroethane	67-72-1	5.0	330
Indeno(1,2,3-cd)pyrene	193-39-5	5.0	330
Isophorone	78-59-1	5.0	330
Naphthalene	91-20-3	5.0	330
Nitrobenzene	98-95-3	5.0	330
N-Nitrosodimethylamine	62-75-9	5.0	330
N-Nitroso-di-n-propylamine	621-64-7	5.0	330
N-Nitrosodiphenylamine	86-30-6	5.0	330
N-Nitrosodipyrrolidine	930-55-2	5.0	330
Pentachlorophenol	87-86-5	25	830
Phenanthrene	85-01-8	5.0	330
Phenol	108-95-2	5.0	330
Pyrene	129-00-0	5.0	330

* The Shealy primary standard is the standard normally used at Shealy. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.

** 2,2'-oxybis(1-chloropropane) was formerly known as bis(2-chloroisopropyl)ether.

TABLE DoD-II. Semi-volatile Organic Surrogate Compounds and Control Limits

Surrogate Compounds	Concentration in Standard (µg/mL)	Aqueous Control Limits		Solid Control Limits	
		Lower	Upper	Lower	Upper
2,4,6-Tribromophenol	100	40	125	35	125

2-Fluorobiphenyl	100	50	110	45	105
2-Fluorophenol	100	20	110	35	105
Nitrobenzene-d5	100	40	110	35	100
Phenol-d5/-d6	100	N/A	N/A	40	100
Terphenyl-d14	100	50	135	30	125

TABLE DoD-III. Aqueous LCS/MS Control Limits for Semi-volatile Organic Target Compounds

Analyte	Aqueous Control Limits			
	Lower	Upper	Lower ME	Upper ME
Polynuclear Aromatics				
2-Methylnaphthalene	45	105	35	115
Acenaphthene	45	110	35	120
Acenaphthylene	50	105	40	115
Anthracene	55	110	45	120
Benz[a]anthracene	55	110	45	120
Benzo[a]pyrene	55	110	45	120
Benzo[b]fluoranthene	45	120	35	130
Benzo[k]fluoranthene	45	125	30	135
Benzo[g,h,i]perylene	40	125	25	135
Chrysene	55	110	45	120
Dibenz[a,h]anthracene	40	125	30	140
Fluoranthene	55	115	45	125
Fluorene	50	110	40	120
Ideno[1,2,3-cd]pyrene	45	125	30	140
Naphthalene	40	100	30	115
Phenanthrene	50	115	40	130
Pyrene	50	130	35	140
Phenolic/Acidic				
2,4,5-Trichlorophenol	50	110	40	120
2,4,6-Trichlorophenol	50	115	40	125
2,4-Dichlorophenol	50	105	40	115
2,4-Dimethylphenol	30	110	15	125
2,4-Dinitrophenol	15	140	10	160
2-Chlorophenol	35	105	25	115
2-Methylphenol	40	110	25	120

TABLE DoD-III. Aqueous LCS/MS Control Limits for Semi-volatile Organic Target Compounds (continued)

Analyte	Aqueous Control Limits			
	Lower	Upper	Lower ME	Upper ME
Phenolic/Acidic continued				

2-Nitrophenol	40	115	25	125
3 & 4-Methylphenol	30	110	20	125
4,6-Dinitro-2-methylphenol	40	130	25	145
4-Chloro-3-methylphenol	45	110	35	120
Pentachlorophenol	40	115	25	130
Basic				
3-3'-Dichlorobenzidine	20	110	10	125
4-Chloroaniline	15	110	10	125
Phthalate Esters				
Bis(2-ehtylhexyl)phthalate	40	125	30	140
Butyl benzyl phthalate	45	115	35	130
Di-n-butyl phthalate	55	115	45	125
Di-n-octyl phthalate	35	135	20	155
Diethyl phthalate	40	120	30	130
Dimethyl phthalate	25	125	10	145
Nitrosoamines				
N-Nitrosodi-n-propylamine	35	130	20	145
N-Nitrosodimethylamine	25	110	10	125
N-Nitrosodiphenylamine	50	110	35	120
Chlorinated Aliphatics				
Bis(2-chloroethoxy)methane	45	105	35	115
Bis(2-chloroethyl)ether	35	110	25	120
Bis(2-chloroisopropyl)ether	25	130	10	150
Hexachlorobutadiene	25	105	15	115
Hexachloroethane	30	95	15	105
Halogenated Aromatics				
1,2,4-Trichlorobenzene	35	105	25	120
1,2-Dichlorobenzene	35	100	20	115
1,3-Dichlorobenzene	30	100	20	110
1,4-Dichlorobenzene	30	100	20	110
2-Chloronaphthtalene	50	105	40	115
4-Bromophenyl phenyl ether	50	115	40	125
4-Chlorophenyl phenyl ether	50	110	40	120
Hexachlorobenzene	50	110	40	120

TABLE DoD-III. Aqueous LCS/MS Control Limits for Semi-volatile Organic Target Compounds (continued)

Analyte	Aqueous Control Limits

	Lower	Upper	Lower ME	Upper ME
Nitroaromatics				
2,4-Dinitrotoluene	50	120	40	130
2,6-Dinitrotoluene	50	115	35	130
2-Nitroaniline	50	115	35	125
3-Nitroaniline	20	125	10	145
4-Nitroaniline	35	120	20	130
Nitrobenzene	45	110	35	120
Neutral Aromatics				
Carbazole	50	115	35	130
Dibenzofuran	55	105	45	115
Others				
1,2-Diphenylhydrazine	55	115	45	120
Benzyl alcohol	30	110	15	125
Isophorone	30	110	40	125

TABLE DoD-IV. Solid LCS/MS Control Limits for Semi-volatile Organic Target Compounds

Analyte	Solid Control Limits			
	Lower	Upper	Lower ME	Upper ME
Polynuclear Aromatics				
2-Methylnaphthalene	45	105	35	115
Acenaphthene	45	110	35	120
Acenaphthylene	45	105	35	120
Anthracene	55	105	45	115
Benz[a]anthracene	50	110	40	120
Benzo[a]pyrene	50	110	40	120
Benzo[b]fluoranthene	45	115	35	125
Benzo[k]fluoranthene	45	125	30	135
Benzo[g,h,i]perylene	40	125	25	140
Chrysene	55	110	45	120
Dibenz[a,h]anthracene	40	125	25	140
Fluoranthene	55	115	45	125
Fluorene	50	110	40	115
Ideno[1,2,3-cd]pyrene	40	120	25	135
Naphthalene	40	105	30	120

TABLE DoD-IV. Solid LCS/MS Control Limits for Semi-volatile Organic Target Compounds (continued)

Analyte	Solid Control Limits			
	Lower	Upper	Lower ME	Upper ME

Phenanthrene	50	110	40	120
Pyrene	45	125	35	135
Phenolic/Acidic				
2,4,5-Trichlorophenol	50	110	40	120
2,4,6-Trichlorophenol	45	110	30	120
2,4-Dichlorophenol	45	110	35	120
2,4-Dimethylphenol	30	105	20	115
2,4-Dinitrophenol	15	130	10	150
2-Chlorophenol	45	105	35	115
2-Methylphenol	40	105	30	115
2-Nitrophenol	40	110	30	120
3 & 4-Methylphenol	40	105	30	120
4,6-Dinitro-2-methylphenol	30	135	10	155
4-Chloro-3-methylphenol	45	115	35	125
4-Nitrophenol	15	140	10	160
Pentachlorophenol	25	120	10	135
Phenol	40	100	30	110
Phthalate Esters				
Bis(2-ehtylhexyl)phthalate	45	125	35	140
Butyl benzyl phthalate	50	125	35	135
Di-n-butyl phthalate	55	110	45	120
Di-n-octyl phthalate	40	130	25	145
Diethyl phthalate	50	115	40	125
Dimethyl phthalate	50	110	40	120
Nitrosoamines				
N-Nitrosodi-n-propylamine	40	115	30	125
N-Nitrosodimethylamine	20	115	10	130
N-Nitrosodiphenylamine	50	115	40	125
Chlorinated Aliphatics				
Bis(2-chloroethoxy)methane	45	110	30	120
Bis(2-chloroethyl)ether	40	105	25	115
Bis(2-chloroisopropyl)ether	20	115	10	130
Hexachlorobutadiene	40	115	25	130
Hexachloroethane	35	110	20	120
Halogenated Aromatics				
1,2,4-Trichlorobenzene	45	110	30	120
1,2-Dichlorobenzene	45	95	35	105
1,3-Dichlorobenzene	40	100	30	110

TABLE DoD-IV. Solid LCS/MS Control Limits for Semi-volatile Organic Target Compounds (continued)

Analyte	Solid Control Limits			
	Lower	Upper	Lower ME	Upper ME
1,4-Dichlorobenzene	35	105	25	115

2-Chloronaphthtalene	45	105	35	115
4-Bromophenyl phenyl ether	45	115	35	130
4-Chlorophenyl phenyl ether	45	110	35	120
Hexachlorobenzene	45	120	35	130
Nitroaromatics				
2,4-Dinitrotoluene	50	115	35	130
2,6-Dinitrotoluene	50	110	35	125
2-Nitroaniline	45	120	30	130
3-Nitroaniline	25	110	15	125
4-Nitroaniline	35	115	20	125
Nitrobenzene	40	115	30	125
Neutral Aromatics				
Carbazole	45	115	30	130
Dibenzofuran	50	105	40	110
Others				
Benzyl alcohol	20	125	10	140
Isophorone	45	110	30	125

TABLE DoD-V. Poor Performing Semi-volatile Organic Target Compounds

Analyte	Control Limits			
	Lower	Upper	Lower ME	Upper ME
Aqueous:				
4-Nitrophenol	0	125	0	145
Benzoic Acid	0	125	0	150
Phenol	0	115	0	135
Phenol-d5/d6 (surrogate)	10	115	0	135
Solid:				
3,3'Dichlorobenzidine	10	130	0	145
Benzoic Acid	0	110	0	130

TABLE DoD-VI. Characteristic Ions for Semi-volatile Organic Target Compounds

Analyte	Primary	Secondary	Tertiary
1,2,4-Trichlorobenzene	180	182	145
1,2-Dichlorobenzene	146	148	111
1,2-Diphenylhydrazine	77	105	182

1,3-Dichlorobenzene	146	148	111
1,4-Dichlorobenzene	146	148	111
1,4-Dichlorobenzene-d14 (Internal Standard)	152	150	115
2,2'-oxybis(1-chloropropane)**	445	77	79
2,4,5-Trichlorophenol	196	132	97
2,4,6-Tribromophenol (Surrogate Standard)	330	332	62
2,4,6-Trichlorophenol	196	198	200
2,4-Dichlorophenol	162	164	98
2,6-Dichorophenol	162	164	98
2,4-Dimethylphenol	122	107	121
2,4-Dinitrophenol	184	154	63
2,4-Dinitrotoluene	165	63	182
2,6-Dinitrotoluene	165	89	121
2-Chloronaphthalene	162	164	127
2-Chlorophenol	128	130	64
2-Fluorobiphenyl (Surrogate Standard)	172	171	N/A
2-Fluorophenol (Surrogate Standard)	112	64	92
2-Methylnaphthalene	142	141	115
2-Methylphenol	108	107	77
2-Nitroaniline	138	65	92
2-Nitrophenol	139	65	109
3,3'-Dichlorobenzidine	252	254	
3-Nitroaniline	138	65	92
4,6-Dinitro-2-methylphenol	198	121	105
4-Bromophenyl phenyl ether	248	250	141
4-Chloro-3-methylphenol	107	142	144
4-Chlorophenyl phenyl ether	204	206	141
3 & 4-Methylphenol	108	107	77
4-Nitroaniline	138	65	92
4-Nitrophenol	109	65	81
Acenaphthene	153	152	154
Acenaphthene-d10 (Internal Standard)	164	162	160
Acenaphthylene	152	151	153
Anthracene	178	176	179
Benzidine	184	92	185
Benzoic Acid	122	105	77
Benzo(a)anthracene	228	229	226
Benzo(a)pyrene	252	253	125

TABLE DoD-VI. Characteristic Ions for Semi-volatile Organic Target Compounds (continued)

Analyte	Primary	Secondary	Tertiary
Benzo(b)fluoranthene	252	253	125
Benzo(g,h,i)perylene	276	138	277
Benzo(k)fluoranthene	252	253	125

Benzyl Alcohol	108	79	77
Bis(2-Chloroethoxy)methane	93	63	95
Bis(2-chloroethyl)ether	93	63	95
Bis(2-ethylhexyl)phthalate	149	167	279
Butyl benzyl phthalate	149	91	206
Carbazole	167	139	N/A
Chrysene	228	226	229
Chrysene-d12 (Internal Standard)	240	236	120
Dibenz(a,h)anthracene	278	279	139
Dibenzofuran	168	139	84
Diethylphthalate	149	177	150
Dimethyl phthalate	163	164	194
Di-n-butyl phthalate	149	150	104
Di-n-octylphthalate	149	150	N/A
Fluoranthene	202	101	100
Fluorene	166	165	167
Hexachlorobenzene	284	142	249
Hexachlorobutadiene	225	223	227
Hexachloroethane	117	201	199
Indeno(1,2,3-cd)pyrene	276	N/A	N/A
Isophorone	82	138	95
Naphthalene	128	129	102
Naphthalene-d8 (Internal Standard)	136	N/A	N/A
Nitrobenzene	77	123	51
Nitrobenzene-d5 (Surrogate Standard)	82	54	128
N-Nitrosodimethylamine	74	42	44
N-Nitroso-di-n-propylamine	70	42	130
N-Nitrosodiphenylamine	169	168	167
N-Nitrosodipyrrolidine	100	41	42
Pentachlorophenol	266	264	268
Perylene-d12 (Internal Standard)	264	260	265
Phenanthrene	178	176	179
Phenanthrene-d10 (Internal Standard)	188	N/A	N/A
Phenol	94	66	65
Phenol-d5/d6 (Surrogate Standard)	99	42	71
Pyrene	202	101	100
Terphenyl-d14 (Surrogate Standard)	244	122	N/A

** 2,2'-oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether.

TABLE DoD-VII. ICV Acceptance Criteria for Semi-volatile Target Organic Compounds

Analyte	%Difference or %Drift
1-Chloronaphthalene	≤ 25
1,2-Dichlorobenzene	≤ 25
1,3-Dichlorobenzene	≤ 25
1,4-Dichlorobenzene	≤ 25

1,2,4-Trichlorobenzene	≤ 25
2-Chloronaphthalene	≤ 25
2-Chlorophenol	≤ 25
2-Methylphenol (o-cresol)	≤ 25
2-Methylnaphthalene	≤ 25
2-Nitroaniline	≤ 25
2-Nitrophenol	≤ 25
2,4-Dichlorophenol	≤ 25
2,4-Dimethylphenol	≤ 25
2,4-Dinitrophenol	≤ 25
2,4-Dinitrotoluene	≤ 25
2,6-Dinitrotoluene	≤ 25
2,4,5-Trichlorophenol	≤ 25
2,4,6-Trichlorophenol	≤ 25
3-Methylphenol (m-cresol)	≤ 25
3-Nitroaniline	≤ 25
3,3'-Dichlorobenzidine	≤ 25
3,3'-Dimethylbenzidine (o-toluidine)	≤ 25
4-Bromophenyl phenyl ether	≤ 25
4-Chloroaniline	≤ 25
4-Chlorophenyl phenyl ether	≤ 25
4-Methylphenol (p-cresol)	≤ 25
4-Nitroaniline	≤ 25
4-Nitrophenol	≤ 25
4-Chloro-3-methylphenol	≤ 25
4,6-Dinitro-2-methylphenol (Dinitro-o-cresol)	≤ 25
Acenaphthene	≤ 25
Acenaphthylene	≤ 25
Anthracene	≤ 25
Azobenzene	≤ 25
Benz(a)anthracene	≤ 25
Benzidine	≤ 25
Benzo(a)pyrene	≤ 25
Benzo(b)fluoranthene	≤ 25
Benzo(g,h,i)perylene	≤ 25
Benzoic Acid	≤ 25

TABLE DoD-VII. ICV Acceptance Criteria for Semi-volatile Target Organic Compounds (continued)

Analyte	%Difference or %Drift
Benzo(k)fluoranthene	≤ 25
Benzyl butyl phthalate	≤ 25
Bis(2-chloroethoxy)methane	≤ 25
Bis(2-chloroethyl)ether	≤ 25

Bis(2-chloroisopropyl)ether	≤ 25
Bis(2-ethylhexyl)phthalate	≤ 25
Carbazole	≤ 25
Chrysene	≤ 25
Dibenz(a,h)anthracene	≤ 25
Dibenzofuran	≤ 25
DEET	≤ 25
Diethylphthalate	≤ 25
Dimethylphthalate	≤ 25
Di-n-butylphthalate	≤ 25
Di-n-octylphthalate	≤ 25
Fluoranthene	≤ 25
Fluorene	≤ 25
Hexachlorobenzene	≤ 25
Hexachlorobutadiene	≤ 25
Hexachlorocyclopentadiene	≤ 25
Hexachloroethane	≤ 25
Ideno(1,2,3-cd)pyrene	≤ 25
Isophorone	≤ 25
Naphthalene	≤ 25
Nitrobenzene	≤ 25
N-Nitrosodimethylamine	≤ 25
N-Nitroso-di-n-propylamine	≤ 25
N-Nitrosodiphenylamine	≤ 25
Pentachlorophenol	≤ 25
Phenanthrene	≤ 25
Phenol	≤ 25
Piperonyl butoxide	≤ 25
Pyrene	≤ 25
Pyridine	≤ 25

*Azobenzene is formed by decomposition of 1,2-diphenylhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

TABLE DoD-VIII. CCV Acceptance Criteria for Semi-volatile Target Organic Compounds

Analyte	% Difference or % Drift
1,2,4-Trichlorobenzene	≤ 30
1,2-Dichlorobenzene	≤ 30
1,2-Diphenylhydrazine	≤ 30
1,3-Dichlorobenzene	≤ 30
1,4-Dichlorobenzene (CCC)	≤ 20
2,2'-oxybis(1-chloropropane)**	≤ 30

2,4,5-Trichlorophenol	≤ 30
2,4,6-Trichlorophenol (CCC)	≤ 20
2,4-Dichlorophenol (CCC)	≤ 20
2,6-Dichorophenol	≤ 30
2,4-Dimethylphenol	≤ 30
2,4-Dinitrophenol	≤ 30
2,4-Dinitrotoluene	≤ 30
2,6-Dinitrotoluene	≤ 30
2-Chloronaphthalene	≤ 30
2-Chlorophenol	≤ 30
2-Methylnaphthalene	≤ 30
2-Methylphenol	≤ 30
2-Nitroaniline	≤ 30
2-Nitrophenol (CCC)	≤ 20
3,3'-Dichlorobenzidine	≤ 30
3-Nitroaniline	≤ 30
4,6-Dinitro-2-methylphenol	≤ 30
4-Bromophenyl phenyl ether	≤ 30
4-Chloro-3-methylphenol (CCC)	≤ 20
4-Chlorophenyl phenyl ether	≤ 30
3 & 4-Methylphenol	≤ 30
4-Nitroaniline	≤ 30
4-Nitrophenol	≤ 50
Acenaphthene (CCC)	≤ 20
Acenaphthylene	≤ 30
Anthracene	≤ 30
Benzidine	≤ 50
Benzoic Acid	≤50
Benzo(a)anthracene	≤ 30
Benzo(a)pyrene (CCC)	≤ 20
Benzo(b)fluoranthene	≤ 30
Benzo(g,h,i)perylene	≤ 30
Benzo(k)fluoranthene	≤ 30
Benzyl Alcohol	≤50

TABLE DoD-VIII. CCV Acceptance Criteria for Semi-volatile Target Organic Compounds (continued)

Analyte	% Difference or % Drift
Bis(2-Chloroethoxy)methane	≤ 30
Bis(2-chloroethyl)ether	≤ 30
Bis(2-ethylhexyl)phthalate	≤ 30
Butyl benzyl phthalate	≤ 30
Carbazole	≤ 30
Chrysene	≤ 30

Dibenz(a,h)anthracene	≤ 30
Dibenzofuran	≤ 30
Diethylphthalate	≤ 30
Dimethyl phthalate	≤ 30
Di-n-butyl phthalate	≤ 30
Di-n-octylphthalate (CCC)	≤ 20
Fluoranthene (CCC)	≤ 20
Fluorene	≤ 30
Hexachlorobenzene	≤ 30
Hexachlorobutadiene (CCC)	≤ 20
Hexachloroethane	≤ 30
Indeno(1,2,3-cd)pyrene	≤ 30
Isophorone	≤ 30
Naphthalene	≤ 30
Nitrobenzene	≤ 30
N-Nitrosodimethylamine	≤ 30
N-Nitroso-di-n-propylamine	≤ 30
N-Nitrosodiphenylamine (CCC)	≤ 20
N-Nitrosodipyrrolidine	≤ 30
Pentachlorophenol (CCC)	≤ 20
Phenanthrene	≤ 30
Phenol(CCC)	≤ 20
Pyrene	≤ 30

APPENDIX SIM – Selected Ion Monitoring (SIM) Analysis

Selected Ion Monitoring (SIM) technique is sometimes required to achieve lower PQL for certain compounds.

For SIM analysis the DFTPP instrument performance check is not required.

A five point initial calibration and daily calibration verification are required before sample analysis can begin. For most operations, the calibration standards are to be prepared at 0.10, 0.20, 0.40, 0.80, and 1.0 ng/µL for each target compound of interest and the associated DMCs. If optional

analysis by SIM is to be performed, the analyst shall add sufficient amount of the internal standard solution to each accurately measured aliquot of sample extract to result in a 0.40 ng/µL concentration of each internal standard.

The acceptance criteria for the initial calibration and calibration verification are project dependent.

The concentration for each of the initial calibration standard is project dependent. The calibration verification standard must be the mid-level (Level 3) standard of the initial calibration.

If the optional analysis by SIM is to be performed, just prior to SIM analysis add sufficient amount of the internal standard solution to an aliquot of water or low-level sample extracts to result in a 0.40 ng/µL concentration of each internal standard.

When setting up the instrument acquisition method, the dwell time and resolution parameters are defaulted to 100ms and low, respectively. In the “dwell” column, enter the amount of time to spend sampling a specific ion. 100 ms is satisfactory for two to three ions. For more than three ions, use a shorter dwell time (such as 30 or 50ms) to ensure there will be enough data points to define the peaks.

Appendix P

Laboratory SOPs

Herbicides

Shealy SOP

S-EX-004 (Preparation)

S-SV-022 (Analysis)

SHEALY ENVIRONMENTAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

CHLORINATED HERBICIDES EXTRACTION

METHOD 8151A

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1. SCOPE AND APPLICATION

1.1 Method 8151 describes the procedure for the extraction of certain chlorinated acid herbicides and related compounds in aqueous, soil and waste materials. Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), this method describes a hydrolysis step that can be used to convert herbicide esters into the acid form prior to analysis. Herbicide esters generally have a half-life of less than one week in soil.

2. SUMMARY OF METHOD

2.1 For aqueous samples – A measured volume of sample, usually 1 liter, is acidified to pH < 2 with 1:1 sulfuric acid. The sample is then extracted with diethyl ether and esterified with diazomethane.

2.2 For solid samples – 50 g of sample is acidified to pH < 2 with 1:1 hydrochloric acid. The sample is then extracted and esterified with diazomethane.

2.3 For Non-Aqueous samples-, 1g of sample is extracted and esterified with diazomethane.

3. DEFINITIONS

3.1 Refer to the QAMP for definition of terms used in this SOP.

4. 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.

4.2 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by detergent washing with hot water, rinses with tap water, rinses with organic-free reagent water, and then with acetone (in that order). After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Immediately prior to use, glassware should be rinsed with acetone and pesticide-quality hexane.

4.2.1 The use of high purity reagents and solvents helps to minimize interference problems. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary.

4.3 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.

4.4 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.

4.5 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed then rinsed to constant pH with organic-free reagent water. Sodium sulfate and glass wool must be acidified.

4.6 Sample extracts should be dried prior to methylation or else poor recoveries will be obtained.

5. SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all Shealy personnel.

5.2 As stated in the Shealy Comprehensive Chemical Hygiene, Safety, and Hazard Communication Plan (P-HS-003), eye protection that satisfies ANSI Z87.1, laboratory coat, and at least latex gloves must be worn while samples, standards, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3 The health and safety hazards of many of the chemicals used in the procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazard is known:

5.3.1 The following material is classified as a **carcinogen**:
Methylene chloride, diazomethane

5.3.2 The following materials are known to be **flammable**:
n-hexane, acetone, methylene chloride

5.3.3 The following materials are known to be **irritants**:
n-hexane, acetone, methylene chloride

5.3.4 The following material is known to have **explosive potential**:
diazomethane

5.3.4.1 Since the explosive potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free from etches, cracks, or chips, and which does not have ground glass joints.

5.3.4.2 Solutions of diazomethane will be kept at temperature below 90°C.

5.3.4.3 Diazomethane must be generated and handled in a fume hood.

5.3.4.4 Store diazomethane away from alkali metals.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 Any accidents and spills above 50 mls must be reported to the lab supervisor, team leader, or safety officer.

5.6 Discard chipped or broken glassware to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.7 All work must be stopped in the event of a known or potential compromise to the health and safety of Shealy personnel. The situation must be reported immediately to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1 Fume hood.

6.2 Timers – Capable of measuring seconds.

6.3 pH indicator paper – pH range including the desired extraction pH.

6.4 Analytical balance – Capable of accurately weighing to 0.0001g.

6.5 Syringe –1 mL.

6.6 Boiling chips – Teflon, approximately 10/40 mesh.

6.7 Vials – 12 mL, glass with PTFE-lined screw caps.

6.8 Pipet – 2 ml Pasteur, glass, disposable.

6.9 Pipet – 10 mL, sterile, disposable.

6.10 Erlenmeyer flask – 250 mL and 500 mL, with a ground-glass joint at the neck.

6.11 Water bath – Capable of holding temperature at 60 ± 2°C.

6.12 Separatory funnel – 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

6.13 Beaker – 150 mL, 250 mL, 400 mL, 600 mL, thick-walled.

6.14 Funnel – 75-mm diameter with 80-mm stem length and 5-mm stem diameter.

6.15 Glass wool, acid washed.

6.16 Graduated cylinder – 1-L, 100 mL.

6.17 Glass powder filter funnels – 75-mm diameter with 35-mm stem and 12-mm stem diameter.

6.18 Filter papers – 15-cm diameter (Whatman No. 1 or equivalent).

6.19 Spatula – Stainless steel, PTFE, or disposable wooden.

6.20 Wrist shaker – Burrell Model 75 or equivalent.

6.21 Clamps to hold K-D flasks, concentrator tubes, and Snyder columns together.

6.22 Kuderna-Danish (K-D) apparatus:

6.22.1 Concentrator tube – 10 mL graduated (Kontes K-570050-1025 or equivalent) with ground-glass stopper.

6.22.2 Evaporation flask – 500 mL (Kontes K-570001-500 or equivalent). Can be attached to concentrator tube with springs, clamps, or equivalent.

6.22.3 Snyder column – Three-ball macro (Kontes K-503000-0121 or equivalent).

6.23 Diazomethane Bubbler – Assemble from two 20 mm × 150 mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The bubbler assembly is explained in Figure 4.

7. REAGENTS AND STANDARDS

- **Note: All stored reagents and standards are labeled with the following information:**

  1. **Name of standard or solution**
  2. **Concentration**
  3. **Analyst's initials**
  4. **Prep date**
  5. **Expiration date**
  6. **Tracking number**
  7. **Warning label of any hazards and/or precautions for use**

7.1 Reagent Water – Shealy employs a series of in-house deionized (DI) tanks to purify the incoming water to the conductivity measurement, 0.056 μmhos/cm (corresponds to resistivity of 18 meg-ohms). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2 Ottawa Sand.

7.3 Sodium sulfate (granular, acidified, anhydrous), Na_2SO_4 – Purify by heating to 450°C for 4 hours. Acidify by slurrying 1000 g sodium sulfate with enough diethyl ether to just cover the solid; then add 1.0 mL of concentrated sulfuric acid in a drop wise manner and mix thoroughly. Place tray of acidified sodium sulfate on water bath heated at 65 ± 5°C and evaporate ether and acid until sodium sulfate is completely dried. Store in oven at 130°C. Good for up to 6 months.

- Note:
  - Heating must be done under a fume hood.
  - To check the pH of the acidified sodium sulfate, add 1 g of the acidified sodium sulfate to 5 mL of organic-free reagent water. The mixture must have pH of <4.

7.4 Sulfuric acid (H_2SO_4) solution, 1:1 (v/v) – Slowly add 50 mL of concentrated H_2SO_4 to 50 mL of organic-free reagent water. Other concentrations of acid solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

7.5 Sulfuric acid (H_2SO_4) solution, 1:3- Slowly add 50mL of concentrated H_2SO_4 to 150 mL of organic-free reagent water. Store at 4°C(± 2).

7.6 Hydrochloric acid (HCl) solution, 1:1 (v/v) – Slowly add 50 mL of concentrated HCl to 50 mL of organic-free reagent water.

- **Note: When preparing diluted acid, always add acid to water. If the water is added to the acid, a violent reaction may occur.**

7.7 Solvents – All solvents must be pesticide quality or equivalent.

7.7.1 Acetone, CH_3COCH_3.

7.7.2 Hexane, C_6H_{14}, boiling point 68.7°C.

7.7.3 Diethyl Ether, $C_2H_5OC_2H_5$ – must be free of peroxides.

7.7.4 Isooctane, $(CH_3)_3CH_2CH(CH_3)_2$.

7.7.5 Methanol, CH_3OH.

7.7.6 Carbitol (diethylene glycol monoethyl ether), $C_2H_5OCH_2CH_2OCH_2CH_2O$.

7.8 Nitrogen gas.

7.9 Diazald – reagent grade.

7.10 Silicic Acid – reagent grade.

7.11 Potassium hydroxide (37% aqueous solution (w/v)), KOH – Dissolve 37.0 g of potassium hydroxide pellets in reagent water in a 100 mL volumetric flask. Bring up to volume with reagent water.

7.12 Sodium hydroxide (NaOH), (10N) solution – Weigh out 1000.0 grams of sodium hydroxide pellets. Place a 2000 mL beaker containing 1000-1200 mL of reagent water on a stir plate and add small portions of the pellets to beaker. **Use caution when adding sodium hydroxide pellets; a substantial amount of heat will be generated by the addition of sodium hydroxide pellets.** After the addition of the 1000.0 grams of sodium hydroxide pellets, transfer the solution to an appropriate storage container. Rinse the beaker with reagent water, and transfer to the storage container. Bring the final volume to 2500 mL with reagent water.

7.13 Stock standard solutions – Commercially available. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to two years and must be replaced sooner if verification from an independent source indicates a problem. See Table

7.14 Spike and surrogate solutions – All matrix and surrogate spiking standards are in free acid form and are purchased from approved vender in solutions. All acid standards have a holding time of 2 months and must be replaced sooner if verification from an independent source indicates a problem. Refer to Table I for appropriate concentration of spiking and surrogate solutions used. Table II shows the specific compounds in each spike and surrogate solution and the concentration of each compound that is added to the sample.

- **Note: All standards prepared for surrogate, LCS, and matrix-spiking solutions must be analyzed by GC or GC/MS prior to use for sample extraction.**

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Aqueous samples are collected in 1-L amber glass bottles; solid samples are collected in 9-oz glass jars.

8.2 Samples must be stored at 4 ± 2°C from the time of receipt until extraction. The holding time for samples in this method is 7 days for aqueous and 14 days for non-aqueous.

9. QUALITY CONTROL

9.1 Initial Demonstration of Capability and MDL:

9.1.1 The initial demonstration of capability (IDOC) and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.2 Extraction Batch – A group of up to 20 samples that are of the same matrix (aqueous, solids, or TCLP) and are processed together using the same procedures and reagents. The batch must contain a method blank (MB), a laboratory control sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD). If insufficient sample volume exists to perform an MS/MSD, a laboratory control sample duplicate (LCSD) must be performed to generate precision data. In some cases, at the request of the client, it may be appropriate to process a matrix spike and a sample duplicate in addition to the MS/MSD. If the clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs. A TCLP batch requires one method blank (MB) for each extraction fluid, a laboratory control sample (LCS), and a matrix spike (MS).

9.3 Sample Count – Laboratory generated QC samples (MB, LCS, LCSD, and MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

9.4 Method Blank (MB) – One method blank must be processed with each batch. The method blank consists of reagent water and all reagents and compounds specific to the method. The method blank is carried through the same extraction procedure as samples. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated concentration of compounds or false positive data. Acceptance criteria of method blanks and corrective actions are contained within the individual analytical method SOP.

9.4.1 The aqueous method blank is prepared by adding 1.0 mL of surrogate spiking solution, containing all specific compounds, to 1000 mL of reagent water. For aqueous TCLP herbicides, samples that are <0.05% solid, the method blank is prepared in the same manner. The method blank is then processed as described in Section 11.

9.4.2 The TCLP method blank is prepared by diluting 100 mL of the TCLP blank leachate to 1000 mL with reagent water and adding 1.0 mL of surrogate spiking solution. The TCLP method blank is then processed as described in Section 11. TCLP Extraction Fluid 1 and TCLP Extraction Fluid 2 must be extracted in separate leachate batches, as well as, prep batches containing the

corresponding samples. One method blank is prepared from each type of extraction fluid.

9.4.3 The solid method blank is prepared by adding 1.0 mL of surrogate spiking solution, containing all compounds specific to the method, to the appropriate reagents. The solid method blank is then processed as described in Section 11.

9.5 Laboratory Control Sample (LCS) – One aqueous LCS must be processed with each batch. The LCS consists of all compounds specific to the method, and 1.0 mL of matrix spiking solution, containing known amounts of all compounds of interest. The LCS must be carried through the entire extraction procedure described in Section 11. The LCS is used to monitor the accuracy of the extraction process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Acceptance criteria of LCS and corrective actions are contained within the individual analytical method SOP.

9.5.1 The aqueous LCS is prepared by spiking 1000 mL aliquot of reagent water with 1.0 mL of surrogate spiking solution, and 1.0 mL of the appropriate matrix spiking solution (see Table II). The LCS is then processed as described in Section 11. The aqueous TCLP herbicide LCS is prepared in the same manner using the matrix spiking solution specific to TCLP herbicides.

9.5.2 The TCLP LCS is prepared by diluting 100 mL of TCLP blank filtrate to 1000 mL with reagent water and adding 1.0 mL of surrogate spiking solution and 1.0 mL of the appropriate matrix spiking solution (see Table II). The LCS is then processed as described in Section 11.

9.5.3 The solid LCS is prepared by adding 1.0 mL of the surrogate spiking solution, and 1.0 mL of the appropriate matrix spiking solution to the appropriate reagents. The LCS should be processed as described in Section 11.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – One MS/MSD pair must be processed for each aqueous and solid batch. TCLP herbicide extraction requires each batch to contain a matrix spike (MS) only. A matrix spike (MS) is a field sample to which known concentrations of all compounds of interest have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in addition to MS/MSD. The MS/MSD results are used to determine the

effect of a matrix on the precision and accuracy of the analytical process. If MS/MSD are not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits. **Samples identified as field blanks cannot be used for MS/MSD analysis**. Acceptance criteria of MS/MSD and corrective actions are contained within the individual analytical method SOP.

9.6.1 The aqueous matrix spike sample is prepared by spiking 1000 mL aliquot of the designated sample with 1.0 mL of surrogate spiking solution and 1.0 mL of the appropriate matrix spiking solution (see Table II). The MS/MSD are then processed as described in Section 11. The aqueous TCLP herbicide MS is prepared in the same manner using the matrix spiking solution specific to TCLP herbicides. A matrix spike duplicate (MSD) is not required for TCLP herbicide extraction.

9.6.2 The TCLP matrix spike is prepared by diluting 100 mL of TCLP blank filtrate to 1000 mL with reagent water and adding 1.0 mL of surrogate spiking solution and 1.0 mL of the appropriate matrix spiking solution (see Table II). The TCLP MS is then processed as described in Section 11.

9.6.3 The solid matrix spike is prepared by adding 1.0 mL of the surrogate spiking solution, and 1.0 mL of the appropriate matrix spiking solution to 50 g of the designated sample containing specific reagents and solvents to the method. The MS should be processed as described in Section 11.

9.6.4 If MS/MSD are not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be extracted and analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

10. CALIBRATION AND STANDARDIZATION

10.1 The balance calibration is checked at the beginning of each day using a certified weight set and recorded in a logbook.

10.2 The check must weigh within ±10% (i.e., 0.1 mg) at 1 mg and ± 0.5% (i.e., 5.0 mg) at 1000 mg. If values are not within these limits, recalibrate the balance.

11. PROCEDURE

- **NOTE: BEFORE ANY QUALITY CONTROL OR FIELD SAMPLES ARE PROCESSED, ALL GLASSWARE USED IN THE PROCEDURE FOR ALL SAMPLES MUST BE RINSED WITH HEXANE.**

11.1 Preparation of aqueous and TCLP samples:

11.1.1 Aqueous sample volume measurement:

11.1.1.1 Transfer 1 L of reagent water into each of 2 separatory funnels for aqueous method blank and laboratory control sample.

11.1.1.2 If aqueous sample is collected in a container larger than 1 L, use a properly cleaned graduated cylinder to measure 1 L of sample and transfer to a 2 L separatory funnel.

11.1.1.3 Alternatively, mark the sample level on the sample container and transfer the entire contents of the 1 L aqueous sample bottle into a separatory funnel. Refill the sample container with water to the mark and then measure using a 1 L graduated cylinder. Record the volume to the nearest 5 mL.

11.1.1.4 If high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 1 L with reagent water.

- Any reduction in the volume of a sample should be approved by a supervisor, lab director, or QA Officer and completely documented using a Nonconformance Memo. The client shall be notified and the NCM filed in the project file. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.1.2 TCLP leachate/Aqueous TCLP sample volume measurement:
Refer to
Sections 11.1.2.1 - 11.1.2.3 for TCLP leachate sample volume measurement. For aqueous TCLP sample volume measurement,
refer to Sections 11.1.2.4 to 11.1.2.6.

11.1.2.1 Transfer 100 mL of TCLP blank leachate to each of 2

separatory funnels and dilute to 1000 mL with reagent water
for TCLP method blank and laboratory control sample.

11.1.2.2 For TCLP samples, transfer 100 mL of the TCLP leachate to a
2 L separatory funnel and dilute to 1000 mL with reagent
water.

11.1.2.3 An additional 100 mL aliquot of a sample designated for the MS should be transferred to a 2 L separatory funnel and diluted to 1000 mL with reagent water.

11.1.2.4 For aqueous TCLP herbicides, samples that are <0.05% solid,
1 L of reagent water is used for both the method blank and the laboratory control sample.

11.1.2.5 If the TCLP sample is aqueous, the sample must be filtered before preparation. The aqueous portion collected is defined as the TCLP filtrate. Transfer 100 mL of the aqueous filtrate to a 2 L separatory and dilute to 1000 mL with reagent water.
.

11.1.2.6 An additional 100 mL aliquot of a designated filtrate should be prepared in the same manner as the sample for the MS.

11.1.3 Using a syringe, add 1.0 mL of the surrogate spiking solution (refer to Section 7.12) to the method blank, LCS, each sample, and the MS (MSD, if applicable).

11.1.4 To each, the LCS and MS (MSD, if applicable) using a syringe, add 1.0 mL of the appropriate matrix spiking solution (refer to Section 7.12).

11.1.5 Record the unique chemical ID’s of the surrogate and matrix spiking solutions, expiration dates, and volumes used on the prep batch sheet. These chemical ID’s will be entered into LIMS during batch promotion.

11.1.6 Add 250g of NaCl to the method blank, LCS/D,MS/MSD, and samples, seal and shake to dissolve the salt.

11.1.7 If samples are being extracted for herbicide esters, hydrolysis must be performed.

Refer to Section 11.2.1 for hydrolysis procedure.

11.1.8 If samples are being extracted for herbicide acids only, refer to Section 11.2.2.

11.2 Extraction of aqueous and TCLP samples:

11.2.1 HYDROLYSIS of Aqueous Samples: Use this step only if herbicide esters, in addition to herbicide acids, are to be determined.

- Note: Quality Control (MB, LCS, LCSD, MS/MSD) samples are treated and extracted in the same manner as field samples.

11.2.1.1 Add 10-12 mL of 10N NaOH 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 10 N NaOH. Let the sample sit at room temperature until the hydrolysis step is completed (usually 1-2 hours), shaking the separatory funnel and contents periodically.

11.2.1.2 Add 60 mL of methylene chloride to rinse the graduated cylinder used in transferring the sample (or sample bottle if the sample was transferred directly from the bottle). Transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 minutes, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10

minutes. If the emulsion interface between the layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods. Discard the methylene chloride phase.

- Note: Record the chemical ID of the methylene chloride used for extraction for subsequent entry into LIMS.

11.2.1.3 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. Perform a third extraction in the same manner.

11.2.2 Add approximately 15-20 mL of 1:1 sulfuric acid to the sample (or hydrolyzed sample), seal, and shake to mix. For samples that are being extracted for only herbicide acids, a smaller portion of acid, 5-10 mL, should be sufficient to adjust the pH. Check the pH of the sample with pH paper. If the sample does not have a pH <2, adjust the pH by adding more acid.

- Note: Lesser strengths of acid solution may be used, provided that it does not result in a significant change (e.g., <1%) in the volume of sample extracted.

11.2.3 Add 180 mL of diethyl ether directly to the separatory funnels for the hydrolyzed samples or use 180 mL of diethyl ether to rinse the cylinder used in transferring sample (or sample bottle if the sample was poured directly from the bottle) and transfer this rinse solvent to the separatory funnel. Record the chemical ID of the diethyl ether used for extraction for subsequent entry into LIMS.

11.2.4 Seal and shake the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure.

- Note: Diethyl ether creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the

separatory funnel has been sealed and taken off the holding rack before being shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors.

11.2.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between the layers is more than one third of the volume of the solvent layer, the analyst must employ mechanical techniques to complete phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, centrifugation, or other physical methods.

11.2.6 Collect the aqueous layer (bottom layer) in a 1 L Erlenmeyer flask or original sample container. Drain the diethyl ether extract (top layer) into a 250 mL or 500 mL glass stoppered Erlenmeyer flask. Rinse the separatory funnel with a small portion of diethyl ether and collect the rinsate in the Erlenmeyer flask.

11.2.7 Return the aqueous phase to the separatory funnel. Using 60 mL of diethyl ether, repeat the extraction procedure (Section 11.2.3-11.2.6) a second time, combining the extracts in the 250/500 mL Erlenmeyer flask. Perform a third extraction with 60 mL diethyl ether in the same manner. After all three portions of extracts are combined, refer to Section 11.5.

11.3 Extraction of soil, sediment, or other solid samples by shaker extraction or ultrasonic extraction.

11.3.1 Shaker Extraction

- All samples must be homogenized prior to obtaining the aliquot to be used for extraction. See Sub-Sampling SOP S-QA-010 for sub sampling instructions

11.3.1.1 Add 50 g of Ottawa Sand to the Method Blank and LCS in a 500mL Erlenmeyer flask.. Add 50 of the well-mixed solid sample to a 500 mL Erlenmeyer flask. Two 50 g aliquots of the same designated sample must be weighed for the MS/MSD. Adjust the pH to 2 with 1:1 HCl and place stopper on flask. Monitor the pH for 15 minutes with occasional stirring. If necessary, add additional HCl until the pH remains <2.

11.3.1.2 Designate two flasks, one for the method blank (MB) and one for the LCS.

11.3.1.3 Using a syringe, add 1.0 mL of surrogate spiking solution (refer to Section 7.12) into the method blank, LCS, LCSD (if applicable), each sample, and MS/MSD.

11.3.1.4 To the LCS and MS/MSD, using a syringe, add 1.0 mL of the appropriate matrix spiking solution (refer to Section 7.12).

- Note: After surrogate and/or matrix spiking solution(s) have been added to an individual sample, replace the stopper. DO NOT leave sample unstopped; doing so may lead to the loss of surrogate and/or target compounds in the sample.

11.3.1.5 Record the unique chemical ID's and expiration date of the surrogate and matrix spiking solutions, and volumes used on the batch sheet. These chemical ID's will be entered into LIMS during batch promotion.

11.3.1.6 Immediately following the addition of the surrogate and matrix spiking solutions, add 20 mL of acetone to each of the flask, and place stopper on the flask. After all flasks have had the spiking solutions and solvents added and have been stoppered, mix the contents with the wrist shaker for 20 minutes. Add 80 mL of diethyl ether to the same flask and shake again for 20 minutes. Record the chemical ID of the acetone and diethyl ether used for extraction for subsequent entry into LIMS.

11.3.1.7 Using a glass powder funnel and filter paper (Whatman No. 1 or equivalent) filter the extract into a clean, solvent-rinsed, 250/500 mL Erlenmeyer flask. The filter paper should be pre-moistened with diethyl ether before the transfer of the extract. Immediately rinse the filter paper with 5-10 mL of ethyl ether after the sample extract drains through.

11.3.1.8 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 minutes and the acetone-ether extract filtered into the corresponding Erlenmeyer flask.

11.3.1.9 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent (i.e. 225 mL). If this is not the case, additional extraction is required using 10 mL of acetone and 40 mL of diethyl ether.

11.3.1.10 Transfer the extracts to 2-L separatory funnels containing 250 mL of reagent water. If an emulsion forms, slowly add 5 g of

acidified sodium sulfate (anhydrous), until the solvent-water mixture separates. A quantity of sodium sulfate equal to the weight of the sample may be added, if necessary.

11.3.1.11 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to pH < 2, using 1:1 HCl.

- Note: Lesser strengths of acid solution may be used, provided that it does not result in a significant change (i.e. <1%) in the volume of extract.

11.3.1.12 Gently shake the contents of the separatory funnel for 1 minute and allow 10 minutes for the layers to separate.

11.3.1.13 Collect the aqueous phase in a clean 600 mL beaker and the extract phase (top layer) in a 500 mL ground glass stoppered Erlenmeyer flask.

11.3.1.14 Transfer the aqueous phase back into the separatory funnel and extract a second time using 25 mL of diethyl ether, shaking contents for 1 minute and allowing 10 minutes for layers to separate.

11.3.1.15 After sufficient time has passed for layers to separate, drain and discard the aqueous layer. Combine the ether extracts in the Erlenmeyer flask. Proceed to 11.5

11.3.2 Ultrasonic Extraction

11.3.2.1 Add 50g of the well-mixed solid sample to a 9oz jar. Adjust the pH to 2 with concentrated hydrochloric acid and thoroughly mix the contents. Add acidified sodium sulfate, if needed to attain a sandy free flowing mixture.

11.3.2.2 Add 1.0 ml of the surrogate spiking solution to all samples, including the MB, and LCS and MS/MSD, if applicable. To the LCS and each of the sample aliquots weighed for MS/MSD, if applicable, add 1.0 ml of appropriate spiking solution.

11.3.2.3 Immediately after adding the surrogate and spiking solutions, to appropriate samples, add 100 ml of methylene chloride/acetone (80ml:20ml), (v/v).

11.3.2.4 Place the bottom surface of the tip of the ¾” disruptor horn about ½” below the surface of the solvent, but above the sediment layer. Do not use a micro tip probe.

- Note: Be sure the horn is properly tuned according to the manufacturer's instructions.

11.3.2.5 With the power control knob set at 10 (full power), press the START key to run the program. The sample will be extracted ultrasonically for three minutes. (Output control knob at 10 (full power), mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle set at 50% (energy on 50% of the time and energy off 50% of the time). Allow the solids to settle. Transfer the organic layer to a 500 ml Erlenmeyer flask through a filter paper containing 7-10g of acidified sodium sulfate.

11.3.2.6 Ultrasonically extract the sample twice more using 100 ml of methylene chloride with the same ultrasonic conditions. Add 7-10g of sodium sulfate to each extract and allow the extracts to sit and dry for 2 hours, stirring occasionally.

11.3.2.7 After drying for 2 hours,transfer the extract to a 500ml K-D flask with a 10ml concentrator tube attached. Add 2-3 boiling chips and attach the macro Snyder column. Concentrate the extract, using a water bath set at 75°C, to a volume of approximately 5mls. Add 50mls of hexane and transfer the flask to the waterbath set at 90°C and let the extracts concentrate to a volume of approximately 5mls. Remove the flask from the water bath and allow them to cool. If hydrolysis is not needed proceed to 11.5.

11.3.3 HYDROLYSIS of Solid Samples: Use this step only if herbicide esters, in addition to herbicide acids, are to be determined.

11.3.3.1 Add 5ml of 37% aqueous potassium hydroxide and 30ml of organic reagent water to the extract. Add an additional 2-3 boiling chips. If extract was in a turbo vap tube, add the potassium hydroxide and water and transfer to a K-D flask. Reflux the mixture on a water bath at 60-65°C until the hydrolysis step is completed (usually 1-2 hours). Remove the flasks from the water bath and allow to cool to room temperature.

- CAUTION: the presence of residual acetone will result in the formation of aldol condensation products which will cause GC interference.

11.3.3.2 Transfer the hydrolyzed aqueous solution to a 2000ml separatory funnel and extract the solution three times with 100ml portions of methylene chloride allowing 10 minutes between extraction. Discard

the methylene chloride phase. At this point, the basic (aqueous) solution contains the herbicide salts.

11.3.3.3 Adjust the pH of the solution to <2 with cold (4°C) 1:3 sulfuric acid and add 40ml of diethyl ether. Shake for 2 minutes and let stand for 10 minutes. Collect the extract in a 9oz jar. Extract and collect twice more with 20ml of ether. Add 10g of acidified sodium sulfate and swirl extract. Add sodium sulfate slowly until free flowing and allow the extract to remain in contact with the drying agent for a minimum of 2 hours. Proceed to 11.6.

11.4 Extraction of Non-Aqueous samples:

11.4.1 All samples must be homogenized prior to obtaining the aliquot to be used for extraction. See Sub-Sampling SOP S-QA-010 for sub sampling instructions

11.4.2 Add 1g of sample to a 12 ml sample vial.

11.4.3 Two 1 g aliquots of the same designated sample must be weighed for the MS/MSD.

11.4.4 Designate two 12ml vials, one for the method blank (MB) and one for the LCS (add additional vial for a LCSD if insufficient sample for an MS/MSD).

11.4.5 Add approximately 3.0 mls of ethyl ether to MB, LCS, LCSD (if required), each sample, and MS/MSD.

11.4.6 Using a syringe, add 1.0 mL of surrogate spiking solution (refer to Section 7.12) into the method blank, LCS, LCSD, each sample, and MS/MSD.

11.4.7 To the LCS, LCSD and MS/MSD, using a syringe, add 1.0 mL of the appropriate matrix spiking solution (refer to Section 7.12).

11.4.8 Record the unique chemical ID's and expiration date of the surrogate and matrix spiking solutions, and volumes used on the batch sheet. These chemical ID's will be entered into LIMS during batch promotion.

11.4.9 If the sample is to be analyzed for both herbicide esters and acids, then the sample extract must be hydrolyzed. In this case, transfer 1.0 ml (a smaller volume or a dilution may be required if herbicide concentrations are large) to a 250ml Erlenmeyer flask. Proceed to section 11.3.5 for hydrolysis.

11.4.10 Proceed to 11.7 for completion

11.5 Drying of Aqueous extracts:

11.5.1 Add 30 – 50 g of acidified sodium sulfate to the Erlenmeyer flask containing extract. Depending on the sample, more sodium sulfate may be necessary to ensure dryness. The amount of sodium sulfate is adequate when, some free flowing crystals are visible when swirling the flask. If the sodium sulfate solidifies or there is no free flowing sodium sulfate, add additional grams of acidified sodium sulfate and again test by swirling.

11.5.2 Allow the extract to remain in contact with the sodium sulfate for approximately 12 hours at room temperature. If a time limitation does not allow for the extract to be dried overnight, the extract may be dried for 2 hours, minimum, at $4 \pm 2^{o}C$.

- Note: The drying step is very critical to ensuring complete esterification. Any moisture remaining in the ether will result in low herbicide recoveries.

11.6 Concentration of extract using the Turbo Vap:

- NOTE: **IMMEDIATELY PRIOR TO USE, RINSE EACH piece of glassware, AS WELL AS FUNNELS AND TURBO VAP TUBES, WITH HEXANE.**

11.6.1 Turbo Vap Concentration:
Label Turbo Vap tubes accordingly. Filter the dried extract through a funnel plugged with acid washed glass wool into the corresponding Turbo Vap Tube. Place the Turbo vap tubes in the turbo vap at approximately 35°C. Concentrate the extract to approximately 0.5mL. Transfer the extract to a 10mL condenser.

11.7 Esterification of concentrated extract – Diazomethane derivatization – Bubbler method:

- CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

The following precautions must be taken:

- Do not heat above 90°C – Explosion may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, and glass stirrers – Explosion may result.
- Store away from alkali metals – Explosion may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

11.7.1 Add 1.0 mL of isooctane and 0.5 mL of methanol, using 10 mL sterile pipets, to the extract. Dilute to a final volume of 4.0mL with diethyl ether.

11.7.2 Assemble the diazomethane bubbler (see Figure 4).

11.7.2.1 In the first test tube, add 5.0 mL of diethyl ether.

11.7.2.2 In the second test tube, add 1.0 mL of diethyl ether, 1.0 mL of carbitol, 1.5 mL of 37% KOH, and 0.1 – 0.2 g of Diazald.

- Note: The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1 – 0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 minutes of total esterification.

11.7.3 Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists.

11.7.4 Remove the concentrator tube and cover sample. Place in a hood at room temperature for 20 minutes.

11.7.5 Destroy any unreacted diazomethane by adding 0.1 – 0.2 g of silicic acid to the concentrator tube. Allow samples to stand covered, until the evolution of nitrogen gas has stopped.

11.7.6 Using 2 mL Pasteur pipet, transfer the extract to a calibrated 12 mL vial with PTFE lined cap, adjust the extract volume in 10 mL with hexane. Label vial with sample ID, method, and prep batch number, and store away from light at 4 ± 2°C.

11.8 The extract may now be analyzed for herbicides.

11.9 Procedural Variations – This section applies to all samples except South Carolina compliance samples. One time procedural variations are allowed, only if deemed necessary in the professional judgment and supervision of a knowledgeable analyst, to accommodate variation in matrix, chemistry, sample size, or other parameters. Any variation in analytical procedure must be approved by a technical director, the QA Officer, or the client, and must be fully documented (flagged and/or narrated) on the final report. The analyst must use an NCM to notify the appropriate parties and to document the variance. The project manager uses the information on the NCM to notify the client and flag/narrate the final report accordingly. A copy of the NCM is stored with the raw data and the original is filed with the final report.

11.8.1 For South Carolina compliance samples, all procedures outlined in this SOP must be followed without exception. In the event that a deviation from this SOP cannot be avoided (i.e., demonstrated and uncorrectable matrix interference, non-compatible matrix, insufficient sample amount due to client or laboratory error) it is imperative that an NCM is completed that clearly documents the anomaly. This anomaly must be communicated to the client such that the corrective action activity including the sample recollection can be performed. Based upon the type and severity of anomaly, the results may not be appropriate for compliance reporting. Discussions between the client, the appropriate regulator authority, and Shealy will be necessary to resolve certain anomalies. In any case, it is essential that any anomaly be documented in an NCM.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Not applicable.

13. METHOD PERFORMANCE

13.1 Method performance is determined by the analysis of MS and MSD samples as well as method blanks and laboratory control samples. The MS/MSD and LCS must fall within the percent recovery limits and the method blank must meet the criteria specified in determinative SOP.

13.2 Method Detection Limit - Each laboratory must generate a valid method detection limit for each analyte of interest. The procedure for the determination of the method detection limit is in the Shealy QAMP.

13.3 Initial Demonstration - Each laboratory must make an initial demonstration of capability for each individual method. This requires analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The QC check may also be obtained from an outside source. (For certain tests, more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

13.3.1 Four aliquots of the QC check samples are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample must be equal to the LCS concentration.

13.3.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria for the corresponding analyte in the LCS. Calculations and acceptance criteria for the LCS are given in the analytical SOP.

13.3.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet the criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and corrective action.

13.4 Non-standard analytes - For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed on with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and single point calibration.

13.5 Training Qualification - The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience performs this procedure

14. POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1 Waste generated in the procedure including hexane must be segregated and disposed of according to the SHEALY Waste Management Plan (P-HS-001) and per the local, state, and federal regulations. The Safety Officer should be contacted if additional information is required.

15.2 Standards should be purchased and prepared in volumes consistent with laboratory use, to minimize the volume of expired standards to dispose of.

15.3 Wastes that are classified as non-hazardous will be neutralized with sodium hydroxide pellets before being disposed of.

16. REFERENCES

16.1 SW-846, Test Method for Evaluating Solid Waste, Third Edition – Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization, Method 8151A, Revision 1, December 1996.

16.2 Shealy Quality Assurance Management Plan (QAMP), Q-QA-001, Revision 7, July 2010

16.3 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 3, January 2006.

17. MISCELLANEOUS

17.1 All glassware use in this procedure (including new glassware) must be washed with detergent, rinsed with tap water, then with reagent water, then with acetone and finally with hexane.

- Note: The used hexane must be collected and stored in a sealed container to be disposed of properly.

Figure 1. Herbicides Extraction for Aqueous/TCLP Samples

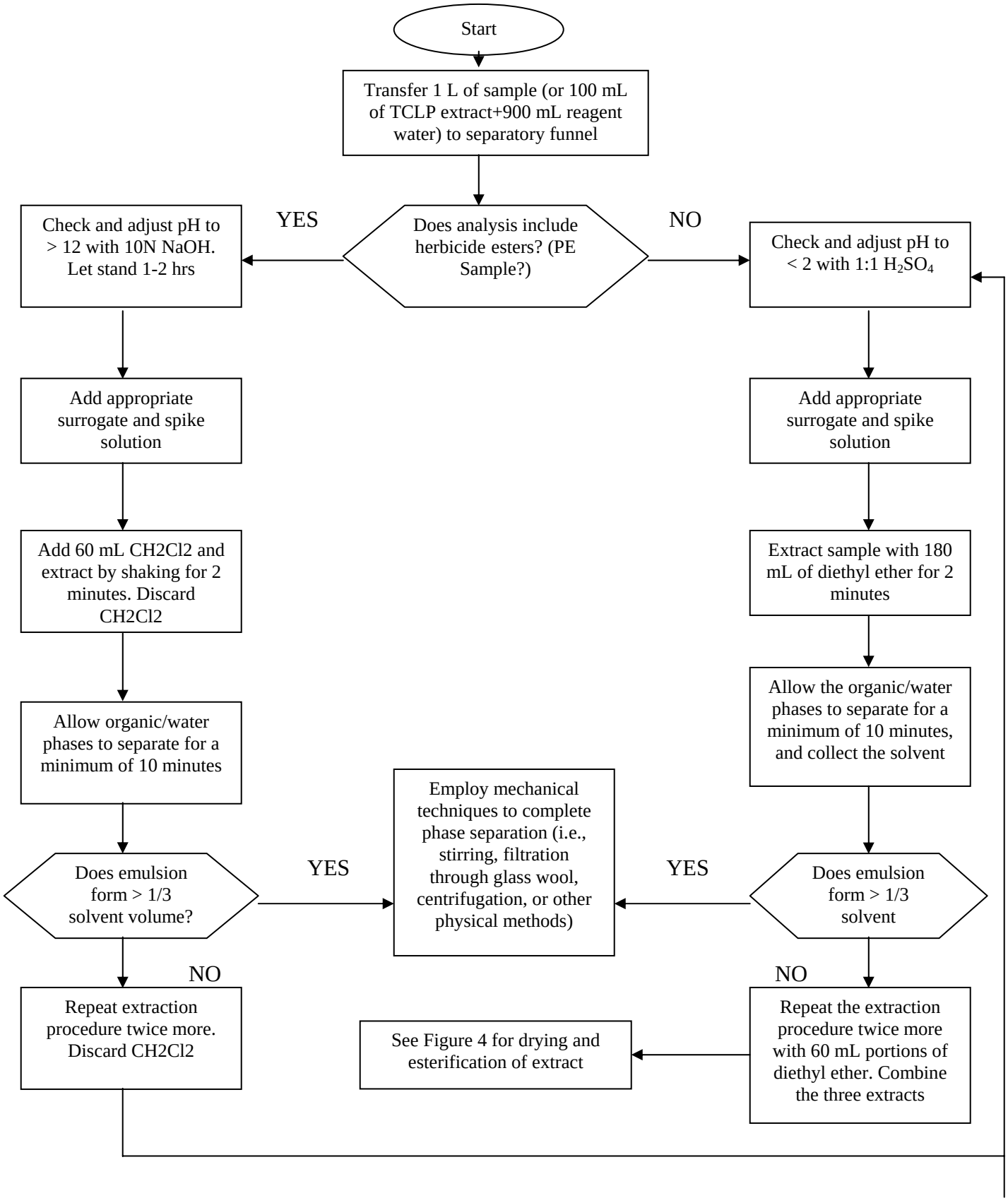


Figure 2. Herbicides Extraction for Solid Samples

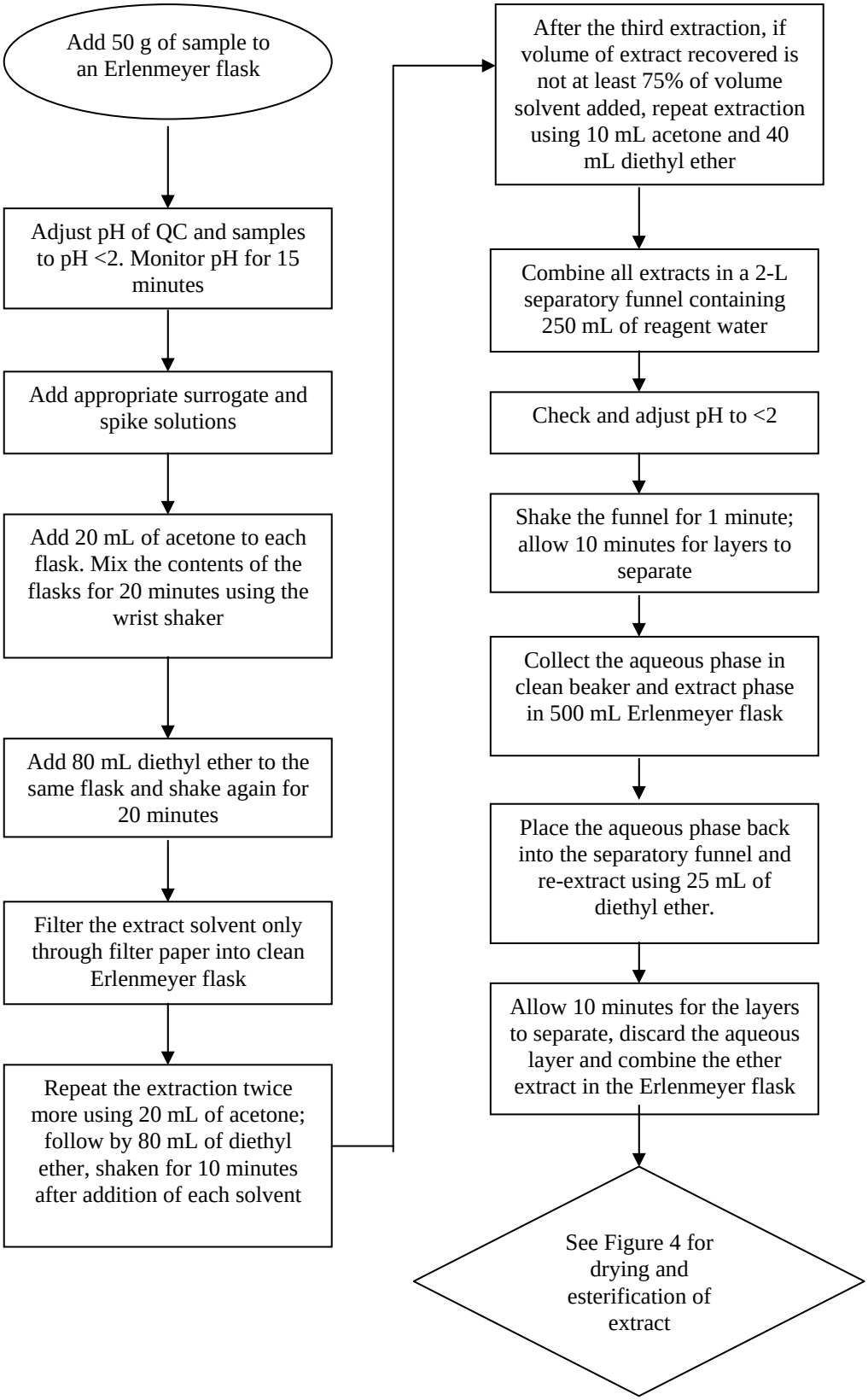


Figure 3. Extraction for Non-Aqueous Samples

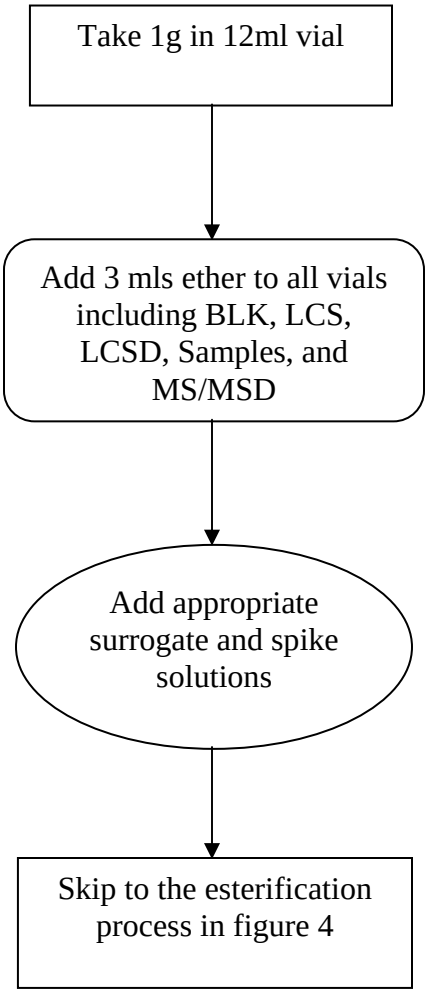
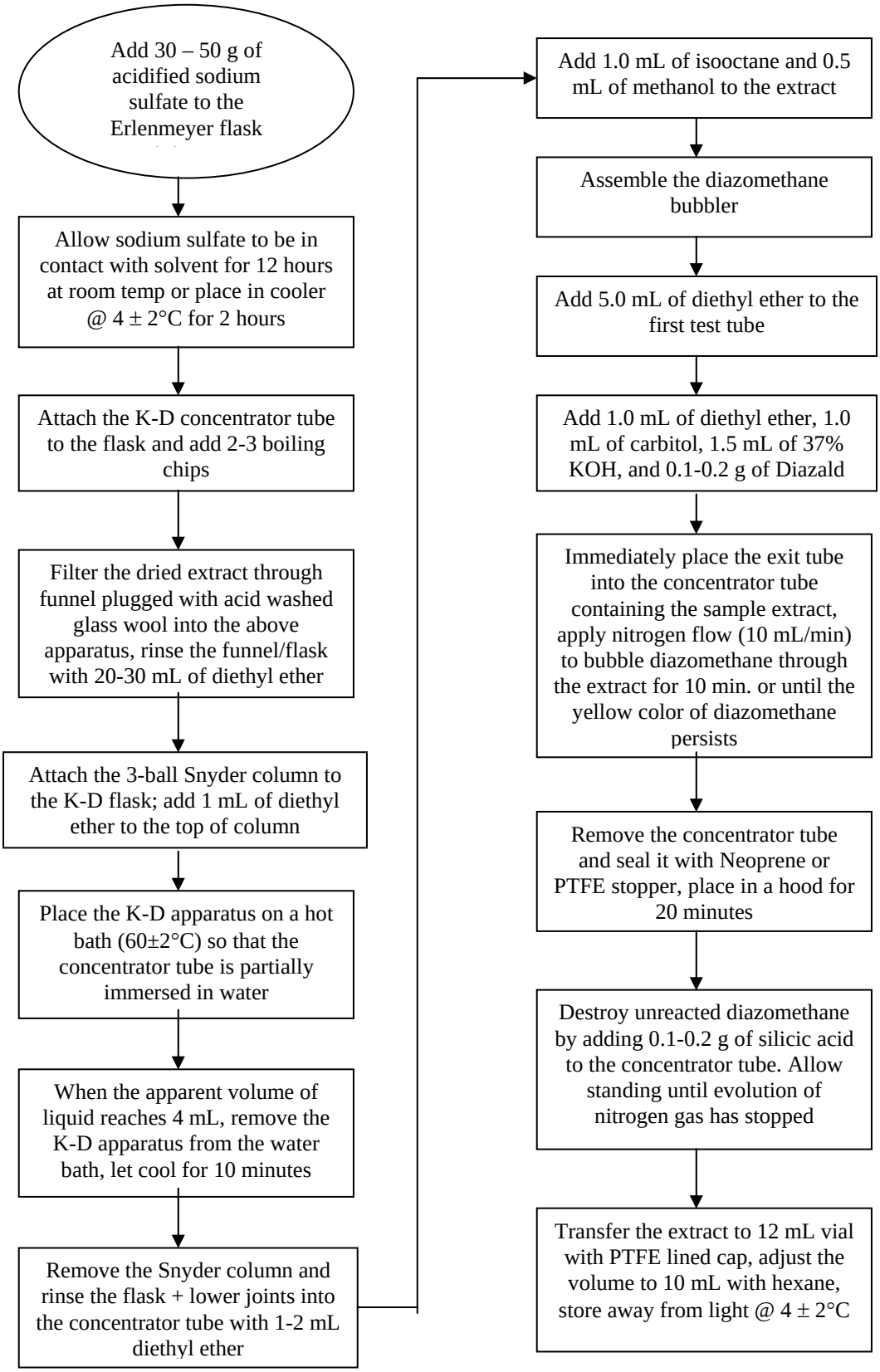


Figure 4. Drying and Esterification of Extracts



APPENDIX A

TABLES

Table I. Spike and Surrogate Compounds and Vendors for Herbicides

	Concentration of Stock Solution (µg/ mL)	Concentration in Final Extract (µg/mL)[1]	Amount Added (mL)	Diluted to (mL)	Vendor	
Spike Compound				50.0	**AccuStandard**	
2,4,5-T	100	10	5.0			
2,4-D	100	10	5.0			
2,4-DB	100	10	5.0			
Dalapon	100	10	5.0			
Dicamba	100	10	5.0			
Dichloroprop	100	10	5.0			
Dinoseb	100	10	5.0			
MCPA	10,000	1000	5.0			
MCPP	10,000	1000	5.0			
Silvex (2,4,5-TP)	100	10	5.0			
Pentachlorophenol	2000	10	0.25			
TCLP Spike Compound				100	Ultra Scientific	
2,4-D	2000	20	1.0			
Silvex (2,4,5-TP)	2000	20	1.0			
Surrogate Compound					Ultra Scientific	
DCAA	5000	50	1.0	100		

Table II Stock Standard Compounds and Vendors for Herbicides

Standard/Solution	Concentration of Stock Solution (µg/ mL)	Concentration in Final Extract (µg/mL)[1]	Amount Added (mL)	Diluted to (mL)	Vendor
Dinoseb	100	10	1	10	Supelco
Chlorinated Herb Acids				10	Supelco
2,4-D	100	10.0	1		
2,4-DB	200	20.0	1		
2,4,5-T	25	2.5	1		
2,4,5-TP	25	2.5	1		
Dalapon	250	25.0	1		
Dicamba	50	5.0	1		
Dichloroprop	100	10.0	1		
MCPA	10,000	1000.0	1		
MCPP	10,000	1000.0	1		
DCAA	100	10.0	1		
Pentachlorophenol	10	1.0	1		

APPENDIX – DoD

Table III. Spike and Surrogate Compounds for Herbicides

	Concentration of Stock Solution (µg/ mL)	Concentration in Final Extract (µg/mL)[1]	Amount Added	Diluted to(mL)	Vendor
Spike Compound				50.0	**AccuStandard**
2,4,5-T	100	10	5.0		
2,4-D	100	10	5.0		
2,4-DB	100	10	5.0		
Dalapon	100	10	5.0		
Dicamba	100	10	5.0		
Dichloroprop	100	10	5.0		
Dinoseb	100	10	5.0		
MCPA	10,000	1000	5.0		
MCPP	10,000	1000	5.0		
Silvex (2,4,5-TP)	100	10	5.0		

SHEALY ENVIRONMENTAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

GAS CHROMATOGRAPHIC ANALYSIS BASED ON EPA SW-846 METHODS 8000B and 8151A

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TABLE DoD-G Chlorinated Herbicide Target Analyte List for DoD

TABLE DoD-H LCS/MS Control Limits for Chlorinated Herbicides for DoD

1. SCOPE AND APPLICATION

1.1 This SOP describes procedures for analysis of organic analytes by Gas Chromatography (GC). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA). Individual analytes and methods are described in the appendices.

1.2 North Carolina and Department of Defense-Quality Systems Manual (DoD-QSM) requirements discussed in the appendices of this SOP supersede the requirements of normal procedures.

2. SUMMARY OF METHOD

2.1 After the initial preparation step, SOP S-EX-004, the sample is introduced to the GC and concentrations of target analytes are measured by the detector response within a defined retention time window, relative to the response to standard concentrations. Internal or external standardization procedures are used as specified in the method appendices.

3. DEFINITIONS

3.1 Batch – The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a laboratory control sample (LCS), and a method blank (MB). In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Batches are defined at the sample preparation stage. Batches should be kept together through the entire analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the Shealy Quality Assurance Management Plan (QAMP) for further details of the batch definition.

3.2 Method Blank – An analytical control consisting of all reagents, internal standards, and surrogate standards that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

3.3 LCS (Laboratory Control Sample) – A blank spiked with the parameters of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.4 MS (Matrix Spike) – Aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.5 MSD (Matrix Spike Duplicate) – A second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method.

3.6 ICV (Initial Calibration Verification) / Second Source Calibration Verification – A standard that is prepared from a different source than the initial calibration standards. The ICV is analyzed after the initial calibration and is used to verify the accuracy of the calibration.

3.7 CCV (Continuing Calibration Verification) – A standard prepared from the same parent standard as the initial calibration. The CCV is used to verify that the instrument response is reliable, and has not changed significantly from the initial calibration curve being used.

3.8 The definitions of any additional terms used in this SOP may be found in the Shealy Quality Assurance Management Plan (QAMP), Q-QA-001.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. If interference is detected, it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2 The use of high purity reagents, solvents, and gases helps to minimize interference problems. Refer to P-QA-006 Solvent Purity Check policy for the procedure for testing the purity of solvents used for extraction.

4.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples.

4.5 Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results.

5. SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all Shealy employees.

5.2 As stated in the Shealy Comprehensive Chemical Hygiene, Safety, and Hazard Communication Plan (P-HS-003), eye protection that satisfies ANSI Z87.1, laboratory coat, and at least latex or nitrile gloves must be worn while samples, standards, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. Specific hazards are covered in the appendices.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers should be kept closed unless transfers are being made. In addition, opened containers of neat standards will be handled in a fume hood.

5.5 All work must be stopped in the event of a known or potential compromise to the health and safety of a Shealy employee. The situation must be reported immediately to a laboratory supervisor and the EHSO (Environmental Health and Safety Officer).

6. EQUIPMENT AND SUPPLIES

6.1 An analytical system with a gas chromatograph containing an injection port(s) and dual Electron Capture Detectors (ECD) is required.

6.2 A data system capable of measuring peak area and/or height is required.

6.3 Recommended equipment and supplies for individual methods are listed in each method appendix.

7. REAGENTS AND STANDARDS

7.1 Stock Standards – Stock standards are purchased as certified solutions or prepared from pure solutions.

7.1.1 Stock standards are stored according to manufacturer recommendations, either 4°C ± 2°C,–10 to –20°C, or ambient temperature, depending on the media the standards were prepared with. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

7.1.2 Purchased standards, if unopened, expire on the date specified by the manufacturer. Opened stock standards and all working standards expire 6 months from the date opened or prepared or on the expiration date of their parent standards, whichever is sooner. Refer to herbicide standards, Appendix C, Section 7, for more detail of holding times. All standards' expiration dates are checked prior to use and disposed of if not within that expiration date.

7.2 Calibration Standards – Semivolatile calibration standards are prepared as dilutions of the stock standards. Surrogates standards are used as specified in the method appendices. Prepared semivolatile calibration solutions must be kept refrigerated at 4 ± 2 °C and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.3 Gases for carrier and make-up: Hydrogen and Nitrogen.

7.4 Quality Control (QC) Standards – QC standards (LCS and matrix spiking standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independent from the calibration standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Aqueous samples are collected in two 1-liter amber glass containers. Solid samples are collected in 4-oz glass containers. Samples are stored at 4 ± 2°C.

8.2 Aqueous samples are extracted within 7 days of collection. Solid samples are extracted within 14 days of collection. The extracts are analyzed within 40 days of extraction.

9. QUALITY CONTROL

9.1 Initial Demonstration of Capability:

9.1.1 For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in the Shealy QAMP must be acceptable before analysis of samples may begin.

9.1.2 For non-standard, non-regulatory analytes, an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2 Batch Definition – Batches are defined at the sample preparation stage. Batches should be kept together through the entire analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the Shealy QAMP for further details of the batch definition.

9.2.1 Quality Control Batch – The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The quality control batch must contain a matrix spike/spike duplicate (MS/MSD), a laboratory control sample (LCS), and a method blank (MB). Laboratory generated QC samples (MB, LCS, and MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count but cannot be used for matrix spikes. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate.

9.3 Control Limits –**In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS/LCSD).** These limits must be determined annually. The recovery limits are mean recovery ± 3 standard deviations. Control limits for compliance with the DoD-QSM can be found in DoD tables for each determinative method.

9.3.1 All surrogate, LCS/LCSD, and MS/MSD recoveries must be entered into Shealy LIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.3.2 Refer to the QAMP, Q-QA-001, for further details of control limits.

9.4 Method Blank (Laboratory Reagent Blank) – One method blank must be processed with each preparation and/or analytical batch. The method blank consists of a similar matrix to the batch of associated samples in which no target

analytes or interferences are present at concentrations that impact the analytical results. The method blank is to contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Refer to Appendix DoD for method blank acceptance criteria for samples analyzed for the Department of Defense.

9.4.1 The method blank must not contain any analyte of interest at or above the PQL. If the method blank contains an analyte of interest at or above the PQL, then the method blank and associated samples must be reanalyzed. If the method blank contamination is confirmed, the entire batch must be re-prepared and reanalyzed. The following exceptions apply:

9.4.1.1 If the method blank contains analytes of interest at or above the PQL, then:

9.4.1.1.1 The method blank concentration must be less than 5 % of the regulatory limit associated with that analyte for that sample. If not, re-prep and reanalyze all samples which do not fall within this criterion.

9.4.1.1.2 The method blank contamination must be less than 5 % of the sample concentration. If not, re-prep and reanalyze all samples which do not fall within this criterion.

9.4.2 To clarify the compounds of interest that are associated with each sample the LIMS generated worksheet printout for each sample will be contained in the batch data file. This worksheet printout will list the required target compounds and the reporting limits.

9.4.3 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, corrective action should be taken. The method blank should be reanalyzed if the analyst feels that the failure was attributed to instrument problems. If the failure is due to a poor extraction, the entire batch must be sent for re-extraction.

9.5 Instrument Blank – Instruments must be evaluated for contamination during each 12-hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. The solvent used for the instrument blank may vary with instrumentation. Surrogate standards may be added to the instrument blank for additional quality control. The instrument blank is evaluated in the same way as the method blank.

9.6 Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD) are also known as Laboratory Fortified Blank and Laboratory Fortified Blank Duplicate – Analyze an LCS for each batch of samples. In the unlikely event that an MS/MSD pair cannot be performed, an LCS/LCSD pair must be performed. The LCS and LCSD are prepared in the same manner. Both the LCS and LCSD contain all or a majority of the analytes of interest, and must contain the same analytes as the matrix spike(s). **The LCS/LCSD is of a different source than the ICAL.** If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. The initial corrective action will be to check all calculations. If the calculations are correct, the ensuing corrective action will be the re-preparation and reanalysis of the batch.

9.6.1 The LCS does require confirmation; therefore, each analyte is required to pass on both columns for the LCS and the CCV. Any analyte reported for the LCS must be bracketed by passing CCVs on that column.

9.6.2 Refer to individual test appendices for LCS compounds and surrogate recovery criteria for the LCS.

9.6.3 Some clients require additional analytes for spiking in the LCS. The added compounds must be statistically evaluated to determine if the in-house recovery limits are achievable and realistic.

9.7 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) are also known as the Laboratory Fortified Matrix and Laboratory Fortified Matrix Duplicate – For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and concentrations are the same as the LCS/LCSD. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory specific, historically generated limits.

9.7.1 If any individual recovery falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check all calculations. If the calculations are correct, check the recovery of that analyte in the laboratory control sample (LCS). If the recovery of the analyte in the LCS is within limits, then matrix interference has been demonstrated and the laboratory operation may proceed.

9.7.2 If the recovery for any component is outside QC limits for the matrix spike/spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action may include re-preparation and reanalysis of the batch. An NCM must be generated to document this occurrence.

9.7.3 Every effort is made to ensure that an MS/MSD pair is included in every batch. On the rare occasion that this is not possible (sample bottle was broken, etc.) then an LCS duplicate must be analyzed.

9.7.4 The matrix spike/spike duplicate must be analyzed at the same dilution as the parent sample (the un-spiked sample).

9.8 Surrogates – Every sample, blank, and QC sample is spiked with at least one surrogate compound. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. The compounds routinely included in the surrogate spiking solutions, along with recommended standard concentrations, are listed in the appendices for each analysis.

9.8.1 If any surrogate is outside the acceptance limits, an NCM must be written and the following corrective actions must take place (except for dilutions > 5x).

- Check all calculations for error.
- Ensure that instrument performance is acceptable. If the system is demonstrated to be out of control, all steps taken to return the system to control must be fully documented as part of the corrective action.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveals a problem.
- If the above corrective actions have taken place and the result is a surrogate that is outside of the limits, re-extract and reanalyze the sample. If the re-extract is outside of limits, flag the data as “Estimated Concentration” due to demonstrated matrix effect.
- It is only necessary to re-extract/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.9 Nonconformance and Corrective Action – Any deviations from QC procedures must be documented with a nonconformance memo (NCM), with applicable cause and corrective action(s) approved by the QA Manager.

9.10 Quality Assurance Summaries – Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.11 Shealy QC Program – Further details of QC and corrective action guidelines are presented in the Shealy QAMP. Refer to this document if the samples are from a state other than South Carolina, or if the samples are for non-regulatory reporting.

10. CALIBRATION AND STANDARDIZATION

10.1 All herbicide calibration standards must go through the esterification process. These standards are called procedural standards. Follow the procedure provided in the herbicide preparation SOP (S-EX-004).

10.2 If external calibration is used, prepare standards containing each analyte of interest at a minimum of five concentration levels. Analyze from low to high concentration. The low level standard should be at or below the PQL. The other standards define the working range of the detector. Recommended calibration levels are given in the appendices.

10.3 A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns, replacing the ECD detector, etc. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance. All maintenance must be recorded in the instrument's maintenance log with the date and initials of the analyst performing the maintenance.

10.4 With the exception of Section 10.5 below, it is not acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest of the curve and the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve.

10.5 A level may be removed from the calibration if the reason can be clearly documented, for example, a broken vial. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions; all points must be analyzed within 24 hours.

10.6 External Standard Calibration – Quantitation by the external standard method assumes a proportional relationship between the calibration run and the analyte in the sample. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

$$\text{Calibration Factor (CF)} = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Concentration of Standard } (\mu\text{g/mL})}$$

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. However, if matrix interferences would make quantitation using peak area inaccurate for a particular sample, then peak height may be used as a substitute.

10.7 Calibration curve fits – Average calibration factor, linear regression, may be used to fit the data. Average calibration factor may be used if the % RSD of the calibration factor of the analyte in the calibration standard is ≤ 20 %. A linear fit may be used if the % RSD is > 20 %. The correlation coefficient for the fit must be ≥ 0.995. The Target data system uses R^2 to measure the fit, R^2 must be ≥ 0.990. **The ICAL cannot be forced through zero. No sample analysis may be performed unless these criteria are met on both columns.**

The equation for average calibration factor is:

$$\text{Average calibration factor} = \overline{CF} = \frac{\sum_{i=1}^{n} CFi}{n}$$

Where: n = Number of calibration levels

$\sum_{i=1}^{n} CFi$ = Sum of response factors for each calibration level

10.7.1 Linear regression – The response must increase with increasing concentration. The linear fit uses the following functions:

10.7.1.1 External Standard

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where:

y = Instrument response
x = Concentration
a = Slope
b = Intercept

10.8 Non-standard analytes are sometimes requested. For these analytes, it may be acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. This action must be with client approval. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation.

10.9 Initial Calibration Verification (ICV)/Second Source Calibration Verification – The ICAL is verified by analyzing an ICV. The ICV is a standard obtained from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. The ICV is analyzed immediately after the initial calibration. The value of the second source must agree within 30 % of the expected value of the ICAL before sample analysis can begin. If the ICV fails, repeat. If the second ICV fails, maintenance must be performed and two consecutive ICVs must pass or a new ICAL must be analyzed before sample analysis can begin.

10.10 Continuing Calibration Verification (CCV), also known as the Instrument Performance Check.

10.10.1 Opening CCV – The ICAL must be verified at the beginning of each analytical sequence, after every 20 field samples, and at the end of the sequence. The opening CCV must pass all analytes of interest within ± 15 %. Any CCV that has samples reported after it is considered an opening CCV, even if it is analyzed in the middle of a sequence.

10.10.1.1 If the opening CCV fails, repeat once. If the second analysis fails, instrument maintenance must be performed and two consecutive CCVs must pass or a new ICAL must be performed before sample analysis can occur.

10.12.1.2 The center of each retention time window is updated with each 12-hour CCV. The widths of the windows will remain the same (refer to Section 11.6 for details).

- After any major maintenance (e.g. column change), the RT window must be calculated for each analyte and surrogate.

10.10.2 Closing CCV – Any CCV analyzed after samples is considered a closing CCV for those samples.

10.10.2.1 If the samples preceding the closing CCV are non-detect and the closing CCV is >115 %, the data may be reported.

10.10.2.2 If the closing CCV < 85 %, all associated samples must be reanalyzed.

10.10.2.3 If the samples preceding the closing CCV have a concentration > PQL, the closing CCV must agree within ± 15 %. If the closing CCV fails, all associated samples must be reanalyzed.

10.10.3 A single CCV may be considered both an opening and a closing CCV if the CCV is in the middle of a sequence. At no time can there be more than 12 hours between bracketing CCVs.

10.10.4 Non-detect results: A single sample may be reported from a combination of front and back column results. If only one column passes the CCV criteria, only ND results may be reported for that column, and that analyte.

10.10.5 When a concentration above the PQL (or MDL if "J" flags are required) is detected and confirmed, the higher of the two results is reported. In this case, both front and back columns must pass the opening and closing CCV. (Some client specific programs may require that the lower or both results will be reported.)

10.10.6 Samples quantitated by external standard methods must be bracketed by calibration verification standards that meet the criteria listed above.

10.10.7 % Difference Calculation

10.10.7.1 % Difference for External Standard Method

$$\%\ D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where:

CF_c = Calibration factor from the continuing calibration

$\overline{CF}$ = Average calibration factor from the initial calibration

10.10.8 % Drift Calculation - % Drift is used for comparing the continuing calibration to a linear curve. The criteria for % drift are the same as for % difference.

$$\%\ Drift = \frac{\text{Calculated Conc. - Theoretical Conc.}}{\text{Theoretical Conc.}} \times 100\ \%$$

10.10.9 The retention times of all the analytes in the continuing calibration verification standards must be within the retention time windows as determined in the initial calibration.

11. PROCEDURE

11.1 Extraction – Extraction procedures are referenced in the appendices.

11.2 Cleanup – Cleanup procedures are referenced in the appendices.

11.3 Gas Chromatography – Chromatographic conditions for individual methods are presented in the appendices.

11.4 Sample Introduction – In general, Semivolatile analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.5 Analytical Sequence – An analytical sequence starts with an initial calibration or a daily calibration. Refer to the individual method appendices for method specific details of daily calibrations and analytical sequences.

11.5.1 The daily calibration includes analyses of standards containing all target analytes and updating the retention time windows.

11.5.2 If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration.

11.6 Retention Time Windows

11.6.1 Retention time windows must be determined for all analytes and surrogates. Make an injection of all analytes of interest each day over a 72-hour period. Record the retention time for each single component analyte and surrogate to three decimal places. Calculate the mean and standard deviation of the three absolute retention times for each analyte and surrogate.

11.6.2 If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

11.6.3 The width of the retention time window for each analyte and surrogate is defined as plus or minus three (± 3) times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation in Section 11.6.2 is used, the width of the window will be ± 0.03 minutes.

11.6.4 The centers of the windows are updated with the mid-point of the initial calibration or the CCV that starts the analytical sequence. The centers of the windows must be updated every 12 hours. The widths of

the windows will remain the same until new windows are generated following the installation of a new column.

11.6.5 For DOD, the laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated before performing initial calibrations or analyzing samples.

11.6.6 Corrective Action for Retention Times – The retention times of all compounds in the continuing calibration that starts the sequence must be within the RT windows established during the initial calibration. If this condition is not met, a new initial calibration must be performed. Each subsequent continuing calibration must be within the retention time windows established by the CCV that started the 12-hour analytical sequence. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

11.7 Daily Retention Time Windows – The center of the retention time windows are determined in Section 11.6.4. The retention time windows must be updated by the CCV at the beginning of each analytical sequence, but not for any other calibration verification standards.

11.8 Percent Moisture – Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to S-IN-023, Method 160.3/160.4 for determination of percent moisture.

11.9 Procedural Variations – This section applies to all samples <u>except</u> South Carolina compliance samples. One time procedural variations are allowed, only if deemed necessary in the professional judgment and supervision of a knowledgeable analyst, to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in analytical procedure must be approved by a technical director, the QA Officer, or the client, and must be fully documented (flagged and/or narrated) on the final report. The analyst must use an NCM to notify the appropriate parties and to document the variance. The project manager uses the information on the NCM to notify the client and flag/narrate the final report accordingly. A copy of the NCM is kept with the raw data and the original is filed with the final report.

11.9.1 For South Carolina compliance samples, all procedures outlined in this SOP must be followed without exception. In the event that a deviation from this SOP cannot be avoided (i.e., demonstrated and uncorrectable matrix interference, non-compatible matrix, insufficient sample amount due to client or laboratory error) it is imperative that an NCM is completed that clearly documents the anomaly. This anomaly must be

provided to the client such that corrective action activity including sample recollection can be performed. Based upon the type and severity of anomaly, the results may not be appropriate for compliance reporting. Discussions between the client and the appropriate regulatory authority will be necessary to resolve certain anomalies.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative Identification

12.1.1 Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if "J" flags are required. Confirmation is required on a second column. Refer to the appendices for test specific requirements for confirmation. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (MDL if "J" flags required). For confirmed results, the higher of the two results is reported.

12.1.2 If the relative percent difference (RPD) between the responses on the two columns is > 40 %, or if in the opinion of an experienced analyst the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

$$RPD = \frac{R_1 - R_2}{\frac{1}{2}(R_1 + R_2)} \times 100$$

Where R = Result

12.1.3 The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2 Calibration Range – If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half of the calibration range. It may be necessary to dilute samples due to matrix. In this case, an NCM is required.

12.3 Dilutions – Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hit or hits below 20 % of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must

be reanalyzed at a dilution targeted to bring the largest hit above 50 % of the calibration range.

12.3.1 Guidance for Dilutions Due to Matrix – If the sample is initially run at a dilution and only minor matrix peaks are found, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination.

12.3.2 Reporting Dilutions – The most concentrate dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.4 Interferences – If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5 Calculations – Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in an appendix attached to this document.

12.5.1 External Standard Calculations

12.5.1.1 Aqueous Samples

$$\text{Concentration } (\mu g/L) = \frac{A_x \times V_t \times DF}{CF \times V_o}$$

Where:

A_x = Response for the analyte in the sample
DF = Dilution factor
V_t = Volume of total extract, µL
V_o = Volume of sample extracted or purged, mL
CF = Calibration factor, area or height/µg/mL, Section 10.4

If linear regression is used the following calculation is used:

$$X = \frac{(y-b)V_t DF}{aV_o}$$

Where:

y = Instrument response
x = Concentration

a = Slope
b = Intercept

12.5.1.2 Non-aqueous and Solid Samples

$$\text{Concentration (mg/kg)} = \frac{A_x \times V_t \times DF}{CF \times W \times D}$$

Where:

W = Weight of sample extracted, g

$$D = \frac{100 - \%\text{Moisture}}{100} \qquad (D = 1 \text{ if wet weight is required})$$

If linear regression is used the following calculation is used:

$$x = \frac{(y - b)V_t DF}{aWD}$$

Where:

y = Instrument response
x = Concentration
a = Slope
b = Intercept

12.5.2 Surrogate Recovery – Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equation:

$$\%\ \text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100$$

13. METHOD PERFORMANCE

13.1 Method Detection Limit – Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in Shealy QAMP.

13.2 Initial Demonstration – Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. The standard used is of a

different source than the ICAL. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests, it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in each appendix.

13.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3 Training Qualification – The team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1 Waste generated in this procedure must be segregated and disposed according to the Shealy Waste Management Plan (P-HS-001). The Safety Officer should be contacted if additional information is required.

16. REFERENCES

16.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996, Section 8000B, 8151A

16.2 Shealy Quality Assurance Management Plan (QAMP), Q-QA-001

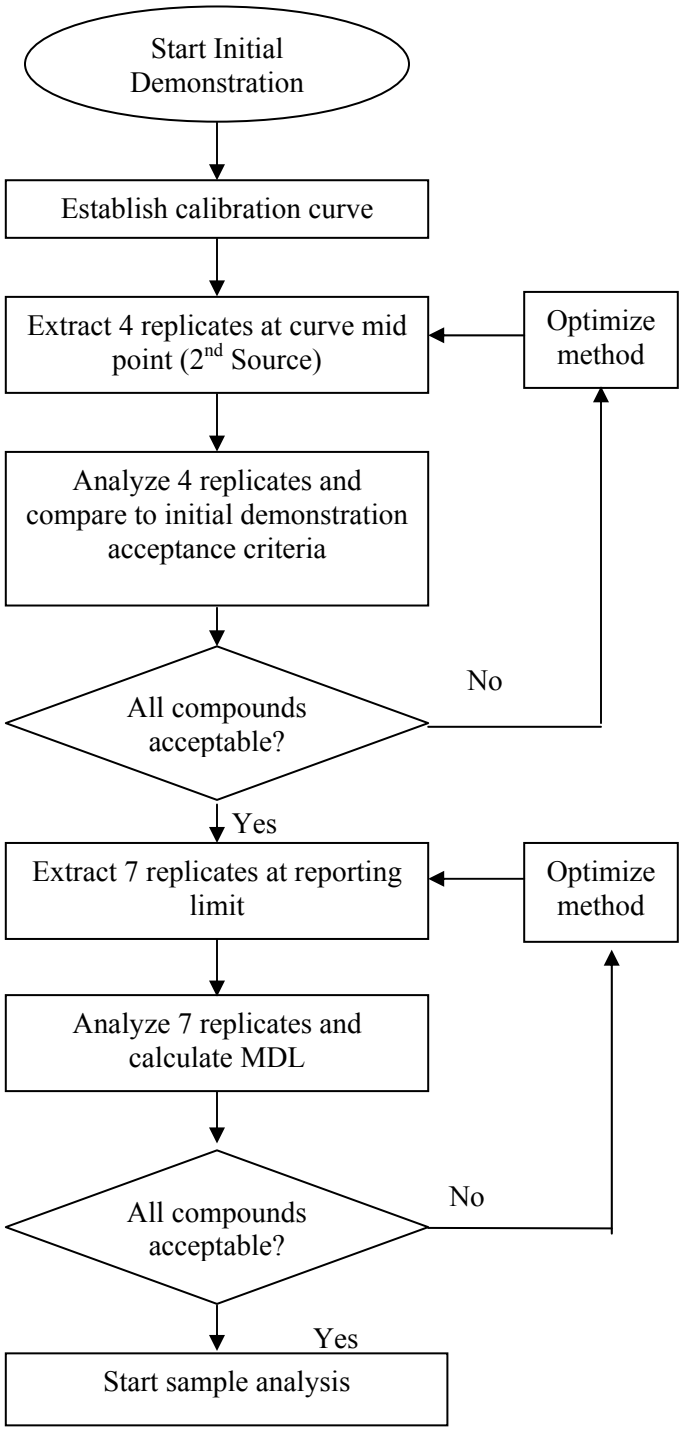
16.3 Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.1, April 2009.

17. MISCELLANEOUS

17.1 Modifications from Reference Method – Chapter 1 of SW-846 states that the Method Blank should not contain any analyte of interest at or above the Method Detection Limit. This SOP states that the Method Blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed to be up to 5 times the reporting limit in the blank following consultation with the client.

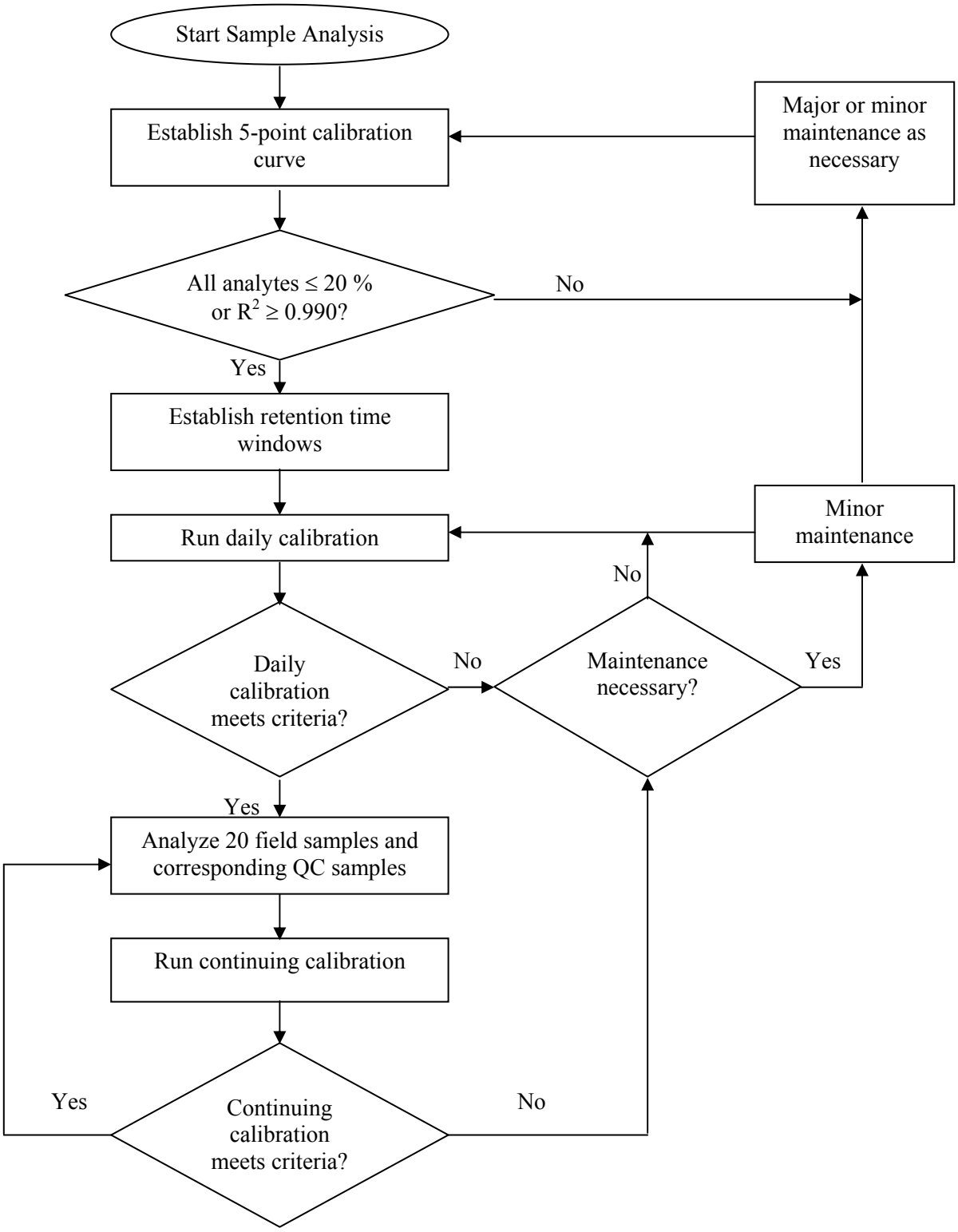
17.2 Flow Diagrams

17.2.1 Initial Demonstration and MDL[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

17.2.2 Sample Analysis



APPENDIX A

ANALYSIS OF PHENOXY ACID HERBICIDES
BASED ON METHOD 8151A

1. SCOPE AND APPLICATION

1.1 This method is applicable to the gas chromatographic determination of Chlorinated phenoxy acid herbicides, and includes all extracts derived from solid, aqueous, or non-aqueous matrices that have been prepared according to SOP S-EX-004. The herbicides listed in Table C-1 are routinely analyzed. Other chlorinated acids may be analyzed by this method if the quality control criteria in Section 9 and the initial demonstration of method performance in Section 13 are met.

2. SUMMARY OF METHOD

2.1 This method presents conditions for the analysis of prepared extracts of phenoxy acid herbicides by gas chromatography. The herbicides, as their methyl esters, are injected onto the column, separated, and detected by electron capture detectors. Quantitation is by the external standard method. Final results are reported as acid.

3. DEFINITIONS

3.1 Refer to the QAMP for definitions of terms used in this document. Definitions may also be found in the method 8000B section of this SOP.

4. INTERFERENCES

4.1 Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

4.2 Chlorinated acids and phenols cause the most direct interference with this method.

4.3 Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups for the herbicide extracts are described in the sample preparation SOP.

5. SAFETY

5.1 Refer to Section 5 of the method 8000B section of this SOP for general safety requirements.

6. EQUIPMENTS AND SUPPLIES

6.1 Refer to Section 6 of the method 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2 Refer to Table C-2 for analytical columns.

6.3 Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1 Refer to Section 7 of the method 8000B section of this SOP for general information of reagents and standards.

7.1.1 Instrument calibration standards are purchased from vendor in acid form. These standards must undergo esterification procedures; refer to prep SOP, S-EX-004 Section 11.7.

7.1.2 Unopened standards have a manufacturer determined expiration date.

7.1.3 Opened standards have a two-month expiration date from date of being opened to date of esterification.

7.1.4 After esterification, the calibration standards have a expiration date of 6 months.

7.2 Refer to Table C-3 and C-4 for details of calibration and other standards.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

8.1 Refer to Section 8 of the method 8000B section of this SOP.

9. QUALITY CONTROL

9.1 Refer to Section 9 of the method 8000B section of this SOP for quality control requirements except surrogate information.

9.2 Surrogates – Every sample, blank, and QC sample (excluding instrument blanks) is spiked with a surrogate compound. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.2.1 The current surrogate recovery limits are located in the LIMS. A hard copy is kept in the laboratory, and is available upon request.

9.2.2 QC: The surrogate must pass for a single column for the MB and the LCS. If this criterion is not met, all effected samples must be re-prepared and reanalyzed.

9.2.3 Samples: The surrogate must pass recovery limits for at least one of the two columns.

9.2.3.1 Shealy policy is to report the higher result between the two columns. If the surrogate failed for the reported column, the surrogate from both columns must be reported to show that at least one of the surrogates passed (documenting that the prep procedure was performed within performance limits).

9.2.3.2 If the surrogate fails for both columns, the following corrective actions must take place (except for ≥5x dilutions):

9.2.3.3 Check all calculations for error.

9.2.3.4 Ensure that instrument performance is acceptable.

9.2.3.5 Recalculate the data and/or reanalyze the extract if either of the above checks reveals a problem.

9.2.4 If the results are confirmed, re-prepare and reanalyze the sample once. Re-preparation is not necessary if there is obvious chromatographic interference. In any case, an NCM must be filed to document the specifics.

9.2.4.1 If the reanalysis shows failing surrogate recoveries, matrix interference has been demonstrated and an NCM must be written so that the data can be reported with a flag.

9.2.4.2 If the reanalysis shows a passing surrogate recovery, the re-prep results are reported.

9.2.5 If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate then matrix effect has been demonstrated for that sample and re-preparation is not necessary. If only one is out of control, then re-preparation or flagging of the data is required. Each scenario requires an NCM.

9.2.6 Refer to the Shealy QAMP for further details of the corrective actions.

9.3 Refer to Table C-5 for minimum performance criteria for the initial demonstration of capability.

9.4 Refer to Table C-5 for the components and levels of the LCS and MS mixes.

10. CALIBRATION AND STANDARDIZATION

10.1 Refer to Section 10 of the method 8000B section of this SOP for general calibration requirement.

External standard calibration is used for this method.. A five point calibration curve is run from standards prepared from stock standards which have undergone the esterification process. These standards are called procedural standards. Follow the procedure provided in Section 11.7 of the prep SOP (S-EX-004).

10.2 A mid level standard is used for the continuing calibration. The center(s) of retention time windows for any analytes included in the daily calibration are updated. The widths of the windows will remain the same. See Section 11.6 of the SOP for method 8000B for details.

10.3 Refer to Table C-2 for details of GC operating conditions.

11. PROCEDURE

11.1 Refer to the method 8000B section of this SOP for procedural requirements.

11.2 Extraction – The extraction procedure is described in SOP S-EX-004.

11.3 Cleanup – The alkaline hydrolysis and subsequent extraction of the basic solution described in the extraction procedure provides an effective cleanup.

11.4 Analytical sequence – The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.4.1 The daily calibration consists of mid level standards of all analytes of interest. The center of retention time windows must be updated with the daily calibration.

11.4.2 A continuing calibration verification (CCV) is run after every 10 field samples or 12 hours, which ever comes first.

11.5 Gas Chromatography – Chromatographic conditions are listed in Table C-2.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Refer to the method 8000B section of this SOP for identification and quantitation of single component analytes.

12.2 All standards must go through the esterification process. These standards are called procedural standards. Follow the procedure provided in Section 11.7 of the prep SOP (S-EX-004).

13. METHOD PERFORMANCE

13.1 Multiple laboratory performance data has not been published by the SOP for this method. Table C-5 lists minimum performance standards required by Shealy for the four replicate initial demonstration of capability (required by Section 13.2 of method 8000B section of this SOP) for this method. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1 Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996, Section 8000B and 8151A.

16.3 Shealy Quality Assurance Management Plan (QAMP) Q-QA-001

16.4 Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.1, April 2009.

17. MISCELLANEOUS

17.1 Modifications from Reference Method – Refer to the method 8000B section of this SOP for modifications from the reference method.

17.3 Tables DoD -G and H have been added to Appendix C for LCS, matrix spike, and surrogate control limits for all DoD samples.

TABLE C-1. Standard Analyte List, Method 8151A

Compound	CAS Number	Reporting Limit		
		Aqueous (µg/L)	Soil (µg/Kg)	TCLP (mg/L)
2,4,5-T	93-76-5	0.5	10	NA
2,4,5-TP (Silvex)	93-72-1	0.5	10	0.02
2,4-D	94-75-7	2.0	40	0.005
2,4-DB	94-82-6	4.0	80	NA
Dalapon	75-99-0	5.0	100	NA
Dicamba	1918-00-9	1.0	20	NA
Dichloroprop	120-36-5	2.0	40	NA
Dinoseb	88-85-7	2.0	40	NA
MCPA	94-74-6	200	4000	NA
MCPP	93-65-2	200	4000	NA
Pentachlorophenol	87-86-5	1.0	20	NA

- The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.	Dilution Factor
Ground water	1000 mL	10 mL	10
Low-level soil	50 g	10 mL	10
TCLP	100ml	10 mL	10
Non-aqueous waste	1 g	10 ml	10

- Specific reporting limits are highly matrix dependent. The reporting limits listed above are provided for guidance only and may not always be achievable. For special projects, the extracts may be analyzed without any dilution, resulting in reporting limits 10 times lower than those in Table C-1.

TABLE C-2. Recommended Instrumental Conditions, Method 8151A

Parameter	Recommended Conditions
Injection port temperature	200°C
Detector temperature	325°C
Temperature program	50°C hold 2min, 30°C/min to 300°C, hold 0.5min
Column 1	DB-XLB 25m x 0.32mm x 0.25µm Capillary
Column 2	DB-35MS 25m x 0.32mm x 0.25µm Capillary
Injection	1 µL
Carrier gas	Hydrogen
Make up gas	Nitrogen
Instrument configuration	Single injection using a y-split, dual detector, dual column

- Recommended conditions should result in resolution of all analytes listed in Table C-1.

TABLE C-3. Calibration Levels, Free Acids[1] (µg/L), Method 8151A

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
2,4,5-T	2.5	10	20	50	250
2,4,5-TP (Silvex)	5	10	20	50	250
2,4-D	10	40	80	200	1000
2,4-DB	20	80	160	400	2000
DCAA (Surrogate)	10	40	80	200	1000
Dalapon	25	100	200	500	2500
Dicamba	5	20	40	100	500
Dichloroprop	10	40	80	200	1000
Dinoseb	10	40	80	20	1000
MCPA	1000	4000	8000	20000	100000
MCPP	1000	4000	8000	20000	100000
Pentachlorophenol	1	4	8	20	100

[1] The reporting limits listed in Table C-1 will be achieved with these calibration levels and a 10- fold dilution of the sample extract. Lower reporting limits can be achieved with lesser dilutions of the sample extract.

TABLE C-4. LCS/Matrix Spike and Surrogate Spike Levels, Method 8151A

Compound	Aqueous (µg/L)	Soil (ug/Kg)	Waste (ug/Kg)	TCLP (mg/L)
2,4,5-T	10	200	10000	N/A
2,4,5-TP (Silvex)	10	200	10000	0.20
2,4-D	10	200	10000	0.20
2,4-DB	10	200	10000	N/A
Dalapon	10	200	10000	N/A
Dicamba	10	200	10000	N/A
Dichloroprop	10	200	10000	N/A
Dinoseb	10	200	10000	N/A
MCPA	1000	20000	1000000	N/A
MCPP	1000	20000	1000000	N/A
Pentachlorophenol	10	N/A	N/A	N/A
DCAA (Surrogate)	50	1000	50000	0.5

TABLE C-5. Aqueous LCS, MS, MSD, Surrogate, and Initial Demonstration of Capability Recovery Limits, Method 8151A

Compound	Initial Demonstration, Mean % Recovery Limits	Initial Demonstration, % RSD Limits
2,4,5-T	56-125	40
2,4,5-TP (Silvex)	56-132	40
2,4-D	59-139	40
2,4-DB	67-142	40
Dalapon	47-142	40
Dicamba	61-110	40
Dichloroprop	66-118	40
Dinoseb	45-140	40
MCPA	66-145	40
MCPP	76-149	40
Pentachlorophenol	70-130	40
DCAA (Surrogate)	62-117	NA

TABLE C-5. Solid LCS, MS, MSD, Surrogate, and Initial Demonstration of Capability Recovery Limits, Method 8151A

Compound	Initial Demonstration, Mean % Recovery Limits	Initial Demonstration, % RSD Limits
2,4,5-T	58-129	40
2,4,5-TP (Silvex)	58-135	40
2,4-D	63-142	40
2,4-DB	74-142	40
Dalapon	62-131	40
Dicamba	67-111	40
Dichloroprop	68-131	40
Dinoseb	50-130	40
MCPA	72-146	40
MCPP	82-149	40
DCAA (Surrogate)	44-114	NA

TABLE DoD-G. Chlorinated Herbicide Target Analyte List for DoD

Compound	CAS Number	Reporting Limit	
		Aqueous (µg/L)	Soil (µg/Kg)
2,4,5-T	93-76-5	0.5	10
2,4,5-TP (Silvex)	93-72-1	0.5	10
2,4-D	94-75-7	2.0	40
2,4-DB	94-82-6	2.0	40
Dalapon	75-99-0	1.0	20
Dicamba	1918-00-9	1.0	20
Dichloroprop	120-36-5	2.0	40
Dinoseb	88-85-7	0.5	10
MCPA	94-74-6	200	4000
MCPP	93-65-2	200	4000

TABLE DoD-H. LCS/MS Control Limits for Chlorinated Herbicides for DoD

Compound	AQUEOUS		SOLID	
	Upper	Lower	Upper	Lower
2,4,5-T	35	110	45	135
2,4,5-TP (Silvex)	50	115	45	125
2,4-D	35	115	35	145
2,4-DB	45	130	50	155
Dalapon	40	110	-	-
Dicamba	60	110	55	110
Dichloroprop	70	120	75	140
Dinoseb	20	100	-	-
MCPA	60	145	-	-

APPENDIX – DoD QSM Requirements

Sections found in this appendix supersede and/or supplement the existing sections of the SOP. These requirements must be met when analyzing samples for the Department of Defense as stipulated in the DOD Quality Systems Manual (Version 4.1, April 2009).

9. QUALITY CONTROL

9.4 Method Blank Acceptance Criteria – replaces Section 9.4 and 9.4 sub-sections.

Method Blank (MB) – One method blank must be processed with each preparation and/or analytical batch. The method blank consists of a similar matrix to the batch of associated samples in which no target analytes or interferences are present at concentrations that affect the analytical results. The method blank is to contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

9.4.1 For a method blank to be acceptable for use with the associated samples, the concentration of analytes detected in the blank must be ≤ one-half (½) the practical quantitation limit (PQL) or project specific reporting limits.

9.4.1.1 The acceptance criterion for common laboratory contaminants is that no analytes should exceed the PQL.

9.4.2 If the MB does not meet the criteria above, the source of the contamination shall be investigated and measures taken to minimize or eliminate the problem. The affected samples shall be reprocessed or data shall be appropriately qualified. All steps taken to return the system to control must be fully documented.

9.4.2.1 If reanalysis is not possible due to limited sample volume or holding time, then the samples associated with the contaminated blank must be evaluated as to the best corrective action for the samples (e.g., reprocessing or data qualifying codes). In all cases, the corrective action(s) must result in the completion of an NCM.

9.12 Analysis Carryover Study – An analysis carryover study must be performed annually for each technology for each instrument model. The study will also need to be repeated after any changes have been made (e.g. instrument conditions) that could effect the carryover. The carryover study demonstrates the concentration at which a target or non-target analyte may be detected without contaminating the subsequent sample(s). A carryover verification standard (CVS) is analyzed at the same concentration as the highest point in the initial calibration and will be followed immediately by an instrument blank. The maximum carryover criteria are as follows:

9.12.1 The resultant carryover must be ≤ ½ the applicable PQL.

9.12.2 If a sample is nondetect after being analyzed immediately after a sample with high concentrations of target and/or non-target compound(s), the sample results may be reported.

Additional studies may be performed to identify how many blanks are required in the contiguous sequence to achieve the ≤ ½ PQL criteria. These studies need to be fully documented and readily available to all analysts.

10. CALIBRATION AND STANDARDIZATION

10.7.2 Non-linear regression – The coefficient of determination (COD) R^2 must be ≥ 0.990. The COD is presented in the Target data system as R^2. Six points shall be used for the second order. The non-linear fit uses the following functions:

10.7.2.1 External Standard

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

Where:

y = Instrument response
x = Concentration
a = Slope
b = Intercept

10.7.2.2 Coefficient of Determination

$$COD = \frac{\sum_{i-1}^{n}\left(Y_{obs} - \bar{y}\right)^2 - \left(\frac{n-1}{n-p}\right)\sum_{i-1}^{n}\left(Y_{obs} - Y_i\right)^2}{\sum_{i-1}^{n}\left(Y_{obs} - \bar{y}\right)^2}$$

Where:

Yobs = Observed response (area) for each concentration from the initial calibration standard

$\overline{Y}$ = Mean observed response from the initial calibration

Yi = Calculated (or predicted) response at each concentration from the original calibration(s)

n = Total number of calibration points (i.e., 6 for a quadratic model)

p = Number of adjustable parameters in the polynomial equation (i.e., 2 for a second order polynomial)

10.10 Initial Calibration Verification (ICV)/Second Source Calibration Verification – The ICAL is verified by analyzing an ICV. The ICV is a standard obtained from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. The ICV is analyzed immediately after the initial calibration. The value of the second source must agree within 20 % of the expected value of the ICAL before sample analysis can begin. If the ICV fails, repeat. If the second ICV fails, maintenance must be performed and two consecutive ICVs must pass or a new ICAL must be analyzed before sample analysis can begin.

10.11 Continuing Calibration Verification (CCV), also known as the Instrument Performance Check.

10.11.1 Opening CCV – The ICAL must be verified at the beginning of each analytical sequence, after every 10 field samples, and at the end of the sequence. The opening CCV must pass all analytes of interest within $\pm$ 20 %. Any CCV that has samples reported after it is considered an opening CCV, even if it is analyzed in the middle of a sequence.

10.5.1 Lower Order of Quantitation (LOQ) Verification – This is an analysis of a QC sample containing the analytes of interest in each matrix 1-2 times the claimed LOQ

10.5.1.1 A successful analysis is one where the recovery of each analyte is within the established test method acceptance criteria or client data quality objectives for accuracy.

10.5.1.2 This single analysis is not required if the bias and precision of the measurement system is evaluated at the LOQ.

10.5.1.3 The LOQ must not be set any lower than the low-level calibration standard for multi-point calibration or no lower than a low-level calibration check sample for single level calibration.

12. DATA ANALYSIS AND CALCULATIONS

12.1.2 If the relative percent difference (RPD) between the responses on the two columns is > 40 %, the result will be qualified with a "J" flag. If the result is not confirmed the result from the column with the detection will be reported and qualified with a "Q" flag. RPD is calculated using the following formula:

$$RPD = \frac{R_1 - R_2}{\frac{1}{2}(R_1 + R_2)} X\ 100$$

Where R = Result

Appendix P

Laboratory SOPs

TPH Extractables

Test America SOP

EDS-GCS-011

Title: QUANTITATION OF SEMIVOLATILE PETROLEUM PRODUCTS IN WATER, SOIL, SEDIMENT AND SLUDGE [NJDEP OQA-QAM-025]

Approvals (Signature/Date):

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1.0 Scope and Application

NJDEP Method OQA-QAM-025, "Quantitation of Semivolatile Petroleum Products in Water, Soil, Sediment and Sludge" (current revision) is used to determine the presence of Total Semivolatile Petroleum Products (TPHC) in environemental samples. TPHC includes paraffinic, naphthenic and polynuclear aromatic hydrocarbons (PAH).

1.1 Analytes, Matrix(s), and Reporting Limits

Analyte	Matrix	Reporting Limit
TPH	Solid	6.7 mg/kg
TPH	Aqueous	0.1 mg/L

Note: For a complete listing of current Method Detections Limits (MDLs) and Reporting Limits (RLs) please refer to TestAmerica Edison Work Instruction No. EDS-WI-071 (*NJDEP OQA-QAM-025: Current MDLs and Reporting Limits, most current revision*).

1.2. On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Sections 7 (Review of Work Request) and 20 (Test Methods and Method Validation) of TestAmerica Edison's Quality Assurance Manual (ED-QA-LQM).

2.0 Summary of Method

Petroleum residues are extracted from samples with Methylene Chloride. All samples are spiked with ortho-terphenyl and chlorobenzene surrogate prior to extraction. The Methylene Chloride extract is analyzed utilizing GC/FID instrumentation. The concentration of TPHC range organics is determined using a summation of the area response of all resolved peaks and the unresolved "envelope" in the time window established during initial calibration. This time window starts at the time of initial rise of peak C8 and ends at the time of final elution of peak C40.

3.0 Definitions

For a complete list of definitions refer to Appendix 5 in the most current revision of TestAmerica Edison's Quality Assurance Manual (ED-QA-LQM).

4.0 Interferences

4.1 All glassware must be washed with hot soapy water and then rinsed once with 50:50 Methylene Chloride/Acetone followed by two rinsings with Methylene Chloride to reduce any contaminants.

4.2 There is a baseline shift that occurs during temperature programming of the GC column oven. Therefore, this "area" must be determined by injecting a Methylene Chloride instrument blank and subtracted from the total area from the actual samples run. If this area is not subtracted out, the resulting "Total TPHC" value reported will be falsely high. As the concentration of "Total TPHC" in the sample

approaches the detection, the baseline correction becomes very critical. Therefore it is essential that the GC/FID be in optimal condition.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

- During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard.
- The block that the extraction beaker sits is hot enough to burn unprotected skin. Use caution when removing extraction beakers that haven't had time to cool and use appropriate protective equipment (e.g., insulated gloves or tongs).
- The use of Kevlar gloves is required for the assembly/disassembly of ground glass joints in addition to those tasks that present the potential risk for injury.
- The use of separatory funnels to extract aqueous samples with Methylene Chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted, periodic venting may be necessary during the extraction. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, the use of a face shield over safety glasses or goggles is recommended. Keep the sash on the fume hood as low as reasonably possible.
- The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.
- There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section.

Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sulfuric Acid	Corrosive Oxidizer Dehydra-dator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1. Instrumentation:

6.1.1 Gas Chromatograph (GC): The system used is an HP and an Agilent Technologies (Avondale, PA) model 5890/6890 GC. Each GC is equipped as described below. The GC oven is temperature programmable.

6.1.2 Injection System: Sample injection is accomplished by an HP7673 autosampler with a 10uL syringe. The auto injector is serviced by a robot arm that shuttles samples between the sample tray and the injection turret.

6.1.2.1 A splitless injection port with electronic pressure control (EPC) is used. Fifty seconds after sample injection, the purge valve is turned on to facilitate the sweeping of any remaining residual solvent/sample from the injection port. The EPC is used in the ramp pressure mode.

6.1.2.2 The injection port liner used is a 4mm splitless sleeve (Restek Catalog No. 11868-773. This liner/glass wool combination performs several functions. The glass wool serves as a heat sink rapidly vaporizing solvent and samples resulting in higher response factors. The liner also protects the column head from accumulation of high boiling residuals and particulates.

6.1.3 Oven and Columns: Temperature programmable gas chromatographic ovens are required capable of integrated temperature control between 35°C and 360°C.

6.1.3.1 The analytical column is a Rtx®-5MS (Fused Silica), 15 meter x 0.25mm ID capillary, film thickness 0.5 micron (Restek Catalog No. 12368).

6.1.4 Detector: Flame Ionization Detector (FID)

6.1.5 Data System

6.1.5.1 Chemstation: The Chemstation is utilized for automation of runs and acquisition. The system is dedicated to a single GC and does not multitask. Therefore, data manipulation cannot be done while sample analysis is in progress. The data system acquires and stores all chromatographic data.

6.1.5.2 Target: Target is utilized for the processing of the data files. Calibrations, verification standards and samples are processed and reviewed using this database. All reports are also generated by Target.

6.2. Supplies - Water extraction:

6.2.1 250 ml Erlenmeyer Flask, AMK Glass ERL-0252 or equivalent

6.2.2 2000 ml Separatory Funnel, AMK Glass SFC-0095 or equivalent

6.2.3 100 mm o. d. glass funnels, Fisher or equivalent

6.2.4 10 ml jacketed, gx`raduated Concentrator Tubes, AMK Glass KD-0018 or equivalent

6.2.5 19/22 Ground Glass Stoppers

6.2.6 3 Ball Snyder Columns, TEC Glass TG6-03 or equivalent

6.2.7 1 ml Gastight Syringe, Hamilton 81317 or equivalent

6.2.8 150 ml Centrifuge Tube

6.2.9 100 ml Graduated Cylinder

6.2.10 Pasteur 5¾" Disposable Pipets, Fisher 13-678-20B or equivalent

6.2.11 Kuderna Danish Flask (500 ml), TEC Glass TG7-01 or equivalent

6.2.12 Separatory funnel rotator, APR Machine or equivalent

6.2.13 Analytical Evaporator (N-Evap) Organomation

6.2.14 Centrifuge, Varifuge F; Hereaus Sepatech

6.2.15 Glass Wool

6.2.16 Dessicator

6.2.17 Standard Taper Clamps (Size 19, blue)

6.2.18 Boiling Stones, Troemner P/N 133- B or equivalent, rinsed with Methylene Chloride

6.2.19 pH Paper

6.2.20 Watch Glass

6.2.21 Wax Pencil

6.2.22 1 Liter Graduated Cylinder

6.2.23 Marking Tags

6.2.24 Six Position Steam Bath, Fisher 15-496 or equivalent

6.2.25 Muffle Oven, Thermolyne 6000 or equivalent

6.3 Supplies - Soil Extraction:

6.3.1 Automated Soxhlet Extraction System (Soxtherm, O.I. Analytical).

6.3.2 Glass extraction thimble, metal clip and beaker. (Soxtherm).

6.3.3 10ml concentrator tube.

6.3.4 Analytical balance –capable of weighing to 0.01 g.

6.3.5 Glass wool.

6.3.6 Drying Agent

6.3.7 Sodium sulfate (granular anhydrous), Mallinkrodt MA8020-06 or equivalent.

6.3.8 Drying agents must be purchased pre-cleaned or heated at 4OO°C for 4 hours in a shallow tray.

6.3.9 1000ul gastight syringe

6.3.10 500ul gastight syringe

6.3.11 Boiling stones

6.3.12 Weigh boats

6.3.13 Tongue depressors, wood.

6.3.14 Pipettes.

6.3.15 Nitrogen Evaporator. (N-EVAP, Organomation)

7.0. Reagents and Standards

7.1. Reagents

7.1.1. Methylene Chloride, pesticide grade equivalent

7.1.2. Acetone, pesticide grade

7.1.3. Sodium sulfate crystals. Sodium sulfate crystals must be baked at 400°C for four hours prior to use.

7.1.4. De-ionized water

7.1.5. Concentrated Sulfuric acid

7.2. Standards

7.2.1. Normal Paraffinic Calibration Standard: Prepared using Supelco TPH Mix 3 (Supelco Catalog Number 861394-U). This mixture contains the following 17 hydrocarbons at a concentration of 1,000 ug/ml each in carbon disulfide:

Number of Carbons	Compound
C6	hexane
C7	n-heptane
C8	n-octane
C9	n-nonane
C10	n-decane
C11	n-undecane
C12	n-dodecane
C14	n-tetradecane
C16	n-hexadecane
C18	n-ocatadecane
C20	n-eicosane
C24	n-tetracosane
C28	n-octacosane
C32	n-dotriacontane
C36	n-hexatriacontane
C40	n-tetracontane
C44	n-tetratetracontane

7.2.2. The calibration standard is prepared (as described in the table in Section 7.3.1) based on the concentration of total C6-C44 parafinnic hydrocarbons in the solution (17,000 ug/ml) but only the 14 C8-C40 paraffinic hydrocarbons are used when calibrating for this method. The prepared total C6-C44 hydrocarbon concentration is corrected for the C8-C40 concentration by multiplying by 0.8235 (i.e., 14/17). For example, the 25 ug/ml total C6-C44 standard solution actually contains 20.6 ug/l C8-C40 (25 * 0.8235).

7.2.3. A certified separate lot of this same standard solution is used for preparing the Initial Calibration Verification (ICV) standard as well as the spiking standard (see Section 7.3)

7.2.4. An example chromatogram for this mixture can be found in Attachment A and an example Certificate of Analysis for this mixture can be found in Attachment B.

7.2. Surrogate standard: Two surrogate compounds are used: o-Terphenyl (Supelco Catalog Number 47580-U, 10000 ug/ml) and chlorobenzene (Supelco Catalog Number 46860-U, 10000 ug/ml). A 20 ug/ml Surrogate Solution is prepared by adding 200 ul of each of the above referenced standards into 98 ml of Methylene Chloride and bringing up to a 100 ml final volume (again with Methylene Chloride)with acetone. This 20ug/ml standard is used to spike all field samples and QC samples (matrix spikes, method blanks and LCS) prior to extraction.

7.3. Preparation of the 5-Point Calibration Standards:

7.3.1. Prepare 5-point TPHC calibration standards in methylene chloride as described in the following table using the TPH Mix 3 described in Section 7.1 (Supelco Catalog Number 861394-U) and the o-Terphenyl/Chlorobenzene surrogate solution described in section 7.2 :

Concentration of Standard: Total C6-C44/Total C8-C40 (ug/ml)	Vol. of TPH Mix 3 (Supelco 861394-U)	Concetration of OTP/Chlorobenzene Surrogate (ug/ml)	Vol. of OTP/chlorobenzene Surrogate (20ppm)	Final Volume in Methylene Chloride
100 / 88	29.4 uL	0.25	62.5 uL	5 ml
500 /441	147 uL	1.25	312.5 uL	5 ml
1000 /883	294 uL	2.5	625 uL	5 ml
2500 /2207	1.47 ml	6.25	3125 uL	10 ml (Midpoint)
5000 /4413	1.47 ml	12.5	3125 uL	5 ml

7.4. Preparation of the Initial Calibration Verification (ICV)/Spiking Standard:

A second source Initial Calibration Verification (ICV) standard at the midpoint level of 2500 ug/ml (without O-Terphenyl/Chlorobenzene) will be prepared by diluting 1.47 ml of certified separate lot SS TPH Mix 3 (Supelco Catalog Number 8S61394-U) to a final volume of 10 ml with Methylene Chloride. This standard serves as both the ICV and as the spiking solution for the MS/MSD (see Section 10).

7.5. Preparation of Laboratory Control Sample (LCS):

The Laboratory Control Sample (LCS) spiking solution consisting of #2 Fuel Oil is prepared at a concentration of 2000 ug/ml by diluting 1 ml of 20,000 ug/ml (ppm) #2 Fuel Oil (Accustandard Catalog Number FU-002-D-40X or equivalent) in Methylene Chloride to a final volume of 10 ml of Methylene Chloride. This standard is used for spiking the LCS as described in Section 10.

7.6. All standards preparation information must be logged into the BNAGC Standard Preparation Log Book. All pertinent information must be entered: Date prepared, Lot #'s, Expiration dates, Solvents used, Lab Lot # (expiration date), Manufacturer and Verification signature.

8. Sample Collection, Preservation, Shipment and Storage

8.1. Samples must be stored at 4°C.

8.2. Water samples must be preserved to a pH of <2 and be extracted within 14 days of collection. If unpreserved, water samples must be extracted within 4 hours of collection.

8.3. Soil samples must be extracted within 14 days of collection.

8.4. For sample homogenization refer to TestAmerica Edison SOP No. ED-GEN-007 (*Subsampling*).

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Glass	1L	HCL, pH < 2; Cool 4 ± 2°C	14 days to extraction, 40 days after extraction	NJDEP-OQA-QAM-025
Soils	Glass	4 oz	Cool 4 ± 2°C	14 days to extraction, 40 days after extraction	NJDEP-OQA-QAM-025

9. Quality Control

9.1. **Sample QC** - The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	< Rpt. Limit
Laboratory Control Sample (LCS)[1]	1 in 20 or fewer samples	Statistical Limits [4]
Matrix Spike (MS)[2]	1 in 20 or fewer samples	Statistical Limits [4]
MS Duplicate (MSD)[2]	1 in 20 or fewer samples	Statistical Limits [4]
Surrogates	every sample[3]	Statistical Limits [4]

[1] LCS Duplicate (LCD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
[2] The sample selection for MS/MSD are randomly selected, unless specifically requested by a client….predetermined by the extraction lab.
[3] Analytical and QC samples (MB, LCS, MS/MSD)
[4] Statistical control limits are updated annually and are updated into LIMS

9.1.1. **Method Blanks** are extracted with each sample batch on each day that sample are extracted. For the method blank to be considered acceptable,

it must contain less than the reporting limit of petroleum hydrocarbons. If a target analyte is detected in the method blank at a concentration higher than the reporting limit, the extract is first reanalyzed for confirmation. If results are still outside of limits the entire batch of samples associated with the method blank must be re-extracted and reanalyzed.

9.1.2. Laboratory Control Sample (LCS): A Laboratory Control Sample (LCS) or blank spike must be extracted and analyzed for with each batch of 20 environmental samples. The LCS is prepared as detailed in Section 7.5. The LCS data is used to assess performance if the MS/MSD recoveries fall outside of established limits. The recoveries of the LCS must fall within lab generated acceptance criteria. If the spiked sample recovery results fall outside the laboratory generated limits (refer to TestAmerica Edison Work Instruction No. EDS-WI-061, *NJDEP OQA-QAM-025 Current QC Limits*), the LCS recovery is evaluated. If LCS recovery is within limits the poor sample recovery results are attributed to matrix interference. If the LCS recovery results are outside QC limits, first the extract is reanalyzed and if it is still outside the limits the entire QA batch must be re-extracted and reanalyzed.

9.1.3. Matrix Spike/Matrix Spike Duplicate (MS/MSD): A Matrix Spike/Matrix Spike Duplicate (MS/MSD) pair is extracted and analyzed with every batch of 20 environmental samples. The matrix spiking standard is prepared as detailed in Section 7.4. MS/MSD recoveries are evaluated against lab generated limits (refer to TestAmerica Edison Work Instruction No. EDS-WI-061, *NJDEP OQA-QAM-025 Current QC Limits*). If the MS/MSD recovery limits fall outside of lab limits the LCS recovery is evaluated and corrective action is taken as described in 9.1.2.

9.1.4. Surrogate Standards: All samples, blanks and QC samples are spiked with a 2 component surrogate standard mix containing o-terphenyl & chlorobenzene (see Section 7.2). The percent recovery of the surrogate standards is calculated and compared to lab generated limits (refer to TestAmerica Edison Work Instruction No. EDS-WI-061, *NJDEP OQA-QAM-025 Current QC Limits)*. If surrogate recovery is outside of acceptance limits, follow the steps detailed below. If the recoveries are still outside of limits after following these corrective actions, the sample must be re-extracted and reanalyzed or the data flagged as “estimated concentration”.

9.1.4.1. If a dilution was performed on the extract, remake the dilution and re-analyze.

9.1.4.2. Verify the final volume of the extract is correct and re-inject the extract.

9.1.4.3. If the surrogate fails after re-analysis, re-extract and re-analyze the sample (if sample volume permits).

9.2. Instrument QC

9.2.1. Initial Calibration Range and Initial Calibration Verification (ICV)

9.2.1.1. Initial Calibration Range: A five point initial calibration range is analyzed prior to the analysis of any samples. The initial calibration standards are prepared as detailed in Section 7.3. (Note: Prior to the analysis of the five point calibration range, a methylene chloride blank is analyzed to determine the area response generated by normal baseline bleed. This area response is determined by integrating the area between the initial and final peaks of the TPHC component standard. This area is subtracted from all standards, blanks, samples and QC samples prior to calculation of results). The initial calibration analyzed and evaluated as described in Section 9.2.3.

9.2.1.2. Initial Calibration Verification (ICV): An Initial Calibration Verification (ICV) standard is analyzed immediately after the Initial Calibration Range and before any samples are analyzed. The ICV is prepared from a source separate from the initial calibration standards as detailed in Section 7.5. The ICV is evaluated as detailed in Section 9.2.3.

9.2.2. Continuing Calibration Verification (CCV): A mid-point Continuing Calibration Verification (CCV) standard is analyzed every 12 hours or after every 10 environmental samples (whichever is more frequent) and at the end of each analytical sequence. The CCV consists of the 2500 ug/ml standard analyzed with the initial calibration range (see Section 7.3 for details on preparation of this standard). The CCV is evaluated as detailed in Section 9.2.3.

9.2.3. Calibration Acceptance Summary :

9.2.3.1. Retention Time Windows: Retention time (RT) windows must be established to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. All gas chromatographs used for analysis of TPHC by NJDEP OQA-QAM-025 at TestAmerica Edison are equipped with electronic pressure control (EPC). The use of EPC results in little retention time variability between analyses. Accordingly, retention time variability for the purpose of retention time window determination for standards analysis is extremely small. The default retention time window option must therefore be employed as follows to accommodate the excellent precision of EPC equipped systems.

9.2.3.1.1. Establish the retention time windows by making 3 injections of the 500 ug/ml calibration standard over the course of a 72 hour period. Record the retention times for each of the surrogate standards (o-terphenyl and

chlorobenzene) in each of the 3 injections. Calculate the standard deviation of the three absolute retention times for each surrogate. The retention time window is defined as ± 3 times the standard deviation of the absolute retention time. (If the standard deviation is zero, used ± 0.1 minutes as the retention time window).

9.2.3.1.2. Retention times must be monitored for each continuing calibration standard, method blank, environmental sample and QC sample. The RT for the o-terphenyl and chlorobenzene surrogate in the continuing calibration standard must not vary more than 0.1 minutes from the RT of the OTP/chlorobenzene from the initial calibration. If the RT of the OTP/chlorobenzene fails to meet this criterion in the continuing calibration standard a new 5-point calibration must be analyzed.

9.2.3.1.3. The RT of the o-terphenyl and chlorobenzene surrogate in blanks, samples, and QC samples must not vary more than 0.1 minutes from the RT of the o-terphenyl and chlorobenzene surrogate in the Continuing calibration standard. If the RT of the o-terphenyl and chlorobenzene surrogate fails to meet this criterion the samples must be re-analyzed.

9.2.3.2. Initial Calibration Range: External standard calibration is employed for this method. The response factor (RF), defined as the ratio of the area to the standard concentration, is calculated for each both TPHC and each surrogate standard at each calibration concentration.

$$RF = \frac{\text{Total Area of Standard}^{(1)}}{\text{Amount of Std Injected}}$$

(1): Total area of TPHC is defined as the time window from the initial rise of the C8 peak to the end of the elution of the C40 peak (do not include peak area for the surrogates).

9.2.3.2.1. The average response factor may be used for quantitation if the % Relative Standard Deviation (RSD) across the 5 point range is <20%. Alternatively, linear regression may be used if the correlation coefficient (r1) is $\geq$ 0.95. Calibration is verified every 12 hours or after every ten (10) samples, whichever comes first, by analysis of the CCV as detailed in Section 9.2.2.

9.2.3.3. Initial Calibration Verification (ICV): An ICV is analyzed as described in Section 9.2.1.2. The calculated concentration of the ICV must be within ±20% difference (%D) of expected concentration. If the %D exceeds 20%, the analyst should take corrective action (check the standard solutions, perform instrument maintenance, etc..) and re-inject the ICV once. If the

ICV is still outside of the 20%D acceptance criteria, a new initial calibration range must be analyzed. Any samples analyzed after a non-compliant verification standard must be analyzed under a passing standard.

9.2.3.4. Continuing Calibration Verification (CCV): The CCV is analyzed as described in Section 9.2.2. The calculated concentration of the CCV must be within ±20% difference (%D) of expected concentration. If the %D exceeds 20%, the analyst should take corrective action (check the standard solutions, perform instrument maintenance, etc...) and re-inject the CCV once. If the CCV is still outside of the 20%D acceptance criteria, a new initial calibration range must be analyzed. Any samples analyzed after a non-compliant verification standard must be analyzed under a passing standard.

9.2.3.5. Mass Discrimination Check: Mass discrimination can take place in the injection port. The heavier molecules do not enter the column as a defined plug of vapor with the lighter molecules. Mass discrimination is minimized by placing a small plug of silanized glass wool in the injection port liner. The end of the column should be placed about 1 cm inside the liner.

9.2.3.5.1. The continuing calibration check is checked for mass discrimination. The response factor ratio of C32/C20 should be greater then 0.8. If the ratio is less, reposition the column in the glass liner until mass discrimination is within the acceptance criteria.

Instrument QC Requirement Summary				
Step	***Standards***	***Type***	***Control Limit***	***Frequency***
Method # NJDEP OQA-QAM-025				
Initial Calibration	100, 500, 1000, 2500 and 5000 ug/ml	*Average response factor or 1st order linear regression*	*For average RF: <20% RSD. For linear regression: r >0.95*	*As required. Initially and when ICV or CCV do not meet requirement.*
ICV	2500 ug/ml (second source)	*Average*	*±20% Difference*	*Once after each initial calibration*
CCV	2500 ug/ml	*Average*	*±20% Difference*	*Every 12 hours or 10 samples, whichever is more frequent*
Mass Discrimination Check	2500 ug/ml (CCV)	*RF*	*RF ratio of C32/C20 should be >0.8*	*Every 12 hours*

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10. Procedure

10.1. Sample Prep

10.1.1 Sample Prep – Aqueous

10.1.1.1 Obtain a sufficient number of 2000-ml separatory funnels and 250-ml Erlenmeyer flasks for each environmental sample and QC sample to be extracted. Rinse each separatory funnels and Erlenmeyer flasks three (3) times with methylene chloride.

10.1.1.2 Place a small amount of glass wool into a 100-mm funnel and fill with pre-baked sodium sulfate crystals. Rinse three (3) times with methylene chloride (also rinse the outside of the funnel stem 3 times with methylene chloride, as it is likely to come into contact with the extract). Allow time for all of the rinsate to drain out of the funnel into a waste container.

10.1.1.3 Mark the lab sample numbers on the separatory funnels with a red wax pencil.

10.1.1.4 Make up tags with the following information and place on a 250ml Erlenmeyer flask:

- Fraction (TPHC)
- Sample number
- date of extraction

10.1.1.5 Place the 100-mm funnel containing rinsed sodium sulfate crystals onto the flask.

10.1.1.6 Mark the fluid level on sample bottles with a black marking pen.

10.1.1.7 Rinse a 1000 ml graduated cylinder 2-3 times with deionized organic free water. Obtain 1000 ml of deionized organic free water for each of the Method Blank and the LCS (blank spike).

10.1.1.8 Pour the Method Blank and LCS into their corresponding separatory funnels.

10.1.1.9 Rinse syringes 8 to 10 times with Methylene Chloride.

10.1.1.10 Add 1ml of the o-terphenyl and Chlorobenzene surrogate (See Section 7.2) to each separatory funnel.

10.1.1.11 If you are extracting Matrix Spike (MS) and Matrix Spike Duplicates (MSD), add 1ml of the Spiking Solution (see Section 7.4) to the appropriate separatory funnels. (When spiking, make sure to get all bubbles out of the syringe. In addition, hold the syringe just above the level of the liquid when adding the spike. Don't touch the tip of the syringe to the liquid or the side of the separatory funnel).

10.1.1.12 If you extracting an LCS, add 1ml of the LCS Spiking Solution (see Section 7.5) to the appropriate separatory funnel. (When spiking, make sure to get all bubbles out of the syringe. In addition, hold the syringe just above the level of the liquid when adding the spike. Don't touch the tip of the syringe to the liquid or the side of the separatory funnel).

10.1.1.13 Add 60 ml of Methylene Chloride to each sample bottle.

10.1.1.14 Swirl the bottle and add the 60-ml of Methylene Chloride to its corresponding separatory funnel. Also add 60 ml of Methylene Chloride to separatory funnel containing a QC sample (MS/MSD/LCS).

10.1.1.15 After making sure the funnels are properly secured start the rotators. Stop the rotator and vent the funnels after about 10 seconds. Resume rotating for 2 minutes.

10.1.1.16 Let the sample settle.

10.1.1.17 Drain the bottom layer (organic layer) of the sample into the funnel/Erlenmeyer apparatus.

10.1.1.18 Repeat steps 10.1.1.13 through 10.1.1.17 twice, adding the Methylene Chloride directly to the separatory funnel, rather than rinsing the sample container as in 10.1.1.3.

10.1.1.19 The aqueous layer can be discarded once the 3 extraction cycles have been completed.

10.1.1.20 Fill the empty sample bottles that were marked with a black marker with tap water up to the black line. Pour this into the graduated cylinder used for measuring sample volumes. Note the volume on the Organic Extraction Data Sheet.

10.1.1.21 Rinse a KD concentration tube apparatus and a Snyder column three times with Methylene Chloride.

10.1.1.22 Pour the Methylene Chloride extracts from the Erlenmeyer flasks into a KD concentration tube apparatus. Rinse the Erlenmeyer flask from which the sample came twice with Methylene Chloride and pour both rinsates into the KD apparatus. Transfer the ID tag from the Erlenmeyer flask to the KD apparatus.

10.1.1.23 Attach the Snyder column to the top of the KD apparatus.

10.1.1.24 Concentrate the extract to approximately 5-ml in Steam Bath.

10.1.1.25 Remove the Snyder column from the top of the KD flask. Remove blue taper clamp from the ground glass joint and dry the exterior with a Kimwipe. Transfer the concentrator tube with the 5ml extract to the N-Evap and "blow down" the extract until the volume is 1.0 ml.

10.1.1.26 If an emulsion forms during extraction, rinse a centrifuge tube well with Methylene Chloride and then drain the lower layer from the large separatory funnel into the tube. Centrifuge for 3 to 5 minutes at 2000 rpm. Make sure the levels (and weights) of the samples directly opposite one another in the centrifuge are approximately equal. After the centrifuging process is finished, there will be two layers: water on top and the Methylene Chloride with the desired sample extract on the bottom. A 1 ml disposable pipet should be used to transfer the bottom layer from the centrifuge tube to the appropriate Erlenmeyer flask. With this method, care must be taken not to transfer any of the top layers. The top layer that remains is poured back into the 2000 ml separatory funnel with the rest of the original sample.

10.1.2 Sample Prep – Solid:

10.1.2.1 Solid samples (soils/sediments) – Obtain the solid samples requiring extraction. Decant and discard any water layer from sediment samples. Mix the sample thoroughly. Discard any foreign objects such as sticks, leaves, and rocks.

10.1.2.2 Weigh approximately 15 grams (±0.05 grams) of the solid sample into a weigh boat. Mix the sample with approximately 30 grams of pre-baked sodium until a free-flowing mixture is obtained.

10.1.2.3 Place small amount of glass wool into the bottom of an extraction thimble and rinse three times with methylene chloride. Discard the rinsate. Transfer the prepared sample into an extraction thimble.

10.1.2.4 Rinse an extraction beaker three times with methylene chloride. Discard the rinsate. Record the lab sample ID number on the extraction beaker with a red wax pencil.

10.1.2.5 Add 3-5 boiling chips to the extraction beaker.

10.1.2.6 Rinse a clip three times with methylene chloride, attach to extraction thimble and place the extraction thimble into the extraction beaker.

10.1.2.7 Spike each sample with 1 ml the Surrogate Spiking Solution (see Section 7.2) and (in the case of samples selected for MS/MSD) 1 ml of the Spiking Standard (See Section 7.4).

10.1.2.8 Add exactly 100ml of Methylene Chloride to each extraction beaker.

10.1.2.9 Ensure that the following settings are loaded into the Soxtherm Automated Soxhlet Extraction Unit (each of these parameters is defined in the sections below):

- Boiling Time: 55minutes
- Solvent Reduction A: 5 minutes
- Extraction Time: 55 minutes
- Solvent Reduction B: 5 minutes
- Solvent Cooling Time: 20-30 minutes

10.1.2.10 Load the extraction beaker onto the the Soxtherm Automated Soxhlet Extraction Unit: For sample loading, the condensers of the Soxtherm should be in their raised position. Install the extraction beakers into position on the unit. Center the extraction beaker over the aluminum-heating block. The Teflon extraction cylinder makes a seal with the extraction beaker, so the beaker must not have any chips.

10.1.2.11 Press the ENTER button to start the extraction cycle. The Soxtherm Automated Soxhlet Extraction unit is designed to run largely unattended. Operator intervention is typically not required until the second solvent reduction cycle (i.e. Solvent Reduction B) (approximately 2 hours after the start of the extraction).

10.1.2.12 The Soxtherm unit enters the first stage of extraction (Boiling). During this stage the sample is immersed into the boiling solvent

mix. This ensures very rapid intimate contact between the sample and solvent and rapid extraction of the organic analytes. The system is in reflux during this stage of extraction.

10.1.2.13 During the next cycle (Solvent Reduction A) a pre-set amount of solvent is removed. The system is not in reflux. The condensate is collected in the 15ml reservoir cups and a pulse of nitrogen transfers the aliquot to the solvent recovery tank. Performing this 5 times removes 75ml of the extraction solvent. At the conclusion of this cycle the extraction solvent level in the extraction beaker should now be below the extraction thimble.

10.1.2.14 In the next cycle (Extraction Time) the system is again in total reflux and there is no net change in solvent volume. During this phase, condensed solvent runs through the sample in the extraction thimble and drips out into the extract below.

10.1.2.15 At the end of the Extraction Time cycle the system enters the Solvent Reduction B phase. During this cycle a single 15ml aliquot of condensed solvent is removed and collected in the solvent recovery take (See Solvent Reduction A). This is the point where analyst intervention may be needed. Theoretically 10ml of solvent should be left in the extraction beaker (100ml initial volume with 90ml removed during the Solvent Reduction cycles). Due to system limitations, this is not always the case. The operator has to carefully monitor this reduction step and remove the beaker if the extract volume becomes too low (i.e., if the volume is less than 10 ml). If an extraction beaker has to be removed, the analyst must raise the condensers and use tongs to remove the beaker. The condensers should then be lowered and solvent reduction can proceed on the remaining samples.

10.1.2.16 The final Soxtherm cycle is Solvent Cooling Time. At the beginning of this cycle, power to the heater is stopped, but cooling water continues running through the condensers. Reflux and rinsing of the thimble will continue for some time, but no additional solvent reduction occurs during this period. The sample extracts should still be monitored closely and removed if the solvent level becomes too low.

10.1.2.17 At the end of the cooling cycle, water to the condensers is shut-off and the extraction beakers are raised several millimeters above the hot plate. The extract is now ready for concentration. The analyst must quantitatively

transfer the extract to a pre-rinsed 10ml concentrator tube and place on the N-Evap for final concentration. After final concentration the final extract volume must be adjusted to 1ml with Methylene Chloride.

10.2 Instrument Setup and Calibration

10.2.1. Instrument Setup: Prior to calibration and analysis the instrumentation detailed in Section 6.1 must be setup with the following operating conditions:

10.2.1.1 Injection System: A splitless injection port with electronic pressure control (EPC) is used. Fifty seconds after sample injection, the purge valve is turned on to facilitate the sweeping of any remaining residual solvent/sample from the injection port. The EPC is used in the ramp pressure mode. The ramp constant pressure program is setup as follows:

Initial Pressure	Initial Time	Final Pressure	Hold
35 psi	0.5 min	35 psi	6.56 min

For TPHC by OQA-QAM-025 analysis the normal operating conditions of the injection port are as follows:

Injection Temperature:	335^{o}C
Injection Port Pressure:	35 psi
Column flow:	21.4 ml/minute
Detector (FID)	360C
Hydrogen flow	15.0 ml/min
Air flow	350.0 ml/min
Makeup flow	5.0 ml/min
EPC	ramp pressure mode

10.2.1.1.1 The injection port liner used is a 4mm splitless sleeve (Restek Catalog No. 20782-211.5). This liner/glass wool combination performs several functions. The glass wool serves as a heat sink rapidly vaporizing solvent and samples resulting in higher response factors. The liner also protects the column head from accumulation of high boiling residuals and particulates.

10.2.1.1.2 Regular maintenance is performed on the injection port. Prior to performing maintenance the injection port, oven and detector temperatures are lowered to ambient prior to "cracking" the system. This is so as to introduce a minimum of damaging oxygen molecules into the system.

10.2.1.1.3 After the system has cooled, the old liner is removed. The injection port should be checked for particulate residues and cleaned as needed. A flashlight is usually required for this. After a new liner has been prepared it is placed into the injection port. A graphite seal is placed around the liner. The edges of the seal must be flat, not knife-edged, and free of nicks or burrs. If any of these conditions are not met, the graphite seal must be replaced as well. The graphite seal is critical to proper operation of the injection port. If in doubt, replace it.

10.2.1.1.4 The locking ring on the top of the injection port should be turned, with the wrench, about 1/8 turn past finger tight. The septum nut should never be tightened more than finger tight. After the injection port is reassembled, all column nuts inside the oven should be checked for leaks using Snoop (Supelco) or another suitable leak tester.

10.2.1.1.5 The septa should be changed each time the injection port is opened. Another routine maintenance operation to improve column performance is the removal of the first 3 cm of the column. Document all such column maintenance in the instrument maintenance log.

10.2.1.1.6 Once the signal from both detectors has stabilized, it is time to re-heat the zones. The zones should be heated in the order of detectors, oven and then injectors. This is to ensure that volatilized contaminants do not condense on the column or detector.

10.2.1.2 **Oven**: Temperature programming is employed to achieve higher resolution of compounds and shorter run times than could be accomplished using isothermal methods. The oven temperature program and pressure ramping for QAM analysis is employed for all columns as follows:

Initial Temp:	35°C
Initial Time:	0.50 minutes
Ramp #1:	80°C/minutes for 4 minutes
Final Temp:	360°C
Final Hold:	2.0 minutes

10.2.2. Calibration: Refer to Section 9.2 for instrument calibration requirements.

10.3 Sample Analysis

10.3.1. Sample analysis may begin after an acceptable initial calibration has been performed meeting the criteria in Section 9.2.3.

10.3.2. Analyze all method blanks, environmental samples and associated QC samples. Analyze the CCV standard (see Section 9.2.3.4) every 12 hours

or after every 10 injections (whichever is more frequent) and at the end of the sequence. The CCV must meet the criteria as outlined Section. 9.2.3.4. If the CCV fails to meet these criteria, all samples analyzed preceding it must be re-analyzed under a passing CCV.

10.3.3. If any sample concentration exceeds the upper end of the calibration range, the extract must be diluted and re-analyzed. NOTE: Methylene chloride blanks should also be analyzed after a sample suspected to be highly concentrated to prevent carryover.

10.3.4. Calculate final concentrations in aqueous and solid samples using the calculations found in Section 11.0 (Calculations/Data Reduction).

Idealized Analytical Sequence with Initial Calibration	
1. MeCl2 2. Subtraction Blank 3. Level - 1 4. Level - 2 5. Level - 3 6. Level - 4 7. Level -5 8. ICV 9 thru 18. Ten samples*	19. CCV 20 thru 29. Ten samples 30. CCV 31-40. Ten samples 41. CCV

*May be up to 10 samples or 12 hours from the start of the calibration verification standards

11.0. Calculations / Data Reduction

11.1. Accuracy:

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$$

11.2. Precision (RPD):

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.3. Calculate the concentration of the TPHC organics in the sample using a summation of peak response for all chromatographic peaks in the time window within which the target analytes elute. Use the following equations:

11.3.1. Aqueous Samples:

$$\text{Concentration mg/L} = \frac{(Ax)\ (Vt)\ (D)}{(RF)\ (Vs)}$$

Where: Ax = sum of area for TPHC range organics in the sample
RF = response factor from continuing calibration standard
Vt = final volume of extract (ml)
Vs = initial volume of sample extract (L)
D = dilution factor

11.3.2. Solid samples

$$\text{Concentration mg/kg.} = \frac{(Ax)\ (Vt)\ (D)}{(RF)\ (Vs)\ (Dw)}$$

Where: Ax = sum of area for TPHC range organics in the sample
RF = response factor from continuing calibration standard
Vt = final volume of extract (ml)
Vs = initial weight of sample extract (mg)
D = dilution factor
Dw = Dry weight correction factor $\left(\frac{100 - \%\ \text{moisture}}{100}\right)$

12.0. Method Performance

12.1. Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in Section 20 (Test Methods and Method Validation) of TestAmerica Edison's Quality Assurance Manual (ED-QA-LQM). MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2. Demonstration of Capabilities

For DOC procedure refer to Section 20 in the most current revision of TestAmerica Edison's Quality Assurance Manual (ED-QA-LQM).

12.3. Training Requirements

Refer to TestAmerica SOP No. ED-GEN-022, *Training*, for the laboratory's training program.

13.0. Pollution Control

13.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places

pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

13.2. The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage

14.0. Waste Management

14.1. The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.2. The following wastestreams are generated when using this method:

- Auto sampler vials and expired standards: These vials are collected in satellite accumulation within the instrument laboratory. The vials are then placed into a 55 steel open top drum in the waste room. When the drums are full, the drum will be collected by the waste vendor for disposal. This waste is treated for incineration.
  Teris Profile Number: 50016652
  Onyx Profile WIP Number: 282493

- Mixed Solvent Waste: Mixed solvent waste is collected in a small beaker inside the bench top hood. This waste is then transferred into the satellite accumulation container in the Organic Prep. Lab. on a daily basis. This material is transferred into 5 gallon solvent cans as satellite accumulation. These cans are emptied every 24 hours into a steel drum in the waste room. This drum is kept in the walk in hood until it is full. The full drum is then removed from the hood and placed on secondary containment in the waste room.
  Teris Profile Number: 50016624
  Onyx Profile WIP Number: 545240

15.0. References / Cross-References

15.1. NJDEP Method OQA-QAM-025, "Quantitation of Semivolatile Petroleum Products in Water, Soil, Sediment and Sludge" (current revision)

15.2. TestAmerica Edison Document No. ED-QA-LQM, *Laboratory Quality Manual*, most current revision.

15.3. TestAmerica Edison Work Instruction No. EDS-WI-061, *NJDEP OQA-QAM-025 Current QC Limits,* most current revision.

15.4. TestAmerica Edison Work Instruction No. EDS-WI-071 *NJDEP OQA-QAM-025: Current MDLs and Reporting Limits,* most current revision.

15.5. TestAmerica SOP No. ED-GEN-022, *Training,* most current revision.

15.6. TestAmerica Edison SOP No. ED-GEN-007, *Subsampling*, most current revision.

15.7. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, most current revision.

16.0. Attachments

Attachment 1: Example Standard Chromatogram, TPH Mix 3 (Supelco Catalog Number 861394-U).

Attachment 2: Example Certificate of Analysis, TPH Mix 3 (Supelco Catalog Number 861394-U).

17.0. Revision History

- Revision 1, dated January 2007
  - Throughout document:Removed all references to DRO (Diesel Range Organics)
  - Section 1.1: Replaced reference to Method 8015B with correct method reference: NJDEP OQA-QAM-025.
  - Section 7: Clarified language regarding the preparation of all standards.
  - Section 10.3.5:Replaced 'QAM' with 'TPHC by OQA-QAM-025'
  - Section 10.3.21: Replaced reference to Sections 10.3.5-10.3.6 with reference to Section 10.3.19.
  - Section 10.3.24.1: Replaced reference to 10.3.6 and 10.3.7 with reference to Section 10.3.20.
  - Section 10.3.24.2: Replaced reference to Section 10.3.6 with reference to Section 10.3.20.
  - Section 10.3.25: Replaced reference to Section 10.3.8 with reference to Section 10.3.20.
  - Section 11.1.2:Removed existing Section 11.1.2 which contained references to spikes as these are covered in Section 11.3. Replaced Section 11.1.2 with existing Section 11.1.3.
  - Section 11.3: Renamed as 'Matrix Spikes and Blank Spike (LCS)'
  - Section 11.3.1.1: Revised to include the spike recovery limits of 70%-130% and the RPD limit of 20% until such time as the lab has sufficient data to generate in-house limits.
  - Appendix B:Added at this revision Appendix B consists of an example Certificate of Analysis for the Supelco TPH Mix 3 cited in Section 7.

- Revision 2, March 2007
  - Section 8.2: Revised to read as follows: "Water samples must be preserved to a pH of <2 and be extracted within 7 days of collection. If unpreserved, water samples must be extracted within 4 hours of collection."
  - Section 8.3: Revised to read as follows per method requirements: "Soil samples must be extracted within 7 days of the time of collection." This section had

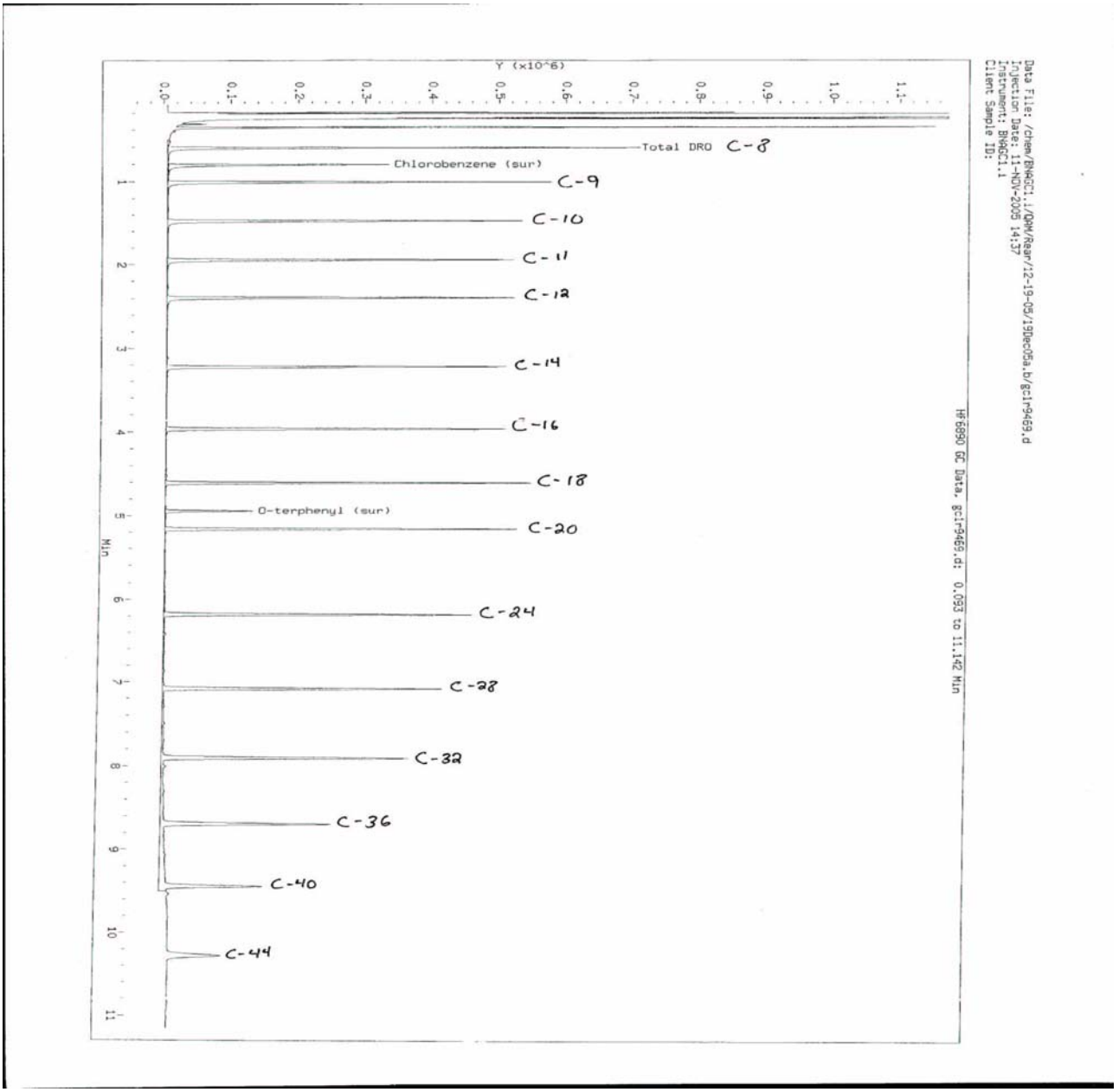
previously listed a 14 day holding time.
- Section 11.2.1: First sentence revised to read as follows: "The O-terphenyl and Chlorobenzene surrogate recoveries must fall within lab generated limits for all blanks and samples (including MS/MSD and Blank Spikes)."

- Revision 3, dated June 2008

  - Revised SOP format in accordance with TestAmerica Corporate Quality SOP No. CW-QS-002 (Rev 0) Writing a Standard Operating Procedure (SOP).
  - Section 1.1: Added reference to work instruction containing current MDLs/RLs.
  - Section 1.1: Added reference to Quality Assurance Manual for method modifications.
  - Section 2: Expanded to include references to applicable prep SOPs.
  - Section 3: revised to reference new location for definitions.
  - Section 5: Revised to include most up to date corporate health and safety references and information.
  - Section 6: Revised to include complete list of instrumentation and supplies.
  - Section 7.2.1: Added table detailing components found in TPH 3 Mix.
  - Section 7.3: Updated the instructions for preparation of the 5 point calibration range standards.
  - Section 8: Updated the extraction holding times for both soils and waters from 7 days to 14 days per the current revision (Rev. 7) of NJDEP OQA-QAM-025.
  - Section 9.1: Expanded QC sample preparation, analysis, evaluation and corrective action details.
  - Section 7.5 and 9.1.2: Revised to replace the parrafinic hydrocarbon LCS with a #2 Fuel Oil LCS solution.
  - Section 9.2: Expanded details of preparation, analysis, evaluation and corrective action for initial and continuing calibration and calibration verifications. Added a table summarizing Instrument QC Requirements.
  - Section 9.2.3.4: Revised acceptance criteria for CCV from 20%RSD to 20%D.
  - Section 10.1.2: Revised to require that soil extractions be performed with methylene chloride only.
  - Section 10.1.2: Revised to include specific details of Soxtherm Operation.
  - Section 10.2.1.2: Updated the oven temperature program used for QAM-025 analysis.
  - Section 11.3.2: Revised formulas for calculation of final concentration in soils to include a correction for % moisture.
  - References: Expanded to include more specific SOP references.

Attachment 1

Example Standard Chromatogram,
TPH Mix 3
Supelco Catalog Number 861394-U



Attachment 2

Example Certificate of Analysis,
TPH Mix 3
Supelco Catalog Number 861394-U

Certificate of Analysis

DESCRIPTION: SS TPH Mix 3

CATALOG NO.: 8S61394-U MFG DATE: Jun-2006

LOT NO.: LB40555 EXPIRATION DATE: Jun-2009

SOLVENT: CARBON DISULFIDE

ANALYTE (1)	CAS NUMBER	PERCENT PURITY(2)	WEIGHT(3) CONCENTRATION	ANALYTICAL(4) CONCENTRATION	STD DEV	SUPELCO LOT NO
HEXANE, SS	110-54-3	99.3	1001	1002	+/- 13.9	LA89053
N-DECANE, SS	124-18-5	99.9	1002	1071	+/- 147.1	LA91224
N-DODECANE, SS	112-40-3	99.9	1000	1056	+/- 137.4	LA91225
N-DOTRIACONTANE, SS	544-85-4	97.0	1001	1054	+/- 141.7	LB15677
N-EICOSANE, SS	112-95-8	99.9	1001	1055	+/- 142.9	LA91222
N-HEPTANE, SS	142-82-5	99.4	1001	1042	+/- 75.7	LA94367
N-HEXADECANE, SS	544-76-3	99.9	1000	1048	+/- 138.3	LA91220
N-HEXATRIACONTANE, SS	630-06-8	99.9	1002	1051	+/- 142.5	LB15736
N-NONANE, SS	111-84-2	99.9	1000	1063	+/- 108.6	LB15566
N-OCTACOSANE, SS	630-02-4	99.9	1001	1052	+/- 143.3	LB16041
N-OCTADECANE, SS	593-45-3	99.6	1001	1053	+/- 141.1	LA91221
N-OCTANE, SS	111-65-9	99.9	1002	1075	+/- 102.6	LB15563
N-TETRACONTANE, SS	4181-95-7	98.3	1002	1056	+/- 140.2	LB15570
N-TETRACOSANE, SS	646-31-1	96.8	1000	1051	+/- 143.4	LB15568
N-TETRADECANE, SS	629-59-4	99.6	1002	1050	+/- 137.8	LA91219
N-TETRATETRACONTANE, SS	7098-22-8	96.2	1001	1056	+/- 142.7	LB15569
N-UNDECANE, SS	1120-21-4	99.7	1001	1046	+/- 136.6	LB15567

(1) Listed in alphabetical order.
(2) Determined by capillary GC-FID, unless otherwise noted.
(3) NIST traceable weights are used to verify balance calibration with the preparation of each lot. Concentration of analyte in solution is ug/ml +/- 0.5%, uncertainty based upon balance and Class A volumetric glassware. Weights are corrected for analytes less than 98% pure.
(4) Determined by chromatographic analysis against an independently prepared reference lot. Mean of replicate injections.

These products have identical formulations but are prepared from independently sourced raw materials, and are quality controlled independently. Products denoted as Separate Source standards afford the convenience of working with Supelco as a single vendor while enabling you to meet independent calibration and quality control requirements of the US EPA

Elwood Doughty
Quality Control Supervisor

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SUPELCO
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Phone (814) 359-3441

Appendix P

Laboratory SOPs

TAL Metals + titanium

Shealy SOPs

S-IM-013 (Preparation)

S-IM-022 (Analysis)

SHEALY ENVIRONMENTAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

METHOD 3050B

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1. SCOPE AND APPLICATION

1.1 This procedure describes the preparation of soil samples for the analysis of certain metals by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP).

1.2 Samples prepared by the protocols detailed in this SOP may be analyzed for the elements listed in Table I (Appendix A). Other elements and matrices may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3 This method is not total digestion, but will dissolve almost all metals that could become “environmentally available”. By design, metals bound in silicate structures are not dissolved by this procedure as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludges, wastes and sediments.

2. SUMMARY OF METHOD

2.1 A representative 1-2 gram (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. For ICP analysis, the digestate is refluxed with hydrochloric acid before being filtered and diluted to 50 mL.

3. DEFINITIONS

3.1 Total Metals – The concentration determined on an unfiltered sample following vigorous digestion. Note that this method is designed to determine the total environmentally available metals.

3.2 Refer to the QAMP for the definitions of other terms used in this SOP.

4. INTERFERENCES

4.1 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them (refer to Appendix B).

4.2 Boron and silica from the glassware will grow into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic lab ware should be used.

4.3 Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents, and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.4 Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.5 Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs, the sample must be re-prepared. Antimony is easily lost by volatilization from hydrochloric media.

4.6 Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all Shealy personnel.

5.2 As stated in the Shealy Comprehensive Chemical Hygiene, Safety, and Hazard Communication Plan (P-HS-003), eye protection that satisfies ANSI Z87.1, laboratory coat, and at least latex gloves must be worn while samples, standards, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1 The following materials are known to be **corrosive**: hydrochloric acid and nitric acid.

5.3.2 The following materials are known to be **oxidizing agents**: nitric acid and hydrogen peroxide.

5.3.3 All heating of samples must be carried out in a fume hood.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened,

transferred and prepared in a fume hood, or under other means of mechanical ventilation.

5.5 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides and sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of a Shealy employee. The situation must be reported immediately to a laboratory supervisor/team leader.

5.7 The preparation of reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.

5.8 Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9 Acid/peroxide spills must be neutralized immediately with sodium bicarbonate, flushed with water, and cleaned up using appropriate spill kits.

5.10 Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.11 Any and all accidents and spills must be reported to the lab supervisor, team leader, or safety officer.

6. EQUIPMENT AND SUPPLIES

6.1 Environmental Express Hotblock (Cal 3300) or equivalent, capable of maintaining a temperature of 95 ± 2°C.

6.2 Thermometer that covers a temperature range of 0-100°C.

6.3 Environmental Express disposable plastic digestion tubes with screw caps.

6.4 Watch glasses – ribbed.

6.5 Whatman No. 41 filter paper or equivalent.

6.6 Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.7 Bottletop Dispensers or suitable reagent dispensers.

6.8 Calibrated automatic pipets with corresponding pipet tips or Class A volumetric pipets.

6.9 Class A volumetric flasks.

7. REAGENTS AND STANDARDS

- **Note: All standards and reagents are made using reagent water and volumetric glassware unless otherwise noted. Lot numbers or in-house chemical ID numbers, where applicable for reagents and standards, are documented on the sample prep batch sheets.**

- **Note: All stored reagents and standards are labeled with the following information:**

    1. **Name of standard or solution**
    2. **Concentration**
    3. **Analyst's initials**
    4. **Prep date**
    5. **Expiration date**
    6. **Tracking number**
    7. **Warning label of any hazards and/or concentration of acid or base**

7.1 Refer to S-QA-007 for all glassware cleaning procedures before using any glassware.

7.2 Reagent Water – Shealy employs a series of in-house deionized (DI) tanks to purify the incoming water to the conductivity measurement, 0.056 μmhos/cm (corresponds to resistivity of 18 meg-ohms). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in determinative SOPs.

7.3 Laboratory Control Samples (LCS/LCSD and matrix spike (MS/MD) stock standards are purchased as custom multi-element mixes or as single-element solutions. All stocks must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.4 Working ICP LCS/LCSD/MS/MD spike solutions – The working ICP LCS/LCSD/MS/MD spike solutions are the same as LCS/LCSD/MS/MD stock standards (7.3), no further preparation is necessary. Refer to Table II (Appendix A) for details regarding the concentration of each element in the working spike solution and in the spiked LCS/LCSD/MS/MD samples.

7.5 The LCS/LCSD and MS/MD samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom solution, a solution must be purchased from a vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.6 Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.7 Nitric acid solution, 1:1 – Dilute concentrated HNO_3 with an equal volume of reagent water.

- **Note: When preparing diluted acids always add acid to water. If the water is added to the acid, a violent reaction may occur.**

7.8 Hydrochloric acid (HCl), concentrated, trace metals grade or better.

7.9 30% Hydrogen peroxide (H_2O_2), reagent grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Sample holding times for metals under the scope of this SOP is 180 days from time of collection to the time of analysis.

8.2 Solid samples do not require chemical preservation and can be stored at room temperature.

9. QUALITY CONTROL

9.1 Initial Demonstration of Capability:

9.1.1 The initial demonstration of capability (IDOC) and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.2 Preparation Batch – A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, a laboratory control sample (or LCS/LCSD pair) and a matrix spike/matrix spikes duplicate (MS/MD pair) for the first set of 10 samples. The remaining samples in the preparation batch, ≤ 10, must be associated with an MS only. If there are 10 or fewer samples in the preparation batch, an MS/MD pair is required. In some cases, at the request of the client, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MD. If clients specify specific samples for MS/MD, the batch may contain multiple MS/MD pairs.

9.3 Sample Count – Laboratory generated QC samples (MB, LCS/LCSD, and MS/MD) are not counted towards the maximum 20 samples in a batch. Field QC samples are also included in the batch count.

9.4 Method Blank (MB) – One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks and corrective actions are contained within the individual analytical method SOP's.

9.4.1 Soil method blank is prepared by taking 1.0 gm of reagent water through the procedure described in Section 11.5.

9.5 Laboratory Control Sample (LCS/LCSD) – One soil LCS/LCSD must be processed with each preparation batch. The LCS/LCSD must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS/LCSD is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS/LCSD results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for acceptance of LCS/LCSD results and corrective actions are contained within the individual analytical method SOP's. Table II provides the details regarding the stock, working solutions and final spike concentrations for ICP.

9.5.1 The ICP LCS/LCSD is prepared by spiking a 1.0 gm aliquot of reagent water with 1.0 mL of each of the working ICP LCS/LCSD/MS/MD spike solutions (Section 7.4). The LCS/LCSD is then processed as described in Section 11.5. DoD samples require 1.0g water in the associated LCS.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MD) - The batch must contain a method blank, a laboratory control sample (or LCS/LCSD pair) and a matrix spike/matrix spikes duplicate (MS/MD pair) for the first set of 10 samples. The remaining samples in the preparation batch, ≤ 10, must be associated with an MS only. If there are 10 or fewer samples in the preparation batch, an MS/MD pair is required. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MD's. The MS/MD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. **Samples identified as field blanks cannot be used for MS/MD analysis.** Criteria for acceptance of MS/MD and corrective actions are

contained within the individual analytical method SOP's. Table II provides details regarding the stock, working solutions and final matrix spike concentrations for ICP.

9.6.1 The ICP soil matrix spike sample is prepared by spiking 1-2 grams of sample with 1.0 mL of each of the working ICP LCS/LCSD/MS/MD spike solutions (Section 7.4). The matrix spike sample is then processed as described in Section 11.5.

10. CALIBRATION AND STANDARDIZATION

10.1 The hot block temperature should be verified daily for each unit used by measuring the temperature of reagent water in a tube placed on the heated hot block using a thermometer. Record this temperature in the temperature verification logbook.

10.2 Bottletop dispensers must be verified daily to assure the correct volume of reagent is being dispensed. Class A volumetric glassware is used to verify the volume the dispenser is set to provide. The results must be documented in the bottletop dispenser calibration verification logbooks.

10.3 Automatic pipets are calibrated daily by weighing the volume of water the pipet dispenses and documented in the pipets calibration logbook.

10.4 Analytical balance must be calibrated daily using a certified weight set and document in the balance calibration logbook.

11. PROCEDURE

11.1 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2 All heating of samples must be carried out in a properly functioning hood.

11.3 Samples are typically logged in as either aqueous or solids. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment, etc.) contact the team leader or project manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.4 Proper sample identification is extremely important in any preparation procedure. Labeling of digestion tubes must be done in a manner to ensure connection with the

proper sample. Bottles used to store digestates should be labeled with sample ID, method of preparation, and prep batch number.

11.5 Preparation of Solids, Sediment, and Sludge for Analysis by ICP.(for silicon digestion see section 18)

11.5.1 Obtain a well-mixed, homogenized sample with a clean plastic or wooden spoon or spatula. All samples must be homogenized prior to obtaining the aliquot to be used for digestion.

- Note: If the sample container is full with no headspace, it is important to empty the contents of the container into a clean vessel and mix well before weighing. If the sample container has headspace, stir the sample in the original sample container to avoid the possibility of contamination.

11.5.2 For ICP digestion procedure, weigh 1-2 g of sample into a digestion tube and record the exact weight to the nearest 0.01 gram. Do not target a specific weight.

11.5.3 Measure additional portions of the designated samples for the MS and MD analyses.

11.5.4 Add 1.0 gm of reagent water into each digestion tubes for the MB and LCS/LCSD.

11.5.5 Spike the LCS/LCSD, MS, and MD samples with 1.0 mL of each of the working ICP matrix spike solution (7.3) for ICP analysis.

11.5.6 Add 10 mL of 1:1 HNO_3 and mix the sample by gently swirling the tube.

11.5.7 Cover tube with ribbed watchglass, heat sample on hotblock at 95 ± 2°C and gently reflux for 10 minutes without boiling.

- Note: **Do not allow sample to boil or go dry during any part of the digestion**. Doing so will result in the loss of analyte and the sample must be reprepared.

11.5.8 Remove from hotblock and allow sample to cool to room temperature.

11.5.9 Add 5.0 mL of concentrated HNO_3 and replace watchglass.

11.5.10 Heat sample at 95 ± 2°C for 2 hours or until sample is reduced to approximately 5 mL. (Do not let the volume of solution reduced to less than 5 mL.)

- If brown fumes are observed, repeat step 11.5.9 and 11.5.10 until no more fumes are evolved.

11.5.11 Remove from hotblock and allow sample to cool to room temperature.

11.5.12 Remove the ribbed watchglass and add 2.0 mL DI water and 3.0 mL of 30% H_2O_2. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

11.5.13 Continue heating at 95 ± 2°C for another 2 hours or until the volume is reduced to approximately 5 mL.

11.5.14 Remove from hotblock and allow sample to cool to room temperature.

11.5.15 Remove watchglass, add 10 mL of concentrated HCl.

11.5.16 Replace watchglass and heat for an additional 15 minutes without boiling.

11.5.17 Remove from hotblock and allow sample to cool to room temperature.

11.5.18 Wash down tube wall and watchglass with reagent water.

11.5.19 Dilute to 50-mL mark with reagent

11.5.20 Filter sample through Whatman No. 41 filter paper into clean tube and screw on cap. The sample is now ready for analysis.

11.6 Nonconformance documentation shall be filed in the project file along with performing 11.7 or 11.7.1.

11.7 Procedural Variations – This Section applies to all samples <u>except</u> South Carolina compliance samples. One time procedural variations are allowed, only if deemed necessary in the professional judgment and supervision of a knowledgeable analyst, to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in analytical procedure must be approved by a technical director, the QA Officer, or the client, and must be fully documented (flagged and/or narrated) on the final report. The analyst must use an NCM to notify the appropriate parties and to document the variance. The project manager uses the information on the NCM to notify the client and flag/narrate the final report accordingly. A copy of the NCM is kept with the raw data and the original is filed with the final report.

11.7.1 For South Carolina compliance samples, all procedures outlined in this SOP must be followed without exception. In the event that a deviation

from this SOP cannot be avoided (i.e., demonstrated and uncorrectable matrix interference, non-compatible matrix, insufficient sample amount due to client or laboratory error) it is imperative that an NCM is completed that clearly documents the anomaly. This anomaly must be communicated to the client such that corrective action activity including sample recollection can be performed. Based upon the type and severity of anomaly, the results may not be appropriate for compliance reporting. Discussions between the client, the appropriate regulatory authority, and Shealy will be necessary to resolve certain anomalies. In any case, it is essential that any anomaly be documented on an NCM. The project manager uses the information on the NCM to notify the client and flag/narrate the final report accordingly.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Not Applicable

13. METHOD PERFORMANCE

13.1 Method Detection Limit – Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in Shealy QAMP.

13.2 Initial Demonstration – Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equal to the LCS concentration.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria for the corresponding analyte in the LCS.

13.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3 Training Qualification – The team leader has the responsibility of ensuring that this procedure is being performed by an employee who has been properly trained and has the required experience.

14. POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1 Waste generated in the procedure must be disposed of according to the Shealy Waste Management Plan (P-HS-001) and per the local, state, and federal regulations. The Safety Officer should be contacted, if additional information is required.

15.2 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1 SW-846, Test Method for Evaluating Solid Waste, Third Edition – Acid Digestion of Sediments, Sludges, and Soils, Method 3050B, Revision 2, December 1996.

16.2 EPA/600/4-79-020 – Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 200.7, Revised March 1983.

16.3 EPA/600/R-94/111 – Methods for the Determination of Metals in Environment Samples – Supplement I, May 1994.

16.4 Shealy Quality Assurance Management Plan (QAMP), Q-QA-001

16.5 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.1, January 2006.

17. MISCELLANEOUS

18. SOIL DIGESTION FOR SILICON

18.1 Obtain a well-mixed, homogenized sample with a clean plastic or wooden spoon or spatula. All samples must be homogenized prior to obtaining the aliquot to be used for digestion.

- Note: If the sample container is full with no headspace, it is important to empty the contents of the container into a clean vessel and mix well before weighing. If the sample container has headspace, stir the sample in the original sample container to avoid the possibility of contamination.

18.2 For ICP digestion procedure, weigh 1-2 g of sample into a digestion tube and record the weight. Do not target a specific weight.

18.2.1 Measure additional portions of the designated samples for the MS and MD analyses.

18.2.2 Add 25 gm of reagent water into each digestion tubes for the MB and LCS/LCSD, and to the samples and MS/MSD.

18.2.3 Spike the LCS/LCSD, MS, and MD samples with 1.0 mL of each of the working ICP matrix spike solution (7.3) for ICP analysis.

18.2.4 Add 5 mL of 1:1 HNO_3 and mix the sample by gently swirling the tube.

18.2.5 Cover tube with ribbed watchglass, heat sample on hotblock at 95 ± 2°C and gently reflux for 5 minutes without boiling.

- Note: **Do not allow sample to boil or go dry during any part of the digestion**. Doing so will result in the loss of analyte and the sample must be reprepared.

18.2.6 Remove from hotblock and allow sample to cool to room temperature.

18.2.7 Add 5.0 mL of concentrated HNO_3 and replace watchglass.

18.2.8 Heat sample at 95 ± 2°C for 1 hour

18.2.9 Remove from hotblock and allow sample to cool to room temperature.

18.2.10. Remove the ribbed watch-glass and add 2.0 mL DI water and 3.0 mL of 30% H_2O_2. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

18.2.11 Continue heating at 95 ± 2°C until the volume is reduced to approximately 25 mL.

18.2.12 Remove from hotblock and allow sample to cool to room temperature.

18.2.13 Remove watchglass add 10 mL of concentrated HCl.

18.2.14 Replace watchglass and heat for an additional 8 minutes without boiling.

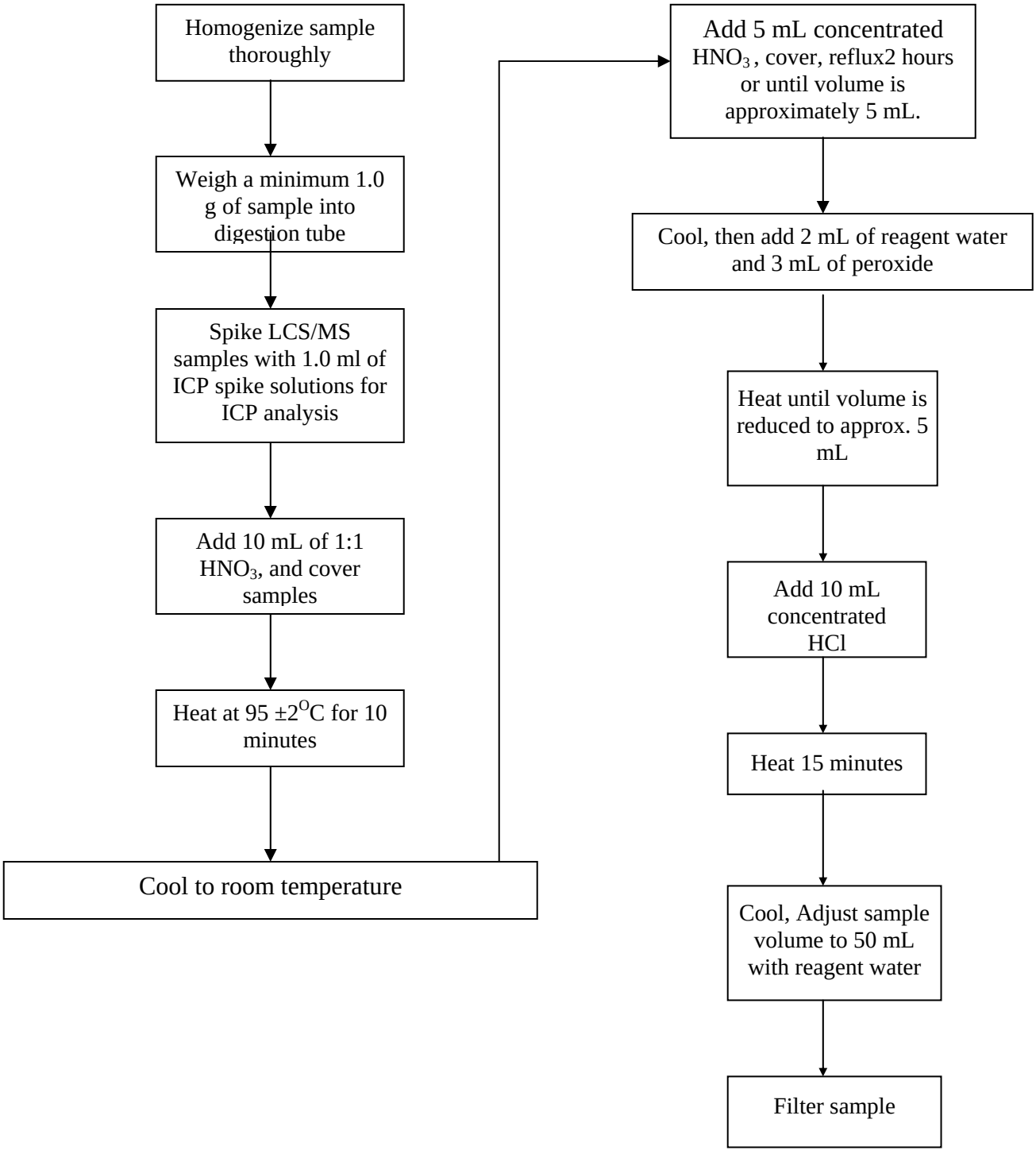
18.2.15 Remove from hotblock and allow sample to cool to room temperature.

18.2.16 Wash down tube wall and watchglass with reagent water.

18.2.17 Dilute to 50-mL mark with reagent water

18.2.18 Filter sample through Whatman No. 41 filter paper into clean tube and screw on cap. The sample is now ready for analysis.

FIGURE 1. Solid Sample Preparation (Section 11.5)



APPENDIX A - TABLES

TABLE I. Method 3050B Approved Analyte List

ICP ELEMENTS	SYMBOL	CAS NUMBER
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic *	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Boron*	B	7440-42-8
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-4824
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Potassium	K	7440-09-7
Selenium*	Se	7782-49-2
Silica*	Si	7740-21-3
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Thallium	Tl	7440-28-0
Tin*	Sn	7440-31-5
Titanium*	Ti	7440-32-6
Uranium*	U	7440-06-11
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

*These elements are not approved for this technology based on the EPA prep method 3050B, but may be approved by local, state, or EPA regional bodies for certification. Please refer to Shealy's state certificates for individually approved elements.

TABLE II. Solid and Aqueous ICP LCS/D and MS/MD Spike Levels

ELEMENT	Working LCS/LCSD MS/MD Spike Solution (mg/L)	Aqueous LCS/LCSD, MS/MD Level * (µg/L)	Solid LCS/LCSD, MS/MD Level ** (mg/kg)
Aluminum	1000	20	1000
Antimony	20	0.40	20
Arsenic	20	0.40	20
Barium	100	2.0	100
Beryllium	100	2.0	100
Boron	100	0.40	100
Cadmium	20	0.40	20
Calcium	2000	40	2000
Chromium	100	2.0	100
Cobalt	100	2.0	100
Copper	100	2.0	100
Iron	1000	20	1000
Lead	20	0.40	20
Magnesium	2000	40	2000
Manganese	100	2.0	100
Molybdenum	100	2.0	100
Nickel	100	2.0	100
Potassium	2000	40	2000
Selenium	20	0.40	20
Silica	200	2.0	200
Silver	20	0.40	20
Sodium	2000	40	2000
Thallium	40	0.80	40
Tin	20	0.40	20
Titanium	20	0.40	20
Uranium	100	NA	100
Vanadium	100	2.0	100
Zinc	100	2.0	100

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS/LCSD or matrix spike based on the addition of 1.0 mL of each working spike solutions (7.3) to 50 mL of sample.

** Final soil spike concentration based on the addition of 1.0 mL of each working spike solutions (7.3) to 1.0 g of sample/50 mL final volume (assumes 100% solid) when it is converted to mg/kg. This concentration is the same as the aqueous mg/L LCS/D as it appears on the raw data before the solid conversion.

APPENDIX B. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by de-ionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only Non-powered, vinyl, or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipet tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The marking on glass beakers have been found to contain lead.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

SHEALY ENVIRONMENTAL SERVICES, INC.

STANDARD OPERATING PROCEDURE

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY

SPECTROMETRIC METHOD for TRACE ELEMENT ANALYSES METHOD 6010C

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1. SCOPE AND APPLICATION

1.1 This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010C. Table I lists the elements appropriate for analysis by Methods 6010C. Additional elements may be analyzed under Method 6010C provided that the method performance criteria presented in Section 13 are met.

1.2 ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will very with the matrices and instrumentation used. For instance, in comparison to conventional ICP techniques, ICP-Trace can achieve detection levels comparable to those determined using the graphite furnace atomic absorption spectroscopy (GFAAS) technique.

1.3 Method 6010C is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, TCLP, and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of dissolved samples and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

2. SUMMARY OF METHOD

2.1 This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer. The intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed.

2.2 Refer to appropriate SOPs for details on sample preparation methods.

3. DEFINITIONS

3.1 Dissolved Metals – Those elements that pass through a 0.45 μm membrane. (Sample is acidified after filtration.)

3.2 Suspended Metals – Those elements that are retained by a 0.45 μm membrane.

3.3 Total Metals – The concentration determined on an unfiltered sample following vigorous digestion.

3.4 Total Recoverable Metals – The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

3.5 Preparation Batch – Composed of 1 to 20 environmental samples of the same matrix. The maximum time between the start of processing the first and last sample in the batch is 24 hours.

4. INTERFERENCES

4.1 Spectral, physical, and chemical interference effects may contribute to inaccuracies in the determination of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.2 A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.3 Inter-element correction factor (IEC's) is necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-elements corrections must be applied to the analyte to remove the effects of these unwanted emissions.

4.4 Physical interferences are generally considered to be effects associated with sample transport, nebulization, and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant

inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard, and/or use of a high solids nebulizer can reduce the effect.

4.5 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching, or standard dilution procedures.

5. SAFETY

5.1 Procedures shall be carried out in a manner that protects the health and safety of all Shealy personnel.

5.2 As stated in the Shealy Comprehensive Chemical Hygiene, Safety, and Hazard Communication Plan (P-HS-003), eye protection that satisfies ANSI Z87.1, laboratory coat, and at least latex gloves must be worn while samples, standards, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3 The health and safety hazards of many of the chemicals used in the procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1 The following materials are known to be **corrosive**: sulfuric acid, hydrochloric acid, nitric acid, and hydrofluoric acid. (NOTE: sulfuric acid and hydrofluoric acids are used in cleaning the ICP torch and hydrofluoric acid is also commonly used in air toxics preparations.)

5.3.2 The following materials are known to be **oxidizing agents**: nitric acid and hydrogen peroxide.

5.3.3 The plasma emits strong UV light and is harmful to vision.

- **Note: Avoid looking directly at the plasma.**

5.3.4 The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 The preparation of standards and reagents will be conducted in a fume hood or well-ventilated area.

5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of a Shealy employee. The situation must be reported immediately to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1 Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.1.2 ICPs currently in use.

Instrument	manufacturer	model	Date installed
Inductively Coupled Plasma-Trace (ICP4)	Thermo Jarrell Ash	ICAP6500	02/01/08
Inductively Coupled Plasma-Trace (ICP3)	Thermo Jarrell Ash	61E	12/2000
Inductively Coupled Plasma-Trace (ICP2)	Thermo Jarrell Ash	61E	07/1998

6.2 Radio Frequency Generator.

6.3 Argon gas supply, welding grade or equivalent.

6.4 Coolflow or appropriate water-cooling device.

6.5 Peristaltic Pump.

6.6 Filter paper – Whatman No. 41 or equivalent.

6.7 Calibrated automatic pipets with appropriate pipet tips or class A volumetric pipets.

6.8 Class A volumetric flasks.

6.9 Autosampler tubes.

7. REAGENTS AND STANDARDS

- **Note: All stored reagents and standards are labeled with the following information:**

    1. **Name of standard or solution**
    2. **Concentration**

3. **Analyst's Initials**
4. **Prep date**
5. **Expiration date**
6. **Tracking number**
7. **Warning label of any hazards and/or concentration of acid or base**

7.1 Intermediate standards are purchased as custom multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon or unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solution may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

7.2 Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acids.

7.3 Refer to Tables II-V for details regarding the working standard concentrations for calibration, calibration verification, interference correction, and spiking solutions.

7.4 Concentrated nitric acid (HNO_3), trace metal grade or better.

7.5 Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6 Reagent Water – Shealy employs a series of in-house deionized (DI) tanks to purify the incoming water to the conductivity measurement, 0.056 μmhos/cm (corresponds to resistivity of 18 meg-ohms). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.7 Internal standard (Li/Y) solution – Dilute 10 mL of Lithium stock (10,000 mg/L) and 10 mL of Yttrium stock (1,000 mg/L) to 1 L with reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Sample holding times for metals are six months from time of collection to the time of analysis.

8.2 Aqueous samples are preserved with nitric acid to a pH of < 2 and may be stored in either plastic or glass. If boron or silica is to be determined, plastic containers are preferred. Refrigeration is not required. Preservation is verified during sample login according to the procedure in the sample receiving SOP.

8.2.1 Dissolved samples must be filtered through a 0.45 μm pore diameter membrane filter at the time of collection or as soon thereafter as possible.

Acidify the filtrate with (1:1) nitric acid immediately following filtration to pH <2.

8.2.2 For total recoverable elements, preservation may be added at time of collection, or, upon receipt at the laboratory. The time allowed for traveling to the laboratory should not to exceed two weeks from the sample collection date. Following acidification, the sample should be mixed, held for 24 hours, and then verified to be pH <2 just before analysis or prep (if prep required). If pH is not <2, add more acid and hold for 24 more hours until verified to be pH <2.

8.3 Soil samples do not require chemical preservation but must be stored at 4 ± 2°C until the time of preparation.

9. QUALITY CONTROL

Table VI provides a summary of quality control requirements including type, frequency, acceptance criteria, and corrective action.

9.1 Initial Demonstration of Capability:

9.1.1 The initial demonstration of capability (IDOC) and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.1.2 Instrument detection limit (IDL) studies must be done before analysis of samples may begin.

9.1.2. Method 6010C: Calculate the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. IDLs must be determined at least every three months and kept with the instrument logbook.

9.2 Linear Dynamic Range Verification (LDR) – The linear range must be determined at least every six months for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample. The standards used to define the linear range limit must be analyzed during a routine analytical run. For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard should be near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10% different from the expected level The highest calibration standard for each analyte contains the analyte at the upper limit of the linear dynamic range and is run as part of each calibration run; therefore, the linear dynamic range is verified with each run. If the

instrument is adjusted in any way that may affect the LR's, new dynamic ranges must be determined. The LR data must be documented and kept on file.

9.2.1 Linear Range (LR) check standards are analyzed daily. Refer to Table III-B for LR standards and concentrations.

9.3 Background Correction Points – To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference.

9.4 Inter-element Corrections (IEC's) – ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IEC's, the IEC's must be redetermined. When initially determining IEC's for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA). Published wavelength tables can also be consulted to evaluate the validity of the IEC's. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than ± the PQL as defined in Tables I or II. To determine IEC's, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the observed concentration of the "interfering element."

- Note: Trace ICP IEC's are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IEC's will be required on a more frequent basis for the Trace as reflected by the ICSA response.

9.5 Rinse Time Determination – Rinse times must be determined annually. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see Section 9.2) should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < PQL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analytes not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range

level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

9.6 Method Blank (MB) – One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest $\geq$ the reporting limit. If the MB contains an analyte of interest $\geq$ the reporting limit:

9.6.1 Re-run method blank once and if still unacceptable, re-preparation and reanalysis of all samples associated with a contaminated method blank is required. If the method blank exceed the reporting limit, but the samples are below the reporting limit , then the sample data may be used. If the method blank is less than 10% of the reporting limit, less than 10% of the regulatory limit or less than 10% of the sample concentration , then the blank is acceptable.

9.6.2 If the client requests that the results be reported down to "J" values and there is a "J" value in the method blank, all sample analyses with a positive result for that analyte must be flagged. The samples do not have to re-prepared or reanalyzed unless the method blank contamination is above the reporting limit..

9.6.3 If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. Such action must result in the completion of a NCM. Refer to Section 11.19, Procedural Variations, for more detail.

9.7 Laboratory Control Sample (LCS) – One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire procedure, including preparation and analysis. Aqueous LCS spike levels are provided in Table II (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable precision guidelines.

9.7.1 If any analyte is outside established control limits, re-run the LCS once. If the LCS fails the second run, then the system is out of control and corrective action must be taken., For Method 6010C, a control limit of 80 – 120 % recovery must be applied. Corrective action will be re-preparation and reanalysis of the batch.

9.7.2 In the event that MS/MD analysis is not possible (not enough sample) a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.8 Matrix Spike/Matrix Spike Duplicate (MS/MD) – One MS/MD pair must be processed in each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MD) is a second aliquot of the same sample (spike identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MD. The MS/MD results are used to determine the effect of a matrix on the accuracy and precision of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MD analysis. Spiking levels are provided in Tables II (Appendix A).

9.8.1 If any analyte recovery falls outside the acceptance range, interference tests should be performed. These tests include post digestion spike addition and/or a dilution test(see 9.9 and 9.10).. For 6010C, control limits of 75% - 125% recovery and 20% RPD must be applied to the MS/MD.. MS/MD results, which fall outside the control limits, must be addressed in the narrative.

9.8.2 If the native analyte concentration in the MS/MD exceeds 4x the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated).

9.8.3 If the MS and/or MS/MD pair fails the recovery criteria, and a 5x or greater dilution was required, reanalysis of the MS/MD is not required. The result is considered over-diluted. This high dilution may allow for an inaccurate determination of matrix effect and must be noted as such in a NCM.

9.8.4 The MS and/or MS/MD pair must be prepared and analyzed at the same dilution as the parent sample (the un-spiked sample) so that a direct relationship and matrix effect can be evaluated.

9.9 Post Digestion Spike Addition- If the MS/MSD recoveries are unacceptable, spike the parent sample of the MS/MSD with a post digestion spike. Another sample from the same preparation batch can be used as an alternative if the parent sample of the MS/MSD can not be used. Recovery should be within 80-120% of the known value. The spike should produce a minimum level of 10x and a maximum level of 100x the PQL. If both the MS/MSD and the post digestion spike fail, then matrix interferences exists.

9.10 Dilution Test – A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5x (1:4) dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted samples, after correction for dilution, should agree within 10% of the original sample determination when the original sample concentration is greater than 10x the PQL. If the results are not within 10%, the possibility of chemical or physical interference exists.

9.11 Initial Calibration Verification (LLICV/ICV) – To be considered acceptable, the calibration curve should have a correlation coefficient greater than or equal to 0.998. Calibration accuracy is verified by analyzing both a low-level (LLICV) and a mid-level second source standard (ICV)..The ICV must fall within 10% of the true value for that solution with relative standard deviation < 5% from replicate (minimum of two) exposures. The LLICV should be prepared from the same source as the calibration standards. The suggested acceptance criteria for the LLICV is 30% of its true value. Quantitative sample analyses should not proceed for those analytes that fail the ICV. However, analyses may continue for those analytes that fail the criteria with the understanding these results should be qualified and would be considered estimated values. Once the calibration acceptance criteria is met, either the lowest calibration standard or the LLICV concentration can be used to demonstrate the lower limit of quantitation and sample results should not be quantitated below this lower standard. In some cases depending on project data quality objectives , it may be appropriate to report these results as estimated. However, they should be qualified by reporting the results as below the limit of quantitation. If the LLICV and ICV fails criteria , the cause needs to be determined and the instrument recalibrated . An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result should be less than the reporting limit. If the ICB fail to meet criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

9.12 Continuing Calibration Verification (LLCCV/CCV/CCB) – Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV is a mid-range standard made from a dilution of the calibration standard. The CCV must fall within 10% of the true value for that solution with relative standard deviation < 5% from replicate (minimum of two) exposures. A CCB is analyzed immediately following the CCV. The CCB result should be less than the reporting limit. Sample results may only be reported when bracketed by valid CCV/CCB pairs. The CCV/CCB pair is analyzed every 10 samples. The low-level continuing calibration verification (LLCCV) should also be analyzed at the end of each analysis batch. A more frequent LLCCV analysis , every 10 samples, may be necessary if low-level sample concentrations are anticipated and the system stability at the low end is questionable. This may also minimize the number of re-analysis should the LLCCV fail if only run at the end of the analysis batch. The LLCCV standard is made from the same source as the calibration standards at the laboratory reporting limit. The LLCCV standard acceptance criteria is 30% of its true value. If a LLCCV, CCV, or CCB fails, discontinue analysis, determine the cause, and recalibrate instrument. The samples associated with the LLCCV/CCV/CCB must be reanalyzed

9.13 Lower Limit of Quantitation Check Sample (LLQC)- The lower limit of quantitation check(LLQC) sample should be analyzed at the laboratory reporting limits and on an as needed basis to demonstrate the detection capability. Ideally, this sample and the low-level calibration check (LLICV) will be prepared at the same concentration .The only difference is the LLQC is

carried through the entire preparation and analytical procedure. The LLQC must recover within 30% of the true concentrations.

9.14 Interference Check Analysis (ICSA/ICSAB) – The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferants. Refer to Table IV (Appendix A) for details of ICSA and ICSAB composition. Custom multi-element ICS solutions must be used. All applicable analytes should be spiked into the ICSAB solution, therefore, if a non-routine analyte is required then it should be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. If the ICP will display overcorrection as a negative number then the non-routine elements can be controlled from the ICSA. Elements known to be interferants on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium, and magnesium must always be included in all ICP runs.

9.14.1 The ICSA and ICSAB solutions must be run at the beginning of the run.

9.14.2 ICSA results for the non-interfering elements with reporting limits ≤ 10 µg/L must fall within ± 2x PQL from zero. ICSA results for the non-interfering elements with PQLs > 10 µg/L must fall within ± 1x PQL from zero. If the ICSA results for the non-interfering elements do not fall within ± 2x PQL (PQL ≤ 10) or ± 1x PQL (PQL > 10) from zero the field sample data must be evaluated as follows:

9.14.3 If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.

9.14.4 If the affected element was not required then the sample data can be accepted.

9.14.5 If the interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result greater than ± 2x PQL from zero then the field sample data can be accepted.

9.14.6 If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2x PQL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.

9.14.7 If the data does not meet the above conditions then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the raw results. If the

results are recalculated manually, the calculations must be clearly documented on the raw data.

9.14.8 The ICSAB results for the interferants must fall within 80- 120% of true value. If any ICSAB interferant result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the samples rerun.

9.15 Method of Standard Addition (MSA) – This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample interference that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences, which cause a baseline shift. Refer to Section 11.17 for additional information on when MSA is required as well as Appendix G for specific MSA requirements.

9.16 Analytical Batching – Samples are grouped together by program area and matrix during analysis. A blank (MB, CCB, or Instrument Blank) is analyzed to separate the end of one program area and the beginning of the next to ensure a clean operating system.

10. CALIBRATION AND STANDARDIZATION

10.1 Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.2 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures. Flush the system with the calibration blank between each standard or as the manufacturer recommends. The calibration curve must consist of a minimum of a blank and three standards. Refer to the ICP instrument manual for detailed set up and operation protocols.

10.3 Instrument calibration must be performed daily and the curve verified with an LLICV, ICV, and ICB. Samples may be analyzed continuously for periods exceeding 24 hours as long as all calibration verification (ICV, ICB) and interference check QC criteria are met. The instrument standardization date and time must be included in the raw data.

10.4 Refer to Section 9.0 for calibration verification procedures, acceptance criteria, and corresponding corrective actions.

11. PROCEDURE

11.1 Sludges, soils, and sediments are weighed to 1.0g and are digested according to S-IM-013.

11.2 All dissolved samples (groundwater, and wastewater) must be digested according to S-IM-007, S-IM-008, or S-IM-009.

11.3 All other samples (groundwater and wastewater) are digested according to S-IM-007 or S-IM-009.

11.4 Three exposures are performed for each standard, field sample, and QC sample. The average of the exposures is reported. For lead and selenium, the results of the sum channel must be used for reporting. If the % RSD between the three results is > 20 %, the sample must be reanalyzed once unless the sample result is < reporting limit.

11.4.1 If the % RSD of the reanalysis is < 20 %, report that result.

11.4.2 If the % RSD of the reanalysis is also > 20 % and the sample result is < reporting limit, report that result.

11.4.3 If the % RSD of the reanalysis is also > 20 % and the sample result is > reporting limit, report the result with the lowest % RSD or use analyst judgment to select the most appropriate result.

11.5 Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless by following a protocol outlined in Section 9.5, it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

11.6 The use of an autosampler for all runs is strongly recommended.

11.7 The use of automated QC checks throughout the instrument software is highly recommended for all calibration verification samples (ICV, CCV), blanks (ICB, CCB, and PB), interference checks (ICSA, ICSAB), and field samples (linear range) to improve the data review process.

11.8 To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.9 To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run.

11.10 For unattended overnight auto-runs, it is strongly recommended that the frequency of ICSA/ICSAB analysis be increased to every 4 hours.

11.11 The use of an internal standard is **required** on the Trace ICP. The following procedural guidelines must be followed when using an internal standard:

11.11.1 Typically used internal standards are yttrium or scandium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.11.2 The internal standard (IS) must be added to every sample and standard at the same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing coil. Internal standards should be added to blanks, samples, and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

11.11.3 The concentration of the internal standard should be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

11.11.4 The internal standard raw intensity counts must be printed on the raw data.

11.11.5 The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte).

11.11.5.1 If the internal standard counts fall within ± 30 % of the counts observed in the Calibration Blank then the data is acceptable.

11.11.5.2 If the internal standard counts in the field samples are more than ± 30 % higher than the expected level, the field samples must then be:

(1) Diluted and reanalyze;

(2) The IS concentrations must be raised; or

(3) A different internal standard must be used.

11.12 The following analytical sequence must be used for Methods 6010C

1 LLICV
2 ICV
3 ICB
4 ICSA
5 ICSAB
6 LR I
7 LR II
8 LR III
9 Up to 10 samples (Batch QC are counted as samples)
10 LLCCV

11 CCV
12 CCB
13 10 samples
14 LLCCV
15 CCV
16 CCB
16 Repeat sequence of up to 10 samples between LLCCV/ CCV/CCB pairs as required completing the sequence

Refer to Quality Control Section 9 and Table VI (Appendix A) for Method 6010C quality control criteria.

11.13 Full method required QC must be available for each wavelength used in determining reported analyte results.

11.14 Guidelines are provided in the appendices on procedures minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.15 All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. If an interelement correction exists for an analyte which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an over-range analyte may not be required to be reported for a sample, if that analyte is an interfering element for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

11.16 For TCLP samples, full four-point MSA analysis will be required if all of the following conditions are met:

(1) recovery of the analyte in the matrix spike is not at least 50 %,

(2) the concentration of the analyte does not exceed the regulatory level, and,

(3) the concentration of the analyte is within 20 % of the regulatory level.

The reporting and regulatory limits for TCLP analyses as well as matrix spike levels are detailed in Table V (Appendix A). Appendix G provides guidance on performing MSA analyses.

11.17 Nonconformance documentation shall be filed in the project file along with performing 11.19 or 11.19.1.

11.18 Procedural Variations – This Section applies to all samples except South Carolina compliance samples. One time procedural variations are allowed, only if deemed necessary in the professional judgment and supervision of a knowledgeable analyst, to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in analytical procedure must be

approved by a technical director, the QA Officer, or the client, and must be fully documented (flagged and/or narrated) on the final report. The analyst must use a NCM to notify the appropriate parties and to document the variance. The project manager uses the information on the NCM to notify the client and flag/narrate the final report accordingly. A copy of the NCM is kept with the raw data and the original is filed with the final report.

11.19 For South Carolina compliance samples, all procedures outlined in this SOP must be followed without exception. In the event that a deviation from this SOP cannot be avoided (i.e., demonstrated and uncorrectable matrix interference, non-compatible matrix, insufficient sample amount due to client or laboratory error) it is imperative that a NCM is completed that clearly documents the anomaly. This anomaly must be communicated to the client such that corrective action activity including sample recollection can be performed. Based upon the type and severity of anomaly, the results may not be appropriate for compliance reporting. Discussions between the client, the appropriate regulatory authority, and Shealy will be necessary to resolve certain anomalies. In any case, it is essential that any anomaly be documented on a NCM. The project manager uses the information on the NCM to notify the client and flag/narrate the final report accordingly.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Sample results should be reported with up to three significant figures.

12.2 Appropriate factors must be applied to sample values if dilutions are performed.

12.3 ICV or CCV Percent Recovery:

$$\% \text{ Recovery} = \frac{X_1}{X_2} \times 100$$

Where:

X_1 = observed ICV (or CCV) concentration
X_2 = true ICV (or CCV) concentration

12.4 LCS Percent Recovery:

$$\% \text{ Recovery} = \frac{X}{t} \times 100$$

Where:

X = observed concentration
t = spike concentration

12.5 MS or MD Percent Recovery:

$$\% \text{ Recovery} = \frac{X_S - X}{t} \times 100$$

Where:

X = observed concentration of unspiked sample
X_S = observed concentration of spike sample
t = concentration of added spike

12.6 Relative Percent Difference between MS and MD:

$$RPD = \frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} \times 100$$

Where:

X_1 = the first detected concentration
X_2 = the second detected concentration

12.7 The final concentration for a digested aqueous sample is calculated as follows:

$$\text{mg/L} = \frac{C \times V1 \times D}{V2}$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.8 The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$\text{mg/kg, dry weight} = \frac{C \times V \times D}{W \times S}$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested
S = Percent solids in decimal form

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. Refer to appropriate SOP for the determination of percent solid. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

12.9 The dilution test percent difference for each component is calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

Where:

I = Sample result
S = Dilution test result

13. METHOD PERFORMANCE

13.1 Method Detection Limit – Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in Shealy QAMP.

13.2 Initial Demonstration – Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests, it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equal to the LCS concentration.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria for the corresponding analyte in the LCS.

13.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3 Non-standard analytes – For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

13.4 Training Qualification – The team leader has the responsibility of ensuring that this procedure is being performed by an employee who has been properly trained and has the required experience.

13.5 Refer to Tables I and II in Appendix A for the list of Method 6010C analytes as well as additional analytes that may be analyzed using this SOP.

13.6 Method performance is determined by the analysis of MS and MD samples as well as method blanks and laboratory control samples. The MS or MD should fall within 75-125 % and the MS/MD should compare within 20 % RPD . These criteria apply

to analyte concentrations greater than or equal to 10x IDL. Method blanks must meet the criteria specified in Section 9.6. The laboratory control samples should recover within 20 % for 6010C of the true value

14. POLLUTION PREVENTION

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1 Waste generated in this procedure must be segregated and disposed according to the Shealy Waste Management Plan (P-HS-001). The Safety Officer should be contacted if additional information is required.

15.2 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1 40 CFR Parts 136, Appendix B, Determination of Method Detection Limits.

16.2 SW-846, Test Method for Evaluating Solid Waste, Third Edition – Inductively Coupled Plasma-Atomic Emission Spectrometry, Method 6010C, Revision 3, February 2007.

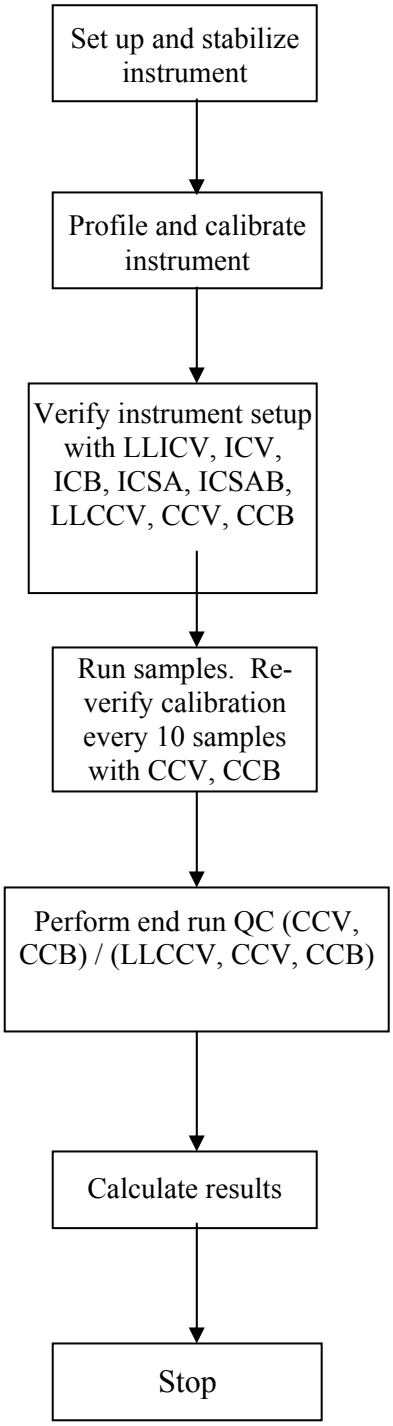
16.3 EPA/600/R-94/111 – Methods for the Determination of Metals in Environmental Samples – Supplement I, May 1994.

16.4 Shealy Quality Assurance Management Plan (QAMP), Q-QA-001

16.5 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.1, April 2009.

17. MISCELLANEOUS

Analysis Flow Diagram



APPENDIX A
TABLES

TABLE I Method 6010C Trace ICP Target Analyte List

ELEMENT	Symbol	CAS #	6010C Analyte	Reporting Limit (mg/L) Aqueous	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	0.20	10
Antimony	Sb	7440-36-0	X	0.010	0.50
Arsenic	As	7440-38-2	X	0.010	0.50
Barium	Ba	7440-39-3	X	0.025	1.3
Beryllium	Be	7440-41-7	X	0.0040	0.20
Boron	B	7440-42-8	X	0.0500	2.5
Cadmium	Cd	7440-43-9	X	0.0020	0.10
Calcium	Ca	7440-70-2	X	5.0	250
Chromium	Cr	7440-47-3	X	0.0050	0.25
Cobalt	Co	7440-48-4	X	0.025	1.3
Copper	Cu	7440-50-8	X	0.0050	0.25
Iron	Fe	7439-89-6	X	0.10	5.0
Lead	Pb	7439-92-1	X	0.010	0.50
Magnesium	Mg	7439-95-4	X	5.0	250
Manganese	Mn	7439-96-5	X	0.015	0.75
Molybdenum	Mo	7439-98-7	X	0.040	2.0
Nickel	Ni	7440-02-0	X	0.040	2.0
Potassium	K	7440-09-7	X	5.0	250
Selenium	Se	7782-49-2	X	0.010	0.50
Silver	Ag	7440-22-4	X	0.0050	0.25
Sodium	Na	7440-23-5	X	5.0	250
Thallium	Tl	7440-28-0	X	0.050	2.5
Tin	Sn	7440-31-5	X	0.050	2.5
Titanium	Ti	7440-32-6	X	0.050	2.5
Uranium	U	7440-06-11	X	0.500	25
Vanadium	V	7440-62-2	X	0.050	2.5
Zinc	Zn	7440-66-6	X	0.020	2.5

TABLE II. Laboratory Control Sample and Matrix Spiking Levels

ELEMENT	AQUEOUS		SOLID/TCLP	
	LCS Spike(mg/L)	Matrix Spike (mg/L)	LCS Spike (mg/L)	Matrix Spike (mg/L)
Aluminum	20	20	1000	1000
Antimony	0.40	0.40	50	50
Arsenic	0.40	0.40	250	250
Barium	2.0	2.0	5000	5000
Beryllium	2.0	2.0	100	100
Boron	0.40	0.40	50	50
Cadmium	0.40	0.40	50	50
Calcium	40	40	2000	2000
Chromium	2.0	2.0	250	250
Cobalt	2.0	2.0	100	100
Copper	2.0	2.0	100	100
Iron	20	20	1000	1000
Lead	0.40	0.40	250	250
Magnesium	40	40	2000	2000
Manganese	2.0	2.0	100	100
Molybdenum	2.0	2.0	100	100
Nickel	2.0	2.0	100	100
Potassium	40	40	2000	2000
Selenium	0.40	0.40	50	50
Silicon	2.0	2.0	100	100
Silver	0.40	0.40	250	250
Sodium	40	40	2000	2000
Thallium	0.80	0.80	40	40
Tin	0.40	0.40	50	50
Titanium	0.40	0.40	50	50
Vanadium	2.0	2.0	100	100
Zinc	2.0	2.0	100	100
Uranium	2.0	2.0	100	100

TABLE III-A. Trace ICP Calibration Standards

ELEMENT	Calibration Level 1 (mg/L)	Calibration Level 2 (mg/L)	Calibration Level 3 (mg/L)
Aluminum	1.0	25	50
Antimony	0.025	0.50	1.0
Arsenic	0.025	0.50	1.0
Barium	0.125	2.50	5.0
Beryllium	0.02	2.50	5.0
Boron	0.25	0.50	1.0
Cadmium	0.01	0.50	1.0
Calcium	25	50.0	100
Chromium	0.025	2.50	5.0
Cobalt	0.125	2.50	5.0
Copper	0.025	2.50	5.0
Iron	0.50	250	50
Lead	0.015	0.50	1.0
Magnesium	25	50	100
Manganese	0.075	2.50	5.0
Molybdenum	0.20	2.50	5.0
Nickel	0.20	2.50	5.0
Potassium	25.0	50.0	100
Selenium	0.025	0.50	1.0
Silicon	2.5	2.50	5.0
Silver	0.025	0.50	1.0
Sodium	25	50.0	100
Thallium	0.05	1.0	2.0
Tin	0.25	0.50	1.0
Titanium	0.25	0.50	1.0
Uranium	0.50	5.0	50
Vanadium	0.25	2.50	5.0
Zinc	0.10	2.50	5.0

TABLE III-B. Trace ICP Calibration Verification Standards

ELEMENT	ICV (mg/L)	CCV (mg/L)	LR I (mg/L)	LR II (mg/L)	LR III (mg/L)
Aluminum	12.5	25	-	500	-
Antimony	0.25	0.50	50	-	-
Arsenic	0.25	0.50	50	-	-
Barium	1.25	2.5	25	-	-
Beryllium	1.25	2.5	25	-	-
Boron	0.25	0.50	-	-	50
Cadmium	0.25	0.50	10	-	-
Calcium	25	50	-	500	-
Chromium	1.25	2.5	50	-	-
Cobalt	1.25	2.5	25	-	-
Copper	1.25	2.5	50	-	-
Iron	12.5	25	-	200	-
Lead	0.25	0.50	25	-	-
Magnesium	25	50	-	500	-
Manganese	1.25	2.5	25	-	-
Molybdenum	1.25	2.5	-	-	50
Nickel	1.25	2.5	25	-	
Potassium	25	50	-	-	100[1]
Selenium	0.25	0.50	50	-	-
Silicon	1.25	2.5		-	50
Silver	0.25	0.50	10	-	-
Sodium	25	50	-	-	100[1]
Thallium	0.50	1.0	50	-	-
Tin	0.25	0.50	-	-	50
Titanium	0.25	0.50	-	-	50
Uranium	2.5	5.0	-	-	50[1]
Vanadium	1.25	2.5	50	-	-
Zinc	1.25	2.5	50	-	-

[1] Potassium, Sodium, and Uranium LR concentrations are contained in Calibration Level 3.

TABLE IV. Interference Check Sample Concentrations

ELEMENT	ICSA (mg/L)	ICSAB (mg/L)
Aluminum	500	500
Antimony	-	1.0
Arsenic	-	1.0
Barium	-	0.50
Beryllium	-	0.50
Boron	-	1.0
Cadmium	-	1.0
Calcium	500	500
Chromium	-	0.50
Cobalt	-	0.50
Copper	-	0.50
Iron	200	200
Lead	-	1.0
Magnesium	500	500
Manganese	-	0.50
Molybdenum	-	1.0
Nickel	-	1.0
Selenium	-	1.0
Silver	-	1.0
Thallium	-	1.0
Vanadium	-	0.50
Zinc	-	1.0

TABLE V. TCLP Reporting Limits, Regulatory Limits, and Matrix Spike Levels

ELEMENT	Reporting Limit (mg/L)	Regulatory Limit (mg/L)	Spike Level (mg/L)
Arsenic	0.10	5.0	5.0
Barium	0.25	100	100
Cadmium	0.020	1.0	1.0
Chromium	0.050	5.0	5.0
Lead	0.030	5.0	5.0
Selenium	0.50	1.0	1.0
Silver	0.050	5.0	5.0

TABLE VI. Summary of Quality Control Requirements for non-DoD Samples

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Three-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criteria is not met.	RSD between duplicate exposures ≤5%	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	. Method 6010C: 90 - 110% recovery.	Terminate analysis; Correct the problem; Recalibrate.
LLICV	Beginning of every analytical run before ICV	+/-30% of the true value	Terminate analysis; Correct the problem; Recalibrate
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be less than reporting limit (Table 1) from zero.	Terminate analysis; Correct the problem; Recalibrate.
CCV	Every 10 samples and at the end of the run.	6010C: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
LLCCV	At end of every analytical batch	+/-30% of the true value	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable LLCCV.
CCB	Immediately following each CCV.	The result must be within ± PQL (Table 1) from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
ICSA	Beginning of every run.	See Section 9.13.2	See Section 9.13.2
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.13.3

***** See Section 11.11 for exact run sequence to be followed.

TABLE VI. Summary of Quality Control Requirements for non-DoD Samples (continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Dilution Test	One per prep batch.	For samples > 50x IDL, dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference per client request.
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be < Reporting Limit (Table 1). Sample results greater than 10x the blank concentration are acceptable. Sample results < Reporting Limit (Table 1) may not require redigestion or reanalysis.	Redigest and reanalyze samples.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% Samples with results < PQL and the LCS results are > 120% may not require redigestion or reanalysis.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125% recovery .	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added.
Matrix Spike Duplicate	See Matrix Spike	75 - 125% recovery; RPD ≤ 20%.	See Corrective Action for Matrix Spike.

APPENDIX B
METALS DATA REVIEW CHECKLIST

ICP Data Review Checklist

Preparation Batch #(s):_____ **Instrument ID #:_____**
Analytical Batch #:_____ **Date:_____**

Area of Review	Level I Review (Y/N)	Level II Review (Y/N)
• Prepared and analyzed per proper Method/SOP		
• Prepared and analyzed within holding time		
• Instrument profiled		
• Initial calibration correct (Int. Std. criteria ±30%) Time 1- Internal Std Range:_____ to _____ ____ 2- Internal Std Range:_____ to _____ ____ 3- Internal Std Range:_____ to _____ ____		
• ICV/CCV criteria met (ICV 10%; CCV 10%)		
• LLICV/LLCCV /LLQC criteria met +/- 30%		
• ICB/CCB criteria met (± Reporting limit)		
• ICSA/ICSAB met criteria (refer to details below)		
• Analysis within linear range		
• LCS criteria met (80% - 120% for 6010C)		
• MB criteria met (<Reporting Limit or sample is 10X blank result)		
• MS/MD Recovery criteria met (75-125%)		
• MS/MD RPD criteria met (20%)		
• %RSD criteria met for samples (individual exposures)		
• %RSD criteria met for QC (individual exposures)		
• Sequence Run Log has been reviewed		
Initials		
Date		

ICSA/B Criteria	SW-846 6010C
	±20%
*Non-Interferant ≤ 10 µg/L	±2x PQL
*Non-Interferant > 10 µg/L	± PQL

*Required by Shealy only, not a method requirement.

Comments:_____
_____

APPENDIX C
TROUBLESHOOTING GUIDE

PROBLEM	POSSIBLE CAUSE/ SOLUTION
High Blanks	Increase rinse time. Clean or replace tip. Clean or replace torch. Clean or replace sample tubing. Clean or replace nebulizer. Clean or replace mixing chamber. Lower torch.
Instrument Drift	RF not cooling properly. Vacuum level is too low. Replace torch (crack). Clean or replace nebulizer (blockage). Check room temperature (changing). Replace pump tubing. Room humidity is too high. Clean torch tip (salt buildup). Check for argon leaks. Adjust sample carrier gas. Reprofile horizontal mirror. Replace PA tube.
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks. Adjust sample carrier gas. Replace tubing (clogged). Check drainage (back pressure changing). Increase uptake time (too short). Increase flush time (too short). Clean nebulizer, torch, or spray chamber. Increase sample volume introduced. Check that autosampler tubes are full. Sample or dilution of sample not mixed. Increase integration time (too short). Realign torch. Reduce amount of tubing connectors.
Cu/Mn Ratio Outside Limits or Low Sensitivity	Plasma conditions changed. Clean nebulizer, torch, or spray chamber. Replace tubing (clogged). Realign torch. Check IECs.
Standards reading twice normal absorbance or concentration.	Incorrect standard used. Incorrect dilution performed.

APPENDIX D
CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only Non-powered, vinyl, or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipet tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The marking on glass beakers have been found to contain lead.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

APPENDIX E
PREVENTIVE MAINTENANCE

As part of the Shealy QAMP, a maintenance schedule has been developed for the ICP and ICP Trace. This information is kept in a maintenance log to document any preventive maintenance or servicing to the instruments.

ICP TRACE

Thermo Jarrel Ash 61E Trace
+ Auto Sampler

ITEM	REFERENCE MANUAL	FREQUENCY
Nebulizer	**Sec. 11, P. 4, Tip #3**	**D**
Vacuum System	**Sec. 11, P. 11, Par. 11.3**	**D**
Auto Sampler Cleaning	**Sec. 5, P. 3**	**D**
Auto Sampler Lubrication	**Sec. 5, P. 3**	**M**
Mixing Chamber	**Sec. 11, P. 8, Par. 11.1.3**	**D**
Plasma Torch	**Sec. 11, P. 9, Par. 11.1.5**	**D**
Vacuum System	**Sec. 11, P.11, Par. 11.3**	**SA**
Water Filter	**Sec. 11, P.14, Par. 11.5**	**SA**

D	**=**	**Daily**	
W	**=**	**Weekly**	
BW	**=**	**Bi Weekly**	
M	**=**	**Monthly**	
Q	**=**	**Quarterly**	**(January; April; July; October)**
SA	**=**	**Semi Annual**	**(January; July)**
A	**=**	**Annual**	**(January)**

APPENDIX E. PREVENTIVE MAINTENANCE (CONTINUED)

ICP

Thermo Jarrel Ash ICAP 61
+ Auto Sampler

ITEM	REFERENCE MANUAL	FREQUENCY
Outer Surface	----	D
Auto Sampler Cleaning	Sec. 5 P. 3	D
Nebulizer Check	----	D
Pump Tubing	----	D
Torch/Spray Chamber	----	D
D Mirror	----	D
RF. Generator Filters	13.1.1	BW
Intel. Controller Filter	13.2.1	BW
Auto Sampler Lubrication	Sec. 5 P. 3	M

D	=	Daily	
W	=	Weekly	
BW	=	Bi Weekly	
M	=	Monthly	
Q	=	Quarterly	(January; April; July; October)
SA	=	Semi Annual	(January; July)
A	=	Annual	(January)

APPENDIX F
CROSS-REFERENCE OF TERMS USED IN METHODS 6010C AND BY SHEALY INC.

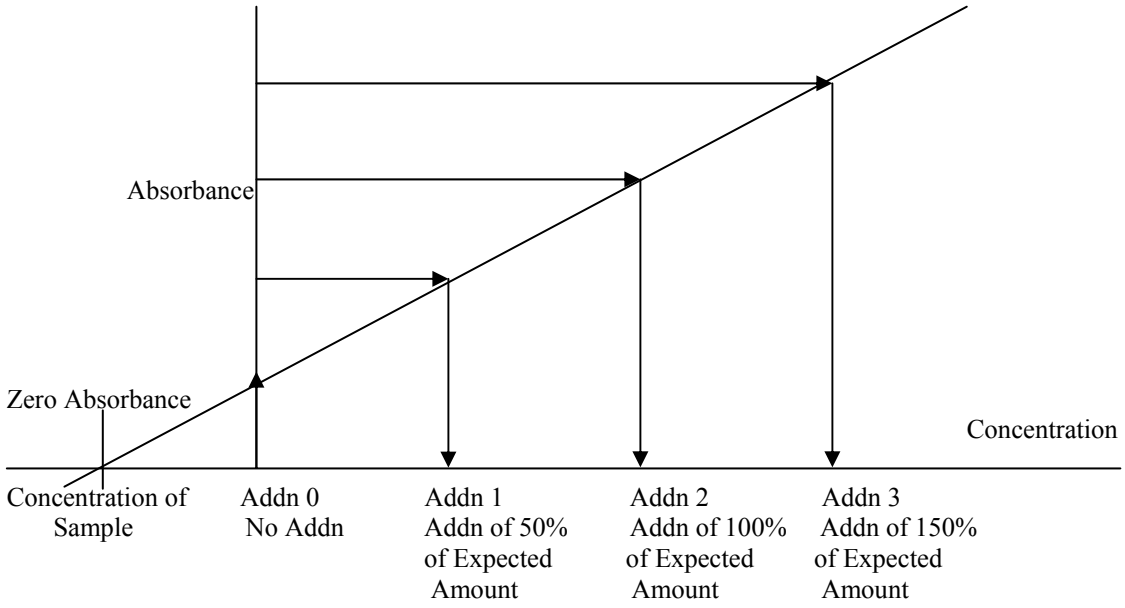
SW6010C	SHEALY INC. SOP
Calibration blank (CB)	Initial and continuing calibration blanks (ICB/CCB)
Dilution test	Dilution test
Instrument detection limit (IDL)	Instrument detection limit (IDL)
Continuing calibration verification (CCV)	Continuing calibration verification (CCV)
Internal standard	Internal standard (IS)
NA	NA
NA	Laboratory control sample (LCS)
Matrix spike and matrix spike duplicate (MS/MD)	Matrix spike and matrix spike duplicate (MS/MD)
Method blank	Method or Prep blank (MB)
Linear dynamic range (LDR)	Linear dynamic range (LDR)
Method detection limit (MDL)	Method detection limit (MDL)
Check standard or Initial calibration verification (ICV)	Initial calibration verification (ICV)
Interference check solution (ICS)	Interference check solution (ICSA/ICSAB)

APPENDIX G
METHOD OF STANDARD ADDITION (MSA) GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standard are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in figure below. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX DoD - QSM Requirements

Sections found in this appendix supersede and/or supplement the existing Sections of the SOP. These requirements must be met when analyzing samples for the Department of Defense-NFESC (Navy) as stipulated in the DOD Quality Systems Manual (version 3, January 2006).

9.0 QUALITY CONTROL

9.1.2.2 For DoD work, the detection limits established from the IDL study must be ≤ MDL.

9.6 Method Blank Acceptance Criteria – replaces Section 9.6 and 9.6 sub-Sections.

9.6.1 Method Blank (MB) – One method blank must be processed with each preparation and/or analytical batch. The method blank consists of a similar matrix to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results. The method blank is to contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

9.6.2 For a method blank to be acceptable for use with the associated samples, the concentration of analytes detected in the blank must be ≤ one-half (1/2) the practical quantitation limit (PQL) or project specific reporting limits.

9.6.2.1 The acceptance criterion for common laboratory contaminants is that no analytes should exceed the PQL.

9.6.3 If the MB does not meet the criteria above, the source of the contamination shall be investigated and measures taken to minimize or eliminate the problem. The affected samples shall be reprocessed or data shall be appropriately qualified. All steps taken to return the system to control must be fully documented.

9.6.3.1 If reanalysis is not possible due to limited sample volume or holding time, then the samples associated with the contaminated blank must be evaluated as to the best corrective action for the samples (e.g., reprocessing or data qualifying codes). In all cases the corrective action(s) must result in the completion of a NCM.

9.8.1 and 13.6 For DoD samples, the matrix spike and matrix spike duplicate control limits are 80-120%, except for silver for solids, which has limits 75-120%.

9.11 For DoD samples, no analyte must be detected at concentrations greater than 2 x the MDL in the CCB which is analyzed before beginning a sample run, after every 10 samples, and at the end of the analysis sequence.

9.12 PQL Standard – A standard that is spiked at the normal PQL concentrations and is analyzed after the calibration and before samples. This standard must recover within ± 20% of the spiked value. Corrective action will be the reanalysis of this standard. If the reanalysis of the PQL standard fails to recover within the acceptable limit, perform instrument maintenance and recalibrate the instrument.

9.13.2 For DoD analysis, when the ICS-A is run, the absolute value of concentration for all non-spiked analytes must be < 2 x MDL, unless higher values found are verified trace impurity from one of the spiked analytes.

9.14 Analysis Carryover Study – An analysis carryover study must be performed annually for each technology for each instrument model. The study will also need to be repeated after any changes have been made (e.g. instrument conditions) that could effect the carryover. The carryover study demonstrates the concentration at which a target or non-target analyte may be detected without contaminating the subsequent sample(s). A carryover verification standard (CVS) is analyzed at the same concentration as the highest point in the initial calibration and will be followed immediately by an instrument blank. The maximum carryover criteria are as follows:

9.14.1 The resultant carryover must be ≤ ½ the applicable PQL.

9.14.2 If a sample is nondetect after being analyzed immediately after a sample with high concentrations of target and/or non-target compound(s), the sample results may be reported.

10.5.1 Lower Order of Quantitation (LOQ) Verification – This is an analysis of a QC sample containing the analytes of interest in each matrix 1-2 times the claimed LOQ

10.5.1.1 A successful analysis is one where the recovery of each analyte is within the established test method acceptance criteria or client data quality objectives for accuracy.

10.5.1.2 This single analysis is not required if the bias and precision of the measurement system is evaluated at the LOQ.

10.5.1.3 The LOQ must not be set any lower than the low-level calibration standard fro multi-point calibration or no lower than a low-level calibration check sample for single level calibration.

Additional studies may be performed to identify how many blanks are required in the contiguous sequence to achieve the ≤ ½ PQL criteria. These studies need to be fully documented and readily available to all analysts.

TABLE I. DoD Method 6010C Trace ICP Target Analyte List

ELEMENT	Symbol	CAS #	6010B Analyte	Reporting Limit (mg/L) Aqueous	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	0.20	10
Antimony	Sb	7440-36-0	X	0.010	0.50
Arsenic	As	7440-38-2	X	0.010	0.50
Barium	Ba	7440-39-3	X	0.025	1.3
Beryllium	Be	7440-41-7	X	0.0040	0.20
Cadmium	Cd	7440-43-9	X	0.0020	0.10
Calcium	Ca	7440-70-2	X	5.0	250
Chromium	Cr	7440-47-3	X	0.0050	0.25
Cobalt	Co	7440-48-4	X	0.025	1.3
Copper	Cu	7440-50-8	X	0.0050	0.25
Iron	Fe	7439-89-6	X	0.10	5.0
Lead	Pb	7439-92-1	X	0.010	0.50
Magnesium	Mg	7439-95-4	X	5.0	250
Manganese	Mn	7439-96-5	X	0.015	0.75
Molybdenum	Mo	7439-98-7	X	0.040	2.0
Nickel	Ni	7440-02-0	X	0.040	2.0
Potassium	K	7440-09-7	X	5.0	250
Selenium	Se	7782-49-2	X	0.010	0.50
Silver	Ag	7440-22-4	X	0.0050	0.25
Sodium	Na	7440-23-5	X	5.0	250
Thallium	Tl	7440-28-0	X	0.050	2.5
Vanadium	V	7440-62-2	X	0.050	2.5
Zinc	Zn	7440-66-6	X	0.020	2.5

TABLE II. DoD Aqueous LCS/MS Control Limits for Metals

ELEMENT	Symbol	Aqueous Control Limits			
		Lower	Upper	Lower ME	Upper ME
Aluminum	Al	80	120	80	120
Antimony	Sb	80	120	80	120
Arsenic	As	80	120	80	120
Barium	Ba	80	120	80	120
Beryllium	Be	80	120	80	120
Cadmium	Cd	80	120	80	120
Calcium	Ca	80	120	80	120
Chromium	Cr	80	120	80	120
Cobalt	Co	80	120	80	120
Copper	Cu	80	120	80	120
Iron	Fe	80	120	80	120
Lead	Pb	80	120	80	120
Magnesium	Mg	80	120	80	120
Manganese	Mn	80	120	80	120
Molybdenum	Mo	80	120	75	120
Nickel	Ni	80	120	80	120
Potassium	K	80	120	80	120
Selenium	Se	80	120	75	120
Silver	Ag	80	120	75	120
Sodium	Na	80	120	80	120
Thallium	Tl	80	120	80	120
Vanadium	V	80	120	80	120
Zinc	Zn	80	120	80	120

TABLE III. DoD Solid LCS/MS Control Limits for Metals

ELEMENT	Symbol	Solid Control Limits			
		Lower	Upper	Lower ME	Upper ME
Aluminum	Al	80	120	75	120
Antimony	Sb	80	120	75	120
Arsenic	As	80	120	80	120
Barium	Ba	80	120	80	120
Beryllium	Be	80	120	80	120
Cadmium	Cd	80	120	80	120
Calcium	Ca	80	120	80	120
Chromium	Cr	80	120	80	120
Cobalt	Co	80	120	80	120
Copper	Cu	80	120	80	120
Iron	Fe	80	120	80	120
Lead	Pb	80	120	80	120
Magnesium	Mg	80	120	80	120
Manganese	Mn	80	120	80	120
Molybdenum	Mo	80	120	75	120
Nickel	Ni	80	120	80	120
Potassium	K	80	120	80	120
Selenium	Se	80	120	75	120
Silver	Ag	80	120	70	120
Sodium	Na	80	120	80	120
Thallium	Tl	80	120	80	120
Vanadium	V	80	120	80	120
Zinc	Zn	80	120	75	120

TABLE IV. Summary of Quality Control Requirements for DoD Samples

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Three-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criteria is not met.	RSD between duplicate exposures ≤5%	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Once after each initial calibration, prior to sample analysis.	Method 6010B: 90 - 110% recovery.	Terminate analysis; Correct problem and verify second source standard. Rerun ICV. If that fails, correct the problem and repeat initial calibration.
ICB	Beginning of every analytical run, immediately following the ICV.	No analytes detected > 2 x MDL.	Terminate analysis; Correct the problem; Recalibrate.
CCV	Every 10 samples and at the end of the analysis sequence.	Method 6010B: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
CCB	Immediately following each CCV.	No analytes detected > 2 x MDL.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
ICSA	Beginning of every run.	See Section 9.12.2	See Section 9.12.2
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.12.3

* See Section 11.11 for exact run sequence to be followed.

TABLE IV. Summary of Quality Control Requirements for DoD Samples (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Dilution Test	Each preparatory batch or when a new or unusual matrix is encountered.	Applicable for samples > 50x MDL, dilutions must agree within ±10% of the original determination.	Perform post-digestion spike (PDS) addition; Narrate the possibility of physical or chemical interference per client request.
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be < ½ PQL (Table I, Appendix DoD). For common laboratory contaminants, no analytes detected > PQL.	Correct problem; refer to Section 9.6 of Appendix DoD. If required reprep and reanalyze method blank and all samples processed with the contaminated blank.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within criteria specified in Table II of Appendix DoD. Solid LCS must be within criteria specified in Table III of Appendix DoD	Terminate analysis; Correct the problem; redigest and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes.
Matrix Spike	One per sample preparation batch of up to 20 samples.	For matrix evaluation, use QC acceptance criteria specified for LCS.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.
Matrix Spike Duplicate	See Matrix Spike	RPD ≤20% (between MS and MD or sample and sample duplicate).	See Corrective Action for Matrix Spike.

Appendix P

Laboratory SOPs

Low Level Mercury

Microbac SOP

Hg-1631

STANDARD OPERATING PROCEDURE FOR MERCURY USING AUTOMATIC FLUORESCENCE SPECTROSCOPY

Revision Author: Randon Lingenfelter

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This SOP is effective upon signed approval by the following:

Troy M. Goehl	8/7/2009
Inorganics Manager	Date
	8/28/2009
QA/QC Manager	Date

DISCLAIMER: This SOP has been developed for use at the Microbac Laboratories, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

Last Review Date:
No Changes Needed
Approved By:

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2.0 SCOPE AND APPLICATION

2.1 This is an atomic fluorescence spectroscopy procedure for the determination of Mercury. This procedure is applicable and restricted to the analysis of aqueous matrix samples. The applicable analytes, detection limits and routine reporting limits (PQL) are listed at the Limits tab of the applicable test codes in LIMS.

3.0 SUMMARY

3.1 The integrity of this procedure is maintained only through the application of proper sample collection, sample handling, storage and analysis using the “clean hands, dirty hands” technique.

3.2 In the container received, the entire sample is oxidized with Bromine monochloride (BrCl) at a ratio of 5-ml BrCl per 500-ml sample. The sample is allowed to oxidize all available Hg to Hg(II) for a minimum of 24-hours. 50-ml of oxidized sample is analyzed where it is sequentially reduced with Hydroxylamine monochloride ($NH_2OH \cdot HCl$) to destroy the free halogens, then with stannous chloride ($SnCl_2$) to convert Hg(II) to volatile Hg(0). The Hg(0) is separated from solution by purging and vapor/liquid separation.

3.3 This procedure is based on the reference methods listed in section 17 of this document. This procedure contains no significant deviations to the reference method.

4.0 DEFINITIONS

4.1 A list of definitions is in the Quality Assurance Plan.

5.0 INTERFERENCES

5.1 Preventing samples from becoming contaminated during the sampling and analysis process constitutes one of the greatest difficulties encountered in trace metals determinations. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing samples for trace metals.

5.2 Samples may become contaminated by numerous routes. Potential sources of contamination include sampling protocol, containers, sampling equipment, labware, reagents, and atmospheric inputs such as dirt and dust. Even human contact can be a source of contamination.

5.3 Contamination Control

5.3.1 Philosophy – The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is free from any material that may contain mercury. Substances in a sample cannot be allowed to contaminate the laboratory work area or instrumentation used for trace Mercury measurements.

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5.3.2 Avoiding contamination – The best way to control contamination is to completely avoid exposure of the sample to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being done.

5.3.3 Use a clean environment – The Mercury clean room has been designed to minimize (if not ultimately eliminate) Mercury contamination from outside sources. Incoming air is appropriately filtered and the airflow designed to pass clean air from the instrument lab into and through the preparation lab. Access is restricted to authorized and trained personnel only. Appropriate sample receipt protocols are used to ensure that only non-externally contaminated samples are brought into the lab. Sample receipt into the lab is by way of an isolated holding area to allow for proper cleaning of sample containers prior to handling inside the preparation lab.

5.3.4 Wear gloves – Analysts must wear clean, non-talc gloves during all operations involving handling of the samples, reagents and standards.

5.3.5 Contamination by carryover – Contamination may occur when a sample is processed immediately after a sample containing a relatively high concentration of Mercury. The Hg concentration at which the analytical system (purge, traps, and detector) will carry greater than 0.5 ng/L of Hg into a succeeding system blank must be determined (see the QA/QC section).

5.4 Interference

5.4.1 At the time of promulgation of the reference method, gold and iodide were known interferences. At a Mercury concentration of 2.5 ng/L and at increasing iodide concentrations ranging from 30 to 100 mg/L, test data have shown that Mercury recovery will be reduced from 100 to 0 percent. At iodide concentrations greater than 3 mg/L, the sample should be pre-reduced with $SnCl_2$ (to remove the brown color) and additional or more concentrated $SnCl_2$ should be added. To preclude loss of Hg, the additional $SnCl_2$ should be added in a closed vessel or analysis should proceed immediately. If samples containing iodide concentrations greater than 30 mg/L are analyzed, it may be necessary to clean the analytical system with 4N HCl after the analysis.

6.0 SAFETY

6.1 Consult the current revision of the Chemical Hygiene Plan. Requirements for the use of personal protective equipment (e.g. safety glasses, lab coats, gloves) as well as other area-specific safety requirements (e.g. gas cylinders) and MSDS sheets are addressed in the CHP.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

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7.1 All volumetric glassware used shall be ASTM Class A. Class B glassware must be verified for accuracy on an annual basis and labeled with an appropriate correction.

7.2 All reagent and standard preparation must be performed in the mercury-free clean room.

7.3 PPE: latex gloves (Fisher #11-394-5C or equivalent); lab coat and safety glasses as specified in the Chemical Hygiene Plan

7.4 Tackymat: Fisher #06-520-5

7.5 Glassware: 100-ml and 1000-ml volumetric flasks

7.6 Pipettes: 10 – 100-ul and 100 – 1000-ul adjustable volume repipetters

7.7 Digestion/Autosampler tubes: SCP Science product, Fisher #S195-500 or equivalent

7.8 Instrument: CETAC M8000

7.9 SCP Digifilter Manifold #010-500-230

7.10 SCP 0.45-micron Digifilters #010-500-070

8.0 REAGENTS AND STANDARDS

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST, when available. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

All reagents are stored in the mercury-free clean room unless otherwise noted. Unless otherwise noted, prepared reagents are stored in appropriate containers, retained in the clean room and prepared on an as needed basis.

8.2.1 Lab pure water (DI water): Analyte free water is prepared as described in the Quality Assurance Plan. DI water is obtained from the designated tap in the clean-room.

8.2.2 Hydrochloric acid, concentrated: Fisher catalog #A508-212 or equivalent.

8.2.3 Nitric acid, concentrated: Fisher catalog #A509-212 or equivalent

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8.2.4 Instrument rinse, 1%: In a 2L fluoropolymer bottle (supplier by CETAC) dilute 20-ml Bromine Monochloride solution to a final volume of 2L with lab pure water. Prepare this reagent on a daily basis.

8.2.5 Bromine Monochloride: In a clear glass jar, combine 1 packet of BrCl solution (Environmental Express #HP9010 or equivalent) and 90-ml concentrated HCl. Prepare fresh monthly.

8.2.6 Hydroxylamine Hydrochloride: In a 250-ml container, dissolve and dilute 75-g Hydroxylamine Hydrochloride (Fisher #H330-1 or equivalent) to the mark with lab pure water. Prepare fresh monthly.

8.2.7 Stannous Chloride: In a 1L container, dissolve and dilute 200g of Stannous Chloride crystals (Fisher #T142-500 or equivalent.) with 100-ml concentrated HCl and lab pure water. Prepare fresh weekly.

8.2.8 10% HCl rinse solution: In a Digitube, dilute 5-ml of conc. HCl to 50-ml with DI water.

8.2.9 10% HNO_3 rinse solution: In a Digitube, dilute 5-ml of conc. HNO_3 to 50-ml with DI water.

8.3 Standards

All standards are stored in the mercury-free clean room unless otherwise noted.

8.3.1 Stock Calibration standard, 1000 mg/l: SPEX catalog # PLHG4-2Y or equivalent.

8.3.2 Intermediate Calibration standard, 1 mg/l: In a 100-ml volumetric flask, dilute 0.1-ml of the stock calibration and 7-ml of 7% HCl to the mark with lab pure water. Prepare fresh monthly.

8.3.3 Working Calibration standard A, 1 ug/l: In a 100-ml volumetric flask, dilute 0.1-ml of the intermediate calibration standard and 7-ml of 7% HCl to the mark with lab pure water. Prepare fresh monthly.

8.3.4 Calibration curve: Prepare the following dilutions in individual 50-ml digestion tubes using 0.50-ml BrCl and lab pure water. The calibration curve standards should be prepared fresh with each calibration. The calibration (system) blanks are prepared by filling a 500-ml sample container with lab pure water, acidifying with 2.5-ml conc. HCl and oxidizing with 5.0-ml BrCl.

Vol. (ml)	Parent Std	Final Conc., ng/l
5.0	Working Cal Std A	100
2.5	Working Cal Std A	50
1.25	Working Cal Std A	25
0.25	Working Cal Std A	5.0
.025	Working Cal Std A	0.5
0	---	0

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8.3.5 Method Blank: In a 500-ml clean bottle add the same reagents as the prep batch and fill with DI water.

8.3.6 IPR / OPR: This is the same as the 5.0-ng/l standard used for instrument calibration.

8.3.7 MS/MSD, 5-ng/l: Add 0.25-ml of the working calibration standard A to 50-ml sample.

8.3.8 Stock Verification standard, 1000 mg/l: CPI catalog # S4400-1000331 or equivalent. This standard must be of a source different than that used for calibration.

8.3.9 QCS Intermediate standard, 1 mg/l: In a 100-ml volumetric flask, dilute 0.1-ml of the stock verification standard and 7-ml of 7% HCl to the mark with lab pure water. Prepare fresh monthly.

8.3.10 QCS Working Standard A, 1-ug/l: In a 50-ml volumetric flask, dilute 0.05-ml of the QCS intermediate standard and 3.5-ml of 7% HCl to the mark with lab pure water. Prepare fresh monthly.

8.3.11 QCS, 5.0 ng/l: In a 50-ml digestion tube, dilute 0.25-ml of the QCS working standard A to 50-ml with 0.5-ml BrCl and lab pure water. Prepare fresh with each calibration.

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted. Samples must be received inside of a double-bag system. The outer bag is considered a dirty bag and the inner bag a clean bag. Refer to the Sample Receipt and Login SOP for details. Samples not received in this manner will be rejected or the discrepancies noted and reported to the client.

9.2 Samples should be collected in a glass container. No thermal or chemical preservation is required during transit. Refer to the Sample Receipt and Login SOP for the criteria used at sample receipt to determine whether or not the sample integrity has been maintained. Samples are stored in the double-door staging area built into the mercury-free clean room. Samples that fail to meet the receipt criteria will be rejected or noted as such on the Cooler Inspection Report during the Login process.

9.3 Chemical preservation is applied as part of the preparation procedure. See the details in the Procedure section.

9.4 Provided that samples are received unpreserved then acidified and oxidized full volume (as described in the procedure section), the maximum allowable hold times are: acidification within 28-days and analysis within 90-days of collection.

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10.0 QUALITY CONTROL

10.1 An *Initial Precision & Recovery (IPR)* study must be performed prior to the initial implementation within the lab and whenever substantial change has occurred in the procedure or instrument. Analyze four consecutive 5 ng/l calibration standards. Submit the data to the QA department for evaluation. Refer to EPA Method 1631E section 9.2.2 for details.

10.2 A *Method Detection Limit (MDL)* study must be performed for each new analyst, annually thereafter, and whenever a significant change in procedure or instrument occurs. Analyze a minimum of seven (maximum of ten) standards prepared in the range of 0.1-1.0 ng/l. These standards must be taken through the entire analytical procedure. Submit the data to the QA department for evaluation. Refer to EPA Method 1631E section 9.2.1 for details.

10.3 A *Carryover Point* study must be performed prior to the initial implementation within the lab and whenever substantial change has occurred in the instrument. The carryover point is the Hg concentration at which the analytical system will carry greater than 0.5 ng/L of Hg into a succeeding system blank. This concentration may be determined by analyzing calibration solutions containing successively larger concentrations of Hg. When an environmental sample contains ½ or greater of this determined Hg concentration, a system blank must be analyzed to demonstrate no carryover at the blank criteria level. Preferably, if analysis of the high calibration standard does not result in the carryover of more than 0.5 ng/l into a succeeding blank, the carryover point is defined as some concentration above the linear range of the instrument and any environmental sample having a Mercury concentration greater than that level must be diluted and reanalyzed. Samples that are known or suspected to contain a high concentration of Mercury should initially be analyzed at an appropriate dilution or after samples containing low or non-detectable levels.

10.4 An *On-going Precision and Recovery (OPR) Standard* must be analyzed immediately after calibration, after every 12 consecutive hours of analysis, and after the sample. The concentration of the OPR is defined in the reference method as 5 ng/L.

10.4.1 Acceptance criteria are defined in the reference method and listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.

10.4.2 OPR standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a “S” qualifier.

10.4.3 The reporting of data associated with a failed OPR must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

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10.4.4 Samples associated with an OPR that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.5 A *Quality Control Sample (QCS)* must be analyzed prior to the analysis of environmental samples at a frequency of 1 per run. The QCS is prepared from a standard source different than that used for the OPR.

10.5.1 Acceptance criteria are nominally set to be the same as the OPR and are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.

10.5.2 QCS' that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.

10.5.3 The reporting of data associated with a failed QCS must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.5.4 Samples associated with an QCS that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.6 A minimum of three *Method Blanks* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day.

10.6.1 The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.

10.6.2 MBLKs that fail to meet the acceptance criteria cause the sample results to be automatically flagged in LIMS with a "B" qualifier. MBLKs that are below the reporting limit but above the MDL are flagged in LIMS with a "b" qualifier. "b" flagged data is considered as meeting the acceptance criteria.

10.6.3 The reporting of data associated with a failed control sample must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.6.4 Samples associated with a MBLK that fails with positive bias can be reported without narration if the sample concentration is < PQL or greater than 10 times the blank contamination.

10.7 A *Matrix Spike and Matrix Spike Duplicate* sample must be prepared and analyzed with each batch of maximum 10 samples per matrix and at a minimum of one per day.

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10.7.1 Acceptance criteria are defined in the reference method and listed in the appropriate test code in LIMS. (Note: the accuracy criteria have been met provided at least either the MS or MSD meet the %R criteria.) If the acceptance criteria are not met, refer to the MS/MSD Corrective Action Flowchart in the QAP.

10.7.2 MS/MSD's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier. MSD's that fail to meet the precision criteria are automatically flagged in LIMS with a "R" qualifier.

10.7.3 The reporting of data associated with a failed MS/MSD must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

10.7.4 Samples associated with a MS/MSD that fails the accuracy criteria with positive bias can be reported without narration if the sample concentration is below the reporting limit.

10.7.5 If the concentration measured in the sample is greater than 4-times the concentration of the spike, the spike amount used is insufficient and the MS/MSD not applicable.

11.0 CALIBRATION AND STANDARDIZATION

Calibration data is documented and retained using the printouts from the instrument software and the report generated using the "1631 Calibration and QC Evaluation" spreadsheet. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

11.1 Instrument calibration is required each day of analysis for each run.

11.2 Perform the required preventative maintenance as necessary. Refer to the maintenance log book for M8000.

11.3 Open the QuickTrace file. A box will appear asking if you want the detector block temperature to stabilize. Choose *Yes*. This can take anywhere from 20 minutes to several hours depending on how long the instrument was off. The remainder of the program will open when the detector temperature has stabilized.

11.4 Create a new data file for the day. This is done by choosing *File*, *New From*. A box will open. Click the *Browse* button next to the template worksheet box. A file directory will open up. Choose *QuickTrace* file and then open the *Worksheets* file. Choose the template you wish to use (typically, use that from the previous day). When the worksheet is open, enter the name for the new worksheet using the naming convention "1631" followed by the date (e.g. 1631 11-10-03).

11.5 Check the tubing on the peristaltic pump for wear and replace if needed. Place the tubing on the pump in the following order from bottom to top: drain (large white-white tubing), autosampler (yellow-yellow tubing), stannous (black-black tubing), and finally the hydroxylamine tubing (red-blue) should be on the top. Turn the

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pump on with the black switch on the front of the pump. Starting with the bottom clamp, apply tension with the locking arm. Check for good flow through the tube and proceed to the next clamp. Continue until all the clamps are locked into place and then recheck all of the flows.

11.6 Place the stannous and the hydroxylamine lines into the container of DI water next to the instrument.

11.7 The Gas Liquid Separator (GLS) must be wet to insure proper liquid gas separation. To do this, open the *instrument control panel* (this button has a screwdriver, hammer, and wrench on it). In the new window that opens up, click on the icon with 3 test tubes on it. This screen will have a gas control box on it. Set the gas flow to 40 and click set gas. Look inside the window at the GLS and make sure there are bubbles rising up. Pinch the drain line that goes into the peristaltic pump. This will cause the GLS to fill with water. Make sure that bubbles reach the top of the GLS to completely wet the center tube of the GLS. Repeat if proper wetting does not occur. An error message will appear on the computer screen and the peristaltic pump will stop. The error will say that a GLS overflow has occurred and to click yes to recover from it. Unpinch the drain tubing and click yes. This will allow all of the liquid to drain from the GLS. If the error shows up again repeat the steps listed to continue the draining of the GLS.

11.8 Remove the stannous and hydroxylamine lines from the DI water and place them into the appropriate containers. Let the instrument set for the couple minutes to stabilize with this new gas setting and close the instrument control box.

11.9 At this time the instrument needs to be profiled to make sure things are flowing and working properly. Open the *method editor* (icon looks like a book with a pencil on it). A new window will open. Click the button that has a green arrow pointing to a blue test tube. This will cause the instrument to zero. If necessary, the instrument will temperature stabilize as well. A new window will open up which shows a diagram of the autosampler. Place the 100 ng/L standard in a location and choose that location on the screen. The autosampler will move to that location and sample this standard. The graph on the computer screen will show the results of this standard. It will take approximately 6-minutes for the sample analysis to complete. When it is done look at the graph to make sure the instrument is reading the sample at the correct time. If this looks okay, look at the profile replicate RSD %. This percentage should be at less than 0.4. If this fails, repeat the peak profile. If it passes close, the method editor box.

11.10 To begin a calibration, open the *sequence editor* box (icon looks like a magic wand). On the sequence page, make sure the sample count is 0 and that the box next to “Begin with Calibration” is checked. Click on the *Auto QC* page and make sure all QC solutions are removed from the “QC Calibration Error Box”. This will let the instrument calibrate and then stop. Click the *Generate Sequence* box. Another box will appear asking if you want to save the changes you have made, click *Yes*.

11.10.1 The analyst has the option of entering the sample IDs. If performed, enter “0” for the number of samples in the run. Turn off OPR at the start and the end of the run.

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11.11 Make sure all of the calibration standards are loaded into the autosampler. Hit the green "*GO*" button to start the calibration. Calibration will take approximately 1-hour to complete. After the calibration is done, the peristaltic pump will go to standby and a box telling you this has occurred will appear on the screen. Click *Yes* to remove the box, and look at the results of the calibration. If the calibration passed, the computer will give you a calibration factor as well as a calibration %RSD. If it fails, you will get a failure message and the calibration must be repeated. Analysis of environmental samples cannot proceed without the generation of an acceptable calibration.

11.11.1 The calibration acceptance criteria are as follows. The instrument software as well as the "1631 Calibration and QC Evaluation" spreadsheet is programmed to calculate and evaluate the calibration criteria.

- 3 system blanks — <0.5 ng/l each
average <0.5 ng/l
standard deviation <0.1 ng/l
- Linearity — $CF_m \leq 15\%$ RSD
75-125 %R for the PQL level standard

12.0 PROCEDURE

12.1 SAMPLE PREPARATION

Preparation data is documented and retained using the Mercury Prep Logsheet for EPA 1631E. Preparation data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

12.1.1 Samples are received through a double-door staging area built into the mercury-free clean room. Put on a new pair of clean gloves and bring the samples from the staging area into the prep lab. Process samples into the lab one at a time.

12.1.2 Open the bag, remove the sample container and rinse the container with lab pure water from the faucet. Place the bag in the trash and the rinsed bottle on a paper towel underneath the hood. Verify the sample label information and the physical condition of the sample container. Notify the Supervisor or Project Manager of any label inaccuracies. Note any container inadequacies such as cracked lids, bottles, etc.

12.1.3 Open the sample container and add conc. HCl at a ratio of 5-ml per 1L sample (2.5-ml per 500-ml sample container). If the container is completely filled with sample volume, be certain to thoroughly shake the sample and pour off a small volume prior to adding the acid. Cap the sample and mix.

12.1.4 Open the acidified sample container and add BrCl reagent at a ratio of 5-ml per 500-ml sample. Cap the sample and mix. NOTE: Be certain to evaluate the batch size as samples are processed. All samples from a given run must be processed with the same reagents.

12.1.5 Allow the samples to oxidize for a minimum of 24-hours prior to analysis.

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12.2 SAMPLE ANALYSIS

Analytical data is documented and retained using the printouts from the instrument generated analytical report, run log, and the "1631 Calibration and QC Evaluation" spreadsheet. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

12.2.1 After the calibration has passed, create an autosampler table if it was not already created. To do this, click on the *sequence editor* box. On the sequence page, enter the number of samples that you will be analyzing and uncheck the "Begin with Calibration" box. On the "Auto QC" page, insert OPR standards at the beginning and end of analysis. Click the *generate sequence* button to make the table. The table will appear in a new window. In this window, type the sample ID for each sample that will be run from the sample prep log. After this is done, click the green "*GO*" button to start the run. If the OPR fails the run will stop; otherwise, the samples will run until completion. Make sure that there is plenty of rinse in the rinse bottle. Running out of rinse will cause the instrument to read erroneously low results and cause the QC samples to fail the applicable criteria.

12.2.2 When the run ends, print the run and the run log. Create a PDF file of the instrument run.

12.2.3 Remove the stannous and hydroxylamine lines and place them into the stannous line in 10% HNO_3 and the hydroxyl line in 10% HCl. Let this solution run through the instrument for 5-minutes to remove any salt buildup that may have occurred.

12.2.4 Place the lines into the bottle of DI water for 5-minutes to rinse the acid solution from the instrument.

12.2.5 Pull the lines from the DI rinse and place them in the empty bottle to let the liquid get removed from the lines.

12.2.6 Pull the rinse line from the bottle and place it in an empty 5000-ml bottle. Pump until all lines are dry.

12.2.7 Open the instrument controls and move the autosampler probe to the up position so that it is also pulling air through the lines.

12.2.8 Once all of the liquid has flushed out of the lines, put the instrument into standby by hitting the *standby button* (looks like a ¼ moon), and release the pump tubing to avoid excess stretching or manually turn off the pump and lamp.

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13.0 CALCULATIONS AND DATA HANDLING

13.1 The instrument software, using the following equation, calculates the sample concentration.

$$\text{Conc., ng/L} = [(\text{uabs}_{samp} - \text{avg uabs}_{blk}) / CF_m] [(PFac) (DF)]$$

Where: CF_m = mean CF from all calibration standards
$CF = (\text{uabs}_{std} - \text{avg uabs}_{blk}) / \text{conc}_{std, ng/l}$
PFac = preparation factor = V_f / V_i
DF = dilution factor

13.2 LIMS calculates the final sample concentration as follows:

Mercury, ng/L = (C) (DF) (Pfac)

Where: C = concentration from curve
DF = dilution factor (prior to adding sample to vial)
Pfac = (Final Volume, ml) / (Sample Size, ml)

13.3 After review, enter final results into the LIMS system. Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. There is less certainty in these data and, if sufficient sample and holding time are available, should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data are in the Analytical Data Entry – Metals SOP.

14.0 METHOD PERFORMANCE

14.1 Initial Demonstration of Capability study data, Method Detection Limit study data and Performance Testing study data are maintained and available from the QA office.

15.0 POLLUTION PREVENTION

15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.

15.2 Prepare the minimum amount of reagent and standard necessary.

16.0 WASTE MANAGEMENT

16.1 Refer to the Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

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17.0 REFERENCES

17.1 USEPA Method 1631E

17.2 CETAC QuickTrace Mercury Analyzer software manual, part #480114, version 1.0

17.3 Microbac Laboratories Quality Assurance Plan, current revision, all sections

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

Copy of the Mercury Prep Logsheet for EPA 1631E (1 page)
Copy of the 1631 Calibration and QC Evaluation report (1 page)
Copy of the M8000 Maintenance Log (1 page)
SOP Revision Notification Form denoting changes made to this revision. (1 page)
Appendix to Method 1631 Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation

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Microbac Laboratories - Chicagoland Division
MERCURY PREP LOG SHEET - EPA 1631E

Analyst: _____ Batch ID: _____

	STD / Reagent ID	Exp. Date	Conc.
HCl			---
BrCl			---
Spike Standard			

Date/Time Samples Available: _____

	Sample ID	Cont ID	Date/Time HCl & BrCl Added	MS**	MSD**	Comments
MBLK 1						
MBLK 2						
MBLK 3						
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						

revision: b_12-03

* - HCl and BrCl added at a ratio of 5 mL each per 1L sample (1.25 mL/250 mL)
** - MS/MSD prepared in 50 mL volumes

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Microbac Laboratories, Inc. – Chicagoland Division

1631 Calibration and QC Evaluation

Date Calibrated	8/2/2006	Analyst	TMG
Data File	1631 08-02-06	Reviewed	

Calibration Statistics			Calibration Blank Data			
STDEV CF	AVG CF	%RSD CF	AVG uABS	STDEV uABS	AVG Conc ng/L	STDEV ng/L
3.071	33.911	9.056	3.546	2.106	0.10	0.06
		PASS			**PASS**	**PASS**
	Limit =	**<15% RSD**		**Limits =**	<0.5 ng/L	< 0.1 ng/L

Standard	Conc, ng/L	uABS	CF	Conc	%Rec	
Blk-1	0	3.156		0.1		
Blk-2	0	5.820		0.2		
Blk-3	0	1.663		0.0		
STD-1	0.5	23.154	39.215	0.6	116	**PASS**
STD-2	5	160.167	31.324	4.6	92	
STD-3	25	834.285	33.230	24.5	98	
STD-4	50	1669.693	33.323	49.1	98	
STD-5	100	3250.091	32.465	95.7	96	
OPR-1	5		---	4.575	91.50	**PASS**
QCS	5	4	---	4.775	95.50	**PASS**
OPR-2	5	3	---	4.845	96.90	**PASS**

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Microbac Laboratories, Inc.
Routine/Scheduled Maintenance Log
Instrument ID: CVAF-2

Month & Year: _____

	Minimum Frequencies																
	Daily							Weekly		Monthly			As Needed				
Date	PMT voltage	Reagent flows	Clean External Gold Trap	Gas pressure	High std hf units	Waste	Check KMnO4 trap	Clean GLS	Check pump tubing	Clean fan filter	Check GLS tubing	Check autosamp. tubing	Change SnCl2 tubing	Change Hydroxyl tubing	Change rinse tubing	Change sample tubing	Comments
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rev: _a_5/01/09

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SOP Revision Notification / Annual Review Form

SOP Name MERCURY USING AUTOMATIC FLUORESCENCE SPECTROSCOPY

[X] *New Revision* Old Revision # 1 New Revision # 2

Summary of changes:
- Section 3.3: Removed the deviations from the reference method.
- Sec. 7.0: (1) Removed shoe covers from the supplies list; (2) Added Tackymat and new instruments to the supplies list.
- Sec 8.2: (1) Removed the specification that reagents must be stored in glass containers. (2) Reduced the preparation volume for Hydroxylamine Hydrochloride; (3) Removed the acid rinse solution; (4) Added 10% HCl Rinse and 10% HNO_3 rinse solutions.
- Sec 8.3: Updated the preparations of the Working Calibration Standard A, calibration standards, method blank, MS/MSD, QCS Working Standard A, and QCS to reflect current lab practices.
- Sec 12.2: Added instructions for using the stannous and hydroxyl lines.
- Sec. 18.0: Added the maintenance log for the M8000.

By signing below, I certify that I have been *notified* about the approval of a *new revision* to the above mentioned SOP. I realize it is *my responsibility* to **read, understand and perform** the procedure as set forth in this new revision.

Initials & Date	Initials & Date	Initials & Date

[ ] *Annual Review* Current Revision # _____

By signing below, I certify that I have **re-read, understand** and **agree to perform** the current revision of the above mentioned SOP.

Initials & Date	Initials & Date	Initials & Date

Form revised 01/18/06

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EPA-821-R-01-013
January 2001

Appendix to Method 1631
Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation

Appendix to Method 1631
Total Mercury in Tissue, Sludge, Sediment, and Soil
by Acid Digestion and BrCl Oxidation[1]

A1.0 Scope and Application

A1.1 This Appendix provides two sample preparation (digestion) procedures for oxidation of total mercury (Hg) in solid and semi-solid sample matrices. These procedures may be used in conjunction with EPA Method 1631B: *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* for determination of mercury in tissue, sludge, sediment, soil, industrial samples, and certified reference materials.

A1.2 The digestion procedures in this Appendix, in conjunction with Method 1631B, allow determination of Hg at concentrations ranging from 1.0 to 5000 ng/g in solid and semi-solid matrices. Higher concentrations can be measured by selection of a smaller sample size and/or dilution of the digestate.

A1.3 The detection limit and minimum level of quantitation in this Method usually are dependent on the level of interferences rather than instrumental limitations. The method detection limit (MDL; 40 CFR 136, Appendix B) for Hg has been determined to be in the range of 0.24 to 0.48 ng/g when no interferences are present (see Appendix Tables A3 and A4). The minimum level of quantitation (ML) has been established as 1.0 ng/g. These levels assume a sample size of 0.5 g.

A1.4 Because Hg concentrations in solids are typically 10^3 - 10^7 times higher than those found in aqueous samples, the sensitivity provided by the dual amalgam trap system and fluorescence detector described in Method 1631B may be more sensitive than necessary, and a single trap and/or cold vapor atomic absorption spectroscopy (CVAAS) instrument may be adequate. These modifications are allowed under the equivalency provisions in EPA Method 1631B. See Method 1631B Section 9.1.2. However, the dual amalgam trap system and fluorescence detector provide greater sensitivity and specificity in the presence of interferences, and this system must be used to overcome interferences, if present, and to achieve the sensitivity required, if necessary.

A2.0 Summary

A2.1 Digestion I—This procedure is preferred for matrices containing organic materials, such as sludge and plant and animal tissues, because the organic matter is completely destroyed. In this procedure, a 0.2 - 1.5 g sample is digested with HNO_3/H_2SO_4. The digestate is diluted with BrCl solution to destroy the remaining organic material.

A2.2 Digestion II—This procedure is preferred for geological materials because of rapid and complete dissolution of cinnabar (HgS), which is otherwise more slowly attacked by the BrCl in Digestion I. In this procedure, a 0.5 - 1.5 g sample is digested with aqua regia (HCl/HNO_3) to solubilize inorganic materials.

A2.3 The Hg concentration in the digestate is determined using EPA Method 1631B.

[1] Based on a standard operating procedure provided by Frontier Geosciences, Inc.

A3.0 Definitions

See the Glossary at the end of Method 1631B for definitions of the terms used in this Appendix.

A4.0 Contamination and Interferences

A4.1 For the complete recovery of mercury by Method 1631B, all Hg in the sample must be converted to Hg(II). This is accomplished by free halogens present in the digestion step.

A4.2 In Digestion I, the addition of BrCl to the sample after it is fully solubilized HNO_3/H_2SO_4 is critical to convert methyl Hg to Hg(II). If the acid digestates are analyzed by Method 1631B without BrCl oxidation of tissues or geological media, a significant low bias may occur.

A4.3 In Digestion II, the reaction between concentrated HCl and HNO_3 in aqua regia generates nitrosyl chloride (NOCl) and free Cl_2, both of which are very strong oxidants for Hg-containing compounds including cinnabar (HgS) and precious metal amalgams that are not attacked by either acid alone. Aqua regia also converts all methyl Hg to Hg(II). The aqua regia procedure in Digestion II leaches but does not dissolve silicate minerals. Crustal elements such as Fe, Al, Cr, Ba, and Si may not be quantitatively recovered in some media using this procedure.

A4.4 Digestates from both Digestion I and II contain free halogens and extreme caution must be taken to avoid purging these free halogens onto the gold sand traps (see Section 4.4.2 in Method 1631B). Introduction of free halogens may be avoided by analyzing an aliquot of the sample digestate smaller than 5 mL (Appendix Section A12.3), and by pipetting aliquots of the digestate into bubbler water already containing $SnCl_2$. The use of hydroxylamine hydrochloride to remove free halogens (as prescribed in Method 1631B for aqueous samples) is not needed for solid sample digestates; there is a sufficient amount of $SnCl_2$ in the bubbler to reduce both Hg(II) and free halogens in digestate aliquots smaller than 5 mL.

A4.5 If iodized coal or other elemental carbon samples are to be analyzed, the final acid concentration in the diluted sample must be greater than 40% (v/v), and all carbon particles must be settled prior to analysis to avoid re-adsorption of Hg on the carbon and an ensuing low bias.

A5.0 Safety

Observe the safety precautions in Method 1631B.

A6.0 Apparatus and Materials

A6.1 Digestion vessel—50-mL borosilicate Erlenmeyer flask, calibrated to 40 ± 0.5 mL; or any other acid-cleaned, flat-bottomed, borosilicate glass container calibrated to 40 ± 0.5 mL.

A6.2 Pressure release digestion cap—Clear glass sphere or inverted fluoropolymer cone, approximately 1.5 - 2.0 cm in diameter, initially cleaned by heating overnight in hot concentrated nitric acid. The sphere or cone acts as a pressure release valve during gas evolution. A common clear glass marble may be used as the sphere, or the cone may be custom manufactured. Colored glass marbles contain high levels of trace metals and must not be used. The cap must completely cover the opening of the digestion vessel without falling in, yet not be so large as to risk falling off when slightly lifted by the gas pressure in the vessel.

A6.3 Electric hot plate—A temperature controlled electric hot-plate capable of maintaining a temperature of 100-110°C. A commonly available fluoropolymer-coated pancake griddle is excellent for this purpose. Do not use the griddle for heating flammable solvents.

A6.4 Dilution vessels—Volumetric flasks, glass, 25, 50.0, and 100.0 mL, cleaned per the procedures in Method 1631B.

A6.5 Digestate storage vessel—VOA vial, glass, 40-mL, with fluoropolymer-lined cap, cleaned per the procedures in Method 1631B, or purchase I-Chem level 300, trace metal clean, with fluoropolymer-lined cap, or equivalent.

A6.6 Balance—Analytical, capable of weighing 1.0 mg.

A7.0 Reagents and Standards

A7.1 Reference matrices

A7.1.1 Biota, including tissue and wet and dry municipal sludge—Chicken breast, skinless, boneless, purchased at a local supermarket, or other tissue demonstrated to be free of mercury at the MDL in Table A1.

A7.1.2 Soil, sediment, and other geological samples—Playground sand or other sand-like material demonstrated to be free from mercury at the MDL in Table A1.

A7.2 Nitric acid (concentrated)—Reagent grade, containing less than 5 pg/mL Hg. The HNO_3 must be pre-analyzed for Hg before use.

A7.3 Sulfuric acid (concentrated)—Reagent grade, containing less than 5 pg/mL Hg. The H_2SO_4 must be pre-analyzed for Hg before use.

A7.4 HNO_3/H_2SO_4 solution—In a fume hood, slowly add 300 mL of concentrated H_2SO_4 (Appendix Section A7.3) to 700 mL of concentrated HNO_3 (Appendix Section A7.2) in a fluoropolymer bottle.

Warning: This mixture gets hot and emits caustic fumes.

A7.5 Dilute BrCl solutions—Use the concentrated (0.2N) BrCl solution in Section 7.6 of Method 1631B to produce the following solutions:

A7.5.1 0.07 N bromine monochloride solution—Dilute 300 mL of 0.2N BrCl solution to 1000 mL with reagent water in a fluoropolymer bottle.

A7.5.2 0.02 N bromine monochloride solution—Dilute 100 mL of concentrated BrCl solution to 1000 mL with reagent water in a fluoropolymer bottle.

A8.0 Sample Collection, Preservation, and Storage

A8.1 Samples are collected into acid-cleaned glass, polyethylene, or fluoropolymer jars. For all except very low level and high water content samples, polyethylene bags are also acceptable. Dry solids

such as coal and ores may be collected and stored in heavy gauge paper pouches commonly used by geologists.

A8.2 Samples are collected using clean gloves. Equipment is rinsed between samples to avoid cross-contamination. In general, follow the sampling procedures in Method 1613B. The ultra-low level sampling procedures in EPA Method 1669 may not be necessary because Hg concentrations in solids are typically 10^3 - 10^7 times higher than those found in water samples.

A8.3 Sample shipment, storage, preservation, and holding times

A8.3.1 Dry samples—Samples such as ores, coal, paper, and wood may be shipped unrefrigerated and stored indefinitely in a cool, dry location known to have an atmosphere that is low in mercury.

A8.3.2 Biota samples—Samples containing biota, including wet and dry sludge, are shipped to the laboratory at 0-4 °C and may be processed and stored in one of the following two ways:

A8.3.2.1 Biota samples large enough to sub-sample are homogenized to a fine paste with a stainless steel mill, or finely chopped with stainless steel tools on an acid-cleaned, plastic cutting board. After homogenization, samples are stored frozen at < -15 °C in an acid-cleaned glass or fluoropolymer jar. The jar should be sized to be filled between 50 - 80% with sample. Samples may be stored frozen for a maximum of 1 year.

A8.3.2.2 If not analyzed upon receipt at the laboratory, biota samples may be lyophilized (freeze-dried) prior to homogenization and storage. Once lyophilized, biota samples may be stored unrefrigerated in a low-mercury atmosphere for a maximum of 1 year.

A8.3.3 Wet sediment samples—Wet sediment samples are chilled and shipped to the laboratory at 0-4 °C. Because freezing and thawing may adversely affect homogeneity by causing clumping and separation of the solids from the liquid, wet sediment samples must be aliquoted and weighed at the laboratory and prior to freezing if they are not analyzed upon receipt. Wet sediment samples may be held for 1 year if aliquoted, weighed, and frozen at < -15 °C. Sediment samples may be lyophilized and stored unrefrigerated for 1 year in a low-mercury atmosphere if only total Hg will be determined and no free elemental mercury (Hg^0) is expected to be in the samples.

A9.0 Quality Control

A9.1 The quality control (QC) measures in Section 9 of Method 1631B must be followed when analyzing samples using this Appendix. In addition, this Appendix requires method blanks. Descriptions of the modifications of the quality control measures in Method 1631B that are required for application to solid and semi-solid matrices are provided below.

A9.2 Initial demonstration of laboratory capability

A9.2.1 Method detection limit (see Section 9.2.1 of Method 1631B)—The laboratory must achieve an MDL that is less than or equal to the MDL listed in Table A1.

A9.2.2 Initial precision and recovery (IPR; see Section 9.2.2 of Method 1631B)—Analyze four aliquots of the appropriate reference matrix (see Appendix Section A7.1), each spiked with 4.0 ng of Hg. This amount will be 8 ng/g for a 0.5 g sample. Calculate the average percent recovery (X) and the RSD of percent recovery. Compare X and RSD with the corresponding IPR limits in Table A1. If X and RSD meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, RSD exceeds the precision limit or X is outside the recovery range, performance of the analytical system is unacceptable. Correct the problem and repeat the test.

A9.3 Matrix spike/matrix spike duplicate (MS/MSD; see Section 9.3 of Method 1631B)

9.3.1 Spike and analyze 1 out of every 10 samples of the same matrix type, in duplicate, at a concentration 2 - 5 times the background concentration of Hg in the unspiked sample or at the concentration in the IPR (Appendix Section A9.2.2), whichever is greater. Calculate the percent recovery in each aliquot and the RPD between the aliquots. The individual recoveries and the RPD shall meet the MS/MSD recovery acceptance criteria in Table A1. If either recovery or the RPD does not meet the acceptance criteria, correct the problem and repeat the test according to the procedures in Sections 9.3.4 and/or 9.3.5 of Method 1631B.

A9.4 Blanks (see Section 9.4 of Method 1631B)

A9.4.1 Because of the high concentrations of mercury in solid samples, as compared to aqueous samples, field blanks (Section 9.4.3 of Method 1631B) and sampler check blanks (Section 9.4.4.2 of Method 1631B) are not required. However, it may be prudent to collect a sampler check blank the first time that a given set of sampling equipment is used and whenever it is suspected to be contaminated.

A9.4.2 Method blank—For each batch of 20 samples (Section 9.1.7 of Method 1631B), digest and analyze a method blank using the most appropriate reference matrix (Appendix Section A7.1). The laboratory may process a greater number of method blanks, if desired, and average the results. The method blank must include all sample processing steps; e.g., homogenization (Appendix Section A8.3.2.1). The concentration of mercury in the method blank, or the average of multiple method blanks, must meet the QC acceptance criteria in Table A1; otherwise, the source of contamination must be eliminated and the batch reanalyzed.

A9.5 Ongoing precision and recovery (OPR; see Section 9.5 of Method 1631B)—The OPR (laboratory control sample) for solid and semi-solid samples is test of the entire analytical system and includes all sample processing procedures; e.g., homogenization (Appendix Section A8.3.2.1) and digestion (Appendix Section A11.1 or A11.2).

A9.5.1 Analyze an aliquot of the appropriate reference matrix (see Appendix Section A7.1), spiked at the concentration in the IPR (Appendix Section A9.2.2). Calculate the percent recovery.

A9.5.2 Compare percent recovery with the OPR limit in Table A1. If percent recovery meets the acceptance criteria, system performance is acceptable and analysis of samples and blanks may continue. If, however, percent recovery is outside of the acceptance range, analytical system performance is unacceptable. Correct the problem and repeat the test according to Section 9.5.2 of Method 1631B.

A9.6 Quality Control Sample (QCS) - Many certified reference materials (CRMs) are available for total mercury in plants, animals, fish, sediments, soils, and sludge. Recovery and precision for at least one QCS per batch of samples must meet the performance specifications provided by the supplier.

A9.7 Replicate samples—Some samples, particularly sediments, may be heterogeneous. Replicates of these samples should be analyzed to characterize this heterogeneity. Replicate samples may also be required by a specific program to assess the precision of the sample collection, transportation, and storage techniques. The relative percent difference (RPD) between replicates should be less than 30%.

A10.0 Calibration and Standardization

A10.1 Calibrate the CVAFS instrument system using the procedures in Section 10 of Method 1631B. The concentration of the calibration solutions is as given in Section 10.1.1.2 of Method 1613B. The amount of Hg in these solutions will be 0.05, 0.5, 2.5, 5.0, and 10.0 ng.

A10.2 Calibration verification (VER)—Calibration of the CVAFS instrument system must be verified periodically using aqueous standards. In Method 1631B, the OPR is used for this verification because the standards are added to water (see Sections 10.2 and 9.5 of Method 1631B). In contrast, the OPR in this Appendix (Appendix Section A9.5) is used to demonstrate that the end-to-end analytical system remains in control. To avoid confusion, the periodic verification of calibration in this Appendix is referred to as "calibration verification" (VER). The VER is a spiked reagent water sample (an aqueous blank spike) and is used to determine that the CVAFS remains in control.

A10.2.1 Prior to and after the analysis of 10 samples, verify calibration of the CVAFS instrument system using the OPR test in Sections 9.5.1 and 9.5.2 of Method 1631B. Record results as calibration verification (VER).

A10.2.2 The requirements in Section 9.5.2 of Method 1631B must be met for sample results to be valid.

A11.0 Digestion

A11.1 Digestion I: Hot re-fluxing HNO_3/H_2SO_4 digestion followed by BrCl oxidation—This procedure is intended for biota, wood, paper, tissue, municipal sludge, and other primarily organic matrices (excluding coal). It does, however, give quantitative recovery for Hg on finely divided geological matrices such as sediments and soils.

A11.1.1 Accurately weigh (to the nearest mg) an aliquot of sample directly into a tared digestion vessel (Appendix Section A6.1). For organic matter such as biota, weigh 0.2-0.4 gram; for tissue (e.g., fish), plant material, or sludge, weigh 0.5-1.5 grams; for dried material

such as wood, paper, and CRMs, weigh 0.2-0.4 gram. The use of too much organic material will consume all of the acid in the digestion, resulting in a low recovery.

A11.1.2 To each sample, add 10.0 mL of HNO_3/H_2SO_4 solution (Appendix Section A7.4). Place the digestion vessel in an acid fume hood and loosely cap with a clean marble or inverted fluoropolymer cone (Appendix Section A6.2). For wood, paper, or other dry carbohydrates that can react violently with the HNO_3/H_2SO_4 solution, allow the sample to sit in the cold acid for at least 4 hours before heating.

A11.1.3 After digesting at room temperature, place the digestion vessel on a hot plate in the hood and slowly bring to a gentle boil by incrementally increasing the plate temperature over a 1-hour period. If excessive sample foaming occurs, bring to temperature more slowly. Reflux for 2-3 hours to fully oxidize remaining organic matter. The mineral portion of soil and sediment samples will not dissolve but will be effectively leached by this digestion.

A11.1.4 After the digestion is complete, bring to the calibration mark on the digestion vessel (40 ± 0.5 mL; Appendix Section A6.1) with 0.02 N BrCl solution (Appendix Section A7.5.2) and mix thoroughly. Shake the sample/BrCl solution to homogenize, and allow to sit at least 4 hours prior to analysis to oxidize remaining dissolved methyl Hg. Analyze the oxidized digestate per Appendix Section A12.0.

Note: Some highly organic matrices will require higher levels of BrCl (Appendix Section A7.5.1) and longer digestion times or elevated temperatures. The amount of reagent added to a sample must be the same as the amount added to the reagent blank to detect contamination in the reagents, and to the method blank and the OPR to demonstrate that mercury can be recovered quantitatively. BrCl oxidation must be continued until it is complete.

A11.2 Digestion II: Cold aqua regia followed by BrCl oxidation—This procedure is intended for coal, ores, sediments, soils, and other geological media. It does, however, give quantitative recovery for Hg on finely divided biological media such as tissues, paper, and wood, because the organic matrix is leached rather than dissolved. Solid, dry geological media such as rocks, ores, and coal must be pulverized using a contamination-free mill prior to digestion. Otherwise, mercury will not be recovered from the interior of large particles.

A11.2.1 Accurately weigh (to the nearest mg) an aliquot of the sample directly into a tared digestion vessel. For wet sediments and soils, weigh 0.5-1.5 grams; for dried materials such as coal, ores, and CRMs, weigh 0.5-1.0 gram. To better assure homogeneity, sediments and soils should be screened through a 2-mm plastic sieve to remove large rocks and sticks before digestion.

A11.2.2 In a fume hood, add 8.0 mL of concentrated HCl (Method 1631B Section 7.3), swirl, and add 2.0 mL of concentrated HNO_3 to the sample in the digestion vessel. Cap the vessel with a clean glass marble or inverted fluoropolymer cone. Allow to digest at room temperature for at least 4 hours but preferably overnight.

A11.2.3 For coal or other elemental carbon-containing sample, dilute the digestate to the calibration mark (40 ± 0.5 mL) with 0.07 N BrCl solution and shake the flask to mix thoroughly. The addition of BrCl ensures that Hg will not re-adsorb to the carbon

particles, producing low recoveries. After dilution and shaking, allow the sample to settle overnight, or centrifuge prior to analysis. Be sure that all fine-grained particles are completely settled prior to analysis. This settling can be hastened by centrifuging for 20 minutes at 3000 RPM or by filtering the sample through a 0.45-mm filter. Analyze per Appendix Section A12.0.

A11.2.4 For other than coal or elemental carbon-containing samples, dilute the digestate to volume (40 ± 0.5 mL) with reagent water so that the meniscus is at the calibration line in the neck of the digestion vessel. Shake vigorously and allow settling until the supernatant is clear prior to analysis. Analyze per Appendix Section A12.0.

A11.3 The diluted digestates may be stored up to one year in glass or fluoropolymer containers prior to analysis, or for future re-analysis, if needed.

A12.0 Digestate Analysis

Diluted digestates are analyzed in a manner analogous to the analysis of standards by Method 1631B (see Section 10.0 of Method 1631B).

A12.1 Pipet a 0.01- to 5.0-mL volume of diluted digestate (Appendix Section A11.1.4, A11.2.3, or A11.2.4) directly into a bubbler containing approximately 100 mL of pre-purged $SnCl_2$-containing water.

Note: The volume of $SnCl_2$-containing water in the bubbler is not critical for the purpose of purging but is assumed to be 0.100 L for the purpose of calculating results (see Appendix Section A13.1.1).

A12.2 Purge the solution onto a gold trap for 20 minutes. These conditions allow measurement of Hg concentrations in the range of 1 – 5,000 ng/g (parts per billion).

A12.3 Change the $SnCl_2$-containing water in the bubbler after a total of 10 mL of digestate has been added. For example, if 2 digestate aliquots of 5 mL each have been added to 100 mL of fresh, pre-purged, $SnCl_2$-containing water, the $SnCl_2$-containing water must be changed and 100 mL of fresh, $SnCl_2$-containing water must be placed in the bubbler and purged for a minimum of 10 minutes prior to addition of another digestate aliquot.

A12.4 For samples known or expected to contain high Hg concentrations, further dilute (usually by a factor of 100) an aliquot of the diluted digestate with 0.02 N BrCl solution, and analyze a sub-aliquot.

A13.0 Data Analysis and Calculations

A13.1 Calculation of solid phase concentrations

A13.1.1 The analytical system in Method 1631B will give analytical results in units of area (or height) for the volume of diluted digestate analyzed. To calculate the solid phase concentration, use the following equation:

$$C_{Hg} = (A_s - A_{BB}) \times V \times d \times 0.1 / (CF_m \times v \times w)$$

where:

C_{Hg}	=	concentration of mercury in the sample (ng/g wet weight)
A_s	=	peak area (or height) for mercury in the sample
A_{BB}	=	peak area (or height) for the average of the bubbler blanks
V	=	volume of diluted digestate (mL) (Appendix Sections A11.1.4, A11.2.3, A11.2.4) = 40 mL
d	=	dilution factor(s); e.g., a factor of 100 in Appendix Section A12.4.
0.1	=	volume in bubbler (L) (Assumed per note in Appendix Section A12.1)
CF_m	=	mean CF from calibration (area (or height))/(ng/L) (Method 1613B Section 10.1.1.4)
v	=	digestate volume analyzed (mL) (Appendix Section A12.1)
w	=	sample weight (g) (Appendix Section A11.1.1 or A11.2.1)

A13.1.2 If desired, determine the moisture content of a sample aliquot and use the dry weight as "w" in the equation above.

A13.2 Reporting

A13.2.1 Report results as required in Method 1631B except use reporting levels and units appropriate to solid samples (ng/g).

A13.2.2 Reagent blank results and method blank results are reported separately and, if requested or required, are subtracted from sample Hg concentrations.

A14.0 Method Performance

A14.1 This Appendix was developed in a single laboratory and validated in a single laboratory. Performance data from these studies are summarized in Tables A2 through A7.

A15.0 References

1. *Development of Digestion Procedures for Determination of Mercury in Solid and Semi-solid Samples*, Frontier Geosciences, available from EPA Sample Control Center DynCorp I&ET, Alexandria, VA 22304 (703-461-2100; SCC@dyncorp.com).

2. *Single Laboratory Validation of Appendix to Method 1631*, June-July 1999, Brooks-Rand Ltd., EPA Sample Control Center Episode Number 6236, DynCorp I&ET, Alexandria, VA 22304 (703-461-2100; SCC@dyncorp.com).

Table A1. Quality control acceptance criteria.

Test	Acceptance Criteria	Spike concentration
Calibration linearity	<15% RSD of CF	0.5, 5, 25, 50, and 100 ng/L = 0.05, 0.5, 2.5, 5.0, and 10.0 ng
Calibration verification (VER)	77-123%	5 ng/L = 0.5 ng
MDL	0.48 ng/g[(1)]	0.8 ng/g
ML	1 ng/g[(2)]	0.05 ng (lowest calibration point)
MS/MSD recovery	70-130%	2x background or level in IPR/OPR, whichever is greater
MS/MSD precision	< 30% RPD	2x background or level in IPR/OPR, whichever is greater
IPR recovery	75-125%	4.0 ng
IPR precision	< 20% RSD	4.0 ng
OPR recovery	70 - 130%	4.0 ng
Method blank	< 0.4 ng or < 0.1x sample, whichever is greater	-

(1) See Appendix Table A4
(2) Assuming a 0.5 g sample

Table A2. Method performance for biological samples and CRMs digested using hot re-fluxing HNO_3 digestion plus BrCl dilution and Method 1631B. Blanks and spikes were on three different instruments, over a period of several weeks. Data provided by Frontier Geosciences.

Test/material	n	Hg concentration (ng/g; ppb)			Performance
		mean	SD	certified[(1)]	
Method blanks	24	0.25	0.13	--	DL = 0.33 ng/g[(2)]
2.0 ng/g matrix spike	28	1.90[(3)]	0.22	2.00	95% rec.; 11% RSD
IRM-007 (sludge)	3	3,680	150	3,150	117% rec.; 4% RSD
DOLT-2 (fish liver)	7	2,164	161	2,140	101% rec.; 7%RSD
DORM-2 (fish muscle)	11	4,682	386	4,640	101% rec.; 8% RSD
NIST-2796 (mussel)	12	60.4	6.7	61.0	99% rec.; 11% RSD

(1) value provided by supplier of reference material
(2) detection limit = 2.5 x SD for 24 method blanks (2.5 = student's t @ 23 degrees of freedom)
(3) net recovered; background concentration (chicken breast) was 0.41 ng/g

Table A3. Method performance for geological samples and CRMs using cold aqua regia digestion and Method 1631B. Data provided by Frontier Geosciences.

Test/material	n	Hg concentration (ng/g; ppb)			Performance
		mean	SD	certified[1]	
Method blanks	23	0.045	0.037	--	DL = 0.09 ng/g[2]
0.5 ng/g blank spike	8	0.465	0.079	0.50	MDL = 0.24 ng/g
NIST-2709 (soil)	9	1393	111	1,400	100% rec.; 8% RSD
NIST-1633 (fly ash)	2	163	3.0	160	102% rec.; 2% RSD
NIST-2710 (soil)	3	30888	2,692	32,610	95% rec.; 9% RSD
IAEA-356 (sediment)	1	7152	--	7.62	94% rec.
PACS-1 (sediment)	1	4402	--	4,540	97% rec.
NIST-1630 (coal)	3	108	5.0	127*	85% rec.; 5% RSD
NIST-1632 (coal)	5	79.3	7.0	78	102% rec.; 9% RSD

(1) value provided by supplier of reference material

(2) detection limit = 2.5 x SD for 24 method blanks (2.5 = student's t @ 23 degrees of freedom)

Table A4. Results of MDL Set 2 analyses (spiked with 0.24 ng; ~0.8 ng/g). Data provided by Brooks-Rand.

Rep	Sample Mass (g)	Measured Hg (ng)	Blank-corrected Hg (ng)	Sample Concentration (ng/g)*
1	1.03	0.39	0.13	0.41
2	1.29	0.50	0.23	0.71
3	1.25	0.48	0.22	0.73
4	1.36	0.53	0.26	0.78
5	1.28	0.49	0.23	0.68
6	1.01	0.39	0.12	0.40
7	1.17	0.45	0.19	0.61
				Average: 0.62 ng/g **Std. Dev.: 0.15 ng/g**
***blank corrected**				**MDL = 0.48**

Table A5. Analyses of spiked catfish samples (spiked with 17 ng of Hg). Data provided by Brooks-Rand

Replicate	Sample Mass (g)	Measured Hg (ng)	Recovered Hg (ng)*	%Recovery*
1	1.02	30.1	17.1	99.3
2	1.21	31.6	16.2	93.7
3	0.97	31.4	19.0	110.2
4	1.17	23.4	8.41	48.7
*background corrected				**Average: 88% Std. Dev.: 27%**

Table A6. Analyses of spiked powdered egg yolk (spiked with 2.9 ng of Hg). Data provided by Brooks-Rand.

Replicate	Sample Mass (g)	Measured Hg (ng)	Recovered Hg* (ng)	%Recovery
1	1.00	3.49	2.34	80.6
2	1.06	3.16	1.94	67
3	1.04	2.56	1.37	47.1
4	1.08	3.75	2.50	86.2
*background corrected				**Average: 70% Std. Dev.: 17%**

Appendix P

Laboratory SOPs

TOC

DESA SOP

C-88

STANDARD OPERATING PROCEDURE

TOTAL ORGANIC CARBON-SEDIMENTS

Signature and Title

Prepared by:	Deborah P. Kay, Environmental Scientist, SCMS	2/9/11 Date
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QA Reviewed by:	Sumy P. Cherukara, Quality Assurance Officer	2/15/11 Date
Approved by:	James Ferretti, Team Leader, SCMS	2/15/11 Date
Approved by:	John Bourbon, Acting Chief, Laboratory Branch	2/15/11 Date

Review

Reviewed by:	Signature	Date
Reviewed by:	Signature	Date

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STANDARD OPERATING PROCEDURE
TOTAL ORGANIC CARBON-SEDIMENTS

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of nonpurgeable organic carbon in solids, sediments and sludges.

1.2 The range of this method is 100 to 20,000 mg/kg and handles particles up to 0.5 mm diameter.

1.3 The reporting limit for this method is 100 mg/kg.

1.4 This SOP is based on a modified version of EPA Method 415.1

2. SUMMARY OF METHOD

Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed is measured directly by a non-dispersive infrared (IR) detector, or thermo conductivity detector (TCD). The amount of CO_2 is directly proportional to the concentration of carbonaceous materials in the sample.

3. DEFINITIONS

See SOP # G-15 for definitions.

4. INTERFERENCES

4.1 The TOC analyzer measures all of the nonpurgeable carbon in a sample. Volatile components are lost with the inorganic carbonates in the pretreatment step.

4.2 Carbonate and bicarbonate carbon represent an interference under the terms of this test and are removed.

4.3 Contaminated glassware, plastic containers and rubber tubing can cause interference.

4.4 Careless sampling, handling and analysis of samples can cause interference.

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5. SAFETY

5.1 The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Always wear safety glasses or full-face shield for eye protection when working with these reagents. Each laboratory is responsible for maintaining a current safety plan, a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this SOP.

5.2 The sample boats/crucibles used during analysis are heated to 680^{o} C during analysis. Use extreme caution when handling the boats. Use only forceps when handling boats.

6. APPARATUS AND MATERIALS

6.1 - Elementar Vario EL CHNOS analyzer or
- Elementar Liqui TOC analyzer with solids module.

6.2 Quartz and Stainless Steel Crucibles

6.3 Tin and Silver Boats

6.4 Syringes 10ul, 25ul, and 50ul

6. 5 Analytical Balance capable of weighing 0.0001 g.

6.6 AQC/SRM - TOC/TKN/Total-P/NH_3 in Soil, Environmental Resource Associates, or equivalent vendor.

6.7 Whatman GF/F glass microfiber filters, 25mm, ashed at 550^{o}C for 1.5 hr.

6.8 60 X 15 Corning Pyrex petri dishes with covers

6.9 Miscellaneous laboratory apparatus such as flasks, funnels, tubing, etc.

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7. REAGENTS AND SOLUTIONS

7.1 Elementar Liqui TOC analyzer with solids module

7.1.1 Potassium Hydrogen Phthalate Solution, 20,000 mg/L.
Dissolve 4.256 g of Primary Standard Grade KHP in distilled water and dilute to 100 mL.

7.1.2 Potassium Hydrogen Phthalate Solution, 10,000 mg/L.
Dissolve 2.128 g of Primary Standard Grade KHP in distilled water and dilute to 100 mL.

7.1.3 Potassium Hydrogen Phthalate Solution, 5,000 mg/L.
Dissolve 1.064 g of Primary Standard Grade KHP in distilled water and dilute to 100 mL.

7.1.4 Potassium Hydrogen Phthalate Solution, 1,000 mg/L.
Dissolve 0.2128 g of Primary Standard Grade KHP in distilled water and dilute to 100 mL.

7.1.5 Potassium Hydrogen Phthalate Solution, 500 mg/L.
Prepare by diluting 2.5 mLs of Potassium Hydrogen Phthalate 20,000 mg/L Stock Solution to 100 mL.

7.1.6 Potassium Hydrogen Phthalate Solution, 100 mg/L.
Prepare by diluting 0.5 mLs of Potassium Hydrogen Phthalate 20,000 mg/L Stock Solution to 100 mL.

7.1.7 Concentrated Nitric Acid.

7.1.8 Carrier Gas: Air, Ultra Zero Grade, CO2-free and containing less than 1 ppm hydrocarbon.

7.2 Elementar Vario EL CHNOS analyzer

7.2.1 Acetanilide

7.2.2 Carrier Gases: Oxygen Ultra Pure Carrier (UPC) grade gas, UPC GR 4.6 with minimum purity 99.995% (CO and CO_2<1ppm), and Helium

7.2.3 Concentrated Hydrochloric Acid

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7.2.4 Hydrochloric Acid 1:1

7.3 Reagent Water (Dionized Type II).

8. SAMPLE COLLECTION, PRESERVATION, STORAGE & HOLDING TIME

8.1 Samples are collected in glass jars. Samples should be homogenized in order to get representative portions.

8.2 The sample should be refrigerated at 4EC. There is no holding time for this method.

8.3 Samples for particulate organic carbon must be filtered through glass microfiber membrane filters as soon as possible after collection but not longer than 48 hours after collection.

9. SAMPLE PREPARATION

9.1 If enough room is in the sample jar, homogenize the sample by stirring sediment with a small metal or plastic spatula until sample is thoroughly mixed. If there is insufficient room to stir the sample in the jar, pour the contents into a container.

9.2 An aliquot of at least 5 g wet weight is then placed in an evaporating dish and placed in a drying oven at 60EC for 48 hours.

9.3 Transfer the dried sediment to a porcelain mortar and thoroughly ground with a porcelain pestle. Obvious large shell, rock or foreign material fragments should be removed with metal forceps, being careful not to contaminate the sample with foreign material.

9.4 Place the dried sediment in a labeled glass or plastic vials with caps.

9.5 Elementar Liqui TOC analyzer with solids module.

9.5.1 Blanks - Using a 40ul syringe transfer 40ul's of dionized water into a pre-burned stainless steel crucible and analyze according to section 10.2

9.5.2 Calibration/Check Standards - Using a 40ul syringe transfer 40ul's of standard KHP solution (see section 7.1) into a pre-burned stainless steel crucible and analyze according to section 10.2

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9.5.3 Samples - Weigh out approximately 10-35 mg of sample into a pre-burned quartz crucible. Place a few drops of nitric acid on the sample and wait until the foaming reaction stops. Place sample in 60EC oven or on a hotplate for a minimum of 20 minutes. Do not let weighed samples sit out overnight. Only prepare those samples that can be analyzed during the course of a day. Analyze according to section 10.2

Filtration procedure for POC

9.6.1 Filter the thoroughly mixed sample in 50 ml aliquots until a maximum of 600 mls have been filtered. If filtration slows due to particulate buildup on the filter, use the maximum sample volume that can be filtered thru the filter. Record the sample volume filtered.

9.6.2 Do not rinse the filter paper after filtration. Continue the vacuum filtration for 30 seconds after the final sample volume passes thru the filter.

9.6.3 If dissolved organic carbon (DOC) is required, preserve an aliquot of the filtrate to pH <2 with sulfuric acid. Analyze according to SOP C-83.

9.6.4 Place each filter paper into a labeled petri dish and store at -20 to -30 ^{o} C.

9.6.5 When ready to begin sample analysis, place a 12” HDPE mesh sieve in the grey acid container in a fume hood. Fill the bin with conc. HCL to one inch below the mesh floor of the sieve. Place the petri dishes on the mesh screen and remove the lids. Allow the vapors to permeate the filters for 24 hours. After 24 hours, wipe the outside of the petri dish to remove any HCL residue and replace the lids.

9.6.6 Filters are now ready for analysis using the Elementar Liqui TOC analyzer with solids module.

9.7 Elementar Vario EL

9.7.1 Blanks - For blanks an empty slot is analyzed.

9.7.2 Standards - Weigh approximately 5 mg of Acetanilide into a tin boat and compress into a small square, capable of fitting into the autosampler.

9.7.3 AQC/SRM - Weigh approximately 10 mg of AQC/SRM material into a tin boat and compress into a small square, capable of fitting into the autosampler.

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9.7.4 Samples - Weigh approximately 5 to 10 mg's of sample as prepared in sections 9.1 through 9.4 into a silver boat, to this sample slowly add 1:1 Hydrochloric Acid drop by drop until the foaming reaction stops, then slowly add concentrated Hydrochloric Acid drop by drop until any visual reaction has stopped. The samples are then placed in an oven at 90^{o} for 4 hours, after cooling the samples, place the silver boat into a larger tin boat and compress into a small square, capable of fitting into the autosampler.

10. INSTRUMENT OPERATING CONDITIONS

10.1 Both TOC instruments should be left in the sleep mode with gas flow off when not in use.

10.2 Elemntar Liqui TOC - The Elemntar Liqui TOC instrument is generally used for the analysis of water samples, and has to be modified to operate in the solids mode. The instructions for Setup, operation, and maintenance can be found in sections 4, 5, and 6 of the Solids Module Operating instructions supplement to the Elemntar Liqui TOC operating manual.

10.3 Elementar Vario EL - The Elementar Vario EL is configured for the analysis of TOC in soil only. The instructions for Setup, operation, and maintenance can be found in the Elementar Vario EL III Operating Manual.

11. CALIBRATION

11.1 Elemntar Liqui TOC - The Elemntar Liqui TOC instrument is calibrated by analyzing duplicate calibration standards as prepared according to section 7.1., using a concentration range of 0 to 20,000 ppm , to derive a first order linear regression curve. A minimum of 5 calibration points is required.

11.2 Elementar Vario EL - The Elementar Vario EL calibration curve is stable for a least six months, and requires calibration only when the daily factor falls outside the range of 0.95 - 1.1 or if major components such as the detector or adsorption columns are changed. See section 6.4 and 7.2 of the Elementar Vario EL III Operating Manual. Prior to analysis 5 Acetanilide standards are analyzed, two as run ins and three for daily factor calculation. The average of the three daily factors are used to calculate the TOC value for balnks, standards, and samples. The daily factor is acceptable if the values fall in the range of 0.95 to 1.1.

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12. SAMPLE ANALYSIS

12.1 Elemntar Liqui TOC - Blanks, check standards, and samples are prepared and analyzed in duplicate. With the blank, check standard, or sample being introduced into the instrument manually. Sample data i.e. sample name, concentration range, and sample weight, is entered into the instrument's computer spread sheet. Weight data for blanks and standards is entered as 40, with sample weight data being entered in mg's. See section 6.2.2 and 6.2.3 in the Solids Module Operating instructions supplement to the Elemntar Liqui TOC operating manual.

12.2 Elementar Vario EL - Blanks, check standards, and samples are prepared and analyzed in duplicate. With the blank, check standard or sample being introduced into the instrument using an autosampler. See section 6.2 of the Elementar Vario EL III Operating Manual.

13. DATA ANALYSIS AND CALCULATIONS

13.1 All calculations are performed by the instruments using either a linear regression curve (Elemntar Liqui TOC) or daily factor (Elementar Vario EL) to calculate sample results in mg/kg or percent Carbon. If the incorrect weight is entered into the software, the calculation can be performed manually as follows:

13.1.1 $$\frac{\text{Raw Data - Blank Value}}{\text{Slope}} = \text{ug C}$$

13.1.2 $$\frac{\text{ug C}}{\text{Vol. (mg)}} \times 1000 = \text{ppm C}$$

14. METHOD PERFORMANCE

A demonstration of capability (DOC) should be performed each time there is a significant change in the chemistry of the method, a major modification to an existing instrument, or a new instrument is installed. A DOC is performed by each analyst designated to analyze samples using this method. An annual check must subsequently be performed and documented for each analyst using this method.

14.1 Accuracy and Precision

14.1.1 Demonstration of Capability

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A demonstration of capability study must be performed and documented for each analyst using this method. The study should consist of the analysis of four standard reference material (SRM) samples. The results of the SRM's must be within the acceptance criteria supplied by the manufacturer , or within 20% of the true value if no acceptance criteria are specified. The % RSD should be within 20%. The results of the accuracy and precision study (true value, % recovery, standard deviation and % RSD) are maintained by the Quality Assurance Officer for each analyst and are located in the Central Branch File.

14.1.2 Continuing Demonstration of Capability

An annual continuing demonstration of capability study must be performed and documented. It may consist of either successfully analyzing a PT sample or analyzing 2 sets of AQC/SRM samples to within control limits as stated in section 14.1.1. The results of the continuing accuracy and precision study (true value, % recovery, standard deviation and % RSD or final report from the PT provider) are maintained by the Quality Assurance Officer for each analyst and are located in the Central Branch File.

14.2 Method Detection Limit (MDL)

An MDL Study was conducted for this method. The study is based on the requirements listed in 40 CFR Part 136 Appendix B. Specific procedures for conducting an MDL study can be found in SOP # G-8. The MDL Study comprised the analysis of seven reagent grade water samples fortified at a level between 2-3x the detection limit. The results of the MDL determination (true value, average concentration, standard deviation and calculated MDL) are maintained by the Quality Assurance Officer for each method and are located in the Central Branch File.

14.3 Limit of Quantitation (LOQ)

The Laboratory performs a Limit of Quantitation (LOQ) study on an annual basis for analytes associated with chemistry methods. The validity of LOQ is confirmed by successful analysis of a Laboratory Fortified Blank (LFB) at approximately 2X the reporting limit. The acceptance criteria for each analyte is $\pm$ 30% of the true value. After this study is completed, it is reviewed and approved by the Laboratory Management. A summary of all LOQ study performance is maintained in the Laboratory's Central File.

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15. QUALITY CONTROL

15.1 Calibration Curve

Acceptance Criteria - A minimum of 5 standards and a blank must be used to generate the calibration curve. The correlation coefficient must be ∃0.995.

Corrective Action - If the correlation coefficient of the calibration curve, consisting of at least four standards and a blank, is <0.995, the calibration is disallowed. The analysis must be terminated, and repeated after correcting the problem.

15.2 Initial Calibration Verification (ICV), and Continuing Calibration Verfication (CCV).

ICV/CCV - Elemntar Liqui TOC - 10,000mg/l (Section 7.1.2) or 5000mg/l (section 7.1.2)

ICV/CCV - Elementar Vario EL - Acetanilide (Section 7.2.1)

Acceptance Criteria - Analyze the ICV for all determinations immediately following each calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the ICV immediately following calibration must verify that the instrument is within ∀15% of the true value. Subsequent analyses of the CCV must be within ∀15% of the true value.

Corrective Action - If the calibration cannot be verified within the specified limits, analysis must be discontinued, the cause determined and/or in the case of drift the instrument re-calibrated. All samples following the last acceptable ICV/CCV must be reanalyzed.

15.3 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

Acceptance Criteria - Analyze the calibration blank immediately following each calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. All ICB/CCB results must be < the Reporting Limit.

Corrective Action - If the results of the ICB/CCB are > Reporting Limit then all associated samples with a concentration of #10x the amount found in the ICB/CCB should be reprepared and reanalyzed (sample results ∃10x the amount

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found in the ICB/CCB are not considered to be affected by the blank contamination or drift).

If the samples cannot be reprepared, then all affected sample results must be either 1) qualified accordingly, or 2) the reporting limit is raised to the amount found in the sample. Check with the team leader/section chief to determine which option should be used.

15.4 Analytical Quality Control Samples (AQC=s), or Standard Reference Materials (SRM's)

Acceptance Criteria - Analyze two LFB/AQC/QCS samples with each batch of 20 or fewer samples. Calculate accuracy as percent recovery using the following equation:

$$\% \text{ Recovery} = \frac{\text{LFB/AQC/QCS}}{s} \times 100$$

where:

LFB/AQC/QCS = control sample results determined by laboratory

s = concentration equivalent of analyte added to fortify the LFB/AQC/QCS solution.

The % recovery of the LFB/AQC/QCS should be within 75-125%. The relative percent difference (RPD) of the duplicates should not exceed 20% for aqueous standards.

Corrective Action - If the % recovery or RPD results are outside the required control limits, the affected samples should be reprepared and reanalyzed. If the samples cannot be reprepared, then all affected sample results must be qualified accordingly.

15.5 Sample Matrix duplicates

Acceptance criteria -All samples for TOC are analyzed in duplicate. The relative percent difference (RPD) of the duplicates should not exceed 50% .

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Corrective action - If the %RPD result is greater than 50%, rerun the sample once for confirmation. If the %RSD of three or more analyses is outside of the acceptance criteria the sample must be qualified accordingly.

16. REPORTING AND VALIDATION

16.1 Reporting Limits

The reporting limits are calculated based on the concentration of the lowest calibration standard analyzed. This reporting limit for this method is 100 mg/kg. The reporting limits are matrix and dilution dependent. All results are reported to 2 significant figures.

16.2 Sample Data Package

The sample data package should include the following items, where applicable. The analyst may also include other information that may be pertinent to the analysis such as project narratives, etc.

1. Sample preparation information
2. Sample analysis data
3. Instrument calibration data
4. Instrument/computer printouts
5. Data summary checklist with all relevant information entered

16.3 Laboratory Information Management System (LIMS)

The analyst enters the data on the LIMS under the appropriate analytical codes.

16.4 Data Validation

The data package is given to the reviewer. The review is done by a peer who was not involved in the analysis. Upon completion of the review, including validation of all the appropriate codes in the LIMS for the particular project(s), the data reviewer will sign and date the QA/QC Checklist.

16.5 Data Records

A copy of each analytical data package is made for each project in the package and placed in the bin identified for the designated project file. The records for

this designated project file are filed in our locked record cabinets once all data from the project, e.g., non-metal inorganic data, organic data, microbiology data, etc. has been reviewed by the appropriate staff.

17. POLLUTION PREVENTION

17.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the USEPA recommends recycling as the next best option.

17.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

17.3 For information about pollution prevention that may be applicable to laboratories, consult ALess is Better: Laboratory Chemical Management for Waste Reduction@, available from the American Chemical Society=s Department of Government Regulations and Science Policy, 115 16th Street N.W., Washington D.C 20036, (202)872-4477.

18. WASTE MANAGEMENT

The USEPA requires that laboratory waste management practice be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any water discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the Region 2 SOP G-6, ADisposal of samples and hazardous wastes in Regional Laboratory@.

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19. REFERENCES

19.1 Standard Methods for the Examination of Water and Wastewater, Method 5310-TOC, 18th Edition, 1992

19.2 Elementar liquiTOC Operating Manual, 2005.

19.3 Elementar liquiTOC Solids Module Operating Manual Supplement, 2004.

19.4 Elementar varioEL Operating Manual, 2005.

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