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December 13, 2012

United States Army Corps of Engineers
Kansas City District
601 East 12th Street, Room 463
Kansas City, Missouri 64106-2896

ATTN:	CENWK-PM-ES/Buckrucker
CONTRACT:	W912DQ-11-D-3004
PROJECT:	Lower Passaic River Restoration Project Remedial Investigation/Feasibility Study Oversight (RI/FS) Lower Passaic River Study Area, New Jersey
SUBJECT:	Quality Assurance Project Plan, Addendum #11 Chemical Water Column Monitoring Study/ High Volume Chemical Data Collection Program

Dear Ms. Vaughn:

CDM Federal Programs Corporation (CDM Smith) is pleased to submit this electronic copy of the Quality Assurance Project Plan, Addendum No. 11 for Oversight of the Remedial Investigation/ Feasibility Study, Chemical Water Column Monitoring Study/High Volume Chemical Data Collection Program 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 Lower Passaic River Restoration Project RI Water Column Monitoring/High Volume Chemical Data Collection, Revision 1 dated September 2012* and address comments from the United States Environmental Protection Agency.

If you have any comments concerning this submittal, please contact me at (703) 814-7325.

Very truly yours,
CDM FEDERAL PROGRAMS CORPORATION

Frank Tsang, P.E.
Project Manager

Attachment

cc: S. Vaughn, EPA
B. Sy, EPA
J. Czapor, CDM Smith (Letter Only)
S. Kirchner, CDM Smith
S. Budney, CHMM, CDM Smith
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Project File

623563

Contract No.: W912DQ-11-D-3004
Task Order No.: 005

U. S. Army Corps of Engineers
Kansas City District

Quality Assurance Project Plan Addendum No. 11 RI Water Column Monitoring High Volume Chemical Data Collection Program

Lower Passaic River Restoration Project

Remedial Investigation/Feasibility Study Oversight

Lower Passaic River Study Area, New Jersey

December 13, 2012

CDM Smith

LOWER PASSAIC RIVER RESTORATION PROJECT
OPERABLE UNIT (OU) 2

Remedial Investigation/Feasibility Study Oversight

Quality Assurance Project Plan

Addendum No. 11

Chemical Water Column Monitoring Study/ High Volume Chemical Data Collection

Lower Passaic River Study Area, New Jersey

USACE CONTRACT No. W912DQ-11-D-3004

TASK ORDER No. 005

December 13, 2012

Prepared for:
U.S. Army Corps of Engineers
Kansas City District

Prepared by:
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Figure 1 See the Cooperating Parties Group (CPG)'s Quality Assurance Project Plan, Remedial Investigation Water Column Monitoring/High Volume Chemical Data Collection QAPP, Introduction Page 8 of 8, September 2012.

List of Appendices
Appendix Q - Laboratory Standard Operating Procedures (SOPs)

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

Acronyms

%	percent
%R	percent recovery
µm	micrometer
µg/L	microgram per liter
A	analytical
ABS	absolute difference
ANSETS	Analytical Services Tracking System
ASC	analytical services coordinator
ASTM	American Society of Testing and Materials
Axys	Axys Analytical Services Limited
CA	corrective action
CAS	Chemical Abstract Service
CCV	continuing calibration verification
CDM Smith	CDM Federal Programs Corporation
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	chain of custody
CPG	Cooperating Parties Group
CRM	certified reference material
CRQL	contract required quantitation limits
CWCM	Chemical Water Column Monitoring
DESA	Division of Environmental Science and Assessment
DL	detection limit
DOC	dissolved organic carbon
DQA	data quality assessment
DQI	data quality indicators
DQO	data quality objectives
DV	data validation
EDL	estimated detection limit
EPA	United States Environmental Protection Agency
EQuIS	Environmental Quality Information System
FASTAC	Field and Analytical Services Teaming Advisory Committee
FID	flame ionization detector
FS	feasibility study
GC/MS	gas chromatograph / mass spectroscopy
HDPE	high density polyethylene
HRGC/HRMS	High Resolution Gas Chromatography / High Resolution Mass Spectrometry
HRGC/LRMS	High Resolution Gas Chromatography / Low Resolution Mass Spectrometry

HV	high volumn
ICV	initial calibration verification
IPR	initial performance recovery
KC	Kansas City
LCS	laboratory control samples
LMCL	lower method calibration unit
LPR	Lower Passaic River
LPRSA	Lower Passaic River Study Area
Ltd	Limited
MB	method blank
MDL	method detection limit
mg/L	milligram per liter
mL	milliliter
mm	millimeter
MPC	measurement performance criteria
MS	matrix spike
MS/ MSD	matrix spikes /matrix spike duplicate
NA	not available or not applicable
NBSA	Newark Bay Study Area
ng/kg	nanogram per kilogram
ng/L	nanogram per liter
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
OS	oversight
OU	operable unit
oz	ounce
PAL	project action limit
PCB	polychlorinated biphenyl
PCDD/PCDF	polychlorodibenzodioxin /polychlorodibenzofurans
PE	performance evaluation
pg	picogram
pg/kg	picogram per kilogram
pg/L	picogram per liter

PM	project manager
POC	particulate organic carbon
PQLG	project quantitation limit goal
PREmis	Passaic River Estuary Management Information System
PUF	Polyurethane Foam
PWCM	Physical Water Column Monitoring
QA	quality assurance
QAC	quality assurance coordinator
QAPP	quality assurance project plan
QC	quality control
QL	quantitation limit
R	recovery
RI/FS	Remedial Investigation / Feasibility Study
RPD	relative percent difference
RM	river mile
RPM	remedial project manager
RSCC	Regional Sample Control Coordinator
RSD	relative standard deviation
S&A	sampling and analytical
SOP	standard operating procedure
SSC	suspended solids concentration
SV	small volume
TBD	to be determined
TSOP	Technical Standard Operating Procedure
TSS	total suspend solids
UFP	uniform federal policy
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 Smith) will accept split co-located high volume chemical water column study aqueous samples from the Cooperating Parties Group (CPG) during the investigation in the Lower Passaic River Study Area (LPRSA).

This Quality Assurance Project Plan (QAPP) Addendum No.11 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 analytical investigation. CDM Smith will use the various plans prepared by the CPG contractors to verify proper execution of the high volume chemical water column study sample handling, preservation and shipment.

The CDM Smith Final QAPP indicated that future oversight tasks assigned to CDM Smith would be appended with selected worksheets. The following worksheets are included in this addendum to reflect only the chemical water column study analytical procedures and requirements of the CPG's QAPPs written by AECOM, *Quality Assurance Project Plan, Remedial Investigation Water Column Monitoring/ High Volume Chemical Data Collection,* Revision 1 dated September 2012:

- Worksheet #1
- Worksheet #2
- Worksheet #3
- Worksheet #9
- Worksheet #10
- Worksheet #11
- Worksheet #12
- Worksheet #14
- Worksheet #15
- Worksheet #16
- Worksheet #18
- Worksheet #19
- Worksheet #20
- Worksheet #23
- Worksheet #24
- Worksheet #28
- Worksheet #29
- Worksheet #30
- Worksheet #36
- Worksheet #37

1.1 Summary of Chemical Water Column Monitoring Sample Acceptance

CDM Smith's oversight program is designed to provide technical review, verify the accuracy of the CPG's High Volume (HV) Chemical Water Column Monitoring *(*CWCM) study and evaluate the CPG implemented QAPP and SOPs for sampling and analysis.

The CPG is performing the HV CWCM study to provide additional data needed to develop improved partition coefficients for polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/PCDF) and polychlorinated biphenyls (PCB) Congeners from areas of low and higher salinity in the study areas; characterize their inputs at the boundary areas by sampling in Kill van Kull and above Dundee Dam; and to characterize dissolved and particulate phase concentrations in surface water. The study will be conducted over the course of eight planned sampling events:

- Five Routine Events
- Two High flow Events
- One Low Flow/Spring Tide Event

CDM Smith will accept split samples from CPG's contractor, AECOM. Split samples will be analyzed for the same selected contaminants as AECOM:

- Polychlorinated biphenyl (PCB) congeners
- Polychlorodibenzodioxin/furan (PCDD/PCDF) congeners
- Dissolved organic carbon (DOC)
- Suspended solids concentration (SSC)/ total suspended solids (TSS)
- Particulate organic carbon (POC)

This oversight QAPP details the planning and execution processes for accepting, preparing and shipping samples for analysis, and evaluation of the data.

QAPP Worksheet #1
Title and Approval Page

Document Title: **Lower Passaic River Restoration Project Quality Assurance Project Plan (QAPP) Addendum No. 11, Chemical Water Column Monitoring Study/ High Volume Chemical Data Collection**

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

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

Preparer's Address, Telephone Number, and E-mail Address: 14 Wall Street, Suite 1702
New York, NY 10005; (212) 377-4536; OxfordJM@cdmsmith.com

Preparation Date (Day/Month/Year): December 13, 2012

Investigative Organization's Project Manager/Date: C. Tsang
Signature

Frank Tsang/CDM Smith

Investigative Organization's Project QA Manager/Date: Vanessa Macua for:
Signature

Jo Nell Mullins/CDM Smith

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 (NA)

QAPP Worksheet #2
QAPP Identifying Information

Site Name/Project Name: Lower Passaic River (LPR) Restoration Project	**Title**: QAPP Addendum No. 11, Chemical Water Column Monitoring Study/High Volume Chemical Data Collection Program
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 Smith)
Contractor Number: W912DQ-08-D-0018	
Contract Title: Unrestricted Indefinite Delivery Contracts for Achitect-Engineer Services within EPA Region 2 and the Northwestern Division (MEGA Phase A).	
Task Order Number: 5	

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
LPR RI/FS Oversight QAPP, Addendum No.9: *River Mile 10.9 Characterization*	August 25, 2011
LPR RI/FS Oversight QAPP, Addendum No.10: *Low Resolution Coring Supplemental Sampling Program*	January 6, 2012

6. Organizational partners (stakeholders) and connection with lead organization: United States Environmental Protection Agency (USEPA), 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 Smith, Louis Berger Group, Inc., HDR|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 QAPP provides all the required worksheets not included herein. *This addendum addresses only the High Volume CWCM study; 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
Stephanie Vaughn	Remedial Project Manager (RPM)	EPA	(212) 637-4427	(212) 637-4393	vaughn.stephanie@epamail.epa.gov
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Sharon Budney	Deputy Project Manager	CDM Smith	(732) 590-4662	(732) 225-7851	BudneySL@cdmsmith.com
Jeniffer Oxford or other assigned quality assurance coordinator (QAC)	Regional QA Coordinator / Project QA Officer	CDM Smith	(212) 377-4536	(212) 785-6114	OxfordJM@cdmsmith.com
George Molnar	Field Task Leader	CDM Smith	(732) 590-4633	(732) 225-7851	MolnarGC@cdmsmith.com
Scott Kirchner	Analytical Services Coordinator	CDM Smith	(732)590-4677	(732) 225-7851	KirchnerSF@cdmsmith.com
James Fitzpatrick	Sediment Transport Modeler	HydroQual	(201) 529-5151	(201) 529-5728	jfitzpatrick@hydroqual.com
Candice Navaroli	Laboratory Manager	Axys Analytical Services limited (Ltd.)	(250) 655-5800 or (888) 373-0881	TBD	cnavaroli@axys.com
John Birri	Laboratory Contact	DESA Laboratory	219-769-8378	(732) 906-6886	Birri.John@epamail.epa.gov

QAPP Worksheet #9-a
Project Scoping Session Participants Sheet

Project Name: High Volume Chemical Water Column Monitoring Projected Date(s) of Sampling: Winter 2012 Project Manager: Frank Tsang- CDM Smith	Site Name: Lower Passaic River Restoration Project (LPR) RI/FS Oversight (OS) Site Location: New Jersey Operable Unit: OU2

Date of Session: November 4, 2010 and December 7, 2010
Scoping Session Purpose: To discuss the CPG SOPs and appropriate oversight analytical methods for split samples and initiate coordination between oversight efforts in the Newark Bay Study Area by The Louis Berger Group, Inc. and oversight efforts on the Lower Passaic River by CDM Smith.

Name	Affiliation	Phone #	E-mail Address	Project Role
Eugenia Naranjo	EPA	212-637-3467	naranjo.eugenia@epa.gov	Project Manager – Newark Bay Study Area RI/FS
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Elizabeth Buckrucker	USACE	816-389-3581	Elizabeth.a.buckrucker@usace.army.mil	Project Manager
Len Warner	Louis Berger Group, Inc.	914-798-3721	lwarner@louisberger.com	Project Manager - Newark Bay Study Area OS
AmyMarie Accardi-Dey	Louis Berger Group, Inc.	914-798-3712	aacardidey@louisberger.com	Oversight Leader - Newark Bay Study Area OS
Sharon Budney	CDM Smith	732-590-4662	budneysl@cdmsmith.com	Deputy Project Manager – LPR OS
Scott Kirchner	CDM Smith	732-590-4677	kirchnersf@cdmsmith.com	Project Chemist/Data Manager
Jeniffer Oxford	CDM Smith	212-377-4536	oxfordjm@cdmsmith.com	Project Chemist

Comments/Decisions:

- Oversight will be conducted by The Louis Berger Group, Inc. in the Newark Bay Study Area and by CDM Smith on the Lower Passaic River. Split samples collected by the two government contractors need to be collected consistently and analyzed following the same analytical procedures to ensure consistency in the split sample dataset.
- The Louis Berger Group, Inc. and CDM Smith will ship samples to the DESA laboratory and the Shealy and Axys subcontract laboratories consistent with CDM Smith's Master Services Agreements. Advantages to this strategy are the minimization of sample volumes and consistency with data generation. .

Action Items:
CDM Smith to send The Louis Berger Group, Inc. copies of the laboratory SOPs.
Complete coordination of analytical services.
CDM Smith and The Louis Berger Group, Inc. will complete DESA analytical services request forms for the split sample program.

QAPP Worksheet #9-b
Project Scoping Session Participants Sheet

Project Name: High Volume Chemical Water Column Monitoring Projected Date(s) of Sampling: Winter 2012 Project Manager: Frank Tsang- CDM Smith	Site Name: Lower Passaic River Restoration Project (LPR) RI/FS Oversight (OS) Site Location: New Jersey Operable Unit: OU2

Date of Session: July 3, 2012
Scoping Session Purpose: To discuss logistics and coordination for HV CWCM split sampling and comments on the additional CPG QAPP worksheets, with a focus on Oversight QAPP development and planning.

Name	Affiliation	Phone #	E-mail Address	Project Role
Eugenia Naranjo	EPA	212-637-3467	naranjo.eugenia@epa.gov	Project Manager – Newark Bay Study Area RI/FS
Len Warner	Louis Berger Group, Inc.	914-798-3721	lwarner@louisberger.com	Project Manager - Newark Bay Study Area OS
AmyMarie Accardi-Dey	Louis Berger Group, Inc.	914-798-3712	aacardidey@louisberger.com	Oversight Leader - Newark Bay Study Area OS
Sharon Budney	CDM Smith	732-590-4662	budneysl@cdmsmith.com	Deputy Project Manager – LPR OS
Scott Kirchner	CDM Smith	732-590-4677	kirchnersf@cdmsmith.com	Project Chemist/Data Manager
Jeff Rakowski	CDM Smith	732-590-4665	rakowskijj@cdmsmith.com	Field Oversight
Jeniffer Oxford	CDM Smith	212-377-4536	oxfordjm@cdmsmith.com	QA Coordinator

Comments/Decisions:

- It is difficult to capture representative split samples and to maintain consistent sample depths due to changing tides and sampler heights. Co-located samples will be collected instead.
- Split samples will follow the small volume (SV), whole water analytical procedures outlined in the CPG SV CWCM QAPP. The Louis Berger Group, Inc. recommended the collection of a subset of large volume, co-located samples in addition to the split samples to test the sensitivity of the 1-liter, whole water methodology; however, EPA directed The Louis Berger Group, Inc. and CDM Smith to collect split samples only and to follow the CPG's proposed analytical procedures.
- Field duplicates will not be collected since the filter cannot be physically split and the sample cannot be simultaneously pumped through two separate filter cartridges. Since this is a field oversight field blank samples will not be split.
- Split samples will be obtained when the CPG's contractor is not taking a duplicate sample.
- Matrix spike/matrix spike duplicate (MS/MSDs) may not be performed for the PCDD/PCDF or PCB Congeners so the internal laboratory quality control (QC) and the polyurethane foam (PUF) sampler spike will be substituted.

Action Items:
CDM Smith will discuss approach to QAPP Addendum with the Louis Berger Group, Inc. and share tasks to avoid duplication.

QAPP Worksheet #10
Problem Definition

The problem to be addressed by the project:

The CPG is conducting a study of the Lower Passaic River (LPRSA) and the Newark Bay Study Areas (NBSA) to provide additional data needed to develop improved partition coefficients for PCDD/PCDF and PCB Congeners from areas of low and higher salinity in the study areas; characterize their inputs at the boundary areas by sampling in Kill van Kull and above Dundee Dam; and to characterize dissolved and particulate phase concentrations in surface water from the LPRSA and NBSA. This data will enhance the remedial investigation (RI) site characterization and modeling efforts. CDM Smith will provide oversight and analysis of split co-located samples collected from the LPR Study Area to verify the CPG's compliance with their approved project plans and accuracy of the derived data. The Louis Berger Inc. group will provide oversight and analysis of split samples collected from the Newark Bay Study Area.

Oversight will include:

- Technical review and evaluation of CPG's HV CWCM QAPP
- Documentation of field activities, observations and deficiencies
- Acceptance of split water samples
- Sample handling, packaging and shipping to off-site laboratories
- Review of CPG-selected sampling locations
- Comparison of the 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?
- Are the CPG and CDM Smith data complete and accurate?
- Are the data sets comparable?
- Is there a graphically or statistically observable analytical bias between the CPG and CDM Smith data?
- Are the relative percent differences (RPDs) between the CPG and CDM Smith data within the measurement performance criteria?

Secondary data: See Worksheet 13 of the CPG QAPP (AECOM 2012)

QAPP Worksheet #10
Problem Definition

The possible classes of contaminants and the affected matrices:

Split surface water samples will be collected for the following chemical analyses:

- Polychlorinated biphenyl (PCB) congeners
- Polychlorodibenzodioxin/furan (PCDD/PCDF)
- Dissolved organic carbon (DOC)
- Suspended solids concentration (SSC)
- Particulate organic carbon (POC)

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 field observations and split sample data will enable CDM Smith to perform technical review and evaluation on the CPG field program, analytical data and reports, and to assess any potential bias in the CPG dataset as compared to the split samples.

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

- If sample results are not comparable with CPGs, then CDM Smith will note deviations in the Data Reports submitted to USACE and EPA. The CDM Smith Project Manager (PM), USACE PM and EPA regional project manager (RPM) will be informed if there are deviations.
- If the CPG team needs to relocate survey locations, reprioritize analytical parameters, or if there are any changes to the planned analytical program, CDM Smith will communicate this change to the USACE and EPA and document it in the Data Reports.

CDM Smith will present the data findings in a Data 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 Smith, and Stakeholders (as necessary).

What Will the Data be Used For?

1) The CPG will use the data to improve existing data quality and quantity to adequately characterize the chemical concentrations in the solid and dissolved phases throughout the LPRSA; 2) reduce the level of uncertainty in the sorption partition coefficients used in the contaminant fate and transport (CFT) model for the LPRSA and 3) characterize the inputs of PCDD/PCDFs and PCBs at the boundaries of the LPRSA and Newark Bay Study Area (NBSA) by HV sampling in Kill van Kull and above Dundee Dam. The results will support the RI characterization and modeling.

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

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. The data comparison will be presented in a table showing the relative percent difference for values that are 5 times the quantitation limits. 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), the data comparison will be completed on select parameters per chemical class. Parameters will be selected by the project chemist/ 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.

CDM Smith's quality control (QC) data will be used to determine CDM Smith's split sample 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 the data quality indicators (DQIs).

To further achieve these objectives, CDM Smith field personnel will observe and monitor the CPG contractor's implementation of the HV QAPP and will note any deviations. Deviations will be brought to the attention of the CPG's contractor, and reported to the CDM Smith project manager who will communicate this information to the USACE PM and EPA RPM. These will be documented in ongoing and Final Reports and include a discussion of the impact of the deviation(s) on the data quality. The CPG contractor's activities will be documented in the field logbook and oversight forms. A copy of the oversight form is provided in Appendix B of CDM Smith's Final QAPP.

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

What Type of Data is Needed?

Co-located water column dissolved and particulate phase sample(s) will be accepted at the location(s) and depth(s) selected by mutual agreement between CDM Smith and the CPG contractor or as directed by the CDM Smith Deputy PM or the USACE/EPA project managers.

Chemical data will be obtained from the split samples accepted from the CPG. Low reporting limits are required for the organic parameters as shown on QAPP worksheet #15.

How much data are needed?

The CPG will only collect six samples so CDM Smith will accept "split" co-located samples from one or two sampling locations; either a dissolved and particulate phase from one location or each phase from a separate location. Worksheets #11 and 18 of the CPG's CWCM QAPP show the planned locations for sampling.

Approximately 10 percent of the samples will be split (one whole sample). Field rinsate blanks and field duplicates will not be accepted. Oversight activities are listed in Worksheet 10.

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

Definitive level data are required to produce the data quality required. Full validation of the data will enable comparison to the CPG generated data set. 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 Smith has attempted to use comparable methods and obtain similar reporting limits to the CPG's. CDM Smith's oversight staff will document whether the HV CWCM study is performed in compliance with the CPG's QAPP. The representativeness of the data is dependent on the sampling design established by the CPG. Split samples will be obtained by the alternate filling of the sample bottles with the CPG's contractor with a sufficient volume to fulfill analytical needs.

The laboratory reporting limits (contract required quantitation limits (CRQLs) for DESA data, or reporting limits (RLs) for subcontract laboratory data), need to be below or equal to the CPG's project required quantitation limits goals (PQLs) or the CPG's achievable laboratory quantitation limits (QLs). CDM Smith will notify EPA's Regional Sample Control Coordinator (RSCC) or the subcontract laboratory and request lower reporting limits to achieve the project data quality objectives for sensitivity as needed.

Validation of the whole water POC, DOC, and SSC data will be performed by Division of Environmental Science and Assessment (DESA)/ EPA; the particulate and dissolved fractions PCDD/PCDF and PCB Congener data will be analyzed by a subcontract laboratory, Axys, and validated by CDM Smith.

In addition, to ensure that measurement performance criteria for usability (criteria for DQIs) are met, all CDM Smith data will be subject to a data usability

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assessment. The inputs will be the EPA generated validation reports and CDM Smith's data validation summary reports. Measurement performance criteria presented in Worksheets No.12, 28, 35 and 36 will be evaluated as discussed on Worksheet No. 37. The results will be presented in a CDM Smith 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.

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

When – Split co-located surface water samples will be accepted from the CPG's contractor Gradient. The CPG's contractor will collect the samples in winter 2012. This HVCWCM survey will be performed according to the CPG's schedule. The exact sampling dates are to be determined.

Where – The surface water will be collected from the LPRSA locations shown on Figure 1 of the CPG QAPP (AECOM 2012). A dissolved phase and a solid phase sample will be accepted from one location or the dissolved phase from one location and the solid phase from another location. The collocated sample location(s) will be determined by the CDM Smith field oversight personnel in consultation with the CDM Smith deputy project manager and EPA.

How – Sampling procedures are described in the CPG's QAPP (AECOM 2012) (various worksheets) and the Field SOPs (Appendix A of the CPG QAPP). True split samples cannot be obtained so CDM Smith will accept co-located samples collected by the CPG's contractor

Who will collect and generate the data?

CDM Smith oversight staff will record field observations in logbooks and on the Field Oversight Form in Appendix O of QAPP Addendum No. 9. The CPG's contractor will provide the required volume or mass of the samples to CDM Smith who will label, pack and ship to the appropriate laboratory. The CPG' contractor will process samples to obtain both dissolved and particulate phases. The analytical laboratories outlined in this Final QAPP Addendum will generate the data.

Summary of the Field Program Sample Collection

The split samples will be collected as collocated samples since splitting the sample by use of an inline splitter or splitting the PUF would be problematic. The collocated split sample will be drawn through a sample tube attached to the environmental sample tube. It will however, be collected using a separated Gravity sampling system that will be kept at the same sampling pump rate and as needed the pump will be turned off to have the filters changed at the same time the environmental sample is being collected.

How will the data be reported?

- Accepted split co-located samples will be recorded as described in CDM Smith's Final QAPP using field logbooks in accordance with technical standard operating procedure (TSOP) 4-1 provided in Appendix C of the Final QAPP.
- Results will be reported in text format and will include a discussion of the data quality, deviations from the QAPP, and oversight data comparability with

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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 Smith for use in the data assessment and evaluation. ▪ Sample results generated by CDM Smith's subcontract laboratory will be e-mailed to CDM Smith for review and validation. ▪ Data reporting is further covered in the Final QAPP.
How will the data be archived? ▪ The Final QAPP contains other archival information.

QAPP Worksheet #12-a1
Measurement Performance Criteria Table

Matrix	Separated Solids (Particulate phase)
Analytical Group	PCB Congeners
Concentration Level	Low

Sampling Procedure	**Analytical Method/ SOP**	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria[2] (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 Smith will accept splits	EPA Method 1668A AXYS Laboratory MLA-010 Revision 10[1]	Precision	RPD ≤ 40% if concentration ≥5 CRQL	Split samples	S & A
		Precision	±20% of mean if concentration >10 DL[3]	Laboratory duplicate to be performed on the sample extract	A
		Accuracy/Bias	Supplier Certified Limits Per laboratory or method SOP (70-130% of native analytes and 50-150% for surrogates)	CRM Calibration Verification Sample (the sediment CRM will be used)	A
		Accuracy/Bias Precision	60-140 %recovery RSD ≤ 40%	Initial Precision and Recovery	A
		Accuracy/Bias	Per laboratory SOP Warning 70-130%R; Accept 50-150 %recovery	LCS or OPR	A
		Accuracy/ Representativeness	0-6 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks DV	S
		Comparability	Comparable units, and methods	Assessed during DQA	S & A
		Completeness	≥ 90% collection and analysis	Assessed during DQA	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15 and laboratory SOP)	Method blanks assessed during DV and DQA	S & A

Notes:

1. AXYS SOP MLA-010 (USEPA Method 1668 Version A), Refer to Worksheet 23 for project specific modifications.
2. The assigned laboratory must perform and meet all the quality assurance requirements specified in the method.
3. The detection limits (DLs) referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits. Since sample duplicates cannot be collected a duplicate analysis may be performed on the sample extract.

QAPP Worksheet #12-a2
Measurement Performance Criteria Table

Matrix	Solids - Sorption Media (PUF) (Dissolved phase)
Analytical Group	PCB Congeners
Concentration Level	Low

Sampling Procedure	**Analytical Method/ SOP**	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria[2] (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 Smith will accept splits	EPA Method 1668A AXYS Laboratory MLA-010 Revision 10[1]	Precision	RPD ≤ 40% if concentration ≥5 CRQL	Split samples	S & A
		Precision	±20% of mean if concentration >10DL[3]	Laboratory duplicate to be performed on the sample extract	A
		Accuracy/Bias	Supplier Certified Limits Per laboratory or method SOP (70-130% of native analytes and 50-150% for surrogates)	CRM Calibration Verification Sample	A
		Accuracy/Bias Precision	60-140 %recovery RSD ≤ 40%	Initial Precision and Recovery	A
		Accuracy/Bias	Per laboratory SOP Warning 70-130%R; Accept 50-150 %recovery	LCS, OPR	A
		Accuracy/ Representativeness	0-6 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks DV	S
		Comparability	Comparable units, and methods	Assessed during DQA	S & A
		Completeness	≥ 90% collection and analysis	Assessed during DQA	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15 and laboratory SOP)	Method blanks assessed during DV and DQA	S & A

Notes:

1. AXYS SOP MLA-010 (USEPA Method 1668 Version A), Refer to Worksheet 23 for project specific modifications.
2. The assigned laboratory must perform and meet all the quality assurance requirements specified in the method.
3. The detection limits (DLs) referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits. Since sample duplicates cannot be collected a duplicate analysis may be performed on the sample extract.

QAPP Worksheet #12-b1
Measurement Performance Criteria Table

Matrix	Separated Solids (Particulate phase)
Analytical Group	PCDD/PCDF
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)[2]	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 Smith will accept split	USEPA Method 1613B Axys Analytical Services SOP MLA-017 rev20[1]	Precision	RPD ≤ 40% if concentration ≥5 QL	Split samples	S & A
		Precision	±20% of mean if concentration >10DL[3]	Laboratory duplicate to be performed on the sample extract	A
		Accuracy/Bias Precision	70-130 %recovery /per laboratory SOP RPD ≤ 40%	CRM LCS/LCSD MS/MSD	S & A
		Accuracy/ Representativeness	0-6 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks DV	S
		Precision	Per laboratory SOP	Initial precision and recovery standard (IPR)	A
		Accuracy/Bias	Various % recovery per laboratory SOP		
		Accuracy/Bias	70-130 %recovery	Ongoing precision and recovery (OPR)	A
		Accuracy/Bias	17-130% recovery	Surrogate standards	A
		Comparability	Comparable units, and methods	Evaluated during DQA	S & A
		Completeness	≥ 90% collection and analysis	Evaluated during DQA	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15 and laboratory SOP)	Method blanks assessed during DV and DQA	S & A

Notes

1. AXYS SOP MLA-017 (USEPA Method 1613 Version B), Refer to Worksheet 23 for project specific modifications.
2. The assigned laboratory must perform and meet all the quality assurance requirements specified in the method.
3. The detection limits (DLs) referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits. Since sample duplicates cannot be collected a duplicate analysis may be performed on the sample extract.

QAPP Worksheet #12-b2
Measurement Performance Criteria Table

Matrix	Solids - Sorption Media (PUF) (Particulate phase)
Analytical Group	PCDD/PCDF
Concentration Level	Low

Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)[2]	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 Smith will accept split	USEPA Method 1613B Axys Analytical Services SOP MLA-017 rev20[1]	Precision	RPD ≤ 40% if concentration ≥5 QL	Split samples	S & A
		Precision	±20% of mean if concentration >10DL[3]	Laboratory duplicate to be performed on the sample extract	A
		Accuracy/Bias Precision	70-130 %recovery (or laboratory SOP) RPD ≤ 40%	CRM LCS/LCSD; MS/MSD	S & A
		Accuracy/ Representativeness	0-6 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks DV	S
		Precision	Per laboratory SOP	Initial precision and recovery standard (IPR)	A
		Accuracy/Bias	Various % recovery per laboratory SOP		
		Accuracy/Bias	70-130 %recovery	Ongoing precision and recovery (OPR)	A
		Accuracy/Bias	17-130% recovery	Surrogate standards	A
		Comparability	Comparable units, and methods	Evaluated during DQA	S & A
		Completeness	≥ 90% collection and analysis	Evaluated during DQA	S & A
		Sensitivity/ accuracy	≤ QLs (WS#15 and laboratory SOP)	Method blanks assessed during DV and DQA	S & A

Notes:
1. AXYS SOP MLA-017 (USEPA Method 1613 Version B), Refer to Worksheet 23 for project specific modifications.
2. The assigned laboratory must perform and meet all the quality assurance requirements specified in the method.
3. The detection limits (DLs) referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits. Since sample duplicates cannot be collected a duplicate analysis may be performed on the sample extract.

QAPP Worksheet #14
Summary of Project Tasks

Sampling Tasks:
The CPG's contractors, AECOM/Gravity Environmental, will pump water through a centrifuge-like vortex solids separation system and through a filter in the sampling train; solids captured in the separation system and the solids on the filter are combined to represent the particulate phase sample. Water is then passed through a PUF sorption medium to capture organic analytes in the filtrate. CDM Smith will accept one co-located sample for the dissolved and one for the particulate phase from the CPG's sampling contractor during the CWCM sampling event. The split co-located sample will be obtained when a duplicate is not being collected by AECOM.

POC, DOC, and SSC will be whole water samples collected as described in the SV CWCM QAPPs. A split of the time weighted composite will be accepted by alternate filling of the CPG Contractor and CDM Smith sample bottles. CDM Smith's oversight staff will package, label and ship the sample fractions to the DESA laboratory and the subcontract laboratory as outlined on QAPP Worksheet 30.

Analysis Tasks:
The sample fractions will be analyzed for PCB congeners, PCDD/PCDF, DOC, POC, and SSC.

Quality Control Tasks: CDM Smith will observe CPG's sampling of the water column under normal flow conditions (400 - 3,000 cubic feet per second) which are consistent with the Small Volume CWCM events. Field duplicate and field rinsate blank samples will not be collected. The CDM Smith 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 Smith. Data generated by the CPG - field program will be used as shown on worksheet 11 of the CPG's Remedial Investigation Water Column Monitoring/High Volume Chemical Data Collection QAPP.

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

Documentation and Records: Records of accepted samples will be documented in accordance with TSOP 4-1 provided in Appendix C of the Final QAPP. The HV CWCM data results will be documented in the following:

1. Data Validation reports
2. Chain of custody (COCs), Analytical Servcices Tracking System (ANSETS), and Trip Report
3. Oversight summary report
4. Data Quality and Usability Summary Report

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

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

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase)
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-1	2051-60-7	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-2	2051-61-8	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-3	2051-62-9	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-4	13029-08-8	50	4.0	See Table 2 of method	See Method	15	4.0
PCB-5	16605-91-7	50	20	See Table 2 of method	See Method	8.4	20
PCB-6	25569-80-6	10	20	See Table 2 of method	See Method	7.7	20
PCB-7	33284-50-3	50	20	See Table 2 of method	See Method	7.9	20
PCB-8	34883-43-7	10	20	See Table 2 of method	See Method	7.2	20
PCB-9	34883-39-1	50	20	See Table 2 of method	See Method	7.5	20
PCB-10	33146-45-1	50	20	See Table 2 of method	See Method	7.9	20
PCB-11*	2050-67-1	40	20	See Table 2 of method	See Method	8.2	20
PCB-12 (Co-elutes with PCB-13)	2974-92-7	50	20	See Table 2 of method	See Method	8.2	20
PCB-13 (Co-elutes with PCB-12)	2974-90-5	50	20	See Table 2 of method	See Method	8.2	20
PCB-14	34883-41-5	50	20	See Table 2 of method	See Method	7.8	20
PCB-15	2050-68-2	10	20	See Table 2 of method	See Method	8.5	20
PCB-16	38444-78-9	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-17	37680-66-3	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-18 (Co-elutes with PCB-30)	37680-65-2	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-19	38444-73-4	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-20 (Co-elutes with PCB-28)	38444-84-7	80	4.0	See Table 2 of method	See Method	0.51	4.0
PCB-21 (Co-elutes with PCB-33)	55702-46-0	50	4.0	See Table 2 of method	See Method	0.50	4.0
PCB-22	38444-85-8	10	4.0	See Table 2 of method	See Method	0.53	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase)
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-23	55720-44-0	10	4.0	See Table 2 of method	See Method	0.52	4.0
PCB-24	55702-45-9	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-25	55712-37-3	10	4.0	See Table 2 of method	See Method	0.50	4.0
PCB-26 (Co-elutes with PCB-29)	38444-81-4	10	4.0	See Table 2 of method	See Method	0.51	4.0
PCB-27	38444-76-7	10	4.0	See Table 2 of method	See Method	1.0	4.0
PCB-28 (Co-elutes with PCB-20)	7012-37-5	80	4.0	See Table 2 of method	See Method	0.51	4.0
PCB-29 (Co-elutes with PCB-26)	15862-07-4	10	4.0	See Table 2 of method	See Method	0.51	4.0
PCB-30 (Co-elutes with PCB-18)	35693-92-6	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-31	16606-02-3	50	4.0	See Table 2 of method	See Method	0.5	4.0
PCB-32	38444-77-8	10	4.0	See Table 2 of method	See Method	0.5	4.0
PCB-33 (Co-elutes with PCB-21)	38444-86-9	50	4.0	See Table 2 of method	See Method	0.50	4.0
PCB-34	37680-68-5	10	4.0	See Table 2 of method	See Method	0.52	4.0
PCB-35	37680-69-6	10	4.0	See Table 2 of method	See Method	0.54	4.0
PCB-36	38444-87-0	10	4.0	See Table 2 of method	See Method	0.52	4.0
PCB-37	38444-90-5	10	4.0	See Table 2 of method	See Method	0.56	4.0
PCB-38	53555-66-1	10	4.0	See Table 2 of method	See Method	0.52	4.0
PCB-39	38444-88-1	10	4.0	See Table 2 of method	See Method	0.52	4.0
PCB-40 (Co-elutes with PCB-41, 71)	38444-93-8	10	4.0	See Table 2 of method	See Method	0.74	4.0
PCB-41 (Co-elutes with PCB-40, 71)	52663-59-9	10	4.0	See Table 2 of method	See Method	0.74	4.0
PCB-42	36559-22-5	10	4.0	See Table 2 of method	See Method	0.75	4.0
PCB-43	70362-46-8	10	4.0	See Table 2 of method	See Method	0.86	4.0
PCB-44 (Co-elutes with PCB-47, -65)	41464-39-5	10	4.0	See Table 2 of method	See Method	0.66	4.0
PCB-45 (Co-elutes with PCB-51)	70362-45-7	10	4.0	See Table 2 of method	See Method	0.70	4.0
PCB-46	41464-47-5	10	4.0	See Table 2 of method	See Method	0.80	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase)
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-47 (Co-elutes with PCB-44, -65)	2437-79-8	10	4.0	See Table 2 of method	See Method	0.66	4.0
PCB-48	70362-47-9	10	4.0	See Table 2 of method	See Method	0.72	4.0
PCB-49 (Co-elutes with PCB-69)	41464-40-8	10	4.0	See Table 2 of method	See Method	0.61	4.0
PCB-50 (Co-elutes with PCB-53)	62796-65-0	10	4.0	See Table 2 of method	See Method	0.67	4.0
PCB-51 (Coleutes with PCB-45)	68194-04-7	10	4.0	See Table 2 of method	See Method	0.70	4.0
PCB-52	35693-99-3	50	4.0	See Table 2 of method	See Method	0.67	4.0
PCB-53 (Co-elutes with PCB-50)	41464419	10	4.0	See Table 2 of method	See Method	0.67	4.0
PCB-54	15968-05-5	10	4.0	See Table 2 of method	See Method	0.54	4.0
PCB-55	74338-24-2	10	4.0	See Table 2 of method	See Method	2.4	4.0
PCB-56	41464-43-1	10	4.0	See Table 2 of method	See Method	2.5	4.0
PCB-57	70424-67-8	10	4.0	See Table 2 of method	See Method	2.4	4.0
PCB-58	41464-49-7	10	4.0	See Table 2 of method	See Method	2.4	4.0
PCB-59 (Co-elutes with PCB-62, -75)	74472-33-6	10	4.0	See Table 2 of method	See Method	0.55	4.0
PCB-60	33025-41-1	10	4.0	See Table 2 of method	See Method	2.4	4.0
PCB-61 (Co-elutes with PCB-70, -74, -76)	33284-53-6	50	4.0	See Table 2 of method	See Method	2.3	4.0
PCB-62 (Co-elutes with PCB-59, -75)	54230-22-7	10	4.0	See Table 2 of method	See Method	0.55	4.0
PCB-63	74472-34-7	100	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-64	52663-58-8	10	4.0	See Table 2 of method	See Method	0.55	4.0
PCB-65 (Co-elutes with PCB-44, -47)	33284-54-7	10	4.0	See Table 2 of method	See Method	0.66	4.0
PCB-66	32598-10-0	10	4.0	See Table 2 of method	See Method	2.3	4.0
PCB-67	73575-53-8	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-68	73575-52-7	10	4.0	See Table 2 of method	See Method	2.3	4.0
PCB-69	60233-24-1	10	4.0	See Table 2 of method	See Method	0.61	4.0
PCB-70 (Co-elutes with PCB-61, -74, -76)	32598-11-1	50	4.0	See Table 2 of method	See Method	2.3	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase)
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-71 (Co-elutes with PCB-40, -41)	41464-46-4	10	4.0	See Table 2 of method	See Method	0.74	4.0
PCB-72	41464-42-0	10	4.0	See Table 2 of method	See Method	2.3	4.0
PCB-73	74338-23-1	10	4.0	See Table 2 of method	See Method	0.56	4.0
PCB-74 (Co-elutes with PCB-61, -70, -76)	32690-93-0	50	4.0	See Table 2 of method	See Method	2.3	4.0
PCB-75 (Co-elutes with PCB-59, -62)	32598-12-2	10	4.0	See Table 2 of method	See Method	0.55	4.0
PCB-76(Co-elutes with PCB-61, -70, -74)	70362-48-0	50	4.0	See Table 2 of method	See Method	2.3	4.0
PCB-77	32598-13-3	10	4.0	See Table 2 of method	See Method	2.7	4.0
PCB-78	70362-49-1	10	4.0	See Table 2 of method	See Method	2.4	4.0
PCB-79	41464-48-6	10	4.0	See Table 2 of method	See Method	2.0	4.0
PCB-80	33284-52-5	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-81	70362-50-4	10	4.0	See Table 2 of method	See Method	2.6	4.0
PCB-82	52663-62-4	10	4.0	See Table 2 of method	See Method	2.7	4.0
PCB-83 (Co-elutes with PCB-99)	60145-20-2	10	4.0	See Table 2 of method	See Method	1.5	4.0
PCB-84	52663-60-2	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-85 (Co-elutes with PCB-116, -117)	65510-45-4	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-86 (Co-elutes with PCB-87, -97, -108, -119, -125)	55312-69-1	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-87 (Co-elutes with PCB-86, -97, -108, -119, -125)	38380-02-8	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-88 (Co-elutes with PCB-91)	55215-17-3	100	4.0	See Table 2 of method	See Method	1.5	4.0
PCB-85 (Co-elutes with PCB-116, -117)	73575-57-2	10	4.0	See Table 2 of method	See Method	1.6	4.0
PCB-90 (Co-elutes with PCB-101, -113)	68194-07-0	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-91 (Co-elutes with PCB-88)	68194-05-8	10	4.0	See Table 2 of method	See Method	1.5	4.0
PCB-92	52663-61-3	10	4.0	See Table 2 of method	See Method	1.4	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase)
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-93 (Co-elutes with PCB-95, -98, -100, -02)	73575-56-1	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-94	73575-55-0	10	4.0	See Table 2 of method	See Method	1.6	4.0
PCB-95 (Co-elutes with PCB-93, -98, -100,-102)	38379-99-6	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-96	73575-54-9	10	4.0	See Table 2 of method	See Method	0.70	4.0
PCB-97 (Co-elutes with PCB-86, -87, -108, -119, -125)	41464-51-1	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-98 (Co-elutes with PCB-93, -95, -100, -102)	60233-25-2	100	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-99 (Co-elutes with PCB-83)	38380-01-7	10	4.0	See Table 2 of method	See Method	1.5	4.0
PCB-100 (Co-elutes with PCB-93, -95, -98, -102)	39485-83-1	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-101 (Co-elutes with PCB-90, -113)	37680-73-2	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-102 (Co-elutes with PCB-93, -95, -98, -100)	68194-06-9	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-103	60145-21-3	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-104	56558-16-8	10	4.0	See Table 2 of method	See Method	0.60	4.0
PCB-105	32598-14-4	10	20	See Table 2 of method	See Method	3.7	20
PCB-106	70424-69-0	10	20	See Table 2 of method	See Method	3.1	20
PCB-107 (Co-elutes with PCB-124)	70424-68-9	10	20	See Table 2 of method	See Method	3.6	20
PCB-108 (Co-elutes with PCB-86, -87, -97, -119, -125)	70362-41-3	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-109	74472-35-8	10	20	See Table 2 of method	See Method	3.3	20

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase)
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-110 (Co-elutes with PCB-115)	38380-03-9	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-111	39635-32-0	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-112	74472-36-9	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-113 (Co-elutes with PCB-90, -101)	68194-10-5	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-114	74472-37-0	10	20	See Table 2 of method	See Method	3.8	20
PCB-115 (Co-elutes with PCB-110)	74472-38-1	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-116 (Co-elutes with PCB-85, -117)	18259-05-7	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-117 (Co-elutes with PCB-85, -116)	68194-11-6	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-118	31508-00-6	10	20	See Table 2 of method	See Method	3.5	20
PCB-119 (Co-elutes with PCB-86, -87, -97, -108, -125)	56558-17-9	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-120	68194-12-7	10	4.0	See Table 2 of method	See Method	0.99	4.0
PCB-121	56558-18-0	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-122	76842-07-4	10	20	See Table 2 of method	See Method	3.8	20
PCB-123	65510-44-3	10	20	See Table 2 of method	See Method	3.8	20
PCB-124	70424-70-3	10	20	See Table 2 of method	See Method	3.6	20
PCB-125	74472-39-2	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-126	57465-28-8	10	20	See Table 2 of method	See Method	4.4	20
PCB-127	39635-33-1	10	20	See Table 2 of method	See Method	3.4	20
PCB-128	38380-07-3	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-129	55215-18-4	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-130	52663-66-8	10	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-131	61798-70-7	10	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-132	38380-05-1	10	4.0	See Table 2 of method	See Method	2.2	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase)
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-133	35694-04-3	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-134 (Co-elutes with PCB-143)	52704-70-8	10	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-135 (Co-elutes with PCB-151 -154)	52744-13-5	10	4.0	See Table 2 of method	See Method	0.95	4.0
PCB-136	38411-22-2	10	4.0	See Table 2 of method	See Method	0.71	4.0
PCB-137	35694-06-5	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-138 (Co-elutes with PCB-129, -160, -163)	35065-28-2	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-139 (Co-elutes with PCB-140)	56030-56-9	10	4.0	See Table 2 of method	See Method	2.0	4.0
PCB-140 (Co-elutes with PCB-139)	59291-64-4	10	4.0	See Table 2 of method	See Method	2.0	4.0
PCB-141	52712-04-6	10	4.0	See Table 2 of method	See Method	1.9	4.0
PCB-142	41411-61-4	10	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-143 (Co-elutes with PCB-134)	68194-15-0	10	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-144	68194-14-9	10	4.0	See Table 2 of method	See Method	0.96	4.0
PCB-145	74472-40-5	10	4.0	See Table 2 of method	See Method	0.81	4.0
PCB-146	51908-16-8	10	4.0	See Table 2 of method	See Method	1.8	4.0
PCB-147* (Co-elutes with PCB-149)	68194-13-8	10	4.0	See Table 2 of method	See Method	2.0	4.0
PCB-148*	74472-41-6	10	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-149* (Co-elutes with PCB-147)	38380-04-0	10	4.0	See Table 2 of method	See Method	2.0	4.0
PCB-150	68194-08-1	10	4.0	See Table 2 of method	See Method	0.75	4.0
PCB-151 (Co-elutes with PCB-135, -154)	52663-63-5	10	4.0	See Table 2 of method	See Method	0.95	4.0
PCB-152	68194-09-2	80	4.0	See Table 2 of method	See Method	0.67	4.0
PCB-153	35065-27-1	10	4.0	See Table 2 of method	See Method	1.6	4.0
PCB-154 (Co-elutes with PCB-135, -151)	60145-22-4	10	4.0	See Table 2 of method	See Method	0.95	4.0
PCB-155	33979-03-2	10	4.0	See Table 2 of method	See Method	0.51	4.0
PCB-156 (Co-elutes with PCB-157)	38380-08-4	10	4.0	See Table 2 of method	See Method	1.8	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase)
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-157 (Co-elutes with PCB-156)	69782-90-7	10	4.0	See Table 2 of method	See Method	1.8	4.0
PCB-158	74472-42-7	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-159	39635-35-3	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-160 (Co-elutes with PCB-129, -138, -163)	41411-62-5	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-161	74472-43-8	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-162	39635-34-2	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-163 (Co-elutes with PCB-129, -138, -160)	74472-44-9	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-164	74472-45-0	10	4.0	See Table 2 of method	See Method	1.6	4.0
PCB-165	74472-46-1	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-166 (Co-elutes with PCB-128)	41411-63-6	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-167	52663-72-6	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-168 (Co-elutes with PCB-153)	59291-65-5	10	4.0	See Table 2 of method	See Method	1.6	4.0
PCB-169	32774-16-6	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-170	35065-30-6	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-171 (Co-elutes with PCB-173)	52663-71-5	10	4.0	See Table 2 of method	See Method	1.0	4.0
PCB-172	52663-74-8	10	4.0	See Table 2 of method	See Method	1.0	4.0
PCB-173 (Co-elutes with PCB-171)	68194-16-1	10	4.0	See Table 2 of method	See Method	1.0	4.0
PCB-174	38411-25-5	10	4.0	See Table 2 of method	See Method	1.0	4.0
PCB-175	40186-70-7	10	4.0	See Table 2 of method	See Method	0.93	4.0
PCB-176	52663-65-7	10	4.0	See Table 2 of method	See Method	0.75	4.0
PCB-177	52663-70-4	10	4.0	See Table 2 of method	See Method	1.0	4.0
PCB-178	52663-67-9	10	4.0	See Table 2 of method	See Method	1.0	4.0
PCB-179	52663-64-6	10	4.0	See Table 2 of method	See Method	0.74	4.0
PCB-180 (Co-elutes with PCB-193)	35065-29-3	10	4.0	See Table 2 of method	See Method	0.90	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase)
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-181	74472-47-2	10	4.0	See Table 2 of method	See Method	1.0	4.0
PCB-182	60145-23-5	10	4.0	See Table 2 of method	See Method	0.95	4.0
PCB-183 (Co-elutes with PCB-185)	52663-69-1	10	4.0	See Table 2 of method	See Method	0.94	4.0
PCB-184	74472-48-3	10	4.0	See Table 2 of method	See Method	0.71	4.0
PCB-185 (Co-elutes with PCB-183)	52712-05-7	10	4.0	See Table 2 of method	See Method	0.94	4.0
PCB-186	74472-49-4	10	4.0	See Table 2 of method	See Method	0.78	4.0
PCB-187	52663-68-0	10	4.0	See Table 2 of method	See Method	0.90	4.0
PCB-188	74487-85-7	10	4.0	See Table 2 of method	See Method	0.62	4.0
PCB-190	41411-64-7	10	4.0	See Table 2 of method	See Method	0.78	4.0
PCB-191	74472-50-7	10	4.0	See Table 2 of method	See Method	0.73	4.0
PCB-192	74472-51-8	10	4.0	See Table 2 of method	See Method	0.73	4.0
PCB-193 (Co-elutes with PCB-180)	69782-91-8	10	4.0	See Table 2 of method	See Method	0.83	4.0
PCB-194	35694-08-7	10	4.0	See Table 2 of method	See Method	0.90	4.0
PCB-195	52663-78-2	10	4.0	See Table 2 of method	See Method	0.85	4.0
PCB-196	42740-50-1	10	4.0	See Table 2 of method	See Method	0.94	4.0
PCB-197 (Co-elutes with PCB-200)	33091-17-7	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-198 (Co-elutes with PCB-199)	68194-17-2	10	4.0	See Table 2 of method	See Method	0.95	4.0
PCB-199 (Co-elutes with PCB-198)	52663-75-9	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-200 (Co-elutes with PCB-197)	52663-73-7	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-201	40186-71-8	10	4.0	See Table 2 of method	See Method	0.95	4.0
PCB-202	2136-99-4	10	4.0	See Table 2 of method	See Method	0.96	4.0
PCB-203	52663-76-0	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-204	74472-52-9	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-205	74472-53-0	10	4.0	See Table 2 of method	See Method	0.96	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase)
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-206	40186-72-9	10	4.0	See Table 2 of method	See Method	0.69	4.0
PCB-207	52663-79-3	10	20	See Table 2 of method	See Method	3.2	20
PCB-208	52663-77-1	10	4.0	See Table 2 of method	See Method	2.5	4.0
PCB-209	2051-24-3	10	4.0	See Table 2 of method	See Method	2.5	4.0

Notes:
1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The project quantitation limit goals (PQLGs) are those listed for the individual PCB Congeners listed in the CPG RI/FS QAPP, *Remedial Investigation Water Column Monitoring/High Volume Chemical Data Collection (September 2012)*.
3. See Method 1688A Table 2 for a list of PCB Congener MDLs. Estimated with interferences.
4. Achievable Laboratory EDLs are based on Axys Analytical Services' "Sample Detection Limits", from the pre-program analytical work with the PUF medium [average of three analytical runs: PUF blank (Lab ID: WG40846-101) and two low level IPR samples (Lab ID: WG40846-106 and 107)], which are determined by converting the area equivalent of 2.5 times the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. These are determined individually for every sample analysis run and accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up.

   Achievable Laboratory QL is based on Axys Analytical Services' "Lower Method Calibration Limit (LMCL)", and is determined by prorating the concentration of the lowest calibration solution for sample size and extract volume, according to the following equation ((lowest level calibration concentration) × (extract volume))/sample size. The Achievable Laboratory QLs account for the pre-program analytical work with the PUF medium.

* PCB 147/149, PCB 148, and PCB 11 in PUF Medium: During the pre-program analytical work of the PUF medium, an IPR study was conducted on the PUF medium; all PCB congeners were recovered within the acceptable range. In addition to this IPR study, two low-level spikes on the PUF medium were evaluated. In this test, PCB 147/149 had a percent recovery of 151; PCB 148 had a percent recovery of 141; and PCB 11 had a percent recovery of 143 (average of two analytical runs). EPA Method 1668 does not have criteria for these PCB congeners; however, it is recognized that the recoveries were outside the guidance of 60-140 percent, which has been established for the other PCB congeners. These PCB co-elutions will be reported in the split sample EDD by the laboratory, and split sample comparisons will be conducted on these co-elutions.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Filtered solids
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low - picogram per gram (pg/g)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-1	2051-60-7	10	4.0	See Table 2 of method	See Method	2.7	4.0
PCB-2	2051-61-8	10	4.0	See Table 2 of method	See Method	1.5	4.0
PCB-3	2051-62-9	10	20	See Table 2 of method	See Method	4.2	20
PCB-4	13029-08-8	50	20	See Table 2 of method	See Method	4.6	20
PCB-5	16605-91-7	50	4.0	See Table 2 of method	See Method	3.5	4.0
PCB-6	25569-80-6	10	4.0	See Table 2 of method	See Method	3.2	4.0
PCB-7	33284-50-3	50	20	See Table 2 of method	See Method	4.7	20
PCB-8	34883-43-7	10	4.0	See Table 2 of method	See Method	3.7	4.0
PCB-9	34883-39-1	50	20	See Table 2 of method	See Method	4.6	20
PCB-10	33146-45-1	50	4.0	See Table 2 of method	See Method	3.2	4.0
PCB-11	2050-67-1	40	100	See Table 2 of method	See Method	25	100
PCB-12 (Co-elutes with PCB-13)	2974-92-7	50	4.0	See Table 2 of method	See Method	3.4	4.0
PCB-13 (Co-elutes with PCB-12)	2974-90-5	50	4.0	See Table 2 of method	See Method	3.4	4.0
PCB-14	34883-41-5	50	4.0	See Table 2 of method	See Method	3.3	4.0
PCB-15	2050-68-2	10	20	See Table 2 of method	See Method	4.7	20
PCB-16	38444-78-9	10	4.0	See Table 2 of method	See Method	3.3	4.0
PCB-17	37680-66-3	10	20	See Table 2 of method	See Method	4.3	20
PCB-18 (Co-elutes with PCB-30)	37680-65-2	50	20	See Table 2 of method	See Method	8.0	20
PCB-19	38444-73-4	10	4.0	See Table 2 of method	See Method	0.83	4.0
PCB-20 (Co-elutes with PCB-28)	38444-84-7	80	20	See Table 2 of method	See Method	17	20
PCB-21 (Co-elutes with PCB-33)	55702-46-0	50	20	See Table 2 of method	See Method	7.4	20
PCB-22	38444-85-8	10	20	See Table 2 of method	See Method	5.2	20
PCB-23	55720-44-0	10	4.0	See Table 2 of method	See Method	0.64	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Filtered solids
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low - picogram per gram (pg/g)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-24	55702-45-9	10	4.0	See Table 2 of method	See Method	0.77	4.0
PCB-25	55712-37-3	10	4.0	See Table 2 of method	See Method	3.0	4.0
PCB-26 (Co-elutes with PCB-29)	38444-81-4	10	20	See Table 2 of method	See Method	7.3	20
PCB-27	38444-76-7	10	4.0	See Table 2 of method	See Method	0.80	4.0
PCB-28* (Co-elutes with PCB-20)	7012-37-5	80	20	See Table 2 of method	See Method	17	20
PCB-29 (Co-elutes with PCB-26)	15862-07-4	10	20	See Table 2 of method	See Method	7.3	20
PCB-30 (Co-elutes with PCB-18)	35693-92-6	50	20	See Table 2 of method	See Method	8.0	20
PCB-31	16606-02-3	50	20	See Table 2 of method	See Method	13	20
PCB-32	38444-77-8	10	4.0	See Table 2 of method	See Method	2.7	4.0
PCB-33 (Co-elutes with PCB-21)	38444-86-9	50	20	See Table 2 of method	See Method	7.4	20
PCB-34	37680-68-5	10	4.0	See Table 2 of method	See Method	0.62	4.0
PCB-35	37680-69-6	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-36	38444-87-0	10	4.0	See Table 2 of method	See Method	0.59	4.0
PCB-37	38444-90-5	10	20	See Table 2 of method	See Method	4.8	20
PCB-38	53555-66-1	10	4.0	See Table 2 of method	See Method	0.59	4.0
PCB-39	38444-88-1	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-40 (Co-elutes with PCB-41, 71)	38444-93-8	10	20	See Table 2 of method	See Method	10	20
PCB-41 (Co-elutes with PCB-40, 71)	52663-59-9	10	20	See Table 2 of method	See Method	10	20
PCB-42	36559-22-5	10	20	See Table 2 of method	See Method	4.1	20
PCB-43	70362-46-8	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-44 (Co-elutes with PCB-47, -65)	41464-39-5	10	100	See Table 2 of method	See Method	20	100
PCB-45 (Co-elutes with PCB-51)	70362-45-7	10	4.0	See Table 2 of method	See Method	2.9	4.0
PCB-46	41464-47-5	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-47 (Co-elutes with PCB-44, -65)	2437-79-8	10	100	See Table 2 of method	See Method	20	100

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Filtered solids
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low - picogram per gram (pg/g)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-48	70362-47-9	10	4.0	See Table 2 of method	See Method	2.7	4.0
PCB-49 (Co-elutes with PCB-69)	41464-40-8	10	20	See Table 2 of method	See Method	13	20
PCB-50 (Co-elutes with PCB-53)	62796-65-0	10	4.0	See Table 2 of method	See Method	2.4	4.0
PCB-51 (Coleutes with PCB-45)	68194-04-7	10	4.0	See Table 2 of method	See Method	2.9	4.0
PCB-52	35693-99-3	50	100	See Table 2 of method	See Method	24	100
PCB-53 (Co-elutes with PCB-50)	41464419	10	4.0	See Table 2 of method	See Method	2.4	4.0
PCB-54	15968-05-5	10	4.0	See Table 2 of method	See Method	0.78	4.0
PCB-55	74338-24-2	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-56	41464-43-1	10	20	See Table 2 of method	See Method	7.4	20
PCB-57	70424-67-8	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-58	41464-49-7	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-59 (Co-elutes with PCB-62, -75)	74472-33-6	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-60	33025-41-1	10	4.0	See Table 2 of method	See Method	3.1	4.0
PCB-61 (Co-elutes with PCB-70, -74, -76)	33284-53-6	50	100	See Table 2 of method	See Method	33	100
PCB-62 (Co-elutes with PCB-59, -75)	54230-22-7	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-63	74472-34-7	100	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-64	52663-58-8	10	20	See Table 2 of method	See Method	8.2	20
PCB-65 (Co-elutes with PCB-44, -47)	33284-54-7	10	100	See Table 2 of method	See Method	20	100
PCB-66	32598-10-0	10	20	See Table 2 of method	See Method	15	20
PCB-67	73575-53-8	10	4.0	See Table 2 of method	See Method	1.0	4.0
PCB-68	73575-52-7	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-69	60233-24-1	10	20	See Table 2 of method	See Method	13	20
PCB-70 (Co-elutes with PCB-61, -74, -76)	32598-11-1	50	100	See Table 2 of method	See Method	33	100
PCB-71 (Co-elutes with PCB-40, -41)	41464-46-4	10	20	See Table 2 of method	See Method	10	20

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Filtered solids
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low - picogram per gram (pg/g)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-72	41464-42-0	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-73	74338-23-1	10	4.0	See Table 2 of method	See Method	0.76	4.0
PCB-74 (Co-elutes with PCB-61, -70, -76)	32690-93-0	50	100	See Table 2 of method	See Method	33	100
PCB-75 (Co-elutes with PCB-59, -62)	32598-12-2	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-76(Co-elutes with PCB-61, -70, -74)	70362-48-0	50	100	See Table 2 of method	See Method	33	100
PCB-77	32598-13-3	50	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-78	70362-49-1	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-79	41464-48-6	10	4.0	See Table 2 of method	See Method	0.99	4.0
PCB-80	33284-52-5	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-81	70362-50-4	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-82	52663-62-4	10	20	See Table 2 of method	See Method	4.2	20
PCB-83 (Co-elutes with PCB-99)	60145-20-2	10	100	See Table 2 of method	See Method	21	100
PCB-84	52663-60-2	10	20	See Table 2 of method	See Method	8.6	20
PCB-85 (Co-elutes with PCB-116, -117)	65510-45-4	10	20	See Table 2 of method	See Method	6.5	20
PCB-86 (Co-elutes with PCB-87, -97, -108, -119, -125)	55312-69-1	10	100	See Table 2 of method	See Method	24	100
PCB-87 (Co-elutes with PCB-86, -97, -108, -119, -125)	38380-02-8	10	100	See Table 2 of method	See Method	24	100
PCB-88 (Co-elutes with PCB-91)	55215-17-3	100	20	See Table 2 of method	See Method	5.6	20
PCB-85 (Co-elutes with PCB-116, -117)	73575-57-2	10	4.0	See Table 2 of method	See Method	1.8	4.0
PCB-90 (Co-elutes with PCB-101, -113)	68194-07-0	10	100	See Table 2 of method	See Method	32	100
PCB-91 (Co-elutes with PCB-88)	68194-05-8	10	20	See Table 2 of method	See Method	5.6	20
PCB-92	52663-61-3	10	20	See Table 2 of method	See Method	6.1	20
PCB-93 (Co-elutes with PCB-95, -98, -100,	73575-56-1	100	100	See Table 2 of method	See Method	26	100

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Filtered solids
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low - picogram per gram (pg/g)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
-02)							
PCB-94	73575-55-0	10	4.0	See Table 2 of method	See Method	1.8	4.0
PCB-95 (Co-elutes with PCB-93, -98, -100,-102)	38379-99-6	10	100	See Table 2 of method	See Method	26	100
PCB-96	73575-54-9	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-97 (Co-elutes with PCB-86, -87, -108, -119, -125)	41464-51-1	10	100	See Table 2 of method	See Method	24	100
PCB-98 (Co-elutes with PCB-93, -95, -100, -102)	60233-25-2	100	100	See Table 2 of method	See Method	26	100
PCB-99 (Co-elutes with PCB-83)	38380-01-7	10	100	See Table 2 of method	See Method	21	100
PCB-100 (Co-elutes with PCB-93, -95, -98, -102)	39485-83-1	100	100	See Table 2 of method	See Method	26	100
PCB-101 (Co-elutes with PCB-90, -113)	37680-73-2	10	100	See Table 2 of method	See Method	32	100
PCB-102 (Co-elutes with PCB-93, -95, -98, -100)	68194-06-9	100	100	See Table 2 of method	See Method	26	100
PCB-103	60145-21-3	10	4.0	See Table 2 of method	See Method	1.5	4.0
PCB-104	56558-16-8	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-105	32598-14-4	10	20	See Table 2 of method	See Method	12	20
PCB-106	70424-69-0	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-107 (Co-elutes with PCB-124)	70424-68-9	10	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-108 (Co-elutes with PCB-86, -87, -97, -119, -125)	70362-41-3	10	100	See Table 2 of method	See Method	24	100
PCB-109	74472-35-8	10	4.0	See Table 2 of method	See Method	1.9	4.0
PCB-110 (Co-elutes with PCB-115)	38380-03-9	10	100	See Table 2 of method	See Method	38	100

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Filtered solids
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low - picogram per gram (pg/g)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-111	39635-32-0	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-112	74472-36-9	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-113 (Co-elutes with PCB-90, -101)	68194-10-5	10	100	See Table 2 of method	See Method	32	100
PCB-114	74472-37-0	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-115 (Co-elutes with PCB-110)	74472-38-1	10	100	See Table 2 of method	See Method	38	100
PCB-116 (Co-elutes with PCB-85, -117)	18259-05-7	10	20	See Table 2 of method	See Method	6.5	20
PCB-117 (Co-elutes with PCB-85, -116)	68194-11-6	10	20	See Table 2 of method	See Method	6.5	20
PCB-118	31508-00-6	10	100	See Table 2 of method	See Method	26	100
PCB-119 (Co-elutes with PCB-86, -87, -97, -108, -125)	56558-17-9	10	100	See Table 2 of method	See Method	24	100
PCB-120	68194-12-7	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-121	56558-18-0	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-122	76842-07-4	10	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-123	65510-44-3	10	4.0	See Table 2 of method	See Method	1.9	4.0
PCB-124	70424-70-3	10	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-125	74472-39-2	10	100	See Table 2 of method	See Method	24	100
PCB-126	57465-28-8	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-127	39635-33-1	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-128	38380-07-3	10	20	See Table 2 of method	See Method	4.5	20
PCB-129	55215-18-4	10	100	See Table 2 of method	See Method	32	100
PCB-130	52663-66-8	10	4.0	See Table 2 of method	See Method	2.3	4.0
PCB-131	61798-70-7	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-132	38380-05-1	10	20	See Table 2 of method	See Method	12	20
PCB-133	35694-04-3	10	4.0	See Table 2 of method	See Method	2.0	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Filtered solids
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low - picogram per gram (pg/g)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-134 (Co-elutes with PCB-143)	52704-70-8	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-135 (Co-elutes with PCB-151 -154)	52744-13-5	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-136	38411-22-2	10	4.0	See Table 2 of method	See Method	3.7	4.0
PCB-137	35694-06-5	10	4.0	See Table 2 of method	See Method	2.4	4.0
PCB-138 (Co-elutes with PCB-129, -160, -163)	35065-28-2	10	100	See Table 2 of method	See Method	32	100
PCB-139 (Co-elutes with PCB-140)	56030-56-9	10	4.0	See Table 2 of method	See Method	1.9	4.0
PCB-140 (Co-elutes with PCB-139)	59291-64-4	10	4.0	See Table 2 of method	See Method	1.9	4.0
PCB-141	52712-04-6	10	20	See Table 2 of method	See Method	5.8	20
PCB-142	41411-61-4	10	4.0	See Table 2 of method	See Method	2.2	4.0
PCB-143 (Co-elutes with PCB-134)	68194-15-0	10	4.0	See Table 2 of method	See Method	2.1	4.0
PCB-144	68194-14-9	10	4.0	See Table 2 of method	See Method	2.6	4.0
PCB-145	74472-40-5	10	4.0	See Table 2 of method	See Method	1.2	4.0
PCB-146	51908-16-8	10	20	See Table 2 of method	See Method	5.2	20
PCB-147 (Co-elutes with PCB-149)	68194-13-8	10	100	See Table 2 of method	See Method	26	100
PCB-148	74472-41-6	10	4.0	See Table 2 of method	See Method	1.5	4.0
PCB-149 (Co-elutes with PCB-147)	38380-04-0	10	100	See Table 2 of method	See Method	26	100
PCB-150	68194-08-1	10	4.0	See Table 2 of method	See Method	1.1	4.0
PCB-151* (Co-elutes with PCB-135, -154)	52663-63-5	10	20	See Table 2 of method	See Method	12	20
PCB-152	68194-09-2	10	4.0	See Table 2 of method	See Method	1.0	4.0
PCB-153	35065-27-1	10	100	See Table 2 of method	See Method	28	100
PCB-154 (Co-elutes with PCB-135, -151)	60145-22-4	10	20	See Table 2 of method	See Method	12	20
PCB-155	33979-03-2	10	4.0	See Table 2 of method	See Method	0.89	4.0
PCB-156 (Co-elutes with PCB-157)	38380-08-4	10	4.0	See Table 2 of method	See Method	2.4	4.0
PCB-157 (Co-elutes with PCB-156)	69782-90-7	10	4.0	See Table 2 of method	See Method	2.4	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Filtered solids
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low - picogram per gram (pg/g)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-158	74472-42-7	10	4.0	See Table 2 of method	See Method	2.9	4.0
PCB-159	39635-35-3	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-160 (Co-elutes with PCB-129, -138, -163)	41411-62-5	10	100	See Table 2 of method	See Method	32	100
PCB-161	74472-43-8	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-162	39635-34-2	10	4.0	See Table 2 of method	See Method	1.5	4.0
PCB-163 (Co-elutes with PCB-129, -138, -160)	74472-44-9	10	100	See Table 2 of method	See Method	32	100
PCB-164	74472-45-0	10	4.0	See Table 2 of method	See Method	2.4	4.0
PCB-165	74472-46-1	10	4.0	See Table 2 of method	See Method	1.7	4.0
PCB-166 (Co-elutes with PCB-128)	41411-63-6	10	20	See Table 2 of method	See Method	4.5	20
PCB-167	52663-72-6	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-168 (Co-elutes with PCB-153)	59291-65-5	10	100	See Table 2 of method	See Method	28	100
PCB-169	32774-16-6	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-170	35065-30-6	10	20	See Table 2 of method	See Method	4.7	20
PCB-171 (Co-elutes with PCB-173)	52663-71-5	10	4.0	See Table 2 of method	See Method	1.6	4.0
PCB-172	52663-74-8	10	4.0	See Table 2 of method	See Method	0.90	4.0
PCB-173 (Co-elutes with PCB-171)	68194-16-1	10	4.0	See Table 2 of method	See Method	1.6	4.0
PCB-174	38411-25-5	10	20	See Table 2 of method	See Method	6.4	20
PCB-175	40186-70-7	10	4.0	See Table 2 of method	See Method	0.85	4.0
PCB-176	52663-65-7	10	4.0	See Table 2 of method	See Method	0.67	4.0
PCB-177	52663-70-4	10	4.0	See Table 2 of method	See Method	2.7	4.0
PCB-178	52663-67-9	10	4.0	See Table 2 of method	See Method	1.5	4.0
PCB-179	52663-64-6	10	4.0	See Table 2 of method	See Method	2.5	4.0
PCB-180 (Co-elutes with PCB-193)	35065-29-3	10	20	See Table 2 of method	See Method	15	20
PCB-181	74472-47-2	10	4.0	See Table 2 of method	See Method	0.91	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Filtered solids
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low - picogram per gram (pg/g)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-182	60145-23-5	10	4.0	See Table 2 of method	See Method	0.88	4.0
PCB-183 (Co-elutes with PCB-185)	52663-69-1	10	20	See Table 2 of method	See Method	5.4	20
PCB-184	74472-48-3	10	4.0	See Table 2 of method	See Method	0.65	4.0
PCB-185 (Co-elutes with PCB-183)	52712-05-7	10	20	See Table 2 of method	See Method	5.4	20
PCB-186	74472-49-4	10	4.0	See Table 2 of method	See Method	0.70	4.0
PCB-187	52663-68-0	10	20	See Table 2 of method	See Method	9.6	20
PCB-188	74487-85-7	10	4.0	See Table 2 of method	See Method	0.60	4.0
PCB-190	41411-64-7	10	4.0	See Table 2 of method	See Method	0.75	4.0
PCB-191	74472-50-7	10	4.0	See Table 2 of method	See Method	1.4	4.0
PCB-192	74472-51-8	10	4.0	See Table 2 of method	See Method	0.68	4.0
PCB-193 (Co-elutes with PCB-180)	69782-91-8	10	4.0	See Table 2 of method	See Method	0.72	4.0
PCB-194	35694-08-7	10	20	See Table 2 of method	See Method	15	20
PCB-195	52663-78-2	10	20	See Table 2 of method	See Method	4.7	20
PCB-196	42740-50-1	10	4.0	See Table 2 of method	See Method	1.6	4.0
PCB-197 (Co-elutes with PCB-200)	33091-17-7	10	20	See Table 2 of method	See Method	4.3	20
PCB-198 (Co-elutes with PCB-199)	68194-17-2	10	4.0	See Table 2 of method	See Method	2.8	4.0
PCB-199 (Co-elutes with PCB-198)	52663-75-9	10	20	See Table 2 of method	See Method	14	20
PCB-200 (Co-elutes with PCB-197)	52663-73-7	10	20	See Table 2 of method	See Method	14	20
PCB-201	40186-71-8	10	4.0	See Table 2 of method	See Method	2.8	4.0
PCB-202	2136-99-4	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-203	52663-76-0	10	4.0	See Table 2 of method	See Method	2.9	4.0
PCB-204	74472-52-9	10	20	See Table 2 of method	See Method	10	20
PCB-205	74472-53-0	10	4.0	See Table 2 of method	See Method	1.3	4.0
PCB-206	40186-72-9	10	4.0	See Table 2 of method	See Method	0.60	4.0

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Filtered solids
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: Low - picogram per gram (pg/g)

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit Goal[2]	Analytical Method 1668A		Axys Achievable Limits[4]	
				MDLs [3]	Method QLs	Estimated Detection Limit (EDLs)	QLs
		pg/sample		pg/g		pg/sample	
PCB-207	52663-79-3	10	20	See Table 2 of method	See Method	9.0	20
PCB-208	52663-77-1	10	4.0	See Table 2 of method	See Method	2.8	4.0
PCB-209	2051-24-3	10	20	See Table 2 of method	See Method	4.6	20

Notes:
1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The project quantitation limit goals (PQLGs) are those listed for the individual PCB Congeners listed in the CPG RI/FS QAPP, *Remedial Investigation Water Column Monitoring/High Volume Chemical Data Collection (September 2012)*.
3. See Method 1688A Table 2 for a list of PCB Congener MDLs. Estimated with interferences.
4. Achievable Laboratory EDLs are based on Axys Analytical Services' "Sample Detection Limits", the pre-program analytical work with the coagulant and filter proof (one analytical run Lab ID: WG41220-103), which are determined by converting the area equivalent of 2.5 times the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. These are determined individually for every sample analysis run and accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up.

   Achievable Laboratory QL is based on Axys Analytical Services' "Lower Method Calibration Limit (LMCL)", and is determined by prorating the concentration of the lowest calibration solution for sample size and extract volume, according to the following equation ((lowest level calibration concentration) × (extract volume))/sample size. The Achievable Laboratory QLs account for the pre-program analytical work with the coagulant and filter proof.

* PCB 28/20 in NIST 1944 Standard Reference Material: During the pre-program analytical work, a standard reference material (NIST 1944) was analyzed with pre-cleaned filters and coagulant. The percent recovery of PCB 20/28 (153%) exceeded the measurement performance criteria. This PCB co-elution will be reported in the split sample EDD by the laboratory; however, no split sample comparison will be conducted on this co-elution.

* PCB 151/135/154 in NIST 1944 Standard Reference Material: During the pre-program analytical work, a standard reference material (NIST 1944) was analyzed with pre-cleaned filters and coagulant. Because of the significant contribution from the co-eluting congeners (PCB 135 and PCB 154), the laboratory reported concentration for PCB 151 is not comparable to the certified reference value, which represents a single PCB congener peak. (Note that EPA Method 1668 requires a SPB-Octyl column whereas the certified value was measured on a DB-5 column, which produces a different co-elution pattern.) This PCB co-elution will be reported in the split sample EDD by the laboratory, and a split sample comparison will be conducted on this co-elution.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: PUF cartridge (Dissolved Phase) and filter solids
Analytical Group: PCDD/PCDF by EPA 1613B
Concentration Level: Low (**pg/sample**)

Analyte	CAS Number	Project Action Limit[1] (pg/sample)	Project Quantitation Limit Goals[2] (PQLG) (pg/sample)	EPA 1613B Analytical Method[3]		Achievable Laboratory Limits[4]	
				MDLs [3]	Method CRQLs[3]	EDLs	QLs
2378-TCDD	1746-01-6	10	10	NA	1.0	0.50	2
12378-PeCDD	40321-76-4	25	10	NA	5.0	0.50	0.50
123678-HxCDD	57653-85-7	25	10	NA	5.0	0.53	10
123478-HxCDD	39227-28-6	25	10	NA	5.0	0.60	10
123789-HxCDD	19408-74-3	25	10	NA	5.0	0.53	10
1234678-HpCDD	35822-46-9	25	10	NA	5.0	0.60	10
OCDD	3268-87-9	25	20	NA	10.0	0.61	20
2378-TCDF	51207-31-9	10	2	NA	1.0	0.50	2
12378-PeCDF	57117-41-6	25	10	NA	5.0	0.52	10
23478-PeCDF	57117-31-4	25	10	NA	5.0	0.51	10
123678-HxCDF	57117-44-9	25	10	NA	5.0	0.51	10
123789-HxCDF	72918-21-9	25	10	NA	5.0	0.50	10
123478-HxCDF	70648-26-9	25	10	NA	5.0	0.50	10
234678-HxCDF	60851-34-5	25	10	NA	5.0	0.50	10
1234678-HpCDF*	67562-39-4	25	10	NA	5.0	0.50	10
1234789-HpCDF	55673-89-7	25	10	NA	5.0	0.50	10
OCDF	39001-02-0	25	20	NA	10.0	0.61	20

Notes:

1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The PQLGs for individual PCDDs/PCDFs are based on the CPG's Achievable Laboratory QLs which are taken from the *Quality Assurance Project Plan, Remedial Investigation Water Column Monitoring/High Volume Chemical Data Collection (September 2012)*. The split sample data reporting limit should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
3. Specific MDLs are not listed in Method 1613B, but the QLs listed are the minimum levels published in Table 2 of the method. The actual detection limits are usually dependent on the level of interference rather than instrument limitations.
4. Achievable Laboratory EDLs are based on Axys Analytical Services' "Sample Detection Limits", from the pre-program analytical work with the PUF medium [average of three analytical runs: PUF blank (Lab ID: WG40846-101) and two low level IPR samples (Lab ID: WG40846-106 and 107)], which are determined by converting the area

equivalent of 2.5 times the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. This is determined individually for every sample analysis run and accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up.

Achievable Laboratory QLs are based on Axys Analytical Services' "Lower Method Calibration Limit (LMCL)", and is determined by prorating the concentration of the lowest calibration solution for sample size and extract volume, according to the following equation ((lowest level calibration concentration) × (extract volume))/sample size. The Achievable Laboratory QLs account for the pre-program analytical work with the PUF medium.

* 1,2,3,4,6,7,8-HpCDF in PUF Medium: During the pre-program analytical work of the PUF medium, the average recovery for the IPR study was 120 percent, which is outside the acceptance criteria for Method 1613B, which is 90-112 percent. This analyte will be reported in the split sample EDD by the laboratory; however, no split sample comparison will be conducted on this analyte.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: (Solid Phase) Filtered solids
Analytical Group: PCDD/PCDF by EPA 1613B
Concentration Level: Low (**pg/sample**)

Analyte	CAS Number	Project Action Limit[1] (pg/sample)	Project Quantitation Limit Goals[2] (PQLG) (pg/sample)	EPA 1613B Analytical Method[3]		Achievable Laboratory Limits[4]	
				MDLs [3]	Method CRQLs[3]	EDLs	QLs
2378-TCDD	1746-01-6	10	2	NA	1.0	0.50	2
12378-PeCDD	40321-76-4	25	10	NA	5.0	0.50	10
123678-HxCDD	57653-85-7	25	10	NA	5.0	0.68	10
123478-HxCDD	39227-28-6	25	10	NA	5.0	0.68	10
123789-HxCDD	19408-74-3	25	10	NA	5.0	1.0	10
1234678-HpCDD	35822-46-9	25	10	NA	5.0	1.8	10
OCDD	3268-87-9	25	20	NA	10.0	4.4	20
2378-TCDF	51207-31-9	10	2	NA	1.0	0.50	2
12378-PeCDF	57117-41-6	25	10	NA	5.0	0.50	10
23478-PeCDF	57117-31-4	25	10	NA	5.0	0.53	10
123678-HxCDF	57117-44-9	25	10	NA	5.0	0.58	10
123789-HxCDF	72918-21-9	25	10	NA	5.0	0.53	10
123478-HxCDF	70648-26-9	25	10	NA	5.0	0.59	10
234678-HxCDF	60851-34-5	25	10	NA	5.0	0.75	10
1234678-HpCDF	67562-39-4	25	10	NA	5.0	1.9	10
1234789-HpCDF	55673-89-7	25	10	NA	5.0	1.4	10
OCDF	39001-02-0	25	20	NA	10.0	3.2	20

Notes:
1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The PQLGs for individual PCDDs/PCDFs are based on the CPG's Achievable Laboratory QLs which are taken from the *Quality Assurance Project Plan, Remedial Investigation Water Column Monitoring/High Volume Chemical Data Collection (September 2012)*. The split sample data reporting limit should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
3. Specific MDLs are not listed in Method 1613B, but the QLs listed are the minimum levels published in Table 2 of the method. The actual detection limits are usually dependent on the level of interference rather than instrument limitations.
4. Achievable Laboratory EDLs are based on Axys Analytical Services' "Sample Detection Limits" from the pre-program analytical work with the coagulant and filter proof

(one analytical run: Lab ID WG41220-103), which are determined by converting the area equivalent of 2.5 times the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. This is determined individually for every sample analysis run and accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up.

Achievable Laboratory QLs are based on Axys Analytical Services' "Lower Method Calibration Limit (LMCL)" and is determined by prorating the concentration of the lowest calibration solution for sample size and extract volume, according to the following equation ((lowest level calibration concentration) × (extract volume))/sample size. Achievable Laboratory QLs account for the pre-program analytical work with the coagulant and filters.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous
Analytical Group: Chemical Water Column Analyses
Concentration Level: Low

Analyte	CAS Number	Project Action Limit [1]	Project Quantitation Limit Goal [2] (mg/L)	Analytical Method		Achievable DESA Laboratory Limits[3]	
				MDLs	Method QLs	MDLs (mg/ L)	QLs (mg/L)
DOC	NA	None	0.3	NA	Not listed in Method SM5310B	0.25	0.5
POC	NA	None	1.3	NA	Not listed in EPA Method 415.1	0.005	0.01
SSC (1.5 µm filter)	NA	None	1.0	NA	Not listed in Method SM 2540D[4]	NA	1.0 (with > 1L volume sample)

Notes:

1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The target PQLGs listed are based on the CPG's. Differences in laboratory detection limits will be considered when comparing the data.
3. Laboratory QL is anticipated to be low enough to allow comparison of the split sample data to the CPG data. Detection limits are based on communications with Jim Ferretti of the DESA laboratory and are derived from a DESA study conducted on water column samples from the New York Bight study. The MDL for POC and DOC are estimates and are one half of the QL.
4. Method SM 2540D is equivalent to ASTM 3977-97 Test Option B.

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 HV CWCM Study to EPA and USACE	CDM Smith	August 23, 2012	August 30, 2012	HV CWCM UFP-QAPP Addendum 11	July 30, 2012
Prepare and submit: Final oversight QAPP Addendum for HV CWCM Study	CDM Smith	As soon as comments are received	August 23, 2012	UFP-QAPP Addendum, Final	TBD
Acceptance of splits and sample handling activities	CDM Smith	August 2012	10 days after commencement date	Summary report of chemical data	TBD
Laboratory Analysis	CDM Smith subcontract laboratory(ies)	August 2012	September 2012 (Exact date to be determined; data collection will be dependent on the CPG schedule)	Data Package	TBD; will be dependent on the CPG schedule For standard analyses, 21 days after the last sample is received; however, specialized analyses may take additional time
Validation and verification of sample data	CDM Smith	Fall 2012	Fall 2012	Validated data report	TBD; will be dependent on CPG schedule
Oversight /Data Evaluation	CDM Smith	TBD	TBD	Oversight data Comparison and Summary Report/ Data Quality Summary Report	TBD
Review Chemical Water Column Study Analysis Data Report	CDM Smith	90 days after each sampling event	1 month after receipt of report	Comments on Chemical Water Column Study Analysis Data Report	1 month after receipt of report

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

Survey Location ID	Media	Depth	Analytical Group	Concentration Level	Estimated Number of Samples (identify field duplicates)	Sampling SOP Reference	Rationale for Sampling Location
Refer to QAPP prepared by AECOM for the CPG and Figure 1 (Lower Passaic Locations only) Location TBD	Separated Solid Phase & Sorption Media (PUF)	1-3 feet from bottom	PCDD/PCDF PCB congeners	Low	Approximately 1 location (or a second location for one sample phase) will be co-located for a "split" sample. Split consist of one PUF cartridge and one filtered solids sample.	Appendix A of CPG's HV CWCM QAPP (AECOM 2012) (also see footnotes)	Split samples will be accepted by the on-site oversight staff in consultation with the PM and USACE/EPA. Decision will be judgmental and dependent on CPG's plan for duplicate sample collection.
	Whole water	1-3 feet from bottom	DOC, POC, and SSC	Low	1		
See Worksheet #20 for number of split samples. See CPG's QAPP Worksheet No.18 for the sampling locations and sampling rationale.							

Notes:
Refer to the QAPP prepared by AECOM for the CPG (Worksheets #10, 11 and 18 and Figure 1) titled*, Quality Assurance Project Plan, Remedial Investigation Water Column Monitoring/High Volume Chemical Data Collection (June 2012)* for sampling information.

Lower Passaic locations include river mile (RM) 4.2, RM 10.4 and Above Dundee Dam.

QAPP Worksheet #19 – Surface Water Analysis
Analytical SOP Requirements Table

Matrix	Analytical Group	Concen-tration Level	Analytical and Preparation Method/SOP Reference[1]	Sample Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light)	Maximum Holding Time (preparation/ analysis)
Separated Solids	PCB Congeners	Low	USEPA 1668A (Axys SOP MLA-010)	Entire Contents of Vortex Cup and Flat Filter	8 ounce (oz) wide mouth glass (amber preferred)	Store in dark at 0-6°C; at the laboratory store in the dark at <-10°C	1 year for preparation and analysis
Solid (PUF)	PCB Congeners	Low	USEPA 1668A (Axys SOP MLA-010)	Entire PUF Sorbent	PR2900 Sorbent Cartridge	Store in dark at 0-6°C; at the laboratory store in the dark at <-10°C	1 year for preparation and analysis
Separated Solids	PCDD/PCDF	Low	EPA 1613B (Axys SOP MLA-017)	Entire Contents of Vortex Cup and Flat Filter	8 ounce (oz) wide mouth glass (amber preferred)	Store in dark at 0-6°C; at the laboratory store in the dark at <-10°C	1 year for preparation and analysis
Solid (PUF)	PCDD/PCDF	Low	EPA 1613B (Axys SOP MLA-017)	Entire PUF Sorbent	PR2900 Sorbent Cartridge	Store in dark at 0-6°C; at the laboratory store in the dark at <-10°C	1 year for preparation and analysis
Aqueous	DOC	Low	DOC: SM5310B (DESA SOP C-88 Modified)	500 mL	(2) 250 mL amber glass bottle or protect from light	Cool to 0-6°C; No headspace Lab will filter, H_2SO_4 to pH <2	Ship to the laboratory for preservation and filtering within 48 hours. Filters and filtrates must be analyzed within 28 days.
Aqueous	POC	Low	POC: USEPA 415.1 (DESA SOP C-83 Modified)				
Aqueous	SSC	Low	SM2540D (DESA SOP C-33 Modified)	1000 mL [2 L per CPG QAPP)	(1) 1 L HDPE or amber glass bottle or protect from light	Cool to 0-6°C; No headspace Weigh entire bottle to nearest 0.1 gram then store in dark	28 days to analysis

Notes:

1. The CDM Smith analytical subcontract laboratory SOPs for these analyses are shown in Appendix Q of this QAPP. Method modifications are outlined on worksheet #23.
2. Solid-phase samples consist (at a minimum) of a glass wound cartridge filter, two 0.7 µm filters (142 mm diameter), and vortex chamber water/solids. Laboratory will handle filtered solids by adding coagulant and treating sample as a "solid" matrix.

3: Dissolved-phase samples consist of a PUF medium

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 or Duplicate) Samples	No. of Equipment Rinsate Blanks	No. of Trip Blanks	No of PE Samples	Total No. of Samples
PUF/filtered solids	PCB congeners	Low	USEPA 1668A (Axys SOP MLA-010)	1	0	NA	0	0	0	1
PUF/filtered solids	PCDD/PCDF	Low	EPA 1613B (Axys SOP MLA-017)	1	0	NA	0	0	0	1
Aqueous	DOC	Low	DOC: SM5310B (DESA SOP C-88 Modified)	1	0	0	0	0	0	1
Aqueous	POC	Low	POC: USEPA 415.1 (DESA SOP C-83 Modified)	1	0	0	0	0	0	1
Aqueous	SSC	Low	SM2540D (DESA SOP C-33 Modified)	1	0	0	0	0	0	1

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 Smith and Louis Berger 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. PCB congeners and dioxin/furans will be analyzed by Axys laboratory. DESA will be requested to perform the remaining wet chemistry parameters.

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?
EPA 1668A for HRGC/HRMS Axys SOP: MLA-10	*Analytical Method for the Determination of: 209 PCB Congeners Laboratory SOP MLA-010, Revision 10, August 2010.*	Definitive	PCB Congeners	HRGC/HRMS	Axys Analytical Services Laboratory 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone:1-888-373-0881	Yes- incorporated in the attached SOP and notes below
EPA 1613B for HRGC/HRMS Axys SOP: MLA-017	*Analytical Method for the Determination of Polychlorinated Dibenzodioxins and Dibenzofurans Laboratory SOP MLA-017, Revision 20, March 2011.*	Definitive	PCDD/PCDF	Isotope dilution - HRGC/HRMS		
SM 5310B - DESA SOP C-83 Modified	Modified: "*Standard Operating Procedure: Total Organic Carbon.*" DESA SOP C-83, Revision 2.1, January 31, 2009.	Definitive	DOC (Dissolved Organic Carbon)	Organic Carbon Analyzer	DESA	Yes – see below
Project-specific Modification: Use combustible 0.7 µm glass fiber filter (Whatman, 25 mm diameter, Model 1825-025). Filter within 48 hours of sample collection and preserve. Expose to HCl fumes to remove inorganic carbon. Combust entire filter to reduce errors. Reported DOC values will be the average of two analyses.						
EPA 415.1- DESA SOP C-88 Modified	Modified: "*Standard Operating Procedure: Total Organic Carbon -Sediment*." DESA SOP C-88, Revision 2.1, January 31, 2009.	Definitive	POC (Particulate Organic Carbon)	Filter and Carbon Analyzer with IR or flame ionization detector (FID) Detector	DESA	Yes – see below
Project-specific Modification: Use a 0.7 µm glass fiber filter (Whatman, 25 mm diameter, Model 1825-025). Filters will be pre-combusted and tared; after filtration, filters will be dried and re-weighed. The mass of suspended solids on the 0.7 µm filter will be reported in the data package. Dried POC filters will be stored frozen until analysis. Prior to combustion, POC filter will be exposed to hydrochloric fumes for 24 hours to remove inorganic carbon. DESA will communicate with CDM Smith if the suspended solids concentration is relatively high and carbon load may saturate the detector. POC will be reported in units of mg/L (i.e., volume of water filtered).						
SM 2540D - DESA SOP C-33 Modified	Modified*: "Standard Operating Procedure: Total Suspended Solids Volatile Suspended Solids."* DESA SOP C-33, Revision 3.1, January 31, 2009.	Definitive	Suspended Solids Concentration	Filter, Oven, balance	FASTAC implementation DESA	Yes – see below
Project-specific Modification: Use 0.7 µm filter (ProWeigh, Environmental Express, Model F93447MM-X). Use entire sample bottle to filter. Rinse with deionized water to capture all the solids or until filter refusal. Filter within 7 days of collection. DESA will communicate with CDM Smith if the suspended solids concentration is relatively high and may clog the filter.						

Notes:
1. The FASTAC policy for procuring analytical services was implemented; DESA will perform analyses. DESA maintains the laboratory's SOP information. The SOP will be modified to facilitate comparison with the CPG data. A trip report is not required for samples shipped to the DESA laboratory.
2. As necessary, the assigned laboratories will perform additional clean-up of split samples (via gel permeation chromatography) prior to analysis of organic compounds.

3. The titles above may change dependent on the assigned laboratories.

4. Pre-Program Analytical Work

- Pre-program analytical work not designed to validate the CPG filtration system or validate the CPG dynamic spike (for assessing potential PUF absorption efficiency) and static spike (for assessing potential PUF wash-out). Pre-program analytical work will instead assess Axys Analytical Services' ability to extract and quantify target analytes from PUF cartridge and filtered solids/filter media/coagulant sample.
- Laboratory will use (1) PUF cartridges from Tisch Environmental (part number: TE-1015; dimensions of 1.5 inches × 3 inches), (2) coagulant from Agilent Technologies (part number: Chemtube Hydromatrix No. 198003), (3) 0.7 micrometer (µm) glass fiber filter (142 millimeter (mm) diameter; Whatman), and (4) 25 µm cellulose wood filter (142 mm diameter; Whatman). Laboratory will pre-clean filters and coagulant prior to analytical work.
- Laboratory will conduct an IPR study to validate the PUF cartridge as an aqueous phase matrix for PCDD/PCDF congeners via Method 1613 Version B and PCB congeners via Method 1668 Version A. The IPR study will consist of one laboratory PUF blank, four mid-level calibration point analyses, and two low-level calibration point analyses. A total of seven samples will be analyzed for PCDD/PCDF and PCB congeners. The IPR study will include the following project-specific details:
  - The IPR mid-level calibration point will be the CS-3 calibration solution per published methods. The low-level calibration point will be a factor of 10 times lower than the CS-3 calibration solution and include all targetted congeners.
  - Laboratory will use internal quantification standards as prescribed in AXYS SOP MLA-017 for PCDD/PCDF and AXYS SOP MLA-010 for PCB.
  - Laboratory will use an alternative in-house PCB and PCDD/PCDF clean-up standard.
  - Laboratory will add IPR and surrogate spikes directly onto the PUF media, extract, analyze, and report concentrations in units of picograms per sampler (pg/sampler).
  - The PUF cartridge will be handled as one sample (separation of front and back end of PUF is not required).
  - For each PUF sample, PCB and PCDD/PCDF compounds will be co-extracted and fractionated on-column.
- The laboratory will use an alternate clean-up standard during extraction of the PUF samples, so that it does not interfere with CPG field spikes (dynamic spike and static spike). For the PCDD/PCDF method, the laboratory will use an in-house prepared solution of $^{13}C_6$-1,2,3,4-TCDD, which will be spiked into each PUF sample at 500 pg/sampler. The laboratory will prepare and validate an in-house PCB clean-up standard. Validation of the PCB standard will include instrumental analysis of two PCB runs plus a single point calibration. PCB clean-up standard will consist of a cocktail ($^{13}C_{12}$-PCB95 and $^{13}C_{12}$-PCB153) that will be spiked into each PUF sample at 2,000 pg/sampler.
- The laboratory will randomly select a pre-cleaned 8 ounce amber sample container and add the following materials to the container (sample will be handled following AXYS SOPs MLA-010 and MLA-017, with coagulant replacing anhydrous sodium sulfate as the desiccant):
  - Two 0.7 µm glass fiber filters (142 mm diameter), wetted, and sandwiched together with approximately 2 grams of NIST 1944 (a standard reference material for New York/New Jersey estuarine sediments).
  - One 25 µm cellulose wood filter (142 mm diameter).
  - 10 milliliter (mL) of laboratory-grade water.
  - A pre-cleaned coagulant at a rate of 10 grams of coagulant per 10 grams of sample (assuming 10 mL sample). If necessary, 15-20 grams may be needed if sample is very wet.
- The laboratory will verify its ability to quantify the performance evaluation material NIST 1944 in the solid-phase coagulant sample for PCDD/PCDF congeners via Method 1613 Version B and PCB congeners via Method 1668 Version A. The verification study will consist of one blank sample (filters, coagulant, and water) and two performance evaluation samples (filters, coagulant, NIST 1944, water, one solvent blank, and one flat filter and wound glass filter blank).
- All analyses will be conducted consistent with Method 1613 Version B (or AXYS SOP MLA-017) for PCDD/PCDF and Method 1668 Version A (or AXYS SOP MLA-010) for PCB. All analyses will be performed using a Dean-Stark extractor and toluene. (It is recognized that toluene can cause interferences in the quantification of the mono-PCB and di-PCB homologue groups due to the formation of toluene-related interference compounds; however, these interferences are expected to be minimal and should not impact the project.) All analyses will be performed with a six-point calibration curve. All analyses will be performed using HRGC/HRMS. The following analytical method modifications will be implemented during the project:

- For PCDD analysis, the laboratory routinely uses M/Z channels 354/356 and 366/368 to confirm and quantify the native and surrogate penta-substituted PCDD, respectively. This modification to the instrumentation from the Method 1613 specification is implemented to avoid a persistent interference in the M/Z channels 356/358 and 368/370. The theoretical ratio for the penta-substituted PCDD M/M+2 ions is 0.61; therefore, the acceptance range is 0.52 - 0.70.
- For PCDD and PCB analyses, when results exceed the linear range of the instrument, the laboratoy performs solvent dilutions. Extracts are diluted with solvent and re-analyzed by GC/MS to bring the instrumental response to within the linear range of the instrument. No additional recovery (internal) standard is added. For very high-level samples, where a smaller sample aliquot may not be representative, extracts are diluted and respiked with labeled 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 labeled quantification standards.

Sample Handling

- Government split samples will consist of (1) PUF cartridge spiked in the field by the CPG with dynamic spike surrogate and static spike surrogate, and (2) “solid” samples, which will be prepared by the CPG and consist of at least two 0.7 µm glass fiber filters, a glass wool pre-filter, and vortex chamber water/solids in an 8 ounce amber glass container.
- The laboratory will follow project-specific procedures to add coagulant to the vortex chamber split sample at a rate of 10 grams of coagulant per 10 grams of sample; if necessary. 15-20 grams may be needed if sample is very wet. The sample is then transferred to a Dean-Stark extractor. Sample volume will be approximately 10 mL. Samples will be handled following AXYS SOPs MLA-010 and MLA-017, with coagulant replacing anhydrous sodium sulfate as the desiccant.
- All government split samples shall be analyzed by Method 1613 Version B (or AXYS SOP MLA-017) for PCDD/PCDF and Method 1668 Version A (or AXYS SOP MLA-010) for PCB. All analyses will be performed using a Dean-Stark extractor and toluene. (It is recognized that toluene can cause interferences in the quantification of the mono-PCB and di-PCB homologue groups due to the formation of toluene-related interference compounds; however, interferences are expected to be minimal and are not expected to impact the oversight split sampling effort.) All analyses will be performed with a six-point calibration curve. All analyses will be performed using HRGC/HRMS. The following analytical method modifications will be implemented during the project:
  - For PCDD analysis, laboratory routinely uses M/Z channels 354/356 and 366/368 to confirm and quantify the native and surrogate penta-substituted PCDD, respectively. This modification from Method 1613 specification is implemented in the instrument method to avoid a persistent interference in the M/Z channels 356/358 and 368/370. The theoretical ratio for the penta-substituted PCDD M/M+2 ions is 0.61; therefore, the acceptance range is 0.52 - 0.70.
  - For PCDD and PCB analyses, when results exceed the linear range of the instrument, laboratoy performs solvent dilutions. Extracts are diluted with solvent and re-analyzed by GC/MS to bring the instrumental response to within the linear range of the instrument. No additional recovery (internal) standard is added. For very high-level samples, where a smaller sample aliquot may not be representative, extracts are diluted and respiked with labeled 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 labeled quantification standards
- The laboratory will not validate the CPG dynamic spike and static spike concentrations; however, the laboratory will report these surrogates using their relative response factors.
- The split sample data will be reported in units of pg/sample (corrected for isotopic dilution recovery only) where the “sample” represents either the PUF cartridge or the filtered solids. PUF cartridge split samples will not be corrected for possible contaminant break-through of the PUF via surrogate correction, possible contaminant wash-out of the PUF via surrogate correction, or suspended solids unit conversion, since these corrections may increase the potential bias in the split sample comparison due to potential difference in professional judgment and handling of the data.

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]
HRGC/ HRMS and HRGC/LRMS	Initial Calibration and calibration verification check: Per laboratory SOP	After set up, after instrument changes or failures of checks and every 12 hours	% 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	EPA 1668A/ Axys SOP MLA-010
	Calibration checks: CCVs per laboratory SOP	Daily: Every 12 hours	% recovery per laboratory SOP	Check, correct; re-calibrate and rerun all samples analyzed after last valid calibration check	Laboratory analyst / QA officer - TBD	Axys SOP for PCDD/ PCDF by EPA 1613B: MLA-017
See CDM Smith Final QAPP for DOC, POC, and SSC instrument calibration information.						

Notes:

1. General GC/MS calibration requirements are presented. Instruments used for analyses follow the calibration frequencies outlined in the method SOPs (Appendix K of the Oversight QAPP, Addendum No. 5) and Appendix Q of this Final QAPP Addendum No. 11. Laboratory specific calibration information is maintained by the laboratories; method specific calibration information is detailed in the methods.

QAPP Worksheet #28-a
QC Samples Table

Matrix	PUF (Dissolved Phase) and filter solids
Analytical Group /Concentration Level	PCB Congeners/ Low (pg/sample)
Sampling SOP(s)	See Worksheet #21 – split of CPG samples
Analytical Method/SOP Reference	EPA 1668A (MLA-010 Full SOP, Rev. 10, Nov 2008)
Sampler's Name /Field Sampling Organization	TBD /CDM Smith
Analytical Organization	Axys Analytical Services Ltd.
No. of Sample Locations	See Worksheets #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 (MPC)
Method Blank	1 per 20 samples	Concentration < 2 pg, 10 pg or 50 pg/sample-See SOP Table 1. Sum of all congeners < 300 pg /sample unless sample concen-trations > 10* blank levels	If sample result is 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
Analysis (Laboratory) Duplicate	1 per 20 samples	± 20% mean for concentrations >10*QL	Flag outliers	Laboratory Analyst	Precision	RPD ≤ 40% for concentrations >10x DL[1]; otherwise ABS <QL
Certified Reference Material or Quality Control Sample	Periodically at least quarterly	50-150% recovery	Check standards; recalibrate if required	Laboratory Analyst	Accuracy	70-130% recovery
Calibration Verification Sample	Beginning of each 12-hour shift	70-130% recovery	Adjust and/or recalibrate	Laboratory Analyst	Accuracy/bias	70-130% recovery
Initial Precision and Recovery	Prior to sample analysis	Per laboratory SOP	Investigate and correct	Laboratory Analyst	Accuracy	60-140% recovery ≤ 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% recovery
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if measurement performance criteria (MPC) is exceeded; address in data quality assessment	CDM Smith ASC	Precision	RPD ≤ 40%; ABS<QL for samples <5x QL
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM Smith of failure and need for additional coolant; check packing procedure.	Laboratory Analyst	Accuracy/ representativeness	≤ 10 degrees Celsius for data validation

Notes:

1. The DLs referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits.

QAPP Worksheet #28-b
QC Samples Table

Matrix	PUF (Dissolved Phase) and filter solids
Analytical Group	PCDD/PCDF
Concentration Level	Low (µg/sample)
Sampling SOP(s)	See Worksheet #21 – split of CPG samples
Analytical Method/SOP Reference	EPA 1613B/ MLA-017 (MSU-017, Rev 4, March 2011)
Sampler's Name/ Field Sampling Organization	TBD /CDM Smith
Analytical Organization	Axys Analytical Services Ltd.
No. of Sample Locations	See Worksheet #18 & 20

QC Sample:	Frequency/ Number	Method/SOP QC Acceptance Limits[1]	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per 20 samples	TCDD/F <0.5 pg/sample, PeCDD/F, HxCDD/F, HpCDD/F <1.0 pg/sample, OCDD/F <5 pg/sample unless sample concentrations > 10* blank levels (per 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	± 20% mean for concentrations >10*QL	Investigate and correct; Flag outliers	Laboratory Analyst	Precision	± 20% of mean if sample concentration >10x DL[2]
Initial Precision and Recovery	Prior to sample analysis	Per laboratory SOP, Table 1	Investigate and correct	Laboratory Analyst	Accuracy	Per method/laboratory SOP
Ongoing Precision and Recovery	1 per batch of 20 samples	Per laboratory SOP, Table 1 (70-130% recovery)	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 Smith ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
Surrogates	1 per 20 samples	25-120% recovery -warning limit 17-130% recovery -control limit	Investigate and correct	Laboratory Analyst	Accuracy/bias	25-120% recovery 17-130% recovery
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM Smith of failure and need for additional coolant; check packing procedure.	Laboratory Analyst	Accuracy/ representativeness	≤ 10 degrees Celsius for data validation

Notes:
1. The laboratory must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in EPA Method 1613B as modified in the attached SOP.
2. The DLs referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits.

Worksheets 28 for POC, DOC and SSC are included in the PWCM QAPP March 2010.

QAPP Worksheet #29
Project Documents and Records Table

Sample Collection Documents and Records	On-Site Analysis Documents and Records	Off-Site Analysis Documents and Records	Data Assessment Documents and Records	Other
SCRIBE Traffic Reports/ COC Records	No on-site analysis will be performed	Sample Receipt, Custody and Tracking Logs	Corrective Action Reports	Purchase Requisition Forms
Airbills	Logbook Notes	Standards Tracking Logs	Analytical sample results	Laboratory SOPs
Sample Tracking Log/Sheets	Photographs	Corrective Action Reports	Laboratory certifications	Technical/QA Review Forms
Field datasheets/logbooks	No on-site analysis will be performed	Corrective Action Forms	Laboratory QA Plan (on file with EPA and CDM Smith)	ANSETS Report Forms
Daily Summary Report via e-mail		Data Packages (Case Narratives, Sample Results, QC Summaries and Raw Data (detailed in SOPs).	QC Audit Reports USEPA Region 2 Data Validation SOPs Data Validation Reports	Telephone Logs
Field Change Request Forms		Trip Reports	Data Package Completeness Checklist Validated Data Reports	Electronic Data Deliverables
Custody Seals		Sample analysis run logs	Self Assessment Checklist	Non-Conformance Reports
ANSETS Forms		Sample Receipt, Custody and Tracking Logs		

QAPP Worksheet #30
Analytical Services Table

Matrix	Analytical Group	Concentration Level	Analytical SOP	Data Package Turnaround Time[1]	Laboratory/Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Solid	PCDD/PCDF	Low	EPA 1613B/ Axys SOP MLA-017	21 days /30 days	AXYS Analytical Services Ltd. 2045 Mills Road West Sidney, BC V8L 5X2, Canada 1-888-373-0881	TBD
Solid	PCB Congeners	Low	EPA 1668A/ Axys SOP MLA-010			
Aqueous	SSC	Low	SM2540D (DESA SOP C-33 Modified)	21 days /30 days	DESA Primary contact: RSCC Adly Michael/Bob Toth 732-906-6161/6171 DESA contact: John Birri 732-906-6886	Master Services Agreement Subcontract Laboratory (TBD)
Aqueous	DOC	Low	SM 5310B (DESA SOP C-83 Modified)			
Aqueous	POC	Low	SM 5310B/ 415.1 (DESA SOP C-88 Modified)			

Notes:
1. 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, 2, 3]	Data Validator (title and organizational affiliation)
IIa /IIb	Solid	PCDD/PCDF	Low	EPA SOP HW-19 or 25, Validating PCDD/PCDF by HRGC/HRMS, Revision 1 or National Functional Guidelines	CDM Smith ASC, Scott Kirchner or designee
IIa /IIb		PCB Congeners	Low	Data Validation Guidelines SOP HW-46, rev 0 or National Functional Guidelines	
IIa /IIb	Aqueous	DOC	Low	DESA validation SOP – Data evaluation will review against QAPP measurement performance criteria	DESA
IIa /IIb		POC	Low		
IIa /IIb		TSS/ SSC	Low		

Notes:

1. DESA laboratory results will be validated by EPA staff.
2. Subcontract laboratory results will be validated by the process of data verification and assessment utilizing the laboratory QC summaries.
3. All validation procedures will utilize the measurement performance criteria in the QAPP and any additional method requirements.

QAPP Worksheet #37
Usability Assessment

The Data Comparability Report will be prepared by CDM Smith personnel. Frank Tsang, Task Order Manager, will be responsible for its content and for assigning work to the CDM Smith personnel who will be supporting this assessment. 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 the data, data validation, 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 as well as an assessment of the split sampling data quality. The following items will be assessed for CDM Smith split samples and conclusions drawn based on their results:

Precision – Split samples will be compared using the RPD for each pair of results reported above the QL. As appropriate, alternative data comparisons will be used. If needed, other statistical determination may be conducted consistent with the Newark Bay split samples collected by Louis Berger Inc. Additional information on data handling is included on Worksheet #11 under the section titled "What will the Data be Used for".

Results of laboratory duplicates will be assessed during data validation and data will be qualified according to the data validation procedures cited on Worksheet #36. RPD acceptance criteria of less than or equal to 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 the data will be described in the report.

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

Overall Accuracy/Bias – The results of instrument calibration and surrogate spike recoveries will be reviewed and data will be qualified according to the data validation guidelines cited on Worksheet #36. A discussion summarizing the results of laboratory accuracy and any limitations on the use of the data will be described in the report.

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 the data will be described in the report.

QAPP Worksheet #37

Usability Assessment

Representativeness – A review of adherence to field procedures and of project QA audits will be performed in order to assess the representativeness of the sampling program. Data validation narratives will also be reviewed, and any conclusions about the representativeness of the data set will be discussed.

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

Completeness – A completeness check will be done on analytical data generated by the laboratories. Completeness will be calculated for each analyte and compared to the project completeness goal of 90 percent. For sampling, completeness will be calculated as the number of samples collected and analyzed divided by the number of samples 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 the 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 the data will be determined. Based on the quality, the usability of the data for each analysis will be determined. Based on the combined usability of the 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 the 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 CPG's sample and CDM split sample or field duplicate

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:

CDM Federal Programs Corporation (CDM Smith). 2010. *Final Quality Assurance Project Plan Physical Water Column Monitoring and Generic Information for Upcoming Tasks*. March 10.

CDM Smith. 2011. *Final Quality Assurance Project Plan Addendum No. 9. River Mile 10.9 Characterization Study*. August 25.

AECOM. 2011. Lower Passaic River Restoration Project. Lower Passaic River Study Area RI/FS. *Quality Assurance Project Plan/Field Sampling Plan Addendum. Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection*. Revision 1. July 2011.

AECOM. 2012. Lower Passaic River Restoration Project. *Quality Assurance Project Plan. RI Water Column Monitoring/High Volume Chemical Data Collection*. Revision 1. September.

Louis Berger Group. 2011. Lower Passaic River Restoration Project. Draft *Oversight Quality Assurance Project Plan for Water Column Monitoring in the Newark Bay Study Area*. May 10.

Figure 1

The CPG's QAPP Remedial Investigation Water Column Monitoring/High Volume Chemical Data Collection QAPP, Introduction Page 8 of 8, September 2012.

Introduction (Continued)

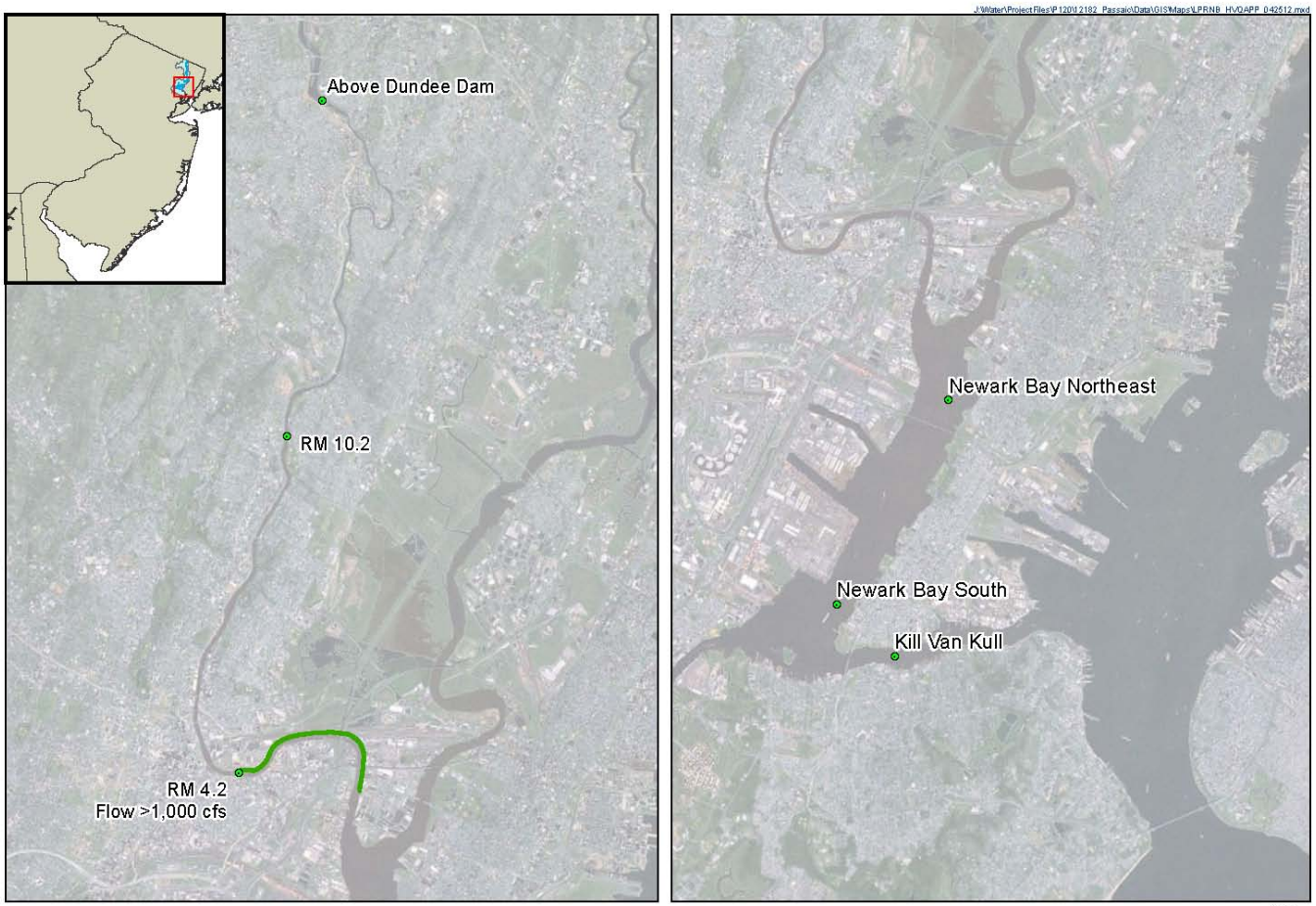

Figure 1. Sampling Locations for High Volume Chemical Water Column Monitoring Program

Appendix Q

Laboratory SOPs

PCDD/PCDF	AXYS
PCB Congeners	AXYS

Appendix Q

Laboratory SOPs

AXYS SOP

MLA-017, Revision 20

Dioxin and Furans (PCDD/PCDF)

By EPA 1613B

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AXYS ANALYTICAL SERVICES LTD.

AXYS METHOD MLA-017: 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]

SCOPE

This analytical method describes the analysis of polychlorinated (tetra-octa) dibenzodioxins and dibenzofurans in solids (sediment, soil, biosolid, pulp), tissues (including blood, serum, plasma and milk), aqueous samples, XAD-2 columns, air samples, particulate filters and solvent extracts. All samples are spiked with ^{13}C-labelled surrogate standards prior to extraction. Solids, tissues, XAD-2 resin, ambient air (PUF and filters) and particulate filters are Soxhlet extracted. Dean-Stark Soxhlet extraction procedures are used for column filters and as an alternate extraction method for solids and XAD-2 resin. Tissue samples, too large to be extracted by Soxhlet extraction, are extracted by base digestion. Aqueous, blood, serum, plasma and milk samples are liquid-liquid extracted. Extracts are routinely cleaned up using the following cleanup columns:

- column chromatography on layered silica gel
- column chromatography on Florisil
- column chromatography on alumina
- column chromatography on carbon/Celite
- column chromatography on Biobeads (optional)

Extracts can also be cleaned up using automated cleanup procedures on an FMS cleanup instrument.

The final extracts are analyzed by high resolution gas chromatography with high resolution mass spectrometric detection (HRGC/HRMS) for concentrations of individual 2,3,7,8 polychlorinated dioxin and furan isomers (tetra - octa) and total congener concentrations. Toxic equivalents for these analytes may also be reported [6,7]. The method is performed according to EPA Method 1613B, which is attached and is considered part of this document.

The MLA-017 procedures conform to methods EPA 1613B, EPA 8290/8290A (Appendix B), and also include options to cover Environment Canada method EPS 1/RM/19 “River Road” (Appendix A) and EPA method DLM02.2 (Appendix C).

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The analysis of non-2,3,7,8-substituted isomers is available as an option and requires no modifications to the analytical method or any additional standards. This option is described in Appendix D.

Approved by: _____ Date: 10 - JUL - 2012
John Cosgrove, President and Senior Technical Director

Approved by: _____ Date: 10-JUL-2012
Shea Hewage, Director of Operations

Approved by: _____ Date: 10-JUL-2012
Dale Hoover, QA Manager

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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 DLM02.2, *Statement of Work (SOW) for Analysis of Chlorinated Dibenzo-p-dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs)*, December 2009.

6. Van den Berg et al. 1998. *Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife.* Environmental Health Perspective, **106** (12), 775-792.

7. *Pilot Study on International Information Exchange on Dioxins and Related Compounds, International Toxicity Equivalency Factor (I-TEF) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds,* North Atlantic Treaty Organization, Report Number 176, August 1988.

8. Environment Canada: *Internal Quality Assurance Requirements for the Analyses of Dioxins in Environmental Samples*, Report EPA 1/RM/23 Oct 1992.

9. USEPA *Determination of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-dioxins and Dibenzofurans in Ambient Air*, Method TO-9A, January 1999.

10. AXYS Method Document MLA-024. *Analytical Method for the Determination of Polybrominated Dioxins and Furans by High Resolution GC/MS*.

11. AXYS Method Document MLA-015. *The Analysis of Ambient Air Samples for Polychlorinated Dioxins (PCDD) and Furans (PCDF), Polychlorinated Biphenyls (PCB) and Polybrominated Diphenylethers (PBDE).*

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CHANGES FROM PREVIOUS REVISIONS AND VERSIONS

The table below lists the details of the changes made from revision 20 version 05 of this document.

Page	Change Details (by June 2012)
22	Section 3.3.4.1: Added instruction for blood/serum/plasma and milk extracts according to EPA 1613/8290. Changed that calibration solutions for Environment Canada method 1/RM/19 should by default be prepared in nonane (not in toluene).
43, 48-52, 58	Sections 5.3.2, 5.5.4.2, 5.6.3, 5.6.4, 5.6.5, 5.7 and 5.11.1: Updated information for cleaning Soxhlet glassware to read pre-Soxhlet with dichloromethane and rinse with dichloromethane.
72	Section 6.9.1: Clarified that nonane is the default final extract solvent for EPA 1613B/8290/8290A and Environment Canada method 1/RM/19. Added instruction for blood/serum/plasma and milk extracts according to EPA 1613/8290.
87	Appendix A: Changed recovery standard solution, final extract and calibration solutions to be prepared in nonane instead of toluene..

The table below lists the details of the changes made from revision 20 version 04 of this document.

Page	Change Details (by June 2012)
1	Scope: Rephrased to clarify that MLA-017 conforms to EPA methods 1613B, 8290 and 8290A, and also includes options to cover EPA method DLM02.2 and EC method EPS 1/RM/19. Deleted reference to PCDD/F analysis in air according to EPA method TO-9A by AXYS method MLA-015. Deleted reference to co-analysis of polybrominated dibenzodioxins and –furans.
14	Section B: Added explanation that the method is not isomer specific for all 2,3,7,8-penta- and hexa-PCDD/F isomers.
16	Table 2: Updated sample size for milk to be 10-30 g (default) or 50-150 g (non-routine).
19	Section 3.1: Added “Stirlenmeyer” flasks to the equipment list.
20, 74	Section 3.1 and section 7: Updated instrument designations.
21, 80	Section 3.3.2 and Section 10 (section 7.11): Clarified that AXYS’ current cleanup standard level is ¼ of the EPA 1613B/ 8290 level.
22, 23	Sections 3.3.4 and 3.3.5: Deleted references to determination of non-2,3,7,8-substituted PCDD/F.
21, 22, 24, 72, 75, 80, 82	Sections 3.3.3, 3.3.4, 6.9, 7, 10 and table 3: Clarified that dilution of calibration solutions and sample extracts in nonane is a requirement for methods EPA 1613/8290 and that the optional use of toluene solvent is a modification not applied to accredited EPA 1613/8290 testing.
22, 86	Section 3.3.4.2 and Appendix A: Clarified that Environment Canada method 1/RM/19 uses recovery and calibration solutions prepared in toluene.
26	Table 5: Corrected levels of 1,2,3,8,9-PeCDF.
32	Section 4: Clarified language about OPR samples. Clarified that aqueous OPR samples are spiked by a combined surrogate and authentic standard solution.
35	Table 7: Clarified QC Parameters “Detection Limit”, “Analyte Peak Response” and “Sensitivity”.
35, 76	Table 7 and Section 8.1: Clarified the Ion Ratio specification according to EPA 1613B standard.
39	Section 5.1.1.4: Deleted mortar grinding instruction. Clarified filter rinsing/pH checking procedure.
45-47	Section 5.5.3.1, 5.5.3.2 and 5.5.4.1: Changed extract drying procedure to filtration through anhydrous sodium sulfate to reflect current practice.
55-56	Section 5.9: Added a milk analysis procedure using sample sizes less than 30 grams and designated this as the default procedure; affected parameters include sample weight, surrogate and recovery standard spiking, addition of cleanup standard, final extract volume, OPR/IPR protocol, and instrumental method acceptance limits. Designated the original milk procedure applicable to larger sample sizes as an optional procedure.. .
67	Section 6.3.3: Added instruction for handling of extracts that leave strong colour in any of the column layers.
70	Section 6.7: Clarified that the extract must be transferred to a centrifuge tube before nitrogen blowdown.
70-71	Sections 6.8.1, 6.8.2 and 6.8.3: Corrected extract blowdown volume to be 300 µL

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74	Section 7: Clarified the number of ions used to monitor compounds. Updated the number of instrument blanks to follow current practice.
77	Table 9: Adjusted quantification ion masses for $^{37}Cl_4$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, $^{13}C_{12}$-1,2,3,6,7,8-HxCDF, $^{13}C_{12}$-1,2,3,7,8,9-HxCDF and $^{13}C_{12}$-2,3,4,6,7,8-HxCDF to be the same as in EPA 1613B. Adjusted quantification ion masses for $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF and $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF to exact masses that differ slightly from EPA 1613B. The adjustments done don't significantly affect the accuracy of the acquisition.
87	Table 10: Adjusted quantification ion masses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDF to be the same as in EPS 1/RM/19. Adjusted quantification ion masses for $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF to an exact mass that differ slightly from EPS 1/RM/19. The adjustments done don't significantly affect the accuracy of the acquisition..
90	Appendix B: Deleted requirement to perform I-Cal immediately following a failed CAL/VER, as this is not an EPA 8290A requirement if RPD is less than 25%/35%.
91	Appendix B: Clarified that the use of cleanup standard is not required by EPA method 8290, but may be added as an internal QC check.
92	Table 12: Corrected typos for a few surrogate names. Adjusted quantification ion masses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDF and $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF to agree with EPA 8290/8290A.
96	Appendix C: Clarified that for EPA method DLM02.2 solid samples are extracted by Dean-Stark Soxhlet extraction and tissue samples are Soxhlet extracted for 18-24 hours.
100	Table 14: Provided four decimals to the ion masses.

The table below lists the details of the changes made from revision 20 version 03 of this document.

Page	Change Details
2, 3	Added reference to Axys method MLA-015.
19, 20	Section 3.3.3 and 3.3.4: Added a conventional EPA 1613B / 8290 procedure for preparation of recovery and calibration solutions in nonane.
22	Added concentrations of recovery standards in nonane to Table 3.
36, 39	Section 5.1 and 5.2: Clarified extraction solvents used with solid samples.
43-45, 93	Section 5.5.1: Added instruction that aqueous samples must be magnetically stirred while spiked with surrogate solution. Section 5.5.3, section 5.5.4.1 and Appendix C: Clarified that all aqueous samples except those analyzed by DLM02.2 are extracted by the default magnetic stirring procedure; extraction is then performed in the same Erlenmeyer flask where the sample was spiked with surrogates. Aqueous DLM02.2 samples must however be extracted using a separatory funnel.
69	Section 6.9: Added a conventional EPA 1613B / 8290 procedure for dilution of extracts with nonane and revised micro-vialing details to match current practice.
77-79	Section 10: Updated modification list (items "Sections 7.13, 14.0, 15.0", "Section 12.3" and "Section 14.2")
87	Appendix B: Clarified applicable modifications by referencing section 10.
93-94	Appendix C: Clarified that all primary column calibration sequences for DLM02.2 work must start and end with the CS-3 solution (which also contains the column performance solution [CPS] compounds). All runs of this solution must be labeled as "CS-3 + CPS" in the run logs. Clarified that all secondary column calibration sequences for DLM02.2 work must start and end with the Isomer Specificity Check (ISC) solution. All runs of this solution must be labeled as "ISC" in the run logs. Clarified that Axys may dilute sample extracts with solvents only after prior agreement with the client.
97	Deleted Appendix D content and renumbered Appendix E as Appendix D.

The table below lists the details of the changes made from revision 20 version 02 of this document.

Page	Change Details
13, 40, 44, 46, 47, 48	Sections B, 5.3.2, 5.5.4.2, 5.6.4, 5.6.5, 5.7: Changed pre-extraction solvent of Soxhlet apparatus to be dichloromethane to reflect current practice.
14	Table 2: Changed sample frozen storage temperature to -20 º C to more closely reflect practice.
17	Section 3.1: Added make of filter to reflect current practice.
19, 35, 38,	Sections 3.3.4, 5.1, 5.2, 5.3, 5.4 and 7: Added identification of a method default procedure

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40, 41, 68	versus an optional procedure.
24	Section 3.4: Clarified type/make of glass fibre filter. Added reference to SLA-108 for instructions pertaining to the glass fibre filter bed.
27-28	Sections 3.6.3 and 3.6.5: Added proofing requirement and pre-elution instructions.
27, 59, 60, 61, 62, 66	Sections 3.6.5, 6, 6.1, 6.3.1, 6.3.2 and 6.8.2: Changed weight of column "DX $AgNO_3$ 30g 44%" to reflect current practice.
29	Section 4.1: Clarified that blank and reference filters must be of the same type and the same cleaning batch as used for the client samples.
33, 43, 50, 51	Sections 5, 5.5.4.1, 5.8.3 and 5.9: Added reference to SLA-124 Liquid-Liquid Supplemental Techniques
37	Section 5.1.1.5: Removed obsolete specification of filter make (GF/F).
37, 39, 44, 60, 76	Sections 5.1.2, 5.2.2, 5.5.4.2, 6.1, 10: Adjusted procedure to spike cleanup standard into separatory funnel when base/acid wash is performed to align with 1613B procedure.
45-46	Sections 5.6.2 and 5.6.3: Changed to describe current practice.
50	Section 5.8.3, point 6: Changed "Lipid Determination" instructions to refer to SLA-020.
51	Section 5.9, point 6: Deleted obsolete reference to fluted filter paper.
61	Section 6.3.1: Changed the typical cutpoint volume for the "DX $AgNO_3$ 30g 44%" column to reflect current practice.
71, 73	Section 8.1 and Table 9: Added chlorinated diphenylether monitoring criteria and ions (Table 9)
72-73, 82, 87	Table 9, 10, 12. Replaced nominal masses with precise masses monitored
various	Renumbered some sections in accordance with updated method formatting standard. Changed "3 significant figures" to "2 decimals" in all weighing instructions. Deleted all references to SLA-030 "Micro Lipid Determination for Human Blood Analysis" that has been archived.

The table below lists the details of the changes made from revision 20 (version 01) of this document.

Page	Section	Change Details
1	Scope	Changed the cleanup column outline in the summary.
25-26, 57ff	3.6.2 - 3.6.5 6	Changed names of the four silica based cleanup columns.
26	3.6.4, 3.6.7	Added details on preparation of the DX 20g 44% column (formerly "large layered acid/base silica column"), specified it as the default column for tissue and blood/serum/plasma extracts. Changed pre-elution details for the DX Carbon/Celite column.
30	4.1	Document correction -changed the default detection limit in Table 7 to 0.5 pg/sample
33	5.1	Changed the default pre-soxhlet solvent from toluene to DCM.
36	5.2	Changed the default pre-clean solvent for the Dean-Stark soxhlet extraction from toluene to DCM.
56	5.12	Deleted the gravimetric splitting procedures, added a reference to SLA-123.
57	6	Added a default procedure outline for manual cleanup. Added a note about changing silica column size, added a note to vortex prior to each transfer.
58	6.2	Added a note that the Biobead column is optional. Clarified procedure language.
58-60	6.3.1-6.3.4	Changed columns, updated procedures.
59	6.3.3	Added language specifying that the large layered silica column is default for tissue analysis.
60	6.4	Specified that a DX Florisil column is default for tissue and optional for solid samples. Added notes on procedure.
60-61	6.5	Added details on the new alumina/carbon Celite combination column.
61-62	6.6	Specified that the standalone alumina column is optional/remedial.
62	6.7	Specified that the standalone DX carbon/Celite column is optional/remedial.
62	6.8	Added requirement to vortex extracts in centrifuge tube prior to every transfer.
66	8	Changed reporting limit for all samples other than blood/serum/plasma to 0.5 pg/sample.
68	9	Changed reporting limit for all samples other than blood/serum/plasma to 0.5 pg/sample.

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The table below lists the details of the changes made from revision 19 of this document.

Page	Section	Change Details
24-25	3.6	Added preparation instructions for the new silica cleanup columns. Clarified names of the silica columns. Clarified instructions.
56-62	6	Updated instructions for all current cleanup options. Clarified which cleanup procedures are default and which are optional. Entered FMS instructions (from previous Appendix F).

The table below lists the details of the changes made from revision 18 of this document.

Page	Section	Change Details
54	6.0	Added reference to an optional automated FMS cleanup procedure.
92	Appendix F	Added information relevant to optional FMS cleanup procedure

The table below lists the details of the changes made from revision 17 of this document.

Page	Section	Change Details
1	Scope	Corrected the manual cleanup column list.
		General change: Automated cleanup using the fluid management system (FMS) is discontinued and all references to it deleted. Only manual cleanup is now performed (section 6).
16, 17, 62	3.3.4, 3.3.5, 7	Clarified which solutions are used for CAL/VER and for resolution checks.
22	Table 5	New table outlining the non-2,3,7,8 substituted compounds in CS-1R and CS-3.
23	3.5	Deleted silver nitrate from the reagent list, changed silica with 10% silver nitrate to be purchased as a finished product.
23-24	3.6	Added a high capacity layered silver nitrate/acid/base silica column to the cleanup column list. Changed preparation solvent to be (pure) hexane for the layered silver nitrate/acid/base columns.
38	5.5.4	Replaced DCM rinse of sample container and filtration apparatus with acetone rinse when the Soxhlet extraction option is used for particulate extraction.
54-60	6	Cleanup section: Deleted all FMS instructions and references. Renamed “acid/base wash” to “base/acid wash”. Moved base/acid wash, Biobead and preparation for GC/MS analysis instructions into this section. Added a High Capacity Layered Silver Nitrate/Acid/Base Silica Column. Changed the order of the sub-sections to reflect the order in which the columns are used. Changed elution solvent for the layered silver nitrate/acid/base silica column to be hexane. Clarified instructions.
61	7	Clarified sub-sections “Sensitivity” and “GC Resolution”.
77	Table 12	Corrected entries under “RRF determined from” to be from individual congeners instead of from the mean of multiple congeners.
81	App. C	Clarified that cleanup standard recovery must be reported from both DB-5 and DB-225 columns. Modifications, item #1: Corrected to cover recovery standard only.

The table below lists the details of the changes made from revision 16 of this document.

Page	Change Details
1-3, 81, 83	Updated reference to DLM02.0 to current revision DLM02.1
20, 22, 47, 48, 49, 50, 66	Changed powdered anhydrous sodium sulphate to be J.T. Baker 12-60 mesh.
26	Table 5: IPR average recovery: Corrected typographical errors for 1,2,3,4,7,8-HxCFD (from 82-108% to 82-118%), 2,3,4,6,7,8-HxCDF (from 74-158% to 74-148%), OCDD (from 86-126% to 89-127%) and $^{13}C_{12}$-OCDD (from 20-138% to 20.5-138%). CAL VER Limits: Corrected for compliance with EPA 8290A limits: 2,3,7,8-TCDD (from 78-129% to 78-125%), 1,2,3,7,8-PeCDD (from 78-130% to 78-125%), 1,2,3,4,7,8-HxCDD (from 78-128% to 78-125%), 1,2,3,6,7,8-HxCDD (from 78-128% to 78-125%), OCDD (from 79-126% to 79-125%) and OCDF (from 70-130% to 75-125%).

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	Added column with sample surrogate acceptance limits specific to Environment Canada method EPS 1/RM/19. Added footnote clarifying that the IPR standard deviation specification is expressed relative to the fortification level
27	Table 6: Added an alternate ion ratio criterion allowable for EPA 1613B applications.
28	Section 5.0 (table): Deleted the reference to SLA-028.
34	Section 5.3.2: Deleted erroneous reference to a second (non-existing) lipid determination method.
43,59	Section 5.8 and Section 8: Added instruction that blood OPR/IPRs should have a FV of 40 µL.

The table below lists the details of the changes made from revision 15 of this document.

Page	Change Details
1	Added document identification to the title.
9	Added reference for definitions (to QDO-001)
9	Added comment that MDLs are kept on file

The table below lists the details of the changes made from revision 14 of this document.

Page	Change Details
32	Section 5.2.2: Deleted requirement to add the toluene in the Dean-Stark receiver to the extract.

The table below lists the details of the changes made from revision 13 of this document.

Page	Change Details
29, 35-37	Sections 5.1.1, 5.5.1, 5.5.3 and 5.5.4.1: New aqueous liquid-liquid extraction procedure using magnetic stirring.

The table below lists the details of the changes made from revision 12 of this document.

Page	Change Details
	Global Changes: Changed the header statement from "This document is the property of AXYS Analytical Services Ltd and contains proprietary and confidential information. It may not be reproduced or distributed without the written permission of the owner. Copyright 13-Apr-2006." to "This document is the Intellectual Property of AXYS Analytical Services Ltd and contains Proprietary and Confidential Business Information. It may not be reproduced or distributed without written permission of the owner. © AXYS Analytical Services Ltd, 2007". Changed address to "2045 Mills Road".
10	Changed in Table 2 the extracted amount of serum to 40 g and the extracted amount of whole blood to 60 g.
46	Changed in section **5.8 Blood Extraction** the extracted amount of serum to 40 g and the extracted amount of whole blood to 60 g.
49	Changed in section **5.9 milk Extraction Procedure** paragraph 6 to be the same as in MLA-013 r06 "Using 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, PCDD/F, and where required, BDE cleanup standards to the extract.". Omitted the filtration of the extract through glass wool.
	4.1 Quality Control Samples: Moved the 30 min equilibration time between native and surrogate spiking to be done after the spiking of both native and surrogate.

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INTRODUCTION

A. ANALYTES OF INTEREST

This analytical method determines the concentrations of the compounds listed below. The analysis of polychlorinated dibenzodioxins and dibenzofurans (tetra - octa) is performed by high resolution GC/MS (HRGC/HRMS).

Table 1. Polychlorinated Dibenzodioxins and Dibenzofurans (PCDD/F)

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)	
1,2,3,6,7,8 HxCDD	1,2,3,4,7,8 Hexachlorodibenzofuran (HxCDF)
1,2,3,7,8,9 HxCDD	1,2,3,6,7,8 HxCDF
Total HxCDD	1,2,3,7,8,9 HxCDF
	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)

A.1 Optional Analytes

The analysis of non-2,3,7,8-substituted isomers is available as an option and requires no modifications to the analytical method or any additional standards. Quantification procedures are described in Appendix D.

The analysis of polybrominated dibenzodioxins and furans may be carried out concurrently with this method, following the procedures described in AXYS Method MLA-024, "*Analysis of Polybrominated Dioxins and Furans by HRGC/MS*".

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B. CONTAMINATION OR 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 of the Analysis Procedures section. The Soxhlet apparatus (including thimble) must be pre-extracted with dichloromethane for a minimum of two hours (three hours if brominated analytes are to be determined) to avoid potential contamination from previous samples.

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

Not all of the possible PCDD/F isomers can be separated on a DB-5 (or any other) GC column; the method is isomer specific for 2,3,7,8-TCDD and for 2,3,7,8-TCDF (through use of a secondary DB-225 column) but results for 2,3,7,8-penta- and hexa-CDD/CDF isomers could be inflated by the presence of co-eluting PCDD/F isomers. The potential for this interference with 2,3,7,8-penta- and hexa-CDD/F isomers is an inherent limitation of the method.

C. SAFETY

Refer to Section 5.0 of EPA Method 1613B for safety precautions when performing the analysis. For general safety procedures refer to SAF-001 “Safety Manual”. Refer to SLA-079 “Agricultural Hazard Protocols for Soils” and SLA-082 “Handling of Human Biohazardous Samples” for procedures for hazardous samples

D. 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 SAF-001 “Safety Manual” and to SAD-014 “Sample Disposal” for procedures for disposing of laboratory wastes.

E. DEFINITIONS

Refer to the definitions in the glossary at the end of EPA Method 1613B, which is appended to this document.

Refer to Axys Analytical Services QA/QC Policies and Procedures Manual (QDO-001, Appendix E) for definitions of general terms used in this document.

F. 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,

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background analyte levels in procedural blanks, and relative percent difference between sample duplicates.

This method has been validated to demonstrate that it is fit for the intended use.

Actual Method Detection Limit (MDL) results are kept on file.

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ANALYSIS PROCEDURES

1. SAMPLE PRESERVATION AND 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[4]	Preservation
Solid (Sed/Soil/Ash/ Sludge)	10 g dry	Glass	<4°C dark	-20°C, dark	(1 year)	1 year	none required
Tissue	10 g wet	Glass or foil wrapped	<4°C dark	-20°C, dark	(1 year)	1 year	none required
Aqueous (water, effluent, wet ash, wet sludge, wet pulp)	1 L	Amber Glass	0 - 4°C	0 - 4°C, dark	(1 year)	1 year	Add 80 mg/L Na_2S2O_3 if +ve for residual Cl If pH>9 adjust to pH 7-9
Dry pulp	20-25 g	Glass	Ambient	Ambient, dark	undefined	undefined	none required
Serum/plasma Whole blood	40 g 60 g	Glass	<4°C	-20°C, dark	(1 year)	1 year	none required
Milk	Up to 30 g (default) 30-150 g (non-routine)	Glass	<4°C	-20°C, dark	(1 year)	1 year	none required
XAD-2 Column	-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 4°C, dark -20°C, dark -20°C, dark	undefined undefined undefined undefined	undefined undefined undefined undefined	none required none required none required none required
Ambient Air	PUF & Filter	Glass	<4°C	-20°C, dark	undefined	undefined	none required
Stack Gas (Sample Trains)	Several Containers[5]	Glass	<4°C	4°C, dark	30 days	undefined	none required
Particulate Filter Papers	whole filter(s)	Glass or foil wrapped	<4°C	-20°C, dark	undefined	undefined	none required
Solvent Extract	1 sample	Glass	<4°C	-20°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 during storage. Samples for brominated analyses must be in amber glass containers.

[2] Storage temperatures quoted are nominal temperatures. Samples stored at a nominal temperature of 4°C are permitted a variance of ±2°C, samples stored at -20 ºC are permitted a variance of 4 ºC.

[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] Hold times for extracts are from time of extraction.

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

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2. SAMPLE PRE-TREATMENT AND PREPARATION

Refer to the following standard operating procedures:

Q-Pulse 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

Refer to EPA Method 1613B, Section 11.2 for the determination of percent solids.

Solid (Sediment/Soil) Samples

Allow a solid sample to thaw prior to homogenization and subsampling following procedures in standard operating procedure SLA-014. Homogenize solid samples 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.

Tissues

Allow a tissue sample to thaw prior to homogenization and subsampling 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 procedure SLA-013.

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

Aqueous Samples

Refer to the standard operating procedure SLA-084 “Preparation of Aqueous Samples for Extraction”.

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Whole Blood/Serum/Plasma

Allow a blood/serum/plasma sample to thaw prior to homogenization and subsampling following procedures in standard operating procedure SLA-014. Homogenize the sample by shaking well.

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.

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.

Particulate Filter Papers

Allow particulate filters papers to partially thaw.

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.

Pulp

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

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

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 Microvials
SLA-041	Reagent Preparation
SLA-044	Activation of Copper Foil, Turnings and Powder
SLA-093	Baking of Anhydrous Sodium Sulphate
SQA-009	Storage and Control of Analytical Standards
SQA-003	Standard Solution Validation

3.1 Equipment List

Extraction

Separatory funnels (125 mL, 500 mL, 1000 mL, 2000 mL)
Erlenmeyer flasks (250 mL, 500 mL, 1000 mL, 2000 mL)
“Stirlenmeyer” flasks (2 L), with attached stopcock (Erlenmeyer flasks modified to allow for efficient extraction of aqueous samples by magnetic stirring)
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
Glass fibre filter paper, Ahlstrom, 161 grade, 1.1 µm, 42.5 mm (or equivalent)
pH paper, range 0-14 (Sigma-Aldrich, Panpeha), 0.5 unit readability
Teflon tape
Aluminum Foil
Spatula - aluminum
Rotary evaporator
Magnetic stirring plate

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Millipore vacuum filtration apparatus
Soxhlet apparatus (pre-cleaned) w/heating mantle
Dean-Stark Soxhlet apparatus (pre-cleaned)
Water bath capable of maintaining up to 50°C
Balance – Top loading and analytical (2-, 3-, & 4-place)
Glassware drying ovens
Sample drying ovens
Muffle furnace
Nitrogen source with manifold apparatus

Instruments

Agilent 6890 Gas Chromatograph, or equivalent

High resolution mass spectrometer VG/Micromass Autospec Ultima, Waters Micromass Autospec Premier, or equivalent (1613B requirement: 28-40 eV electron impact ionization, shall be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately one second.)

GC Columns: DB-5 (60 m, 0.25 mm i.d., 0.10 µm film thickness)
DB-225 (30 m, 0.25 mm i.d., 0.15 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 prior to use.

Glassware must be washed and solvent rinsed following the procedures described in SLA-018.

3.3 Preparation of Standard Solutions

The analysis of PCDD/F by EPA Method 1613B requires the use of the surrogate, cleanup, recovery (internal), authentic spike and calibration solutions described in Section 7.7 - 7.16 of EPA Method 1613B. 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

Modify the preparation of the surrogate spiking solution (EPA Method 1613B, Section 7.10) so that the concentration of the labelled compounds is 100 ng/mL. The volume of the aliquot used has been adjusted so that the same absolute amount of standard, as described in EPA Method 1613B, is added. Note: The lot number of the surrogate stock solution must match the lot number of the calibration series.

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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 (10 µL for blood/serum/plasma or milk samples) is added. 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 3.

3.3.2 Cleanup Standard Solution

Modify the preparation of the cleanup standard spiking solution (EPA Method 1613B, Section 7.12) so that the concentration of the labelled compounds is 10 ng/mL. The volume of the aliquot used has been adjusted so that ¼ of the amount of standard, as described in EPA Method 1613B, is added.

After extraction or drying of the extract, but prior to rotary evaporation or any cleanup step, 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 3.

3.3.3 Recovery (Internal) Standard Solution

Prior to instrumental analysis, cleaned up extracts are spiked with $^{13}C_{12}$-labelled recovery (internal) standards. 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 3.

3.3.3.1 Recovery standard prepared in nonane (mandatory for EPA 1613/8290) – default procedure

Prepare the recovery standard solution in nonane at a concentration of 200 ng/mL. Typically an aliquot of 10 µL (5 µL for blood/serum/plasma or milk extracts) of this solution is added to final extracts.

3.3.3.2 Recovery standard prepared in toluene (not applied to EPA1613/8290 testing) – optional procedure

Prepare the recovery standard solution in toluene at a concentration of 100 ng/mL. Typically an aliquot of 20 µL (10 µL for blood/serum/plasma or milk extracts) of this solution is added to final extracts.

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3.3.4 Calibration Solutions

A series of calibration solutions (CS-1 to 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 concentrations 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 4. Analysis by EPA methods 1613 / 8290 requires the use of nonane solvent, for other applications use of toluene solvent is a permitted option yielding equivalent results.

Where requested, AXYS will expand the initial calibration range specified in method 1613B (Sections 7.13, 14.0, 15.0) to include an extra calibration solution (CS-0.2) that is one-fifth the concentration of CS-1; the concentrations of the other initial calibration solutions, CS-1 through CS-5, remain as stated in the method. Mean calibration RRFs used to quantify sample data are then generated using the six-point initial calibration series of solutions. This extension of the calibration range has the effect of lowering the Minimum Levels to one-fifth of those stated in the method.

The CS-3 solution also contains a suite of PCDD/F compounds (refer to Table 5) to define the GC acquisition windows and to demonstrate GC column isomer specificity.

3.3.4.1 Calibration Solutions Prepared in Nonane (EPA Methods 1613/8290) – default procedure

Prepare five calibration solutions (CS1, CS2, CS3, CS4 and CS5) at the nominal concentrations listed in Table 4 as described in EPA Method 1613B, Section 7.13, using nonane as the diluting solvent. The CS-3 solution is used as the calibration verification (CAL/VER) solution, analyzed every twelve hours to verify GC/MS performance and calibration. The CS-3 solution also contains a suite of PCDD/F compounds (refer to Table 5) used to define the GC acquisition windows, and to demonstrate GC column isomer specificity. When analyzing blood/serum/plasma or milk extracts, the CS-1R solution (refer to section 3.3.5 and Table 5) is used as the CAL/VER solution and to determine GC resolution.

Environment Canada method 1/RM/19 is performed using calibration solutions prepared in nonane.

3.3.4.2 Calibration Solutions Prepared in Toluene (not applied to 1613/8290 testing) – optional procedure

Prepare five calibration solutions (CS1, CS2, CS3, CS4 and CS5) at the nominal concentrations listed in Table 4 as described in EPA Method 1613B, Section 7.13, but using toluene instead of nonane as the diluting solvent. The CS-3 solution is used as the calibration verification (CAL/VER) solution, analyzed every twelve hours to verify GC/MS performance and calibration.

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3.3.5 GC Resolution Test Solutions for Blood/Serum/Plasma and Milk Extracts

When analyzing blood/serum/plasma or milk extracts, the CS-1R solution is used as the CAL/VER solution and to determine the GC peak resolution of the DB-5 column. The CS-1R solution has the same composition as the CS-1 solution, but with 1,2,3,7/1,2,3,8-TCDD added (0.5 ng/mL) for resolution testing. The CS-1R solution also contains a suite of PCDD/F compounds (refer to Table 5).

If confirmation of 2,3,7,8-TCDF is performed on a DB-225 column the resolution between 2,3,7,8-TCDF and 1,2,3,9- and 2,3,4,7-TCDF must be checked using a separate standard solution containing these three compounds at 5 ng/mL each and 1 ng/mL of $^{13}C_{12}$-2,3,7,8-TCDF.

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

Prepare the authentic spiking solution as described in EPA Method 1613B, Section 7.9. 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 (100 µL to each OPR or IPR for blood/serum/plasma or milk). The Batch List indicates the name of the recovery 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 3.

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Table 3. Nominal Concentration of PCDD/PCDF Standard Solutions - GC/HRMS Analysis

Compound Name	Concentration in Standard Solution	Typical Amount Spiked into Every Sample	Typical Amount Spiked into Blood/ Serum/Plasma or Milk OPR Sample	Typical Amount Spiked into all other OPR Samples
Surrogate Std Solution				
$^{13}C_{12}$-2,3,7,8-TCDD	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-OCDD	200 ng/mL	4000 pg	2000 pg	4000 pg
$^{13}C_{12}$-2,3,7,8-TCDF	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100 ng/mL	2000 pg	1000 pg	2000 pg
Cleanup Std Solution				
$^{37}Cl_4$-2,3,7,8-TCDD	10 ng/mL	200 pg	-	200 pg
Recovery Std Solution in Nonane (EPA 1613 / 8290)				
$^{13}C_{12}$-1,2,3,4-TCDD	200 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	200 ng/mL	2000 pg	1000 pg	2000 pg
Recovery Std Solution in Toluene				
$^{13}C_{12}$-1,2,3,4-TCDD	100 ng/mL	2000 pg	1000 pg	2000 pg
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100 ng/mL	2000 pg	1000 pg	2000 pg
Native Spike Solution				
2,3,7,8-TCDD	0.2 ng/mL	-	20 pg	200 pg
1,2,3,7,8-PeCDD	1 ng/mL	-	100 pg	1000 pg
1,2,3,4,7,8-HxCDD	1 ng/mL	-	100 pg	1000 pg
1,2,3,6,7,8-HxCDD	1 ng/mL	-	100 pg	1000 pg
1,2,3,7,8,9-HxCDD	1 ng/mL	-	100 pg	1000 pg
1,2,3,4,6,7,8-HpCDD	1 ng/mL	-	100 pg	1000 pg
OCDD	2 ng/mL	-	200 pg	2000 pg
2,3,7,8-TCDF	0.2 ng/mL	-	20 pg	200 pg
1,2,3,7,8-PeCDF	1 ng/mL	-	100 pg	1000 pg
2,3,4,7,8-PeCDF	1 ng/mL	-	100 pg	1000 pg
1,2,3,4,7,8-HxCDF	1 ng/mL	-	100 pg	1000 pg
1,2,3,6,7,8-HxCDF	1 ng/mL	-	100 pg	1000 pg
1,2,3,7,8,9-HxCDF	1 ng/mL	-	100 pg	1000 pg
2,3,4,6,7,8-HxCDF	1 ng/mL	-	100 pg	1000 pg
1,2,3,4,6,7,8-HpCDF	1 ng/mL	-	100 pg	1000 pg
1,2,3,4,7,8,9-HpCDF	1 ng/mL	-	100 pg	1000 pg
OCDF	2 ng/mL	-	200 pg	2000 pg

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Table 4. Nominal Concentration of PCDD/PCDF Calibration Solutions - GC/HRMS Analysis

	CS-0.2 (ng/mL)	CS-1 (ng/mL)	CS-2 (ng/mL)	CS-3 (ng/mL)	CS-4 (ng/mL)	CS-5 (ng/mL)
Native Compounds						
2,3,7,8-TCDD	0.1	0.5	2	10	40	200
2,3,7,8-TCDF	0.1	0.5	2	10	40	200
1,2,3,7,8-PeCDD	0.5	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	0.5	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	0.5	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	0.5	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	0.5	2.5	10	50	200	1000
1,2,3,7,8,9-HXCDD	0.5	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	0.5	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	0.5	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	0.5	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	0.5	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	0.5	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	0.5	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	0.5	2.5	10	50	200	1000
OCDD	1.0	5.0	20	100	400	2000
OCDF	1.0	5.0	20	100	400	2000
Surrogate Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200	200
Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	0.1	0.5	2	10	40	200
Recovery Standards						
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	100

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Table 5. Nominal Concentrations of additional PCDD/PCDF Compounds in Calibration Solutions CS-1R and CS-3

	CS-1R (ng/mL)	CS-3 (ng/mL)
Additional Compounds		
1,2,3,4-TCDD	0.5	10
1,2,3,7/1,2,3,8-TCDD	0.5	10
1,2,3,9-TCDD	0.5	10
1,2,7,8-TCDD	0.5	10
1,2,8,9-TCDD	0.5	10
1,3,6,8-TCDD	0.5	10
1,3,7,9-TCDD	0.5	10
1,4,7,8-TCDD	0.5	10
1,2,7,8-TCDF	0.5	10
1,2,8,9-TCDF	0.3	6
1,3,6,8-TCDF	0.5	10
1,2,3,8,9-PeCDD	2.5	50
1,2,4,6,8/1,2,4,7,9-PeCDD	2.5	50
1,2,3,8,9-PeCDF	2.5	50
1,3,4,6,8-PeCDF	2.5	50
1,2,4,6,7,9-HxCDD	2.5	50
1,2,3,4,6,8-HxCDF	2.5	50
1,2,3,4,8,9-HxCDF	2.5	50
1,2,3,4,6,7,9-HpCDD	2.5	50

Note: The standard solutions CS-1R and CS-3 also contain the same compounds at the same levels as the CS-1 and CS-3 solutions in Table 4.

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3.4 Preparation of Reagents

Activated Copper is prepared as described in SOP 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 mL) 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 of drying samples) is cleaned by baking at a minimum of 300°C as described in SLA-093.

Anti-Bumping Chips (EM Science) are baked for 8 hours at a minimum of 300°C prior to use and stored in a clean baked jar.

Glass Fibre Filter Papers (Ahlstrom, 161 grade, 1.1 µm, 42.5 mm diameter, or equivalent) are cleaned by baking overnight at a minimum of 300°C.

Glass Fibre Filter Bed – refer to SLA-108 “Preparation of Filter Bedding” for instructions about preparation, cleaning and storage.

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

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

Potassium Hydroxide (KOH, 20% w/v) is prepared by dissolving potassium hydroxide (20 g, Fisher, certified) in ultra pure water (100 mL). The solution is extracted by shaking twice with dichloromethane (2 x 100 mL) and once with hexane (100 mL) and then stored in a baked 4-L bottle.

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

Silanized glass wool is stored in a clean glass jar and solvent rinsed with toluene (2 times) and hexane (2 times) prior to use.

Sodium Hydroxide (NaOH, 1 M) is prepared by dissolving sodium hydroxide pellets (Fisher, 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 a 1 L amber jar with a Teflon lined lid. Typically 3 L is prepared.

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Solvents All solvents used are high purity, distilled in glass solvents, either HPLC or pesticide residue grade. All solvent mixes are prepared on a volume:volume basis, by mixing the appropriate proportions of the solvent together. Solvents must be proofed and approved for use.

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

Sulphuric Acid (H_2SO_4, conc., Seastar Chemicals, quartz distilled) is used as received.

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

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	Preparation of Carbon/Celite Column
SCH-006	Preparation, Use and Maintenance of Biobead Columns

Activated Carbon (AX-21, Anderson Co.) is stored, as received, in Lab 1, in a cupboard on the east wall.

Alumina (Fisher Basic Brockman Activity I, 60-325 mesh) is baked for a minimum of 8 hours at 450°C and deactivated with ultra pure water (typically 1.0% by weight) according to procedures in SCH-001. The degree of activation may vary depending upon the batch of alumina. The deactivated alumina is stored under nitrogen in a stoppered flask and allowed to equilibrate for 24 hours. The 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.

Florisil (Supelco or US Silica, Pesticide grade, 60-100 mesh) is activated by heating at 450°C for a minimum of 8 hours and deactivated with ultra pure water (typically 2.0% by weight) as described in SCH-001. The degree of activation may vary depending upon the batch of Florisil. The 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).

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

10% (w/w) Silver Nitrate on Silica (Aldrich, mesh +230, or equivalent). Prior to use each new lot requires proofing as described in SCH-004. The silica is stored in a foil-wrapped amber jar.

22% H_2SO_4 Acidic Silica is prepared by adding H_2SO_4 (conc., equivalent to 22% of final weight of acidified silica) to baked silica and agitating until homogenous, as described in SCH-004. The mixture is stored in a stoppered round bottom flask.

44% H_2SO_4 Acidic Silica is prepared by adding H_2SO_4 (conc., equivalent to 44% of final weight of acidified silica) to baked silica and agitating until homogenous, as described in SCH-004. The mixture is stored in a stoppered round bottom flask.

28% NaOH Basic Silica is prepared by adding NaOH solution (1M, equivalent to 28% of final weight of basic silica) to baked silica and agitating until homogenous, as described in SCH-004. The silica is stored in a stoppered round bottom flask.

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 before use. The cutpoints are determined prior to use (SCH-003).

3.6 Preparation of Chromatography Columns

3.6.1 Biobeads SX-3 Column

A Biobead gel permeation column (60 g, 3 cm x 50 cm) is prepared and the cutpoints determined as described in SCH-006. Prior to use, the column is cleaned with 20% methanol:dichloromethane and 1:1 dichloromethane:hexane, as described in SCH-006.

3.6.2 DX 4g 44% (formerly "Small Layered Acid/Base Silica Column")

This column is used for cleanup of tissue and blood/serum/plasma extracts and extracts requiring PBDD/F or mono-tri-PCDD/F analysis.

A silica chromatography column (1 cm x 25 cm long) is prepared by sequentially dry-packing in hexane the following, as described in SCH-002:

Silica (neutral, 0.5 g), silica (28% NaOH, 2.0 g), silica (neutral, 0.5 g), silica (44% H_2SO_4, 4.0 g), silica (22% H_2SO_4, 2.0 g) and silica (neutral, 1.0 g).

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3.6.3 DX $AgNO_3$ 4g 44% (formerly "Small Layered Silver Nitrate/Acid/Base Silica Column")

Each supplier lot # of $AgNO_3$ is proofed and if PCDD/F background levels fall below pre-defined limits the pre-elution step is not required.

This column is an optional column that may be used for cleanup of soil, sediment, aqueous, air, XAD-2/filter and solvent extracts. **This column is suitable for the analysis of tetra-octa PCDD/F only. Do not use if brominated dioxin/furan or mono-tri-PCDD/F analysis is required.**

A silica chromatography column (1 cm x 25 cm long) is prepared by sequentially dry-packing in hexane the following, as described in SCH-002:

Pre-elution Required: Dry pack 2.5 g 10% $AgNO_3$ silica in at least 50 mL dichloromethane. Elute the dichloromethane to the top of the bed and discard. Flush the column with 20 mL of hexane and discard. **Do not allow the column to go dry!**

Dry pack the other layers in hexane as follows:

Silica (10% $AgNO_3$, 2.5 g), silica (neutral, 0.5 g), silica (28% NaOH, 2.0 g), silica (neutral, 0.5 g), silica (44% H_2SO_4, 4.0 g) and silica (neutral, 1.0 g).

Pre-elution Not Required: Pack all of the above layers in hexane.

3.6.4 DX 20g 44% (formerly "Large Layered Acid/Base Silica Column")

This is the default column for cleanup of tissue and blood/serum/plasma extracts and extracts requiring PBDD/F or mono-tri-PCDD/F analysis.

A silica chromatography column (2 cm x 30 cm long) is prepared by sequentially dry-packing in hexane the following, as described in SCH-002:

Silica (neutral, 1.0 g), silica (28% NaOH, 10 g), silica (neutral, 1.0 g), silica (44% H_2SO_4, 20 g), silica (22% H_2SO_4, 2.0 g) and silica (neutral, 1.0 g).

3.6.5 DX $AgNO_3$ 30g 44% (formerly "Large Layered Silver Nitrate/Acid/Base Silica Column")

Each supplier lot # of $AgNO_3$ is proofed and if DX Background levels fall below pre-defined limits the pre-elution step is not required.

This column is the default column used for cleanup of soil, sediment, aqueous, air, XAD-2/filter and solvent extracts. It must not be used for tissue sample extracts. **This column is suitable for the analysis of tetra-octa PCDD/F only. Do not use if brominated dioxin/furan or mono-tri-PCDD/F analysis is required.**

A silica chromatography column (2 cm x 30 cm long) is prepared by sequentially dry-packing the following, as described in SCH-002:

Pre-elution Required: Dry pack 2.5 g 10% $AgNO_3$ silica in at least 50 mL dichloromethane. Elute the dichloromethane to the top of the bed and discard. Flush the column with 20 mL of hexane and discard. **Do not allow the column to go dry!**

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Dry pack the other layers in hexane as follows:

Silica (neutral, 1.0 g), silica (28% NaOH, 10 g), silica (neutral, 1.0 g), silica (44% H_2SO_4, 30 g), silica (22% H_2SO_4, 2.0 g) and silica (neutral, 1.0 g).

Pre-elution Not Required: Pack all of the above layers in hexane.

3.6.6 DX Alumina Column

Basic alumina (6 g, 1.0% deactivated) is dry packed in hexane into a glass chromatography column (1 cm x 12 cm), as described in SCH-002. The column is capped with a 1 cm layer of baked granular anhydrous sodium sulphate.

3.6.7 DX Carbon/Celite Column

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

3.6.8 DX Florisil Column

Deactivated Florisil (8 g, 2.0% 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 baked anhydrous granular sodium sulphate.

3.6.9 Glass Wool Column

A glass wool column is prepared by placing a small amount of silanized glass wool into the end of a clean Pasteur pipette, which is then eluted with toluene followed by hexane. The column is used to filter residual particulate (sodium sulphate) from an extract.

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4. QUALITY ASSURANCE/ QUALITY CONTROL

Refer to SLA-016 "Preparation of Quality Control (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. A procedural blank is prepared by spiking an aliquot of the surrogate standard solution into a clean matrix. An aliquot of field surrogate spiking solution is also added if required. 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 blank filter must be of the same type and cleaning batch as used by the client for the sampling. The extraction of the blank filter is started at the acidification step (5.11.1b). Note that the surrogate standard solution is spiked into the filter when it is in the Soxhlet body (5.11.1c).
- 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 for OPR).
- On-going Precision and Recovery (OPR) Samples – On-going Precision and Recovery (OPR) is demonstrated by analyzing with each batch a clean matrix spiked with known amounts of target analytes. The OPR 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, extracted, following procedures in Section 5 of this method.

  Note 1: Aqueous OPR samples are prepared by spiking a combined surrogate and authentic standard solution into the water matrix.

  Note 2: For stationary source air samples, the reference sample (a clean filter of the same type and cleaning batch as used by the client for the sampling) is spiked with an aliquot of authentic spiking standard prior to the extraction, which is started at the acidification step (5.11.1b). Note that the surrogate standard solution is spiked into the filter when it is in the Soxhlet body (5.11.1c)
- 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.

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All elements of the QA/QC program at AXYS Analytical Services are documented in the most recent revision of "AXYS Analytical QA/QC Policies and Procedures Manual". Also refer to SQA-014 "Evaluation of Routine Batch QC Results".

The QA/QC acceptance criteria established for this method are presented in Tables 6 and 7 of this document.

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Table 6. QC Acceptance Criteria for PCDD/F in CAL/VER, IPR, OPR and Test 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)

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Table 7. QC Specifications for 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/serum/plasma and milk:** 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 Requirement (where target concentrations are detectable or sample extracts display atypical interference, SDL values may be higher) **Blood/serum/plasma and milk:** Tetra-penta-CDD/F 0.2 pg/sample, Hexa-octa-CDD/F 0.5 pg/sample **Other matrices**: 0.5 pg/sample
Instrument Carryover and Background: **Toluene Blank** **Samples**	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/serum/plasma and milk 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. <10% contribution from preceding sample (based on observed instrument carryover rate).
Analyte Peak Response	Response must be below the upper 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 (as per section 16.3 of 1613B) 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 in CS-0.2 for 1.0 µL injected, plus for blood/serum/plasma and milk S:N ≥3:1 for 0.05 pg injected 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.

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5. EXTRACTION PROCEDURES

The extraction procedures described in this section are used for the analyses of samples by EPA Method 1613B.

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, authentic and calibration standards required, and any additional information concerning the analysis are documented on a Batch List given to an analyst. Refer to 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 (see 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 Procedure
SLA-020	Gravimetric Lipid Determination by Weight of Extract
SLA-023	Use of Balances
SLA-024	Sealing Ampoules
SLA-027	Completing a Worksheet
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-108	Preparation of Filter Bedding (“Popcorn”)
SLA-124	Liquid-Liquid Extraction Supplemental Techniques

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The following worksheets are available to document the analysis:	
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-tube
FWO-310	Sample Spiking Sheet
FWO-311	Extract Splitting
FWO-312	Cleanup Information
FWO-314	Notes
FWO-317	Extraction – Blood, Milk, Nonylphenols
FWO-318	Extraction – Sample Trains, resin acids, multi-residue pesticides
FWO-319	Ash, acid extractable pesticides
FWO-324	Analysis of Sampling Media, Containers and Solvent and Glassware Proofs
FWO-328	Water Filtration Processing Worksheet
FWO-329	SS Calculation Worksheet
FWO-331	Dean-Stark Extraction Worksheet

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5.1 Soxhlet Extraction of Solids (default procedure)

The solid Soxhlet extraction procedure using toluene-acetone is applicable to the matrices and sample sizes listed below. Alternately, solids may be extracted by Dean-Stark Soxhlet extraction using toluene (Section 5.2).

Matrix	**Sample Size**
Sediments/Soil/Sludge	10 g dry weight
Ash	5 g dry
Pulp	20-25 g (dry)
Black Liquor	25 mL

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

Assemble the Soxhlet apparatus, including the thimble, and thoroughly clean by Soxhlet extracting with dichloromethane for a minimum of two hours (3 hours if brominated dioxins and furan (PBDD/F) are also being determined). Discard the dichloromethane and allow the glassware to dry before using it in the extraction.

5.1.1 Solid Sample Preparation

5.1.1.1 Sediment/Soil/Sludge

Accurately weigh to a minimum of 2 decimals, a solid sample equivalent to 10 g dry (>1% solids) into a clean beaker. Add an aliquot of surrogate standard solution to the sample. Stir well with a clean spatula, cover with clean aluminum foil and allow to equilibrate for at least 30 minutes. 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 to dry to a free-flowing powder (minimum 30 minutes).

Place silica (neutral, baked, 2 g for small thimbles, 5 g for large thimbles) into a pre-cleaned Soxhlet thimble. Quantitatively transfer the dried sample into the Soxhlet thimble. Be sure that the level of sample in the thimble is not higher than the height of the siphon arm. Solvent rinse the beaker (use extraction solvent) and add the rinses to the Soxhlet body. Proceed with the Soxhlet extraction described in Section 5.1.2.

5.1.1.2 Pulp

Place silica (neutral, baked, 2 g for small thimbles, 5 g for large thimbles) into a Soxhlet thimble. Add an accurately weighed (to a minimum of 2 decimals), homogeneous, dried pulp sample onto the silica in the thimble. Be sure that the level of sample in the thimble is not higher

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than the height of the siphon arm. Add an aliquot of surrogate standard solution to the sample and allow to equilibrate for at least 30 minutes. Proceed with the Soxhlet extraction as described in Section 5.1.2.

5.1.1.3 Black Liquor

Accurately weigh to a minimum of 2 decimals, a 25 g subsample of black liquor into a clean beaker. Add an aliquot of the surrogate standard solution, stir well with a clean spatula, cover with clean aluminum foil and allow to equilibrate for at least 30 minutes. Add 150 - 200 g anhydrous sodium sulphate to the sample, in several increments to prevent clumping, and mix well with a clean spatula between additions. Allow to dry to a free-flowing powder.

Place silica (5 g, neutral, baked) into a large, pre-cleaned Soxhlet thimble. Quantitatively transfer the sample to the Soxhlet thimble. Be sure that the level of sample in the thimble is not higher than the height of the siphon arm. Solvent rinse the beaker (use extraction solvent) and add the rinses to the Soxhlet body. Proceed with the Soxhlet extraction as described in Section 5.1.2.

5.1.1.4 Ash, Slag or Ash-like Solids

Accurately weigh to a minimum of 2 decimals an ash sample into a beaker. Using a clean spatula, mix well to break up any lumps. Add an aliquot of the surrogate standard solution, mix well and allow to stand a minimum of 30 minutes. Add hydrochloric acid (HCl, 1 M, 100 mL) to the flask and sonicate for 30 minutes. Using pH paper, check that the pH is <2. If not, add HCl (1 M) dropwise until pH<2 and repeat the sonication step. Filter the mixture using a Millipore filtration apparatus and glass fibre filter/filter bed. Rinse the filter with ultra pure water (approximately 250 mL) until the filtrate is about pH 6 (based on pH of ultra pure water), Check the drips from the Millipore adaptor with pH paper. Dry the particulate (filter paper and filter bed) by mixing with anhydrous sodium sulphate.

Filtrate

Quantitatively transfer the filtrate and rinses to a clean Erlenmeyer flask. Add dichloromethane (300 mL) and a pre-cleaned PTFE magnetic stir bar to the flask and stir 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.

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 that contains toluene (1-2 mL) and concentrate by rotary evaporation to 1-2 mL. Use this flask for the Soxhlet extraction of the particulate as described in section 5.1.2.

Option 2: Dry the dichloromethane extract over anhydrous sodium sulphate for a minimum of 30 minutes. Quantitatively transfer the extract with dichloromethane rinses to the round bottom flask containing the concentrated particulate extract (from 5.1.2) to the filtrate extract. Concentrate the combined extract to 1-2 mL by rotary evaporation.

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Particulate

Place silica (neutral, baked, 2 g for small thimbles, 5 g for large thimbles) into a pre-cleaned Soxhlet thimble. Load the dried particulate into the thimble with solvent rinses (use extraction solvent). Add the rinses to the thimble in the Soxhlet body. Be sure that the level of sample in the thimble is not higher than the height of the siphon arm. Proceed with the Soxhlet extraction as described in Section 5.1.2 below (using the round bottom flask containing the filtrate extract if option 1 was chosen).

5.1.1.5 Aqueous Ash

Filter the ash sample, present as particulate matter in effluent, through a Millipore filter system containing a pre-weighed baked glass fibre filter/filter bed, followed by a rinsing with ultra pure water. Depending on the client's request, the filtrate can be extracted as described in Section 5.5.3 and added to the Soxhlet apparatus' round bottom flask, analyzed as a separate sample, or the filtrate may be discarded. Refer to the Batch List for instructions regarding the filtrate.

Carefully remove the filter/filter bed and air dry in a fume hood overnight. Accurately weigh to a minimum of 2 decimals the dried filter/filter bed with the particulate. Place the filter/filter bed into a clean beaker and add an aliquot of the surrogate standard solution. Allow to equilibrate for at least 30 minutes. Acidify and extract the particulate as described above for ash samples.

5.1.2 Soxhlet Extraction Procedure

Place the Soxhlet thimble containing the sample into a pre-cleaned Soxhlet apparatus. Add anti-bumping granules (4-5 granules) and 80:20 toluene:acetone (300 mL for a small Soxhlet body, 600 mL for a large Soxhlet body) to the Soxhlet apparatus' round bottom flask. Heat the sample under reflux for a minimum of 16 hours; adjust as necessary to achieve a reflux rate of 4 cycles per hour. Allow the solution to cool. If base/acid wash cleanup is required, concentrate the 300 mL extract to 1-2 mL by rotary evaporation and proceed to base/acid wash (Section 6). If base/acid wash cleanup is not required, add an aliquot of cleanup standard to the extract and concentrate the 300 mL extract to 1-2 mL by rotary evaporation.

Proceed to the cleanup procedures (Section 6).

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5.2 Dean-Stark Soxhlet Extraction of Solids in Toluene (optional procedure)

The Dean-Stark Soxhlet procedure is applicable to the matrices and sample sizes listed below.

Matrix	**Sample Size**
Sediments/Soil/Sludge	10 g dry weight
Particulate Filter Paper (wet)	1 – several

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

Assemble the Dean-Stark Soxhlet apparatus, including the thimble, and thoroughly clean by Soxhlet extracting with dichloromethane for two hours (3 hours if brominated dioxins and furan (PBDD/F) are also being determined). Discard the dichloromethane and allow the glassware to dry before using it in the extraction.

5.2.1 Sample Preparation

5.2.1.1 Solids

Accurately weigh to a minimum of 2 decimals a solid sample (>1% solids) equivalent to 10 g dry into a clean beaker. Add an aliquot of surrogate standard solution to the sample. Stir the sample well with a clean spatula, cover with clean aluminium foil and allow it to equilibrate for at least 30 minutes. Add clean reagent sand (100 g) to the sample in the beaker. Mix well with a clean spatula.

Place silica (neutral, baked, 2 g for small thimbles, 5 g for large thimbles) into a pre-cleaned Soxhlet thimble. Transfer the mixture to the thimble. Be sure that the level of sample in the thimble is not higher than the height of the siphon arm. Rinse the beaker and spatula with the extraction solvent. Add the rinses to the Soxhlet body.

5.2.1.2 Particulate Filter Papers

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 Dean-Stark a pre-cleaned Soxhlet thimble that has a layer of silica (neutral, baked, 2 g for small thimbles, 5 g for large thimbles) in the bottom. Be sure that the level of sample in the thimble is not higher than the height of the siphon arm. Add an aliquot of surrogate standard to the sample. Refer to the Bach List for spiking and extract splitting instructions.

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5.2.2 Dean-Stark Soxhlet Extraction Procedure

Place the thimble containing the sample in a pre-cleaned Dean-Stark Soxhlet apparatus. Add anti-bumping granules (4-5 granules) and toluene (300 mL for a small Soxhlet body, 600 mL for a large Soxhlet body) to the flask. Fill the Dean-Stark side arm with toluene. Heat the sample under reflux for a minimum of 16 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 receiver and discard any toluene left in the receiver. Allow the solution to cool. If base/acid wash cleanup is required, concentrate the 300 mL extract to 1-2 mL by rotary evaporation and proceed to base/acid wash (Section 6). If base/acid wash cleanup is not required, add an aliquot of cleanup standard to the extract and concentrate the 300 mL extract to 1-2 mL by rotary evaporation.

Proceed to the cleanup procedures (Section 6).

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5.3 Soxhlet Extraction of Tissues (default procedure)

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 2 decimals, a homogenized tissue sample into a clean beaker. Refer to the Batch List for the sample size. Typical sample sizes are: muscle 10 g, liver 5 g, fat 1 g. Add an aliquot of surrogate standard solution to the sample, stir well with a clean spatula, cover the beaker with clean aluminium foil and allow to equilibrate at least 30 minutes. Add anhydrous sodium sulphate (75 - 100 g) to the beaker, stir the mixture well with a spatula, and allow the mixture to dry until a free-flowing powder is produced (minimum 30 min).

5.3.2 Soxhlet Extraction Method

Assemble the Soxhlet apparatus, including the thimble, and thoroughly clean by Soxhlet extraction with dichloromethane for two hours (3 hours if brominated dioxins and furan (PBDD/F) are also being determined). Discard the dichloromethane. Rinse the apparatus with dichloromethane.

Place silica (neutral, baked, 2 g for small thimbles, 5 g for large thimbles) into a pre-cleaned Soxhlet thimble. Quantitatively transfer the dried sample with solvent 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. Add anti-bumping granules (4-5 granules) and dichloromethane:hexane (1:1, 300 mL) to the Soxhlet apparatus' round bottom flask. Heat the sample under reflux for a minimum of 16 hours; adjust as necessary to achieve a reflux rate of 4 cycles per hour. Allow the mixture to cool. Add an aliquot of cleanup standard to the extract. Concentrate the extract to 1 mL (5 mL if lipid analysis is required) by rotary evaporation.**

** Gravimetric Lipid Analysis: Check the extract for the presence of residual sodium sulphate. If present, filter the extract through a glass wool column. Elute the extract with hexane rinses of the round bottom flask. Collect the eluate in a clean, pre-weighed round bottom flask. Carry out the lipid analysis on the extract according to SLA-020 "Gravimetric Lipid Determination by Weight of Extract". Concentrate the remaining extract to 1–2 mL.

The extract is ready for cleanup procedures (Section 6).

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5.4 Base Digest Extraction Procedure of Tissues (optional procedure)

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

Matrix	**Sample Size**
Tissue	75 - 150 g wet weight.

5.4.1 Sample Preparation

Accurately weigh to a minimum of 2 decimals, 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, stir and allow to equilibrate for at least 30 minutes. Add ethanolic potassium hydroxide (200 mL, KOH, 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. Transfer the ethanolic potassium hydroxide/water mixture to a separatory funnel (1000 mL). Add hexane (150 mL) to the Erlenmeyer, swirl, and then add the hexane to the separatory funnel. Shake the separatory funnel vigorously for 2 minutes. Allow the solution 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 cleanup standard solution to the hexane extract. The extract is ready for one of the following cleanup procedures.

5.4.3 Optional Acid Wash

Prior to manual cleanup procedures, or if the extract has a high lipid content, the following acid wash procedure may be required.

Add concentrated sulphuric acid (conc., H_2SO_4, 100 mL) to the extract and gently shake for two minutes. Allow to sit 15-30 minutes. Discard the lower acid layer. Repeat the sulphuric acid wash (100 mL) 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 for a minimum of 30 minutes. The extract is ready for cleanup on a Biobead column (Section 6).

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5.5 Aqueous Sample Extraction

This extraction procedure is suitable for aqueous samples including drinking water, non-potable water, effluents and aqueous sludge. The typical sample size is 1 litre.

Matrix	**Sample Size**
Aqueous	1 - 4 L

5.5.1 Sample Preparation

Prior to extraction, aqueous samples are homogenized, subsampled and spiked with an aliquot of surrogate standard solution by the analyst. Add a pre-cleaned PTFE magnetic stir bar to the sample and stir while spiking the aliquot of surrogate standard solution. The analyst must refer to SLA-084 "Preparation of Aqueous Samples for Extraction" for complete details of sample homogenization, subsampling, rinsing, surrogate spiking and filtration procedures. Allow surrogates to equilibrate for at least 30 minutes.

5.5.2 Extraction Procedures

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

- Samples with no visible particles are not filtered and are extracted using procedures in Section 5.5.3.
- Samples with visible particulate are filtered prior to extraction by procedures described in Section 5.5.4.

5.5.3 Extraction of Samples with No Visible Particulate

5.5.3.1 Extraction by Magnetic Stirring (Default Procedure)

Note: This extraction procedure must not be used for DLM02.2 work; use instead the separatory funnel extraction procedure below (section 5.5.3.2.)

After homogenization, subsampling and spiking with surrogate standards as described in SLA-084, 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. Liquid/liquid extraction must be done in the same Erlenmeyer flask where the sample was spiked. Quantitatively transfer the solution to a separatory funnel and draw off the dichloromethane layer. Discard the aqueous layer. Dry the extract by filtration into a round-bottom flask through a solvent rinsed glass funnel with a glass wool plug and approximately half full of granular anhydrous sodium sulphate. Rinse the filter with dichloromethane to ensure quantitative transfer. Add an aliquot of cleanup standard solution to the extract. Concentrate the extract to 1-2 mL by rotary evaporation. The extract is ready for chromatographic cleanup procedures (Section 6).

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5.5.3.2 Extraction by Shaking in a Separatory Funnel (Optional Procedure)

After homogenization, subsampling and spiking with surrogate standard, as described in SLA-084, 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. Dry the extract by filtration into a round-bottom flask through a solvent rinsed glass funnel with a glass wool plug and approximately half full of granular anhydrous sodium sulphate. Rinse the filter with dichloromethane to ensure quantitative transfer. Add an aliquot of cleanup standard solution to the extract. Concentrate the extract to 1-2 mL by rotary evaporation. The extract is ready for chromatographic cleanup procedures (Section 6).

5.5.4 Extraction of Samples with Visible Particulate

The analyst must refer to SLA-084 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. For River Road dioxin analysis, where the weight of particulate is required, use an analytical balance to pre-weigh the filter and filter bed (in a tared Petri dish). Record the weight on the worksheet.

   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 the same solvent that will be used for the subsequent Soxhlet extraction. Add the rinses to the thimble in the Soxhlet body.

   OR

   b) Extract the wet filters by Dean-Stark Soxhlet extraction procedures.

   OR

   c) **For River Road dioxin analysis, where the weight of particulate is required,** air-dry the filter/filter bed/particulate in a fume hood overnight. Weigh the dried filter/filter bed/particulate and record the weight on the worksheet. Load the dried filter/filter bed/particulate into a pre-cleaned Soxhlet thimble and place in a pre-cleaned Soxhlet apparatus.

3. If performing Soxhlet extraction of the filter/particulate phase, rinse the container used to hold the sample during the surrogate spiking procedure, and the filtration apparatus (no

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filter!), with approximately 50 mL of acetone and **add this to the toluene:acetone 80:20 solvent mixture used for extraction of the particulate phase** (adjust the toluene solvent amount as necessary to achieve the required 80:20 v/v extraction solvent mixture).

4. If performing Dean-Stark Soxhlet extraction of the filter/particulate phase, acetone is not a suitable solvent. In this case rinse the sample container used to hold the sample during surrogate spiking and the filtration apparatus with the appropriate dichloromethane rinses (refer to SLA-084), **adding the rinses to the filtrate.**
5. Extract the filtrate and particulate separately as described in Sections 5.5.4.1 and 5.5.4.2 and combine the extracts.

5.5.4.1 Extraction of Filtrate

For all analyses except DLM02.2 work extract the filtrate by the default magnetic stirring procedure: Quantitatively transfer the filtrate with dichloromethane rinses to a clean Erlenmeyer flask. Add dichloromethane (300 mL) and a pre-cleaned PTFE magnetic stir bar to the flask and stir the solution (with vortex) for a minimum of 30 minutes. Liquid/liquid extraction must be done in the same Erlenmeyer flask where the sample was spiked. Quantitatively transfer the solution to a separatory funnel and draw off the dichloromethane layer. Discard the aqueous layer.

For DLM02.2 work extract the filtrate using a separatory funnel: Quantitatively transfer the filtrate with dichloromethane rinses to a clean separatory funnel. Add dichloromethane (100 mL or 10% of the volume of the sample) to the separatory funnel and shake vigorously for two minutes. Collect the dichloromethane layer in an Erlenmeyer flask. Repeat the extraction twice more. Combine the dichloromethane layers.

Should problems be encountered for liquid-liquid extraction of complex samples consult AXYS SOP SLA-124 Liquid-Liquid Extraction Supplemental Techniques.

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

Option 1: Dry the dichloromethane extract by filtration through a solvent rinsed glass funnel with a glass wool plug and approximately half full of granular anhydrous sodium sulphate. Filter into a round bottom flask that contains toluene (1-2 mL) and rinse the funnel with dichloromethane to ensure quantitative transfer. Concentrate the extract by rotary evaporation to 1-2 mL. Use this flask for the Soxhlet extraction of the particulate as described in Section 5.5.4.2.

Option 2: Dry the dichloromethane extract by filtration through a solvent rinsed glass funnel with a glass wool plug and approximately half full of granular anhydrous sodium sulphate.. Filter into the round bottom flask containing the concentrated particulate extract (see below) and rinse the funnel with dichloromethane to ensure quantitative transfer. Concentrate the combined extract to 1-2 mL by rotary evaporation.

5.5.4.2 Extraction of Particulate

Assemble the Soxhlet apparatus, including the thimble, and thoroughly clean by Soxhlet extraction with dichloromethane for two hours (3 hours if brominated dioxins and furan

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(PBDD/F) are also being determined). Discard the dichloromethane. Rinse the apparatus with dichloromethane.

Place silica (2 g for small thimbles, 5 g for large thimbles, neutral, baked) into a pre-cleaned Soxhlet thimble. Transfer the dried particulate with solvent 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 80:20 toluene:acetone (300 mL) 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 a minimum of 16 hours; adjust as necessary to achieve a reflux rate of 4 cycles per hour. Allow the solution to cool. If base/acid wash cleanup is required, concentrate the 300 mL extract to 1-2 mL by rotary evaporation and proceed to base/acid wash (Section 6). If base/acid wash cleanup is not required, add an aliquot of cleanup standard to the extract and concentrate the 300 mL extract to 1-2 mL by rotary evaporation.

The extract is ready for cleanup procedures in Section 6.

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5.6 XAD-2 Column Soxhlet Extraction

This procedure is applicable to the analysis of XAD-2 columns. The analysis of an XAD-2 column usually consists of two analyses as the filter(s) and XAD-2 resin are extracted and analyzed separately. The XAD-2 resin is extracted by either by a Dean-Stark Soxhlet extraction (Section 5.6.3) or a Soxhlet extraction (Section 5.6.4). The filter(s) are extracted by a Dean-Stark Soxhlet extraction (Section 5.6.5). Refer to the Batch List for the required extraction procedure. Upon client request, the filter and resin extracts may be combined to form a single extract. Refer to the Batch List for instructions.

5.6.1 Sample Handling Procedures

Refer to 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 extractors. Spike the sample 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 extractors.
3. Rinse the centrifuge tube with acetone (5 mL). Mix the rinsate in the c-tube by vortex mixing. Distribute the rinsate evenly amongst the Soxhlet extractors. 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 pre-cleaned Soxhlet thimble into a beaker.
2. Quantitatively transfer the XAD-2 resin to the pre-cleaned thimble with ultra pure water and allow to drain.
3. Rinse the resin with ultra pure water and allow to drain. Discard the water.
4. Proceed with either a Dean-Stark Soxhlet extraction procedure (5.6.3) or a Soxhlet extraction procedure (5.6.4).

5.6.3 XAD-2 Resin - Dean-Stark Soxhlet Extraction Procedure

1. Assemble a large 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 dichloromethane for two hours (3 hours if brominated dioxins and furan (PBDD/F) are also being determined). Discard the dichloromethane. Rinse the apparatus with dichloromethane.

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2. Transfer the thimble 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.
3. Use a 1000 mL round bottom flask for the solvent.
4. If a single analysis is required, spike the surrogate solution onto 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 apparatus 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.

5.6.4 <u>XAD-2 Resin – Soxhlet Extraction Procedure</u>

1. Assemble a large Soxhlet apparatus, without the thimble. Add a small bed of solvent rinsed glass wool to the bottom of the Soxhlet body to prevent clogging during the reflux procedure. Clean the apparatus by Soxhlet extraction with dichloromethane for two hours (3 hours if brominated dioxins and furan (PBDD/F) are also being determined). Discard the dichloromethane. Rinse the apparatus with dichloromethane.
2. Transfer the thimble 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.
3. Add the appropriate volume of 80:20 toluene:acetone (300 mL for a small Soxhlet body, 600 mL for a large Soxhlet) and anti-bumping granules (4-5 granules) to the Soxhlet apparatus' round bottom flask.
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 XAD-2 resin in the thimble prior to starting the Soxhlet extraction. If multiple analyses are required, spike the surrogates after the extraction procedure. Refer to the Batch List for spiking instructions.
5. Heat the sample under reflux for a minimum of 16 hours; adjust as necessary to achieve a reflux rate of 4 cycles per hour.
6. Allow the solution to cool. Remove water from the extract (Section 5.6.4.1).

   EXTREMELY IMPORTANT – DO NOT CONCENTRATE THESE SAMPLES BY ROTARY EVAPORATION WITHOUT A WATER REMOVAL STEP

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5.6.4.1 Removal of Water from XAD-2 Resin Extracts

The water removal step is dependent on the amount of visible water. If using the 1000 mL round bottom flasks for the Soxhlet extraction, transfer the extract with toluene rinses (3 x 10 mL, vortex the flask with each rinse) to 500 mL round bottom flasks during the evaporation process.

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 sodium sulphate for a minimum of 30 minutes. Return the extract to the round bottom flask with complete toluene rinses. The cleanup standard is added at this point or after the extract has been split. Concentrate by rotary evaporation to 1-2 mL for extract splitting. Refer to the Batch List for spiking and extract splitting instructions.
4. The extract is ready for splitting procedures. (5.12)

5.6.5 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 Soxhlet extraction with dichloromethane for two hours (3 hours if brominated dioxins and furan (PBDD/F) are also being determined). Discard the dichloromethane. Rinse the apparatus with dichloromethane.
2. Place the filter(s) or filter cartridge directly into the pre-cleaned Soxhlet body. Use a large Soxhlet body to hold the filter(s). Be sure that the level of filter(s) 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 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 filter(s) or filter cartridge 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. 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 Method

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 filter papers that are received dry.

Assemble the Soxhlet apparatus, including the thimble, and thoroughly clean by Soxhlet extraction with dichloromethane for two hours (3 hours if brominated dioxins and furan (PBDD/F) are being determined). Discard the dichloromethane. Rinse the apparatus with dichloromethane. The size of Soxhlet apparatus selected is dependent upon the size of sample.

5.7.1 Sample Preparation

5.7.1.1 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 silica (neutral, 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.

5.7.1.2 PUF/Filter

Using clean solvent-rinsed forceps, transfer the PUF and filter(s) to a pre-cleaned Soxhlet thimble that has a layer of silica (neutral, 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 sample in a pre-cleaned Soxhlet apparatus. If a single analysis is required, add an aliquot of the surrogate standard solution to the sample and allow to equilibrate for at least 30 minutes. If multiple analyses are required, refer to the Batch List for surrogate spiking instructions. Add anti-bumping granules (4-5 granules) and 80:20 toluene:acetone (300 mL for a small Soxhlet body, 600 mL for a large Soxhlet body) to the Soxhlet apparatus' round bottom flask. Heat the sample under reflux for a minimum of 16 hours; adjust as necessary to achieve a reflux rate of 4 cycles per hour. Allow the solution to cool. Add an aliquot of cleanup standard to the extract at this point or after the extract has been split. Concentrate the extract to 1-2 mL by rotary evaporation. The extract is ready to be gravimetrically split as described in Section 5.12. Refer to the Batch List for spiking and extract splitting instructions.

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5.8 Blood, Serum or Plasma Extraction

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

Matrix	**Sample Size**
Serum, Plasma	40 g
Whole Blood	60 g

5.8.1 Protocols for Blood/Serum/Plasma Analysis

In order to achieve low detection limits and minimize the background levels of PCDD/F for blood/serum/plasma samples, some routine procedures, typically used for other matrices, are modified. The modified procedures include the following:

- Spiking all blood/serum/plasma OPR and IPR samples with 1/10th the routine amount of native spiking solution (typically 100 µL, see Table 3).
- Spiking all samples and QC samples with ½ the routine amount of surrogate and recovery standard solutions.
- Omitting the addition of cleanup standard.
- Concentrating the extracts to a final volume of 10 µL (Section 6.9), except for OPR/IPR samples where final volume should be 40 µL.

5.8.2 Safety Considerations

Refer to the standard operating procedure SLA-082 'Handling of Human Biohazards" for details of safety precautions when handling blood/serum/plasma 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.

5.8.3 Extraction Procedures

1. Accurately weigh to a minimum of 2 decimals, a sample into a round bottom flask (250 mL). Add an aliquot of surrogate standard solution, cover the flask with clean aluminum foil and allow the solution to equilibrate for at least 30 minutes.
2. Add ethanol, hexane and saturated ammonium sulphate to the sample and extract by shaking on the shaker table for 30 minutes. 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

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Manager including confirmation that the client has been made aware of potential solvent-system effects on gravimetric determination of lipids in blood/serum/plasma matrices. Decant the hexane layer into a separatory funnel (500 mL).

3. 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.
4. Wash the hexane extracts by shaking with ultra pure water (2 x 50 mL) to remove residual ethanol. Discard the aqueous layer.
5. Transfer the hexane extract to an Erlenmeyer flask and dry over anhydrous sodium sulphate for a minimum of 30 minutes.
6. Refer to the Batch List to determine whether a lipid determination is required. If so, carry out the following procedures:

   Lipid Determination: Refer to SLA-020 for lipid determination procedures.
7. Quantitatively transfer the extract with hexane rinses to a clean round bottom flask. The extract is ready for cleanup procedures (section 6).

Should problems be encountered for liquid-liquid extraction of complex samples consult AXYS SOP SLA-124 Liquid-Liquid Extraction Supplemental Techniques.

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5.9 Milk Extraction Procedure

The extraction procedures are suitable for both human and cow's milk. The default sample size is up to 30 g. With prior negotiation and if detection limits lower than approximately 0.02 pg/g are required, an optional non-routine procedure may be used with a sample size of 30-150 g.

5.9.1 Default Protocols for Milk Analysis

In order to achieve low detection limits and minimize the background levels of PCDD/F for milk samples, the default procedures are the same as are used for blood/serum/plasma analysis. The procedures include the following:

- Spiking all milk OPR and IPR samples with 1/10th the routine amount of native spiking solution (typically 100 µL, see Table 3).
- Spiking all samples and QC samples with ½ the routine amount of surrogate and recovery standard solutions.
- Omitting the addition of cleanup standard.
- Concentrating the extracts to a final volume of 10 µL (Section 6.9), except for OPR/IPR samples where final volume should be 40 µL.

5.9.2 Optional Non-Routine Protocols for Milk Analysis

The OPR/IPR protocol, the authentic, surrogate standard and cleanup standard solution spiking amounts, and the final extract volume are the same as for regular aqueous/solid/tissue samples.

5.9.3 Extraction Procedure for Milk Samples

1. Accurately weigh to a minimum of 2 decimals, a subsample of milk (default procedure up to 30 g, optional procedure 30-150 g). For the default procedure, bulk up the sample volume with ultrapure water to a total volume of 30 mL. 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 flask. Return the aqueous layer to the separatory funnel and repeat the extraction with 200 mL hexane. 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).

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5. Drain the hexane extract into an Erlenmeyer flask with hexane rinses and dry over anhydrous sodium sulphate for a minimum of 30 minutes.
6. Quantitatively transfer the dried extract to a pre-weighed round bottom flask and concentrate to ~5 mL by rotary evaporation.
7. Do the following only if the optional procedure is used: Add aliquots of the PCDD/F cleanup standards to the extract.
8. **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 by rotary evaporation.
9. If no lipid analysis is required, concentrate the extract to 1 mL.
10. The extract is ready for column chromatography cleanup procedures. (Section 6)

Should problems be encountered for liquid-liquid extraction of complex samples consult AXYS SOP SLA-124 Liquid-Liquid Extraction Supplemental Techniques.

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5.10 Solvent Extracts

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

5.10.1 Sample Preparation

Determine the weight of the extract as received, as follows:

1. Weigh to a minimum of 2 decimals, the extract in the original container (usually jar or ampoule).
2. Transfer the extract to a centrifuge tube (if received in an ampoule) or to an Erlenmeyer flask with solvent rinses; use the same solvent as in the sample.
3. Reweigh the original container once it has dried.
4. Record all weights on the worksheet.
5. 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 extract splitting and surrogate spiking instructions.

Single PCDD/F and/or PBDD/F Analysis

If only PCDD/F and/or PBDD/F analysis is required, add aliquots of surrogate standard solution(s) and cleanup standard solution to the extract. Dry the extract according to procedures in Section 5.10.2.

Multiple Analyses

If multiple analyses are required, the surrogate and cleanup standards may be spiked before or after extract drying and splitting procedures. Dry the extract according to procedures in Section 5.10.2.

5.10.2 Extract Drying Procedures

1. Inspect the extract for the presence of water. If less than 3 mL water is visible, transfer the extract to an Erlenmeyer flask with solvent rinses (the same solvent as sample).
2. If greater than 3 mL of water is visible, transfer the extract to a separatory funnel with solvent rinses (same solvent as sample) and drain the water from the solvent. Transfer the solvent layer to a clean Erlenmeyer flask.
3. Dry the extract with anhydrous granular sodium sulphate for a minimum of 30 minutes. Quantitatively 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 extract splitting procedures (5.12).

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5.11 Stationary Source Air Samples (Stack Gas)

The analysis of PCDD/PCDF in stack gas involves acidification of the particulate filter to ensure complete recovery of the target analytes. If strict adherence to EPA Method 23 is required, the acidification step is omitted and the front half and back half of the train are extracted separately. Refer to the EPA Method 23 for details.

5.11.1 Sample Processing

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 procedures 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 dichloromethane for two hours. If brominated dioxins and furan (PBDD/F) are also being determined the apparatus must be extracted with dichloromethane for a minimum of 3 hours. Discard the dichloromethane. Rinse the apparatus with dichloromethane.

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 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).

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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 (upper) layer. Proceed with the dichloromethane filter extract as described below.

   Note: Depending upon the mix of solvent in the container, 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) with granular anhydrous sodium sulphate (Na_2SO_4) for a minimum of 30 minutes. Transfer the filtrate 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 2 decimals 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 pH 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).

<u>Back Half of Train</u>

c) Container C (3)

XAD-2 resin is in container C.

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1. Put a layer of silica (neutral, baked, 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 include 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 5.11.1a.
2. If methanol is not present, dry the contents of container D with granular 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.**

1. Transfer the contents of Container E to a separatory funnel. Add the aqueous filtrate from the acidification step (Section 5.11b) 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 dichloromethane extracts, dry with granular 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: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.

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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)

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. This container is not always submitted by the client. **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 in Section 5.11.1a.
2. If methanol is not present, dry the contents of container F with granular 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 Procedure

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 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.
   b. If less than 3 mL of water is visible, quantitatively transfer the entire extract to an Erlenmeyer flask with toluene rinses.
   c. Dry the extract with anhydrous sodium sulphate for a minimum of 30 minutes. Return the extract to the round bottom flask used for the Soxhlet extraction with complete toluene rinses. 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 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 the extract 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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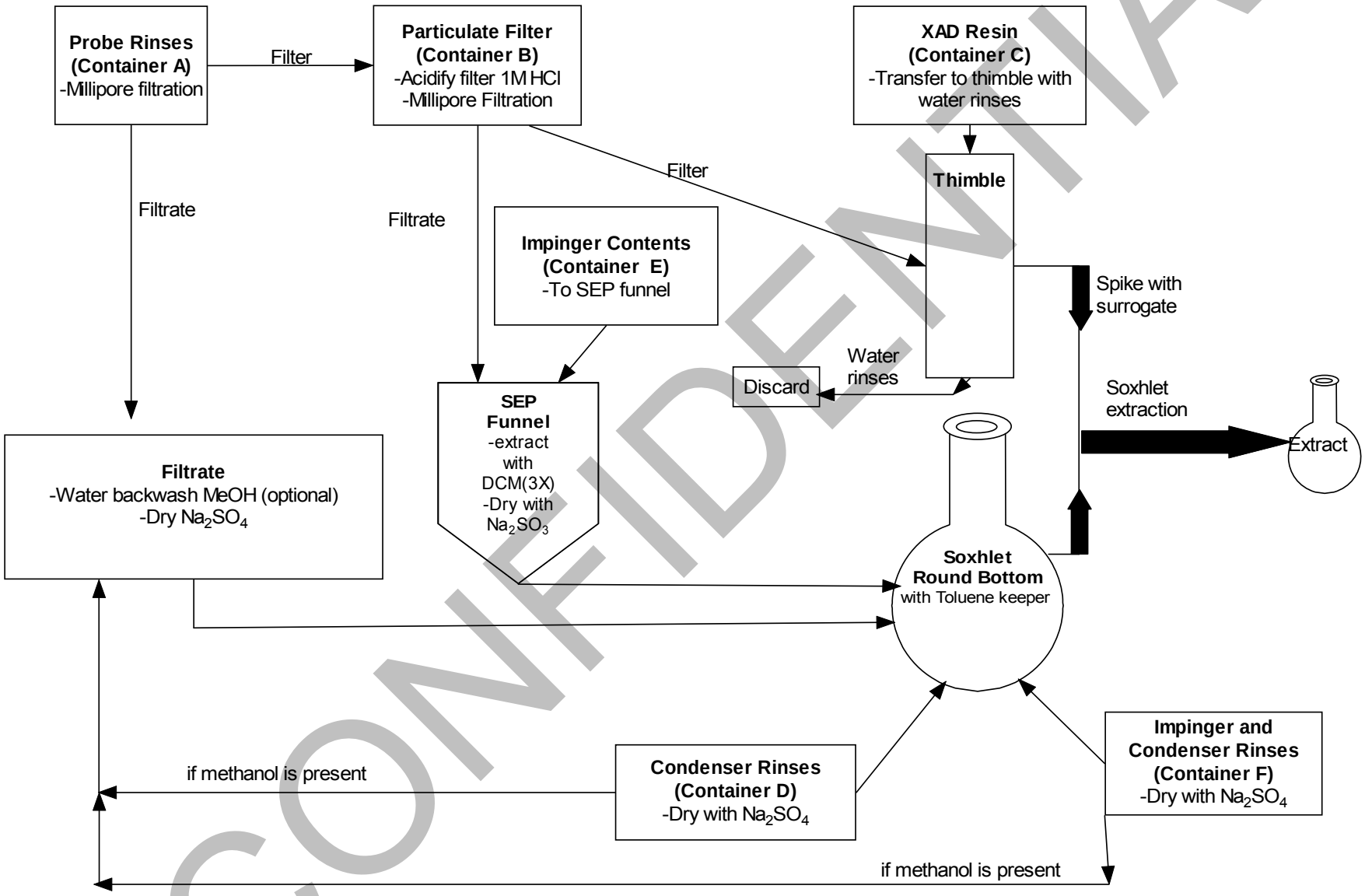
Figure 1. Processing of Sample Trains



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5.12 Gravimetric Splitting Procedures

Refer to SLA-123 “Splitting of Sample Extracts”.

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6. CLEANUP PROCEDURES

An automated FMS (Fluid Management Systems) cleanup may be performed in combination ("hybrid" cleanup) with, or as an alternative to, manual cleanup. The FMS cleanup is equivalent to manual cleanup but may offer efficiency advantages and can be used upon specific approval of the laboratory manager. All operational details of FMS cleanup are listed in Section 6.8.

The cleanup columns are specified in Section 3.6.

The cleanup procedures and column sequences for different matrices are:

Water Soil Sediment XAD-2 adsorbent Air samples Sludge High organic soil	1) <u>Manual</u>: (M base/acid wash →) M DX $AgNO_3$ 30g 44% → (M DX Florisil →) M Copper → M Alumina/carbon/Celite combination column 2) <u>Hybrid</u>: (M base/acid wash →) M DX $AgNO_3$ 30g 44% → F Alumina → F Carbon/Celite 3) <u>Full FMS</u>: (M base/acid wash →) F Jumbo Layered Silica Columns → F Small Layered Silica Columns → F Alumina → F Carbon/Celite
Tissue Blood/serum/ plasma Milk	1) <u>Manual</u>: (M Biobead →) M DX 20g 44% → M DX Florisil → (M Copper →) M Alumina/carbon/Celite combination column 2) <u>Full FMS</u>: (M Biobead →) F Jumbo Acid Silica Column → F Small Layered Silica Columns → F Alumina → F Carbon/Celite

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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

Dioxins adhere to glass. ***Thorough vortexing*** *of round bottom flasks and/or C-tubes when transferring extracts is required.*

The default size of the Manual Layered Silica columns are shown but smaller or larger ones may be used if needed or if required by Project Managers.

An optional Biobead cleanup may be carried out for biosolid sample extracts.

If an aqueous or solids extract shows excessive color, a base/acid wash may be performed based on judgement of the analyst. The base/acid wash can be performed either before or after the DX $AgNO_3$ 30g 44% (formerly "large layered silver nitrate/acid/base silica") column chromatography.

In some cases it may be necessary to modify the column sequence. The Batch List describes any modifications to the chromatographic cleanup procedure. When carrying out a modified procedure, the analyst must consider the following issues:

- the extract must be in hexane to load onto a column.
- a solvent exchange must be performed on extracts that are not in the appropriate solvent, concentrating to 300 µL to remove dichloromethane and 50 µL to minimize toluene.
- toluene is not a suitable solvent for Florisil, alumina and carbon/Celite columns and no more than 50 µL can be present in the extract being loaded onto these columns.
- 1-2 mL of toluene may be present in an extract that is loaded onto a Biobead column.

6.1 Base/Acid Wash Procedure (can apply to manual, hybrid or FMS cleanup)

Base/acid wash may be performed for aqueous or solids extracts showing excessive color (chemist's judgement and sample history apply). The wash can be performed either before or after the DX $AgNO_3$ 30g 44% (formerly "large layered silver nitrate/acid/base silica") column chromatography.

1. Transfer the extract, with rinses (3-5 mL toluene, 3x10 mL hexane)[Note] to a 125 mL separatory funnel, add an aliquot of cleanup standard, and add potassium hydroxide solution (KOH, 20% w/v, 30 mL). Shake the solution for at least one minute. If the solution starts to emulsify or thicken, stop shaking. Allow the phases to separate and continue shaking until a total of one minute of shaking has occurred. Allow the solution to stand for 30 minutes or until a clear separation occurs. Discard the lower aqueous layer. (If the aqueous layer is strongly coloured, repeat the procedure with up to 4 rinses with potassium hydroxide solution, allowing the solution to stand for 15 minutes after each shake.)

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2. Add ultra pure water (30 mL) to the extract in the separatory funnel, shake for ≤1 minute. Discard the aqueous layer. Add concentrated sulphuric acid (30 mL) to the extract and shake for 2 minutes and allow to stand for 30 minutes or until there is a clear separation. (If the acid layer is strongly coloured, repeat the procedure with up to 8 rinses with concentrated sulphuric acid allowing the solution to stand 15 minutes after each shake.) Repeat the extraction with ultra pure water.
3. Transfer the organic layer to a clean 250 mL Erlenmeyer flask and dry over anhydrous sodium sulphate (5-10 g, minimum 30 minutes). The extract is ready for cleanup by column chromatography cleanup procedures.

   Note: If the extract is extremely dirty, coloured or viscous, use a larger volume of hexane and a proportionally larger volume of potassium hydroxide solution in a larger separatory funnel to wash the extract.

6.2 Biobead Column Cleanup (optional for tissue cleanup)

A Biobead column can be used for cleanup of extracts containing up to approximately 1.5 g lipid. If a sample extract contains more than 1.5 g lipid, multiple Biobead columns are required.

Concentrate the extract to 1 mL by rotary evaporation. Load the extract onto a Biobead SX-3 gel permeation column (60 g) with rinses from the elution solvent and elute with 1:1 dichloromethane:hexane. Refer to the most recent cutpoint determination for the elution volume and current cutpoints. Discard the first fraction. Collect the second fraction. Concentrate the collected fraction to 1 mL by rotary evaporation before continuing with the cleanup procedure.

6.3 Manual and Hybrid Layered Silica Column Cleanup

6.3.1 DX $AgNO_3$ 30g 44% (formerly "Large Layered Silver Nitrate/Acid/Base Silica") Column

This is the default silica column for all aqueous, solid, XAD-2 and air sample extracts. Do **not** use it for tissue sample extracts.

Warning: This column is not suitable for brominated dioxins and furans (PBDD/F) or mono-tri-PCDD/F. If either of these analyses is required, use the DX 20g 44% column (section 6.3.3) or the DX 4g 44% column (section 6.3.4) which are also suitable for PCDD/F.

1. Refer to the most recent DX cutpoints for the DX $AgNO_3$ 30g 44% column. Typical cutpoints are as follows: F1 Hexane 200 mL
2. Transfer the extract with hexane rinses (2 x 1-2 mL) to the column. Elute the column with hexane and collect the eluate (F1).
3. If any of the layers are strongly coloured, an additional layered acid/base column, or acid/base washes maybe necessary.
4. Reduce the eluate to 1 mL by rotary evaporation before prior to further extract cleanup.

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6.3.2 DX AgNO3 4g 44% (formerly "Small Layered Silver Nitrate/Acid/Base Silica") Column

Non-routine, optional column for water, soil, sediment, XAD-2 and air sample extracts used only if required in the Project Notes or Batch List.

Warning: This column is not suitable for brominated dioxins and furans (PBDD/F) or mono-tri-PCDD/F. If any of these analyses is required, use the DX 4g 44% column used for tissue extracts in 6.3.4 which is also suitable for PCDD/F.

1. Refer to the most recent DX cutpoints for the DX $AgNO_3$ 4g 44% column. Typical cutpoints are as follows:

   F1 Hexane 50 mL

2. Transfer the extract with hexane rinses (2 x 1-2 mL) to the column. Elute the column with hexane and collect the eluate (F1). Repeat this column procedure with the DX $AgNO_3$ 30g 44% column if any layers are strongly coloured.

6.3.3 DX 20g 44% (formerly "Large Layered Acid/Base Silica") Column

This is the default column for all tissue extracts including blood, serum, plasma and milk extracts. Optional column for sludge and high organic content soil extracts and for extracts requiring PBDD/F analysis, used only if required in the Project Notes or Batch List.

1. Refer to the most recent DX cutpoints for the DX 20g 44% column. Typical cutpoints are as follows:

   F1 Hexane 150 mL

2. Transfer the extract with hexane rinses (2 x 1-2 mL) to the column. Elute the column with hexane and collect the eluate (F1).
3. Reduce the volume to 1 mL.

If any layers are strongly coloured, repeat this column procedure or repeat the cleanup using only the layered packing that was coloured.

6.3.4 DX 4g 44% (formerly "Small Layered Acid/Base Silica") Column

Non-routine, optional column for tissue and blood/serum/plasma extracts and for extracts requiring PBDD/F analysis. It may be used only if required in the Project Notes or Batch List.

1. Refer to the most recent DX cutpoints for the DX 4g 44% column. Typical cutpoints are as follows:

   F1 Hexane 50 mL

2. Transfer the extract with hexane rinses (2 x 1-2 mL) to the column. Elute the column with hexane and collect eluate (F1).
3. Reduce the volume to 1 mL.

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If any layers are strongly coloured, repeat this column procedure or repeat the cleanup using only the layered packing that was coloured.

6.4 DX Florisil Column

This is the default column for tissue extracts including blood, serum, plasma and milk extracts. This column may be used for optional cleanup if required in the Project Notes or the Batch List, or if necessary for remedial cleanup, e.g. for extracts with very high interferences from polychlorinated diphenylethers.

Refer to the most recent DX/PCB cutpoint determination for 2.0% deactivated Florisil for the elution volumes. Typical cutpoints are as follows:

F1	5% dichloromethane in hexane	50 mL
F2	dichloromethane	250 mL

1. The extract must be in hexane prior to loading. Load the extract onto the column using some of the 5% dichloromethane in hexane elution solvent. Elute the column with 5% dichloromethane in hexane (F1) and discard.
2. Elute the column with dichloromethane (F2). Collect the F2 fraction in a 500 mL round-bottom flask. This fraction contains the PCDD/Fs and the most polar pesticides. Concentrate the eluate to 1 mL by rotary evaporation. Transfer to a centrifuge tube with hexane rinses. Be sure to vortex the round bottom flask. Evaporate to 300 µL under a stream of nitrogen. Bulk up the extract to 1 mL with hexane.

6.5 Alumina/ Carbon Celite Combination Column

Extracts with high sulphur levels may at this stage require desulfurization with copper. The extract must be in 1 mL of hexane. Refer to SLA-045 “Removal of Sulphur from Extracts Using Activated Copper”.

The alumina/ carbon Celite combination column is the default cleanup column for all DX extracts.

Refer to the most recent DX cutpoints for 1% deactivated alumina.
Typical alumina cutpoints are as follows:

F1	hexane	50 mL
F2	2% dichloromethane in hexane	10 mL
F3	1:1 dichloromethane:hexane	45 mL

1. The extract must be in hexane prior to loading. Load the extract with some of the hexane elution solvent. Elute the column with hexane (F1) and discard.
2. Elute the column with 10 ml of 2% dichloromethane in hexane. Discard this fraction (F2).
3. While eluting the F1 and F2 fractions from the alumina, pre-elute the carbon Celite columns. Prepare and pre-elute a DX carbon/Celite column as described in Section 3.6.7.

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Note: Watch carefully for the packing slipping in the column. Be generous with the glass wool plugs when packing columns.

4. After fraction F2 has eluted from the alumina remove the glass tip from the stopcock of the alumina column and replace it with the pre-eluted carbon Celite column.
5. Elute the alumina/carbon Celite combination column with 1:1 dichloromethane:hexane (F3). Discard this fraction.
6. Remove the alumina column.
7. Elute the carbon/Celite column with 1:1 dichloromethane:cyclohexane (2 mL) followed by 1:1 ethylacetate:toluene (2 mL). Discard these fractions.
8. Invert the column and elute with toluene. Refer to the most recent cutpoint determination for the toluene elution volume. The typical elution volume is 50 mL. Collect this fraction in a 100 mL round-bottom flask. Concentrate the eluate by rotary evaporation to 1 mL. Transfer the extract with hexane rinses and vortexing to a centrifuge tube. Concentrate the extract under a stream of nitrogen to 300 µL. Proceed to section 6.9 to prepare the extract for GC/HRMS analysis.

6.6 DX Alumina Column

This is an optional cleanup column and may be used if required in the Project Notes or Batch List, or if necessary for remedial cleanup. Ensure that the extract is in hexane prior to loading onto the column.

Refer to the most recent DX cutpoints for 1% deactivated alumina. Typical cutpoints are as follows:

F1	hexane	50 mL
F2	2% dichloromethane in hexane	10 mL
F3	1:1 dichloromethane:hexane	45 mL

1. The extract must be in hexane prior to loading Load the extract with some of the hexane elution solvent. Elute the column with hexane (F1) and discard.
2. Elute the column with 10 ml of 2% dichloromethane in hexane. Discard this fraction (F2).
3. Elute the column with 1:1 dichloromethane:hexane. Collect this fraction (F2) in a round-bottom flask.

6.7 DX Carbon/Celite Column

This is an optional manual cleanup and may be used only if required in the Project Notes or Batch List, or if necessary for remedial cleanup.

1. Prepare and pre-elute a DX carbon/Celite column as described in Section 3.6.7.

   Note: Watch carefully for the packing slipping in the column. Be generous with the glass wool plugs when packing columns.

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2. Load the extract in 1 mL hexane with hexane rinses (2 mL) onto the carbon/Celite column (a total of 3 mL of hexane should be applied to the column). Elute the column with 1:1 dichloromethane:cyclohexane (2 mL) followed by 1:1 ethylacetate:toluene (2 mL). Discard these fractions.
3. Invert the column and elute with toluene. Refer to the most recent cutpoint determination for the toluene elution volume. The typical elution volume is 50 mL. Collect this fraction in a 100 mL round-bottom flask. Concentrate the eluate by rotary evaporation to 1 mL. Transfer the extract to a centrifuge tube with hexane rinses (3 x 1 mL), stirring the extract using a vortex mixer. Concentrate the extract to 300 µL under a gentle stream of nitrogen. Proceed to Section 6.9 “Preparation for GC/HRMS Analysis”.

6.8 FMS Cleanup

The FMS program used is matrix dependent. Refer to the following documents for the appropriate FMS operating parameters for PCDD/F cleanup and FMS operating procedures:

FQA-074	Approved FMS columns, Solvents and Programs
SLA-090	Maintenance and Use of FMS

A trained FMS operator performs the cleanup using the required columns and procedures.

Notify the FMS operator if the samples are known to be high level to ensure that the appropriate wash program is used.

Notify the FMS operator if the lipid content of the extract exceeds 4-5 grams, as this is the capacity of the silica column. Extracts with >4-5 g lipid must be split into appropriate portions and cleaned up on separate FMS modules. The extract portions are combined after FMS cleanup.

Some lot numbers of FMS columns have been shown to have levels of contaminants which require additional cleaning to remove. Refer to FQA-074 for details.

6.8.1 <u>FMS Cleanup of tissue samples (including blood/serum/plasma and milk samples), default FMS procedure</u>

This FMS cleanup is performed on raw sample extracts (or after the Biobead column (Section 6.2), if needed). Prior to FMS cleanup the extracts must be solvent changed to hexane and diluted to 30 mL with hexane. The FMS program uses the following columns:

- Jumbo Acid Silica
- Acid/Base Silica
- Alumina
- Carbon

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Concentrate the extract from the FMS to 1 mL by rotary evaporation. Transfer the extract to a centrifuge tube with hexane rinses (3 x 1 mL), stirring the extract using a vortex mixer. Concentrate the extract to 300 µL in a gentle stream of nitrogen. Proceed to Section 6.9 "Preparation for GC/HRMS Analysis".

6.8.2 Hybrid FMS Cleanup of non-tissue samples, default FMS procedure

This FMS cleanup is performed on sample extracts after manual cleanup on the DX $AgNO_3$ 30g 44% (formerly "Large Layered Silver Nitrate/Acid/Base Silica") Column (Section 6.3.1). Prior to FMS cleanup the extracts must be solvent changed to hexane and diluted to 10 mL with hexane. The FMS program uses the following columns:

- Alumina
- Carbon

Concentrate the extract from the FMS to 1 mL by rotary evaporation. Transfer the extract to a centrifuge tube with hexane rinses (3 x 1 mL) and stir the extract using a vortex mixer. Concentrate the extract to 300 µL in a gentle stream of nitrogen. Proceed to Section 6.9 "Preparation for GC/HRMS Analysis".

6.8.3 Full FMS Cleanup of non-tissue samples, optional FMS procedure

This FMS procedure describes cleanup of raw non-tissue sample extracts.

Quantitatively transfer the extract with hexane rinses to a clean centrifuge tube. Use a vortex mixer to mix each rinse in the round bottom flask to dissolve all residual extract. Concentrate the extract in the centrifuge tube to 300 µL under a gentle stream of nitrogen. Add hexane (~2 mL) to the extract. If particulate is present in the extract, filter the extract by quantitatively transferring the extract with hexane rinses (3 x 1 mL) to a glass wool column. Collect the eluate in a clean centrifuge tube. Repeat the filtering step until the extract is free of residue. Make the volume of extract up to 10 mL with hexane.

The FMS program uses the following columns:

- Jumbo Layered Acid/Base Silica
- Acid/Base Silica
- Alumina
- Carbon

Concentrate the extract from the FMS to 1 mL by rotary evaporation. Transfer the extract to a centrifuge tube with hexane rinses (3 x 1 mL), stirring the extract using a vortex mixer. Concentrate the extract to 300 µL in a gentle stream of nitrogen. Proceed to Section 6.9 "Preparation for GC/HRMS Analysis".

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6.9 Preparation for GC/HRMS Analysis

6.9.1 Dilution of Extracts in Nonane (1613B / 8290 procedure) - default

This is the applicable procedure for preparation of final extracts for analysis by EPA method 1613B, EPA methods 8290/8290A and Environment Canada method 1/RM/19.

Add nonane (10 µL, except for blood/serum/plasma or milk extracts where 5 µL is added) to a clean GC/MS autosampler vial and mark the vial at this volume. Transfer the extract to the autosampler vial. Rinse the centrifuge tube with 300-400 µL of hexane and add the rinse to the autosampler vial. Concentrate the extract under a gentle stream of nitrogen. Make sure the volume of extract does not go below 100 µL. Rinse and vortex the centrifuge tube with 300-400 µL hexane and add the rinse to the autosampler vial.

Concentrate the extract to 10 µL (5 µL for blood/ serum/plasma or milk extracts). Add a 10 µL aliquot of PCDD/F recovery standard prepared in nonane to the autosampler vial (exception: add 5 µL of recovery standard for blood/serum/plasma or milk extracts, and dilute blood/serum/plasma or milk OPRs to 40 µL, or as specified on the Batch List). Cap the autosampler vial. Store the vials in the freezer until just prior to GC/MS analysis (Section 7).

6.9.2 Dilution of Extracts in Toluene (modified 1613B / 8290 procedure) - optional

Transfer the extract to a GC/MS autosampler vial. Rinse and vortex the centrifuge tube with 300-400 µL of hexane and add the rinse to the autosampler vial. Concentrate the extract under a gentle stream of nitrogen. Make sure the volume of extract does not go below 100 µL. Rinse and vortex the centrifuge tube with 300-400 µL hexane and add the rinse to the autosampler vial.

Evaporate to just dryness and add a 20 µL aliquot of PCDD/F recovery standard prepared in toluene to the autosampler vial (exceptions: add 10 µL of recovery standard for blood/serum/plasma or milk extracts, and dilute blood/serum/plasma or milk OPRs to 40 µL, or as specified on the Batch List). Cap the autosampler vial and vortex well. Store the vials in the freezer until just prior to GC/MS analysis (Section 7).

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7. INSTRUMENTAL HRGC/HRMS ANALYSIS

In order to achieve low detection limits and minimize the background levels of PCDD/F for blood/serum/plasma and milk samples, some HRGC/HRMS analysis parameters are modified for these extracts. A summary of the parameters used for blood/serum/plasma and milk vs. other matrices is presented in the table below.

Parameter	**Blood/Serum/Plasma and Milk**	**Other Matrices**
Extract volume	10 µL (OPR/IPR 40 µL)	20 µL
Injection volume	2 µL	1 µL
CAL/VER solution	CS-1R	CS-3
Sensitivity solution	0.025 pg/µL	CS-0.2
GC Res./Window Solution	CS-1R	CS-3

Sensitivity

The sensitivity of the GC/HRMS is checked with every initial calibration procedure by running the lowest-level calibration solution (CS-0.2 calibration solution). Prior to analysis of blood/serum/plasma or milk samples a less concentrated sensitivity standard solution (containing 2,3,7,8-TCDD and 2,3,7,8-TCDF at 0.025 pg/µL) is analyzed and must achieve a S:N≥3:1.

GC Resolution

The GC resolution is checked once every 12 hours by analysing a solution containing either 2,3,7,8-TCDD or 2,3,7,8-TCDF and its closest eluting isomers, and monitoring the valley height between the two peaks.

Blood/serum/plasma or milk samples: The resolution between 2,3,7,8-TCDD and 1,2,3,7/1,2,3,8-TCDD on the DB-5 column must be checked by analyzing the CS-1R solution.

Other matrices: The resolution between 2,3,7,8-TCDD and 1,2,3,7/1,2,3,8-TCDD on the DB-5 column must be checked by analyzing the CS-3 solution. If confirmation of 2,3,7,8-TCDF is performed on a DB-225 column the resolution between 2,3,7,8-TCDF and 1,2,3,9- and 2,3,4,7-TCDF must be checked.

Instrument Calibration

The initial calibration (default calibration procedure) is performed using a series of solutions that encompass the working concentration range of the instrument. 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.

Refer to SIN-028 for details on the frequency of the Initial Calibration procedure.

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Windowing

The CAL VER includes those compounds necessary for defining the elution windows for the PCDDs/PCDFs and is run within 12 hours of the samples being analyzed.

Instrumental Analysis

Analysis is carried out using a high resolution mass spectrometer (VG/Micromass Autospec Ultima, Waters Micromass Autospec Premier, or equivalent) equipped with an Agilent 5890, 6890 or 6890N capillary gas chromatograph, a PAL or CTC autosampler and an Alpha workstation running OPUS or Premier/MassLynx software. The mass spectrometer is tuned daily to have a static mass resolution of 10,000 or greater, in the electron impact (EI) ionization mode. Data are acquired in the voltage selected ion recording mode (SIR) to enhance sensitivity. At least two ions are used to monitor each of the target analytes and ^{13}C-labelled surrogate standards. The cleanup standard (^{37}Cl-2,3,7,8-TCDD) is monitored and quantified using one ion. Five chlorinated diphenylethers are monitored to check for interference using one specific ion for each compound. The masses of the ions monitored for target analytes and surrogate standards are presented in Table 9.

The chromatographic separation is carried out using a DB-5 capillary column (60 m, 0.25 mm i.d., 0.1 µm film thickness). A volume of 1.0 µL from either a 10 µL or 20 µL extract volume is injected (typically 2.0 µL from 10 µL for blood/serum/plasma and milk extracts). A splitless/split injection sequence is used. A second column DB-225 (30 m, 0.25 mm i.d., 0.15 µm film thickness) is used for confirmation of 2,3,7,8-TCDF identification with the exception of blood/serum/plasma extracts, which do not require 2,3,7,8-TCDF identification.

Details of the instrumental analysis, QA/QC requirements, and quantification procedures are described in the instrument method MIN-017.

Analysis Sequence

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

Calibration Sample
Reference Sample
Instrument Blanks [Note]
Procedural Blank
Samples
Calibration Sample

Note: Run as many instrument blanks as necessary to achieve the background specification quoted in Table 7.

See Table 8 for further information on instrumental injection sequence.
Refer to Section 10.0 of EPA Method 1613B for details of calibration procedures.
Refer to Section 14.0 of EPA Method 1613B for details of instrumental analysis.
Refer to Section 15.0 of EPA Method 1613B for details of system and laboratory performance.

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Dilution of extracts

Extracts may be diluted with solvent (with nonane as the default solvent) and re-analyzed by GC/MS to bring the instrumental response to within the linear range of the instrument. Extracts must not be diluted beyond the point at which reliable isotope dilution quantification can be done.

For very high level samples and where allowable by contract, spiking a diluted portion of the extract with an additional aliquot of surrogate standard and subsequent reanalysis is permitted.

Table 8. Suggested Instrumental Injection Sequence

TEST	Maximum Allowable Time *	Cycle
PFK Tune/Mass Res #1		Start of first cycle
CPS run 1 **		
CS3 run 1		
CS1, CS2, CS4, CS5		
Reference Sample		
Instrument Blanks		
Samples (test samples, other QC samples)		
PFK Tune/Mass Res #2	PFK Tune/Mass Res #1 +12.0 hr	
CPS run 2	CPS run 1 +12.0 hr	
CS3 run 2	CS3 run 1 + 12.0 hr	Completion of first cycle
Reference Sample		
Instrument Blanks		
Samples (test samples, other QC samples)		
PFK Tune/Mass Res #3	PFK Tune/Mass Res #2 +12.0 hr	
CPS run 3	CPS run 2 +12.0 hr	
CS3 run 3	CS3 run 2 + 12.0 hr	Completion of second cycle
Reference Sample		
Instrument Blanks		
Samples (test samples, other QC samples)		
…continue cycles or stop as below		
CS3 run 3		
PFK Tune/Mass Res #4	PFK Tune/Mass Res #3 +12.0 hr	Stop

* Times at injection

** Axys currently combines the CPS/CS3 solutions for method 1613B

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8. QUALITATIVE AND QUANTITATIVE DETERMINATION

8.1 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. For 1613B applications only (as per section 16.3 of 1613B) 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.
5. No signal having S:N > 2.5 in the corresponding polychlorinated diphenyl ether channel at the same retention time (± 2 sec.) of a PCDF.

Refer to Section 16.0 of EPA Method 1613B for details of qualitative determination.

Refer to Section 17.0 of EPA Method 1613B for details of quantitative determination. The quantification references are presented in Table 9.

8.2 Reporting Limits

Blood/serum/plasma and milk extracts: For samples and procedural blanks, target analytes are positively identified at concentrations exceeding the sample detection limits (SDL).

Other matrices: For samples, target analytes are positively identified at concentrations exceeding 0.5 pg/sample or exceeding a limit specified by the client. For procedural blanks, target analytes are positively identified at concentrations exceeding the SDL.

Use the acceptance criteria summarized in Tables 6 and 7 to evaluate the data, according to procedures described in SQA-001 *Final Data Checking and* SQA-014 *Evaluation of Routine Batch QC Results*.

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Table 9. Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans by High Resolution GC/MS

Analytes	Quantification Ion (m/z)	Confirmation Ion (m/z)	Surrogate	RRF Determined From
2,3,7,8-TCDD	319.8965	321.8936	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
1,3,6,8-TCDD *	319.8965	321.8936	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
1,3,7,9-TCDD *	319.8965	321.8936	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
1,2,3,7,8-PeCDD	353.8576	355.8546	$^{13}C_{12}$-1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	389.8156	391.8127	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD	389.8156	391.8127	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	389.8156	391.8127	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	423.7767	425.7737	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD
OCDD	457.7377	459.7348	$^{13}C_{12}$-OCDD	OCDD
2,3,7,8-TCDF	303.9016	305.8987	$^{13}C_{12}$-2,3,7,8 -TCDF	2,3,7,8-TCDF
1,2,7,8-TCDF *	303.9016	305.8987	$^{13}C_{12}$-2,3,7,8 -TCDF	2,3,7,8-TCDF
1,2,3,7,8-PeCDF	339.8597	341.8568	$^{13}C_{12}$-1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	339.8597	341.8568	$^{13}C_{12}$-2,3,4,7,8-PeCDF	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	373.8207	375.8178	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDF	407.7818	409.7788	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	407.7818	409.7788	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-HpCDF
OCDF	441.7428	443.7398	$^{13}C_{12}$-OCDD	OCDF
Cleanup Standard				
$^{37}Cl_4$-2,3,7,8-TCDD	327.8847	-	$^{13}C_{12}$-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	331.9368	333.9339	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,7,8-PeCDD	365.8978	367.8949	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	401.8559	403.8530	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	401.8559	403.8530	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	435.8169	437.8140	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-OCDD	469.7780	471.7750	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-2,3,7,8 -TCDF	315.9419	317.9389	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,7,8-PeCDF	351.9000	353.8970	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-2,3,4,7,8-PeCDF	351.9000	353.8970	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	383.8639	385.8610	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	383.8639	385.8610	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	383.8639	385.8610	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	383.8639	385.8610	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	417.8250	419.8220	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	417.8250	419.8220	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	

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Recovery Standards		
$^{13}C_{12}$-1,2,3,4-TCDD	331.9368	333.9339
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	401.8559	403.8530

*Optional isomers which may be reported upon client request.

Cl-DPE Monitoring Ions			
Descriptor	Exact M/Z	M/Z Type	Substance
3	375.8364	M+2	HxCDPE
4	409.7974	M+2	HpCDPE
5	445.7555	M+4	OCDPE
6	479.7165	M+4	NCDPE
7	513.6775	M+4	DCDPE

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9. REPORTING CRITERIA AND PRACTICES

Concentrations and detection limits for the 2,3,7,8-polychlorinated dioxins and furans (tetra-octa) are reported. The internal standard method of quantification, used to determine concentrations of target analytes, corrects the concentrations based on the percent recovery of the surrogate (internal) standards. 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/serum/plasma 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. Results may be expressed in other units if specified by contract.

Sample specific detection limits (SDL's) are determined from the analysis data by converting the minimum detectable area to a concentration following the same quantification procedures used to convert target peak responses to concentrations. The estimated minimum detectable area is determined as 2.5 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.

Percent moisture is reported for all sediments, soils, and ash samples and for tissues when percent moisture is requested. Percent moisture is not reported for pulps and sludge although if is determined for the calculation of a dry weight.

Percent lipid is reported if determined on a sample.

Unless other wise specified, the toxicological equivalent (TEQ) for every dioxin and furan congener is reported. The TEQ represents the concentration of each congener, expressed as an equivalent amount of 2,3,7,8-T_4CDD. The procedures for reporting the TEQ are presented in the SOP SQA-012 'Reporting of the Toxicological Equivalent Amount (TEQ)'.

Reporting Practices

Blood/serum/plasma and milk extracts: For samples and procedural blank, report to the sample detection limit (SDL).

Other matrices: For samples and procedural blank, report to a limit of 0.5 pg/sample or as specified by client.

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10. SUMMARY OF MODIFICATIONS TO EPA METHOD 1613B

The following sections of EPA Method 1613B have been modified as described below.

Section 2.1.2

Aqueous liquid from multiphase samples is liquid/liquid extracted with DCM. The extract from the aqueous phase is then combined with the extract from the solid phase portion of the sample.

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 solution is 100 ng/mL (except for labelled OCDD which is 200 ng/mL) and is prepared in toluene; 20 µL of the labelled compound solution is spiked to solids and tissue samples to yield the method specified concentrations in the final extracts.

Section 7.11

The concentration of the cleanup standard spiking solution is 10 ng/mL, in toluene, and the sample spiking volume is 20 µL. The resulting concentration in the final extracts is ¼ of the concentration specified in the method.

Sections 7.13, 14.0, 15.0

A modified EPA 1613B / 8290 procedure is offered that includes an additional lower level calibration solution, 0.2 times the concentration of CS-1 in the initial calibration series so that initial calibration is based on a six-point series. The calibration solutions are prepared in nonane. A modified EPA 1613B / 8290 procedure using calibration solutions prepared in toluene is also available.

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 specifications for the percent recovery of surrogate standards in samples that are higher than 130% have been lowered to 130%, as presented in Table 6 of this document.

Section 11.5

Multiphase, predominately aqueous, samples containing >1% suspended solids may be prepared and extracted using the same procedure as samples containing ≤1% suspended solids with client approval. This involves separating the solids and aqueous phases by filtration, extracting the solids by Soxhlet extraction, extracting the filtrate by liquid/liquid extraction, and combining the extract from the two phases. Alternatively, with client approval, multiphase, predominately particulate, samples containing >1%

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suspended solids may be processed as solids samples using Soxhlet or Soxhlet Dean-Stark extraction.

Section 12.3

For solids samples with suitable moisture content, an option is offered for drying the sample with anhydrous Na_2SO_4 followed by Soxhlet extraction with 80:20 toluene:acetone. Alternatively, Soxhlet Dean-Stark extraction using toluene is available.

Section 12.3.1 – 12.3.5

Silica or quartz sand is not pre-extracted in the Dean-Stark Soxhlet 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 12.5.3

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. Trends in QC blanks are monitored and diagnostic proofing is conducted if indicated instead of collecting proofs each day and archiving. Historical proofing tests have demonstrated that routine cleaning practices between samples are sufficient to ensure rotary evaporator cleanliness; as an additional safeguard the laboratory segregates processing of samples on the basis of predicted target concentration levels.

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

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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

The EPA 1613B / 8290 procedure uses nonane to dilute extracts. Alternatively a modified EPA 1613B / 8290 procedure using toluene to dilute extracts may be performed.

Section 15.3.5

Table 6 specifications for CAL-VER solution concentrations outside the 70-130% range have been revised to be 70-130%, as presented in Table 6 of this document.

Section 15.5.3

Table 6 specifications for OPR concentrations outside the 70-130% range have been revised to be 70-130%, as presented in Table 6 of this document.

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.

$$Conc_i = \frac{A_i}{A_{si}} \times \frac{M_{si}}{RRF_{i,si}} \times \frac{1}{M_x}$$

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:

$$\frac{A_i}{A_{si}} \times \frac{M_{si}}{M_i}$$

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Calculation of Surrogate Standard Concentrations and Percent Recoveries:

Concentrations of surrogate standards are calculated using the following equation:

$$Conc_{si} = \frac{A_{si}}{A_{rs}} \; x \; \frac{M_{rs}}{RRF_{si,rs}}$$

and, the percent recoveries of the surrogate standards are calculated using the following equation:

$$\%Recovery = \frac{A_{si}}{A_{rs}} \; x \; \frac{M_{rs}}{RRF_{si,rs}} \; x \; \frac{1}{M_{si}} \; x \; 100$$

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

Where acceptable to the client, 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.

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APPENDIX A

ANALYSIS OF PCDD/F by

ENVIRONMENT CANADA METHOD

EPS 1/RM/19

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APPENDIX A - ANALYSIS OF PCDD/F BY ENVIRONMENT CANADA METHOD EPS 1/RM/19

For Canadian regulatory purposes, the concentrations of PCDD/F in effluents are determined and reported according to protocols described in Environment Canada method EPS 1/RM/19. AXYS has modified method EPS 1/RM/19 to allow the use of the surrogate, recovery, authentic spike and calibration solutions used for EPA method 1613B (described in Section 3.3 of this document).

The analysis of PCDD/F by EPS 1/RM/19 may be carried out using the procedures described in this document, with the following modifications, made to satisfy the requirements of EPS 1/RM/19.

1. For the analysis of effluent samples, a proof of the glassware used in the analysis is carried out prior to commencing the analysis.
2. Samples are extracted and cleaned up according to the procedures described in Sections 5.5 and 6 of this document. Samples are spiked with an aliquot of the surrogate standard solution prior to extraction. The use of the cleanup standard is not required, but may be added as an internal QC check. Extracts are spiked with an aliquot of the recovery standard (in nonane) prior to instrumental analysis using the default procedure described in section 6.9.1.
3. The HRGC/HRMS analysis of the extracts is carried out using the procedures described in EPS 1/RM/19 with the following exception:
   - Initial calibration is carried out using four calibration solutions, CS-0.2, CS-1, CS-3, and CS-5 (described in Table 4 of this document) prepared in nonane. A mid-level calibration solution (CS-3) is analyzed every 12 hours as the CAL/VER solution. The mean RRFs determined from the analysis of the initial calibration solution and concentrations of analytes determined in mid-level calibration solution must satisfy the specifications of method EPS 1/RM/19.
   - The sensitivity standard, CS-0.2 is analyzed with every batch of samples.
4. Target analytes are quantified using a select suite of $^{13}C_{12}$ -labelled surrogates as shown in Table 10 of this method.
5. Data is reported using the format in method EPS 1/RM/19.
6. The data is evaluated using the QA/QC criteria described in method EPS 1/RM/19.
7. Detection limits are reported according to procedures in SOP SQA-011 'Dioxins/Furans Detection Limits Reporting'.

Note: Where acceptable to the client and Project Manager, PCDD/Fs may be calculated using RRFs determined from the analysis of the mid-level calibration solution analyzed before and after the analysis of samples.

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Table 10. Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans by High Resolution GC/MS – Method EPS 1/RM/19

Analytes	Quantification Ion (m/z)	Confirmation Ion (m/z)	Surrogate	RRF Determined From
2,3,7,8-TCDD	319.8965	321.8936	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
1,2,3,7,8-PeCDD	353.8576	355.8546	$^{13}C_{12}$-1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	389.8156	391.8127	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD	389.8156	391.8127	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	389.8156	391.8127	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD	423.7767	425.7737	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD
OCDD	457.7377	459.7348	$^{13}C_{12}$-OCDD	OCDD
2,3,7,8-TCDF	303.9016	305.8987	$^{13}C_{12}$-2,3,7,8-TCDF	2,3,7,8-TCDF
1,2,3,7,8-PeCDF	339.8597	341.8568	$^{13}C_{12}$-1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	339.8597	341.8568	$^{13}C_{12}$-1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2,3,4,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDF	407.7818	409.7788	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	407.7818	409.7788	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF
OCDF	441.7428	443.7398	$^{13}C_{12}$-OCDD	OCDF
Labelled Surrogate Stds	**Quantification Ion (m/z)**	**Confirmation Ion (m/z)**	**Recovery Calculated Using**	
$^{13}C_{12}$-2,3,7,8-TCDF	315.9419	317.9389	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-2,3,7,8-TCDD	331.9368	333.9339	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,7,8-PeCDF	351.9000	353.8970	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,7,8-PeCDD	365.8978	367.8949	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	383.8639	385.8610	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	401.8559	403.8530	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	417.8250	419.8220	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	435.8169	437.8140	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-OCDD	469.7780	471.7750	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
Labelled Recovery Stds				
$^{13}C_{12}$-1,2,3,4-TCDD	331.9368	333.9339		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	401.8559	403.8530		

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APPENDIX B

ANALYSIS OF PCDD/F by

EPA Methods 8290 and 8290A

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APPENDIX B - ANALYSIS OF PCDD/F BY EPA METHODS 8290 AND 8290A

The analysis of polychlorinated dioxins and furans by EPA Method 8290 or 8290A is carried out using the procedures described in this document. Electronic copies of methods 8290 and 8290A are available on the AXYS network G:\Information\Published Methods\EPA methods\. The AXYS implementation of EPA Methods 8290 and 8290A includes the following:

1. A sample hold time of 30 days from time of sample collection is recommended.
2. Extract hold time, stored at <-10°C, is 45 days.
3. The same surrogate, recovery, authentic spike and calibration solutions that are used for EPA method 1613B (described in Section 3.3 of this document) are used to perform EPA Methods 8290 and 8290A.
4. A matrix spike/matrix spike duplicate (MS/MSD) sample is analysed with every analysis batch, provided sufficient sample is available. This requirement may be waived by contract.
5. The typical final extract volume is 20 µL but may vary between 10 µL and 50 µL.
6. HRGC/MS analysis is performed according to EPA 1613B protocols described in Section 7 of this document, with the following requirements:
   - An instrumental blank is analyzed at the beginning of every 12-hour analysis sequence, injected following the CAL/VER solution.
   - Should the CAL/VER analysis fail at the end of a 12 hour period by no more than 25% RPD for the native analytes and 35% for the labelled standards, the mean RRF from the two CAL/VER analyses may be used to calculate the analyte concentrations.
7. Using the HRGC/MS data acquired, quantification of target analytes is carried out in accordance with the procedures described in EPA Method 8290 and 8290A, using a minimum number of labelled surrogate standards as summarized in Table 12. The quantification may also be carried out according to EPA Method 1613B, using an expanded suite of surrogate standards as summarized in Table 9 of this document. Section 5.8 of EPA Method 8290A allows for the use of additional labelled surrogates.
8. The QC specifications in Table 11 are used for evaluating data.

Modifications to EPA 8290, 8290A

The following modifications have been made to EPA Methods 8290 and 8290A.

1. Procedures described in Section 10 of this document, 'Modifications made to EPA 1613B', are applicable.
2. The concentrations of the initial calibration solutions, surrogate standard solution and recovery standard solution are modified to be those described in Tables 3 and 4 of this document.
3. The amount of surrogate standard and recovery standard added to each sample are modified to be as described in Table 3 of this document.
4. Sample Specific Estimated Detection Limits (EDL) are reported as Sample Specific Detection Limits (SDL), calculated as described in Sections 8 and 9 of this document.

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In summary, the analysis of PCDD/F by EPA Methods 8290 and 8290A is carried out as follows:

1. Prepare QC samples (procedural blank, spiked reference sample (OPR, MS/MSD), duplicate where applicable) as described in Section 4 of this document.
2. For samples and QC samples, carry out the matrix specific extraction procedure described in Section 5 of this document. Use the surrogate standard described in Section 3.3. Use of a cleanup standard is not required by methods 8290 and 8290A, but may be added as an internal QC check.
3. Clean up the extract using procedures described in Section 6 of this document.
4. Prepare the extract for HRGC/HRMS analysis, as described in Section 6.9 of this document. Use the recovery standard described in Section 3.3.
5. Analyze the extract by HRGC/HRMS according to procedures described in Section 7. Use the acceptance criteria from EPA Methods 8290 and 8290A (summarized in Table 11) to evaluate the data.
6. Quantify the data according to protocols described in EPA Methods 8290/8290A and summarized in Table 12.
7. Evaluate the results using the QC specifications in EPA Methods 8290/8290A, summarized in Table 11.
8. Report final concentrations to a minimum reporting limit of 0.5 pg absolute.

Table 11. QC Criteria for PCDD/F Analysis by EPA 8290/8290A

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

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Table 12. Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans by High Resolution GC/MS – EPA 8290/8290A

Analytes	Quantification Ion (m/z)	Confirmation Ion (m/z)	Surrogate	RRF Determined From
2,3,7,8-TCDD	319.8965	321.8936	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
1,2,3,7,8-PeCDD	353.8576	355.8546	$^{13}C_{12}$-1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	389.8156	391.8127	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD	389.8156	391.8127	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	389.8156	391.8127	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD	423.7767	425.7737	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD
OCDD	457.7377	459.7348	$^{13}C_{12}$-OCDD	OCDD
2,3,7,8-TCDF	303.9016	305.8987	$^{13}C_{12}$-2,3,7,8-TCDF	2,3,7,8-TCDF
1,2,3,7,8-PeCDF	339.8597	341.8568	$^{13}C_{12}$-1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	339.8597	341.8568	$^{13}C_{12}$-1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2,3,4,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	373.8207	375.8178	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDF	407.7818	409.7788	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	407.7818	409.7788	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF
OCDF	441.7428	443.7398	$^{13}C_{12}$-OCDD	OCDF
Labelled Surrogate Stds	**Quantification Ion (m/z)**	**Confirmation Ion (m/z)**	**Recovery Calculated Using**	
$^{13}C_{12}$-2,3,7,8-TCDF	315.9419	317.9389	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-2,3,7,8-TCDD	331.9368	333.9339	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,7,8-PeCDF	351.9000	353.8970	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,7,8-PeCDD	365.8978	367.8949	$^{13}C_{12}$-1,2,3,4-TCDD	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	383.8639	385.8610	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	401.8559	403.8530	$^{13}C_{12}$-1,2,3,7, 8,9-HxCDD	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	417.8250	419.8220	$^{13}C_{12}$-1,2,3,7,8,9 -HxCDD	
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	435.8169	437.8140	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
$^{13}C_{12}$-OCDD	469.7780	471.7750	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	
Labelled Recovery Stds				
$^{13}C_{12}$-1,2,3,4-TCDD	331.9368	333.9339		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	401.8559	403.8530		

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APPENDIX C

Determination of PCDD/F

by EPA Method DLM02.2

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APPENDIX C – ANALYSIS OF PCDD/F BY EPA METHOD DLM02.2

The analysis of polychlorinated dioxins and furans by EPA Method DLM02.2 is carried out using the procedures described in this document and according to the following additional protocols. An electronic copy of DLM02.2 is available on the AXYS network G:\Information\Published Methods\EPA methods\.

1. A hold time of 10 days from sample receipt is applicable to aqueous and solid samples stored at a nominal temperature of 4°C. For solids stored at -20°C, this holding time may be waived with permission by contract.
2. Extract hold time is 30 days.
3. Aqueous samples **must** be liquid-liquid extracted using a separatory funnel (section 5.5.3.2), the magnetic stirring extraction procedure ("default" in section 5.5.3.1) is **not** allowed for DLM02.2 work.
4. Solid samples **must** be extracted using the Dean-Stark Soxhlet extraction procedure, described in Section 5.2.
5. Tissue samples **must** be extracted using Soxhlet extraction for 18-24 hours.
6. Dilutions greater than 20-fold are not permitted; Contact the client to determine further action. Reanalysis of a smaller sample size may be required. Data for both the original extract and diluted extract must be reported.
7. All calibration sequences for the primary column must start and end with the CS-3 calibration solution. The CS-3 calibration solution also contains the CPS (Column Performance Solution) compounds, and must consequently be labeled as "CS-3 + CPS" in the run logs.
8. All calibration sequences for the secondary column must start and end with the Isomer Specificity Check (ISC) solution. The ISC solution runs must be labeled as "ISC" in the run logs.
9. The following additional criterion is applicable to the CAL/VER results:
    a. The percent difference between Relative Responses (RR) from the analysis of the CAL/VER solution and the mean RRs from the initial calibration must be <25% and similarly the difference between the relative response factors (RRF) must be <35%.
10. QC acceptance criteria are those specified in EPA Method DLM02.2.
11. Quantification reports include the signal:noise (S:N) ratio for all analytes and standards.
12. Data reports are in accordance with reporting requirements specified in DLM02.2, Exhibit B Reporting and Deliverables requirements.
13. In cases where an ion abundance area ratio fails, due to co-eluting interferences, a peak height determination of the ion ratio is permitted, provided all other criteria are met and if, in

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the judgement of the analyst, the peak is a CDD/CDF. Analyte concentration is calculated using peak heights for both the native and labelled compounds and data is flagged.

14. Calculation of a total homologue concentration must include any concentrations flagged as 'EMPC' (Estimated Maximum Possible Concentration) and the number of peaks in the total is reported.
15. Cleanup standard recovery must be reported from both DB-5 and DB-225 columns.

Modifications:

The following modifications have been made to the method.

1. Provisional on prior agreement with the client, Axys will dilute sample extracts with solvents to bring responses within range or to minimize interferences, as deemed necessary. No recovery standard is added to diluted extracts.
2. The compounds typically present in the Window Defining Mixture (WDM), the Isomer Specificity Solution (ISC) and the CAL/VER solution are in a single solution that is analyzed as the CAL/VER solution. Analysis of the CAL/VER solution at least once twelve hours satisfies the analysis frequency requirement for the WDM and ISC.
3. Modifications made to EPA Method 1613B, described in Section 10 are applicable.

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APPENDIX D

ANALYSIS OF NON-2,3,7,8-PCDD/F

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APPENDIX D - ANALYSIS OF NON-2,3,7,8-PCDD/F

The concentrations of non-2,3,7,8-PCDD/F may be determined from the GC/MS chromatograms acquired for the analysis of 2,3,7,8-PCCD/F. A Data Interpretation Chemist identifies the non-2,3,7,8 congeners and quantifies them as shown in Table 14 below.

Table 13. Analyte Ions Monitored, Surrogates Used and RRF Determination for Non-2,3,7,8 Substituted Dioxins/Furans by High Resolution GC/MS

PCDD/F Analysis by EPS 1/RM/19				
Analytes	**Quantification Ion (m/z)**	**Confirmation Ion (m/z)**	**Surrogate**	**RRF Determined From**
Tetra-Dioxin	319.8965	321.8936	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8 TCDD
Penta-Dioxin	353.8576	355.8546	$^{13}C_{12}$-1,2,3,7,8-PeCDD	1,2,3,7,8 PeCDD
Hexa-Dioxin	389.8156	391.8127	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	mean of 1,2,3,4,7,8/1,2,3,6,7,8/1,2,3,7,8,9-HxCDD
Hepta-Dioxin	423.7767	425.7737	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD
Tetra-Furan	303.9016	305.8987	$^{13}C_{12}$-2,3,7,8-TCDF	2,3,7,8-TCDF
Penta Furan	339.8597	341.8568	$^{13}C_{12}$-1,2,3,7,8-PeCDF	mean of 1,2,3,7,8/2,3,4,7,8-PeCDF
Hexa Furan	373.8207	375.8178	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	mean of 1,2,3,4,7,8/1,2,3,6,7,8/2,3,4,6,7,8/ 1,2,3,7,8,9-HxCDF
Hepta Furan	407.7818	409.7788	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	mean of 1,2,3,4,6,7,8/1,2,3,4,7,8,9-HpCDF
PCDD/F by EPA 1613B				
Analytes	**Quantification Ion (m/z)**	**Confirmation Ion (m/z)**	**Surrogate**	**RRF Determined From**
Tetra-Dioxin	319.8965	321.8936	$^{13}C_{12}$-2,3,7,8-TCDD	2,3,7,8-TCDD
Penta-Dioxin	353.8576	355.8546	$^{13}C_{12}$-1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDD
Hexa-Dioxin	389.8156	391.8127	Mean of $^{13}C_{12}$-1,2,3,4,7,8/ 1,2,3,6,7,8-HxCDD	mean of 1,2,3,4,7,8/1,2,3,6,7,8/1,2,3,7,8,9-HxCDD
Hepta-Dioxin	423.7767	425.7737	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD
Tetra-Furan	303.9016	305.8987	$^{13}C_{12}$-2,3,7,8-TCDF	2,3,7,8-TCDF
Penta Furan	339.8597	341.8568	Mean of $^{13}C_{12}$-1,2,3,7,8/2,3,4,7,8-PeCDF	mean of 1,2,3,7,8/2,3,4,7,8-PeCDF
Hexa Furan	373.8207	375.8178	mean of $^{13}C_{12}$ -1,2,3,4,7,8/ 1,2,3,6,7,8/2,3,4,6,7,8/ 1,2,3,7,8,9--HxCDF	mean of 1,2,3,4,7,8/1,2,3,6,7,8/2,3,4,6,7,8/ 1,2,3,7,8,9-HxCDF
Hepta Furan	407.7818	409.7788	mean of $^{13}C_{12}$-1,2,3,4,6,7,8/ 1,2,3,4,7,8,9HpCDF	mean of 1,2,3,4,6,7,8/1,2,3,4,7,8,9-HpCDF

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Appendix Q

Laboratory SOPs

AXYS SOP

MLA-010, Revision 11

Polychlorinated biphenyl (PCB) Congeners

By EPA 1668

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AXYS ANALYTICAL SERVICES LTD

ANALYTICAL METHOD FOR THE DETERMINATION OF:

209 PCB CONGENERS BY EPA METHOD 1668A[1], EPA METHOD 1668C[10] 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 covers both EPA Method 1668A and EPA Method 1668C, which are attached and considered to be part of this document.

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 Methods 1668A and 1668C, 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: 23-Dec-2011
John Cosgrove, President and Senior Technical Director

Approved by: _____ Date: 22-DEC-2011
Shea Hewage, Director of Operations

Approved by: _____ Date: 23-Dec-2011
Dale Hoover, QA/QC 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.*

10. EPA Method 1668, Revision C - *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS*, April, 2010. (EPA-820-R-10-005)

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CHANGES FROM PREVIOUS REVISIONS or VERSIONS

The table below lists the details of the changes from revision 11 version 01 of this document.

Page	Change Details
13	Section F: Added “fit for intended use” phrase.
14	Table 1, Changed solids storage temperature to read -20ºC nominal to more closely reflect practice.
17	Section 3.1: Clarified current filter make.
18, 37, 38, 40, 46, 49, 50, 52, 57	Sections 3.2, 5.1.2, 5.2, 5.3.2, 5.5.3.4, 5.6.3, 5.6.4, 5.6.5, 5.7, 5.11: Changed pre-Soxhlet solvent to be dichloromethane.
18-19, 44	Sections 3.3.1 and 5.5.1: Clarified preparation procedures for surrogate standard solution.
23-24	Table 3: Removed “CAL-VER” from the table header (below CS-3)
26	Section 3.5: Changed Florisil deactivation to be by 2.0% water to correspond with current practice.
27	Section 3.6.5: Updated name of cleanup column PB 4g 44%, formerly “Layered Acid/Base Silica Column”. Added section 3.6.6: PB 8g 44% Column.
33	Table 4b: Corrected text error for PCB-170L and PCB-180L; warning limits in sample should be 40-130%.
35, 46	Sections 5 and 5.5.3.3: Added reference to SLA-124 “Liquid-Liquid Extraction Supplemental Techniques”.
37, 39	Sections 5.1.3 and 5.2.3: Changed Biobead cleanup for biosolids from optional to routine.
44	Section 5.5.1: Clarified that aqueous samples are centrifuged, not filtered. Deleted reference to obsolete SLA-086. Added instruction to visually inspect the sample before determining % suspended solids.
45	Section 5.5.2: Clarified aqueous extraction procedures. Deleted reference to obsolete SLA-086.
45-47	Section 5.5.3: Deleted filtration procedures, clarified that centrifugation is the default procedure to separate particulate and aqueous phases. Section 5.5.4: Deleted Biobead cleanup instructions for wastewater, added instead a reference to procedure instructions in section 6.1. Changed wastewater to INFL and EPRO matrices, with EFIN having Biobead as an option.
48	Sections 5.6.2 and 5.6.3: Updated procedure descriptions to current practice.
52	Section 5.7.2: Added instruction to check for separated water phase in the extract.
55-56	Section 5.10: Clarified that minimum sample weight for blood/serum/plasma is 10 g. Updated lipid determination instruction.
62	Section 5.12: Deleted procedure instructions, instead referring to SLA-123 “Splitting of Sample Extracts”.
64	Section 6: Removed all references to FMS procedures.
65	Section 6.1: Clarified that gel permeation cleanup is mandatory for INFL and EPRO extracts, but optional for all other extracts. Added information that the maximum amount of lipid per column is 2 g. Section 6.2: Updated name of cleanup column PB 4g 44%, formerly “Layered Acid/Base Silica Column”. Added Section 6.3: Cleanup column PB 8g 44%.
66	Section 6.4: Updated the typical cutpoints for the alumina cleanup column
82, 84	Table 6a: Corrected that PCB-193 is quantified against PCB-180L. Corrected text error (PCB-170L and PCB-180L were entered twice).
87	Added section 9 Reporting Criteria and Practices.
various	Renumbered some sections in accordance with updated method format standard.

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The table below lists the details of the changes from revision 10 Version 02 of this document.

Page	Change Details
General	Added references to EPA method 1668C where applicable.
2	References: Added EPA method 1668C to the list
9	Clarified how 1668A and 1668C identify congeners 107, 108 and 109
29-30	Table 4a: Pertaining to 1668A only. Added L-PCB-170 and L-PCB-180 specifications.
31-32	Table 4b: Pertaining to 1668C only. Added L-PCB-170 and L-PCB-180 specifications.
36, 37, 39, 41, 44, 45, 47, 48, 63, 64	Section 5.1, 5.2, 5.3, 5.4, 5.5.2.1, 5.5.2.2, 5.5.3.1, 5.5.3.2, 5.5.3.3, 5.6.3, 5.6.4, 6.2, 6.3 and 6.4: Clarified in the section headers which extraction and cleanup options are default and which are optional.
62-63	Section 6: Clarified the two cleanup column sequences that are allowed. Deleted former Figure 2 "Flow chart – Manual Florisil/Silica/Alumina Clean-up Column Sequence".
72-81	Table 6a: Revised PCB 170 and PCB 180 to use 13C-PCB 170 and PCB 180 (respectively) as quantification references.
82	Added Table 6b "Analyte Retention Times, Surrogates Used and RRT Windows for Congener Numbers 107,108, 109 in accordance with 1668A Specification"
83	Added Table 6c "Analyte Retention Times, Surrogates Used and RRT Windows for Optional Reporting of Congener Numbers 107,108, 109 in accordance with 1668C Specification".
84	Section 10: Deleted modification item that powdered rather than granular sodium is used. AXYS currently uses granular.
	Deleted obsolete Appendix E "Optional Reporting of PCB Congeners 107, 108 and 109 in accordance with EPA 1668C specification"

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.

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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.

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

A. 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 conventions used either in EPA Method 1668A or in EPA Method 1668C; these methods differ in how PCB Congener Numbers 107, 108, 109 are assigned to the chromatographic peaks.

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 93, 95, 98, 100, 102
PCB 30, 18	PCB 107, 124 (1668A) or PCB 108, 124 (1668C)
PCB 20, 28	PCB 110, 115
PCB 21, 33	PCB 128, 166
PCB 26, 29	PCB 129, 138, 160, 163
PCB 40, 41, 71	PCB 134, 143
PCB 44, 47, 65	PCB 135, 151, 154
PCB 45, 51	PCB 139, 140
PCB 49, 69	PCB 147, 149
PCB 50, 53	PCB 156, 157[1]
PCB 59, 62, 75	PCB 153, 168
PCB 61, 70, 74, 76	PCB 171, 173
PCB 83, 99	PCB 183, 185
PCB 85, 116, 117	PCB 180, 193
PCB 86, 87, 97 108, 119, 125 (in EPA 1668A) or PCB 86, 87, 97 109, 119, 125 (in EPA 1668C)	PCB 197, 200
PCB 88, 91	PCB 198, 199
PCB 90, 101, 113	

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.

[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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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.

A.1 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, *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*.

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B. 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 dichloromethane 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 6.6 and Appendix B.

C. SAFETY

Refer to Section 5.0 of EPA Method 1668C 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.

D. 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.

E. DEFINITIONS

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

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F. 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.

This method has been validated to demonstrate that it is fit for the intended use.

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ANALYSIS PROCEDURES

1. SAMPLE PRESERVATION AND STORAGE

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	-20°C, dark	(1 year)	1 year	none required
Tissue	5-10 g wet	Glass or foil wrapped	<4°C	-20°C, dark	(1 year)	1 year	none required
Blood	5-20 g	Glass	<4°C	-20°C, dark	(1 year)	1 year	none required
Milk	50 - 150 g	Glass	<4°C	-20°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 -20°C, dark -20°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	-20°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	-20°C, dark	undefined	undefined	none required
Solvent Extract	1 Sample	Glass	<4°C	-20°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 and samples stored at -20°C are permitted a variance of ±4°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 PRETREATMENT AND 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 – PALL, glass fiber, type A/E, 1.0 µm, 102 mm
PTFE tape
Aluminum Foil
Spatula – aluminum
Disposable spoons
Rotary evaporator
Magnetic stirring plate, with pre-cleaned PTFE coated magnetic stirring bars

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Millipore Filtration Apparatus
Soxhlet apparatus (pre-cleaned) with 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)
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 dichloromethane 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 Methods 1668A or 1668C 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 or 1668C (tables 2 and 3 in this method). 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 or 1668C, Section 7.9.1. Modify the preparation of the surrogate spiking solution (Section 7.12, EPA 1668A or 1668C) so that the concentration of the labelled compounds is 100 ng/mL (table 2 of

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MLA-010). The volume of the aliquot used is adjusted so that the same absolute amount of standard, as described in EPA Method 1668A or 1668C 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.

For aqueous samples, the surrogate standard is prepared immediately prior to 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. Prepare the surrogate standard in the laboratory space where it will be used. 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 or 1668C, Section 7.9.2. Modify the preparation of the cleanup standard spiking solution (Section 7.13, EPA Method 1668A or 1668C) so that the concentration of the labelled compounds is 100 ng/mL (table 2 of MLA-010).

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 or 1668C, Section 7.9.3. Prepare the diluted internal (recovery) standard spiking solution as described in EPA Method 1668A or 1668C, Section 7.14 (table 2 of MLA-010).

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.

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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.

CS-1 through CS-5 and CS-0.2

Prepare six calibration solutions as described in EPA Method 1668A or EPA1668C, Section 7.10.1, at the concentrations listed in Table 5 of the EPA method (table 3 of MLA-010). 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 or 1668C, 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 or 1668C, 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	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	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).

2.0% 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 2.0% 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 SCH-004. The silica is stored in a stoppered glass reagent bottle.

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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 granular 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 (granular) and flushed with hexane (~40 mL).

3.6.5 PB 4g 44% (formerly "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).

3.6.6 PB 8g 44% (formerly "Large Capacity Layered Acid/Base Silica Column”)

A silica chromatography column (2 cm O.D. x 30 cm long with glass wool plug in the bottom) is prepared by sequentially dry-packing in hexane the following reagents, as described in SCH-004:

neutral silica (1.0 g), silica (28% NaOH, 4.0 g), neutral silica (1.0 g), silica (44% H_2SO_4, 8.0 g), silica (22% H_2SO_4, 4.0 g) and neutral silica (2.0 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 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 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 Tables 4a and 4b. The applicable AXYS QC acceptance limits meet or exceed the requirements of EPA 1668A or EPA 1668C.

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 4a. QC Acceptance Criteria according to EPA method 1668A for Chlorinated Biphenyls in CAL/VER, IPR, OPR, and Samples

Congener	Cong. No. [2]	Test conc. ng/mL	CAL/VER (%)		IPR [1] (%)		OPR [1] (%)		Labelled compound [1] % recovery in samples	
			Warning limits	Acceptance limits	RSD	$\bar{X}$	Warning limits	Acceptance limits	Warning limits	Acceptance limits
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	-	-
Labeled Compounds										

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Congener	Cong. No. [2]	Test conc. ng/mL	CAL/VER (%)		IPR [1] (%)		OPR [1] (%)		Labelled compound [1] % recovery in samples	
			Warning limits	Acceptance limits	RSD	$\bar{X}$	Warning limits	Acceptance limits	Warning limits	Acceptance limits
$^{13}C_{12}$-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
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
$^{13}C_{12}$-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 Standards										
$^{13}C_{12}$-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

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Table 4b. QC Acceptance Criteria according to EPA method 1668C for Chlorinated Biphenyls in CAL/VER, IPR, OPR, and Samples

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

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Congener	Cong. No.[2]	Test conc. ng/mL	CAL/VER (%)		IPR[1] (%)		OPR[1] (%)		Labelled compound[1] % recovery in samples	
			Warning limits	Acceptance limits	RSD	$\bar{X}$	Warning limits	Acceptance limits	Warning limits	Acceptance limits
$^{13}C_{12}$-2-MoCB	1L	100	65-135	50-145	70	20-135	15-140	15-145	15-130	5-145
$^{13}C_{12}$-4-MoCB	3L	100	65-135	50-145	70	20-135	15-140	15-145	15-130	5-145
$^{13}C_{12}$-2,2'-DiCB	4L	100	65-135	50-145	70	20-135	30-140	15-145	25-130	5-145
$^{13}C_{12}$-4,4'-DiCB	15L	100	65-135	50-145	70	20-135	30-140	15-145	25-130	5-145
$^{13}C_{12}$-2,2',6-TrCB	19L	100	65-135	50-145	70	20-135	30-140	15-145	30-130	5-145
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	65-135	50-145	70	20-135	30-140	15-145	30-130	5-145
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	65-135	50-145	70	20-135	30-140	15-145	30-130	5-145
$^{13}C_{12}$-3,3',4,4'-TCB	77L	100	65-135	50-145	50	45-135	30-140	40-145	30-130	10-145
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	65-135	50-145	50	45-135	30-140	40-145	30-130	10-145
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,3,3',4,4',5-HxCB [3]	156L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB [3]	157L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2',3,3',4,4',5,5'-HpCB	189L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-NoCB	208L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	65-135	50-145	50	45-135	30-140	40-145	40-130	10-145
Cleanup Standards										
$^{13}C_{12}$-2,4,4'-TriCB	28L	100	60-130	65-135	70	20-135	40-125	15-145	40-130	5-145
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	100	60-130	75-125	50	45-135	40-125	40-145	40-130	10-145
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	60-130	75-125	50	45-135	40-125	40-145	40-130	10-145

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Footnotes to Table 4a and Table 4b:

[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 7.1.1 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 Tables 4a and 4b 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 or 1668C.

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
SLA-124	Liquid-Liquid Extraction Supplemental Techniques

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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

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.

5.0.2 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 (Default Procedure)

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 dichloromethane for two hours; three hours if brominated analytes are determined. Discard the dichloromethane. Rinse the apparatus with dichloromethane.

Place a layer of clean silica or granular 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).

5.1.3 Biosolids

In the case of biosolid samples, an optional acid wash may be carried out and a gel permeation chromatographic cleanup procedure will routinely 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 (Optional Procedure)

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 dichloromethane for two hours, three hours if brominated analytes are required. Discard the dichloromethane. Rinse the apparatus with dichloromethane.

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 granular 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 granular 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).

5.2.3 Acid Wash

In the case of biosolid samples, an optional acid wash may be carried out prior to cleanup procedures (Section 6 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). Concentrate the extract to 1 mL by rotary evaporation. The extract is ready for chromatographic cleanup procedures (Section 6).

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5.3 Tissue Extraction Procedure – Soxhlet (Default Procedure)

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 extraction with dichloromethane for two hours, three hours if brominated analytes are required. Discard the dichloromethane. Rinse the apparatus with dichloromethane.

Place a layer of clean silica or granular 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.

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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

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).

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5.4 Tissue Extraction Procedure - Base Digestion (Optional Procedure)

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.

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Transfer the dried extract to a round bottom flask (500 mL) and concentrate to approximately 1 - 2 mL by rotary evaporation.

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).

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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. A typical sample size is 1 litre.

5.5.1 Sample Preparation

The surrogate standard spiking solution must be prepared prior to sample extraction and in the same laboratory space as where the samples are extracted. 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 SLA-084 “Preparation of Aqueous Samples for Extraction” for complete details of sample homogenization, subsampling, rinsing, surrogate spiking and centrifugation procedures.

The aqueous sample extraction procedure depends on the percentage of suspended solids in the sample. Estimate the percent suspended solids by visual inspection. If in doubt of a reasonably accurate visual solid percent estimation, determine the percent suspended solids on a subsample of the sample according to SLA-092 “Determination of Suspended Solids (SS) in a Sample”.

- Samples with ≤1% suspended solids are neither centrifuged nor filtered prior to extraction (Section 5.5.2).
- Samples with >1% suspended solids are centrifuged to separate the particulate and liquid phases. The particulate and liquid phases are extracted separately (Section 5.5.3).

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 centrifuged aqueous samples, 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 (Optional Procedure)

After homogenization, subsampling and spiking with surrogate standard, as described in SLA-084, 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. Transfer the extract to a round bottom flask with dichloromethane rinses. Add an aliquot of cleanup standard solution. Add hexane (2 mL) and concentrate the extract to 1-2 mL. The extract is ready for chromatographic cleanup procedures (Section 6).

Alternate procedure after drying over anhydrous sulphate: Transfer the extract to a Kuderna-Danish flask (500 mL) with dichloromethane. Spike an aliquot of cleanup standard solution. Add hexane (2 mL) and concentrate the extract to 2 mL (water bath 60°C). The extract is ready for chromatographic cleanup procedures (Section 6).

5.5.2.2 Extraction by Magnetic Stirring (Default Procedure)

After homogenization, subsampling and spiking with surrogate standard, as described in SLA-084, 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 to a round bottom flask with dichloromethane rinses. Add an aliquot of cleanup standard solution. Add hexane (2 mL) and concentrate the extract to 1-2 mL (water bath 60°C). The extract is ready for chromatographic cleanup procedures (Section 6).

Alternate procedure after drying over anhydrous sulphate: Transfer the extract to a Kuderna-Danish flask (500 mL) with dichloromethane. Spike an aliquot of cleanup standard solution. Add hexane (2 mL) and concentrate the extract to 2 mL (water bath 60°C). The extract is ready for chromatographic cleanup procedures (Section 6).

5.5.3 Extraction of Samples with >1% Solids

The analyst must refer to the following operating procedures SLA-084 for complete details of sample homogenization, subsampling, rinsing, surrogate spiking and centrifugation procedures. The procedures are summarized below:

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5.5.3.1 Default 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 stainless steel vessel with a clean baked 10 cm filter paper (Pall, type A/E, glass fibre, 1.0 µm) in the bottom of the jar to assist with capturing of the solids. 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 5.5.3.3) or an Erlenmeyer flask (if proceeding according to Section 5.5.3.2). 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 granular 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 in Section 5.5.3.2 or 5.5.3.3.

5.5.3.2 Extraction of the Centrifugate by Magnetic Stirring (Default Procedure)

Quantitatively transfer the centrifugate 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.

5.5.3.3 Extraction of the Centrifugate by Shaking in a Separatory Funnel (Optional Procedure)

Quantitatively transfer the centrifugate to a separatory funnel. Extract the centrifugate 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.

Should problems be encountered for liquid-liquid extraction of complex samples consult AXYS SOP SLA-124 *Liquid-Liquid Extraction Supplemental Techniques*.

5.5.3.4 Extraction of Particulate

Assemble the Soxhlet apparatus, including the thimble, and thoroughly clean by Soxhlet extraction with dichloromethane for two hours (3 hours if brominated analytes are required). Discard the dichloromethane. Rinse the apparatus with dichloromethane.

Place a layer of silica or granular 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

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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 centrifugate 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 round-bottom flask (500 mL) with dichloromethane. Concentrate to 1 mL by rotary evaporation. The extract is ready for chromatographic cleanup procedures (Section 6)

Alternately, after the addition of the cleanup standard transfer the extract into a Kuderna-Danish flask. Add hexane (2 mL) and concentrate the extract to 2 mL (water bath 60°). The extract is ready for chromatographic cleanup procedures (Section 6).

Alternate Procedure for Combining Extracts

If time allows, quantitatively transfer the centrifugate extract with dichloromethane rinses to a round bottom flask. Use this flask for the Soxhlet extraction of the particulate as described in Section 5.5.3.4.

5.5.4 Cleanup of Extracts from Influent and Effluent samples

Extracts from samples with INFL and EPRO as the matrix require a cleanup on a gel permeation column (Section 6.1) prior to the other cleanup procedures described in Section 6. This is an optional step for samples with EFIN as the matrix..

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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 pre-cleaned Soxhlet thimble into a beaker.
2. Quantitatively transfer the XAD-2 resin to the pre-cleaned thimble with ultra pure water and allow to drain.
3. Rinse the resin with ultra pure water and allow to drain. Discard the water.

5.6.3 XAD-2 Resin Soxhlet Extraction Procedure (Default Procedure - **only** if PCDD/F is not determined in the same extract)

1. Assemble a Soxhlet apparatus. Add a small bed of glass wool (weighted down with the pre-cleaned thimble) to the bottom of the Soxhlet body to prevent clogging during the reflux

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procedure. Thoroughly clean the apparatus by Soxhlet extraction with dichloromethane for two hours, three hours if brominated analytes are required. Discard the dichloromethane. Rinse the apparatus with dichloromethane.

2. Transfer the pre-cleaned thimble 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.
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 <u>Removal of Water from XAD-2 Resin Extracts</u>

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 granular 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 <u>Soxhlet/Dean-Stark Extraction of XAD-2 Resin (Default Procedure **when** PCDD/F is determined in the same extract)</u>

This procedure is used only if PCDD/F analysis is required as well as PCB analysis.

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1. Assemble a Soxhlet apparatus 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 dichloromethane for two hours (3 hours if brominated analytes are required). Discard the dichloromethane. Rinse the apparatus with dichloromethane.
2. Transfer the pre-cleaned thimble 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.
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 <u>Filter - Soxhlet/Dean-Stark Extraction</u>

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 dichloromethane for two hours, three hours if brominated analytes are required. Discard the dichloromethane. Rinse the apparatus with dichloromethane.
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'

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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 dichloromethane for two hours, three hours if brominated analyses are required. Discard the dichloromethane. Rinse the apparatus with dichloromethane.

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 granular 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 granular 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. Ensure that the extract doesn't have any water present. 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 granular 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 granular 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).

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5.10 Blood/Serum/Plasma Sample Extraction

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

Matrix	Sample Size
Whole Blood/Serum/Plasma	10 - 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/serum/plasma sample (at least 10 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

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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 ~5 mL. Using standard operating procedure SLA-028, 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).

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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 dichloromethane for two hours. If brominated analytes (PBB) are also being determined the apparatus must be extracted with dichloromethane for a minimum of 3 hours. Discard the dichloromethane. Rinse the apparatus with dichloromethane.

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 granular 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 granular 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 granular 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 granular 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 granular 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 <u>Soxhlet Extraction</u>

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:

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- If less than 3 mL of water is visible, quantitatively transfer the entire extract to an Erlenmeyer flask with toluene rinses.

- 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 granular 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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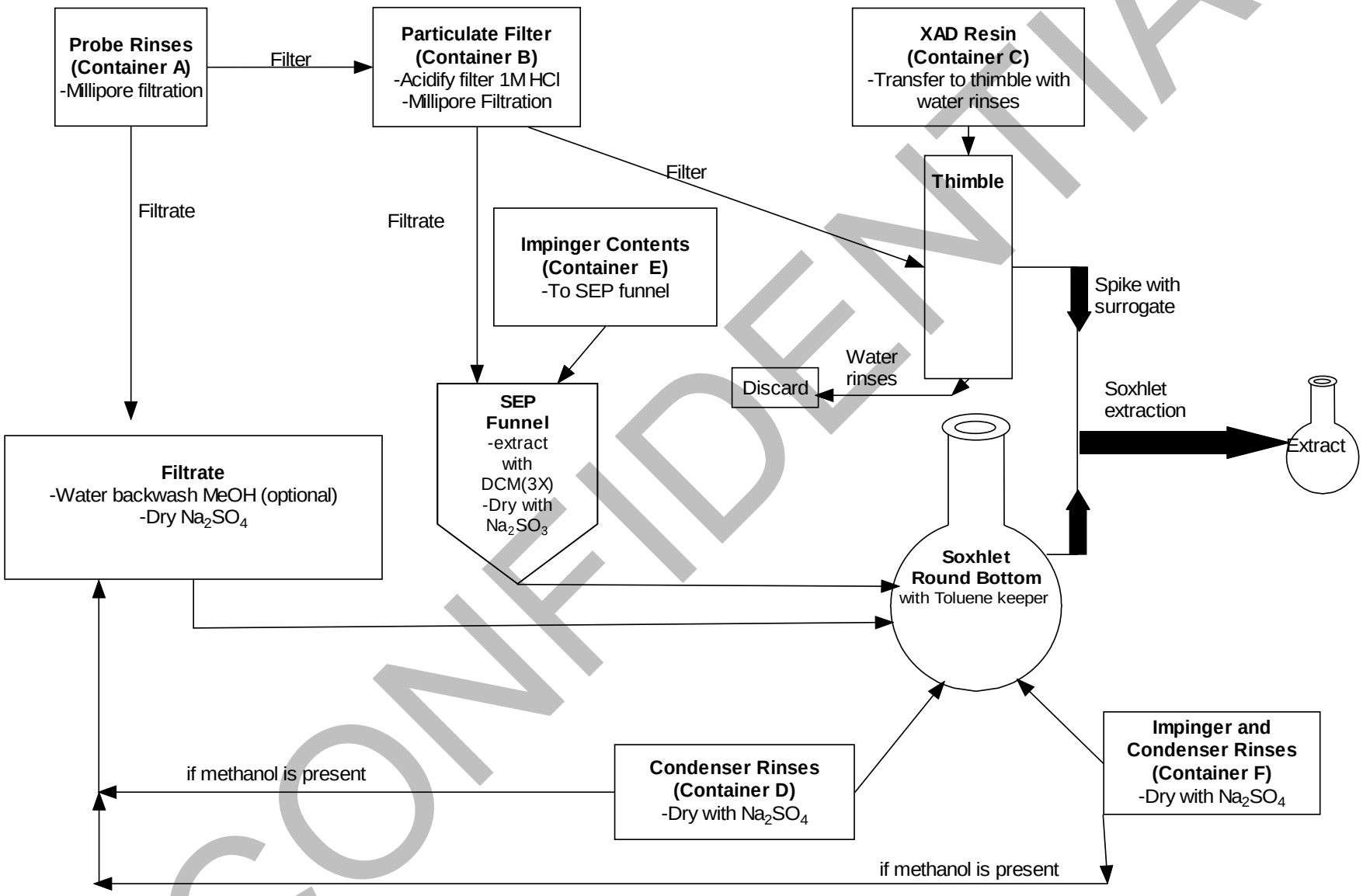
Figure 1: Processing of Sample Trains



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5.12 Extract Splitting Procedures

For detailed instructions refer to SLA-123 "*Splitting of Sample Extracts*".

Gravimetrically split the extract into two portions, one for the PCB analysis and one as backup. 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.

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6. CLEANUP PROCEDURES

The default chromatographic cleanup procedures used for the analysis of 209 PCB congeners are described in Sections 6.2, 6.4 and 6.5. Optional cleanup columns described in Sections 6.1, 6.3 and 6.6 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 cleanup two options for sequencing the Silica/Alumina/Florisil columns are permitted. The default cleanup column sequence is A/B silica, Alumina, Florisil. The alternate sequence is A/B silica, Florisil, Alumina, and this option may be used as necessary to conform to sample turnaround times. Effectiveness of extract cleanup is not affected by the use of the alternate sequence.

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 may be carried out using modified manual cleanup procedures. The analyst is referred to the following documents for details of 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)

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6.1 Gel Permeation Cleanup Column (Default Procedure for Biosolid, INFL and EPRO matrices, Optional Procedure Otherwise. Note that for "tissue" type matrices this step is required and is described in the extraction sections)

Gel Permeation cleanup is mandatory for Biosolid, INFL and EPRO sample extracts (where it should be performed prior to the other cleanup procedures) and optional for other sample extracts, e.g. from sediment, soil, XAD-2 column, ambient air, solvent extract, EFIN and other aqueous samples. The Biobead column may be used prior to the chromatographic sequences described in Section 6.2 and 6.4. 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.

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.

6.2 PB 4g 44% Multi-layered Acid/Base Silica Column (Default Procedure)

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 PB 8g 44% Large Capacity Multi-layered Acid/Base Silica Column (Optional Procedure)

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 3.6.6 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.

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6.4 Alumina Column (Default Procedure)

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:

F1	hexane	10 mL
F2	1:1 dichloromethane:hexane	45 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.

6.5 Florisil Column (Default Procedure)

Florisil columns can be loaded from a round-bottom flask. The extract must be 1 mL in hexane. If other solvents are present a solvent exchange must be carried out as described in section 6.4. 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

6.6 4.5% Carbon/Celite Column (Optional Procedure for 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 6.4). 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.

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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.

6.7 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. The presence of toluene during this final blow down step is essential to reduce losses of the more volatile PCBs.

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:

6.7.1 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.

6.7.2 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.

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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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7. INSTRUMENTAL 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 or 1668C. Instrumental analysis details are described in the most recent revision of AXYS instrumental method MIN-010, *EPA Method 1668A/C - 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 or 1668C 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.

7.1 Initial Calibration

Refer to Section 10.0 of EPA Method 1668A or 1668C 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.

7.1.1 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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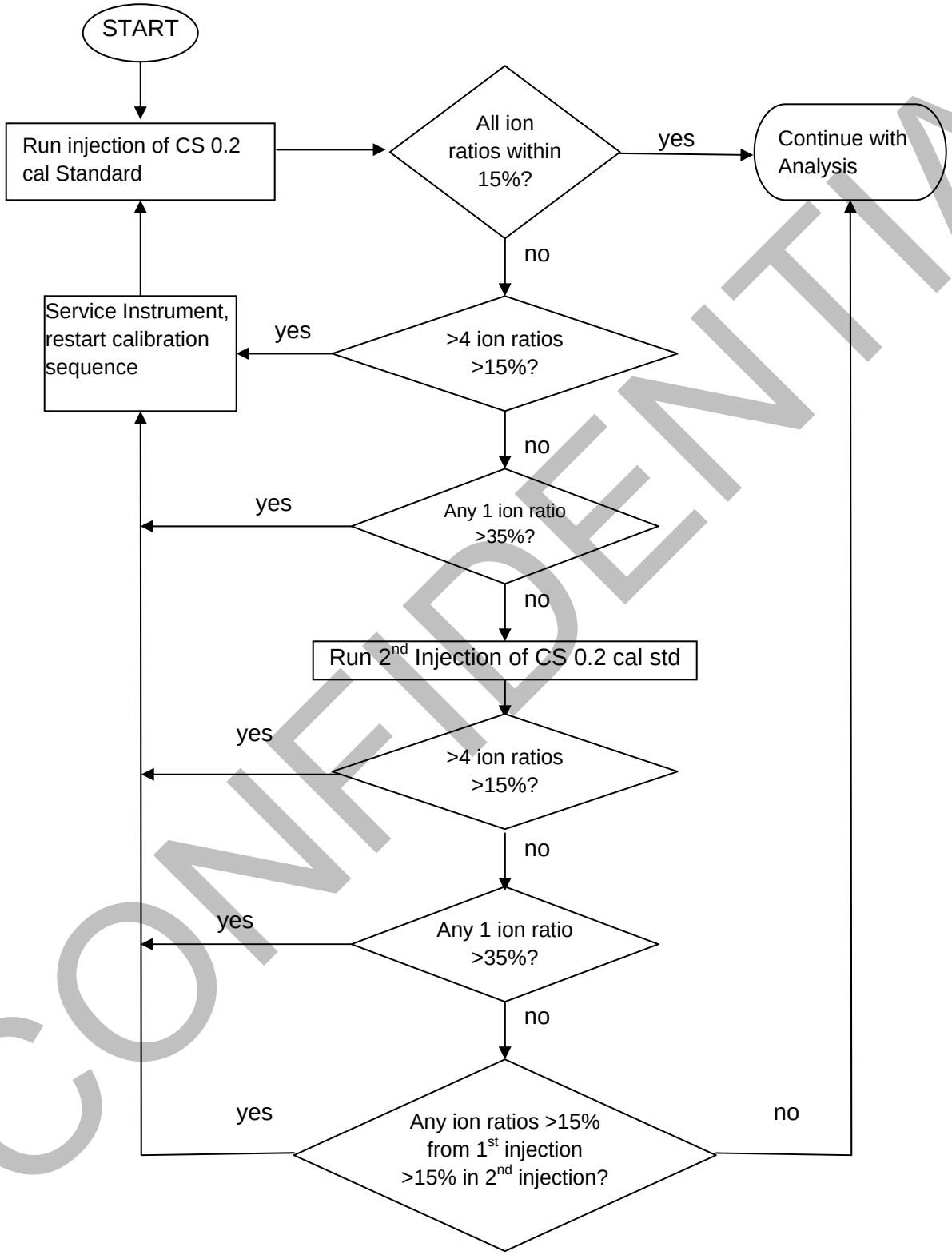
Figure 2. Procedure for Ion Ratio Criteria for CS-0.2 Initial Calibration Standard



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7.2 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 4a (EPA 1668A) or Table 4b (EPA 1668C), must be met prior to the analysis of samples. Details of the calibration verification procedures are described in the EPA Method 1668A or 1668C, Section 15.0.

7.3 Analysis of Samples

Refer to Section 14.0 of EPA Method 1668A or 1668C 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 or 1668C 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.

7.4 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).

7.5 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 and 1668C 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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8. QUALITATIVE AND QUANTITATIVE DETERMINATION

Refer to Section 16.0 of EPA Method 1668A or 1668C for details of qualitative determination and to Section 17.0 of EPA Method 1668A or 1668C 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 Tables 6a, 6b and 6c. 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.

8.1 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	See Tables 6b and 6c for information specific to EPA 1668A or 1668C										
233'45' - PeCB											
22'345 - PeCB											
22'3'45 - PeCB											
2'3456' - PeCB											

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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
22'345' - PeCB											
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											
2'3455' - PeCB	See Tables 6b and 6c for information specific to EPA 1668A or 1668C										
233'46 - PeCB											
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
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/		32:28:00	155L	32:05:00	1.012	6	1.010	1.014

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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
			167L/169L								
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							
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

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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
233'55'6 - 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
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

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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	188L/189L		38:26:00	188L	38:04:00	1.010	6	1.008	1.011
22'344'66' - HpCB	184	74472-48-3	188L/189L		39:00:00	188L	38:04:00	1.025	6	1.023	1.026
22'33'466' - HpCB	176	52663-65-7	188L/189L		39:22:00	188L	38:04:00	1.034	6	1.033	1.035
22'34566' - HpCB	186	74472-49-4	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	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	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	188L/189L		42:15:00	188L	38:04:00	1.110	6	1.109	1.111
22'344'56' - HpCB	182	60145-23-5	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	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	188L/189L	183 + 185							
22'33'456' - HpCB	174	38411-25-5	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	188L/189L		43:35:00	188L	38:04:00	1.145	6	1.144	1.146
22'344'56 - HpCB	181	74472-47-2	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	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	188L/189L	171 + 173							
22'33'455' - HpCB	172	52663-74-8	188L/189L		45:57:00	189L	51:13:00	0.897	6	0.896	0.898
233'455'6 - HpCB	192	74472-51-8	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	180L	180 + 193							
22'344'55' - HpCB	180	35065-29-3	180L	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	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		47:57:00	170L	47:56:00	1.000	6	0.999	1.001
233'44'56 - HpCB	190	41411-64-7	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

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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
22'344'566' - 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
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

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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
13C12-233'44'5' - 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
13C12-22'33'44'5 - HpCB	**170L**		194L		47:57:00	194L	53:25:00	0.898	20	0.891	0.904
13C12-22'344'55' - HpCB	**180L**		194L		46:36:00	194L	53:25:00	0.872	20	0.866	0.879
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
13C12-22'33'44'55'66' - 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

(1) Suffix "L" indicates labelled compound.
(2) C = co-eluting congener

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Table 6b. Analyte Retention Times, Surrogates Used and RRT Windows for Congener Numbers 107, 108 and 109 in accordance with 1668A 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
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
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							
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

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Table 6c. Analyte Retention Times, Surrogates Used and RRT Windows for Optional Reporting of Congener Numbers 107, 108 and 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
23'44'6 - PeCB	119	56558-17-9	104L/123L/114L/ 118L/105L	86 + 87 + 97 + 109 + 119 + 125							
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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9. REPORTING CRITERIA AND PRACTICES

Concentrations and detection limits for target compounds are reported. The isotope dilution/internal standard method of quantification, used to determine concentrations of target analytes, corrects the concentrations based on the percent recovery of the surrogate. Typical reporting units are pg/g, pg/L, or pg/sample. Concentrations for solids are reported on a dry weight basis. Concentrations in tissues (including blood/serum/plasma 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. Results may be expressed in other units if specified by contract.

Sample specific detection limits (SDL's) are determined from the analysis data by converting the minimum detectable area to a concentration following the same quantification procedures used to convert target peak responses to concentrations. The estimated minimum detectable area is determined as 2.5 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.

The lower reporting limit for blood/serum/plasma samples is the SDL, for other matrices the lower reporting limit is 0.5 pg/sample (or as specified by client).

Percent moisture is reported for all sediments, soils, and ash samples and for tissues when percent moisture is requested. Percent moisture is not reported for pulps and sludge although if is determined for the calculation of a dry weight.

Percent lipid is reported if determined on a sample.

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10. SUMMARY OF MODIFICATIONS TO EPA METHODS 1668A and 1668C

The following sections of EPA Methods 1668A and 1668C 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: Sodium sulphate is baked at a minimum of 300°C for 8 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 6.4), 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 6.4), 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 6.6 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:

<u>PCB 81</u> 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.

<u>PCB 123</u> shoulders on the PCB 109 peak on both the SPB-Octyl and the DB-1 columns.

<u>PCB 126</u> 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.

<u>PCB 157</u> co-elutes with a fragment peak from PCB 202 on the DB-1 column.

<u>PCB 169</u> 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 PB21_080 S:27	Pre-Carbon DB1 PB23_102 S:25	POST-Carbon Octyl 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

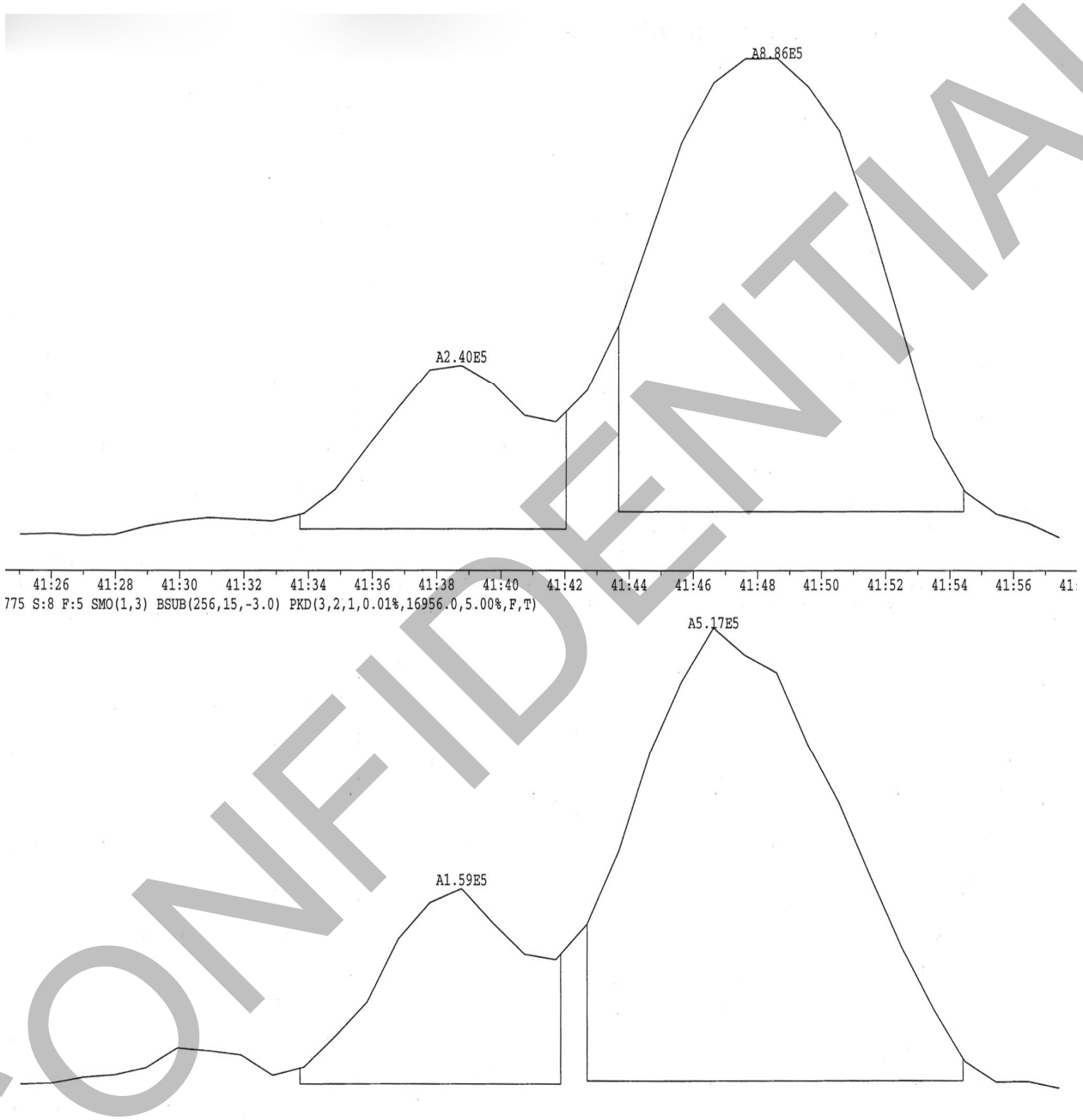

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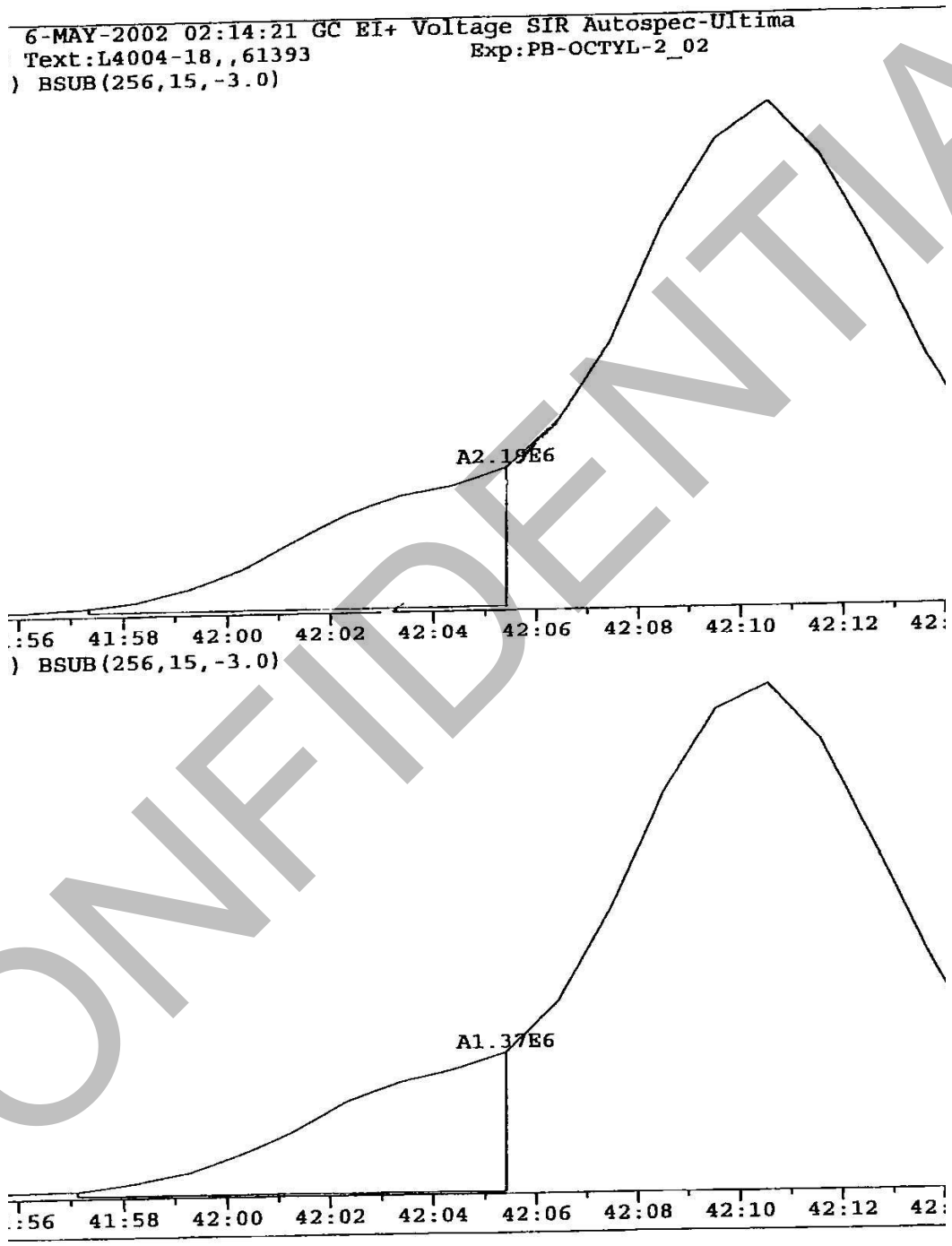
Figure B-2: Typical Chromatogram of a Less-defined Shoulder of PCB-126 on SPB-Octyl Column



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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 1668C, described in Section 10 of this document, are applicable.

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Appendix Q
Laboratory SOPs

DESA SOP

Updated SOPs Available Upon Request for

Dissolved Organic Carbons (DOC)

Suspended Solids Concentrations (SSC) /

Total Dissolved Solids (TSS)

Particulate Organic Carbons (POC)