GREAT LAKES ARCHITECT ENGINEER SERVICES (GLAES)

CONTRACT

FIELD SAMPLING AND QUALITY ASSURANCE PROJECT PLAN

Munger Landing Sediment Characterization
St. Louis River AOC
Minnesota and Wisconsin Site Characterization

Task Order 68HE0518F0693/Contract No. EP-R5-11-09

May 2019

PREPARED FOR

EPA
United States
Environmental Protection
Agency

PREPARED BY

ch2m

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QUALITY ASSURANCE PROJECT PLAN
MUNGER LANDING SEDIMENT CHARACTERIZATION ST. LOUIS RIVER AOC MINNESOTA AND WISCONSIN
Task Order 68HE0518F0693, Contract Number EP-R5-11-09

Prepared by: CH2M HILL (CH2M) Date: May 2019
Approved by:

EPA, GLNPO Date
Contracting Officer's Technical Representative: Bill Murray

EPA, GLNPO Date
Great Lakes Legacy Act Quality Assurance Lead: Mark Loomis

Adrienne M. Korpela 5/24/2019
CH2M Date
Project Manager: Adrienne Korpela

5/24/2019
CH2M Date
Quality Assurance Manager: Jewelle Keiser

11/29/2018
Pace Analytical Date
Project Manager: Steve Mleczko

Kate E Verbeten Digitally signed by Kate Verbeten DN: cn=Kate Verbeten, o=Pace Analytical Services, LLC - Green Bay WI, ou, email=Kate.Verbeten@pacelabs.com, c=US Date: 2018.11.29 14:44:03 -06'00' 11/29/2018
Pace Analytical Date
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Abbreviations and Acronyms

°C	degrees Celsius
µg/kg	microgram per kilogram
AOC	area of concern
ASTM	ASTM International
CH2M	CH2M HILL, Inc.
COTR	contracting officer's technical representative
DQO	data quality objective
DRO	diesel range organics
EB	equipment blank
EDD	electronic data deliverable
EDP	EQuIS Data Processor
EPA	U.S. Environmental Protection Agency
EQuIS	EarthSoft's Environmental Quality Information Systems
EXES	Electronic Data Exchange and Evaluation System
FOP	field operating procedure
GIS	geographic information system
GLLA	Great Lakes Legacy Act
GLNPO	Great Lakes National Program Office
GLSED	Great Lakes Sediment Database
GPS	global positioning system
GRO	gasoline range organics
HASP	health and safety plan
HDPE	high-density polyethylene
ID	identification
IDW	investigation-derived waste
LCS	laboratory control sample
LIMS	laboratory information management system
MDL	method detection limit
MPCA	Minnesota Pollution Control Agency
MS	matrix spike
MSD	matrix spike duplicate
NEIC	National Enforcement Investigations Center
Pace Analytical	Pace Analytical Services, LLC
PAH	polycyclic aromatic hydrocarbons
PARCC	precision, accuracy, representativeness, completeness, and comparability
PCB	polychlorinated biphenyl
PDF	portable document format
PPE	personal protective equipment
QA	quality assurance
QAM	quality assurance manager
QAPP	quality assurance project plan
QATS	Quality Assurance Technical Support
QC	quality control
RA	remedial action
RCRA	Resource Conservation and Recovery Act
RF	response factor
RL	reporting limit

RPD	relative percent difference
RRF	relative response factor
SDG	sample delivery group
SEDD	Staged Electronic Data Deliverable
SOP	standard operating procedure
SOW	Statement of Work
SVOC	semivolatile organic compound
2,3,7,8-TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
TCLP	toxicity characteristic leaching procedure
TEF	toxicity equivalency factors
TEQ	toxicity equivalence
TOC	total organic carbon
USACE	U.S. Army Corps of Engineers
VOC	volatile organic compound
WDNR	Wisconsin Department of Natural Resources

SECTION 1

Project Management

The U.S. Environmental Protection Agency (EPA) requires parties that conduct environmental monitoring and measurement efforts mandated or supported by the EPA Great Lakes National Program Office (GLNPO) to participate under a centrally managed field sampling plan and quality assurance project plan (QAPP). The QAPP was developed in accordance with the QA/R-5 *EPA Requirements for Quality Assurance Project Plans* (EPA 2001). Parties generating data under this program must implement procedures so that the precision, accuracy, representativeness, completeness, and comparability (PARCC) of their data are known and documented. To meet the objective, CH2M HILL, Inc. (CH2M) prepared this QAPP, which covers the data collection activities to be performed. Project participants, including subcontractors, must follow the procedures and protocols outlined in this QAPP.

This document presents the organization, objectives, functional activities, sampling rationale, procedures, and specific quality assurance (QA) and quality control (QC) activities for the sediment investigation being conducted at the Munger Landing site in the St. Louis River Area of Concern (AOC), in Duluth, Minnesota. Figures 1A and 1B present the study area and proposed sampling locations.

This section provides an overall approach for managing the project and describes the following:

- Project organization, roles, and responsibilities
- Problem definition and background information
- Project description and schedule
- Data quality objectives (DQOs) and criteria for measuring data
- Instructions for special training requirements and certification
- Instructions for documentation and records management

1.1 Project Organization

At the direction of EPA GLNPO, CH2M is responsible for performing a sediment investigation in the Munger Landing site in the St. Louis River AOC in Minnesota and Wisconsin.

The work is being conducted for EPA GLNPO in accordance with the Statement of Work (SOW) for Task Order No. 68HE0518F0693 under Contract EP-R5-11-09 (dated January 2016), CH2M's *Draft Data Quality Objectives, Munger Landing Sediment Characterization, St. Louis River AOC, Minnesota and Wisconsin Site Characterization* with contingent approval (2018a), and this field sampling and QAPP.

1.1.1 EPA GLNPO Contracting Officer's Technical Representative

Bill Murray, EPA's contracting officer's technical representative (COTR), has overall responsibility for all phases of the project. The COTR also is responsible for reviewing and approving this QAPP.

1.1.2 EPA GLNPO Alternate Contracting Officer's Technical Representative

Meaghan Kern, EPA's alternate COTR, in absence of the COTR, the alternate COTR has overall responsibility for all phases of the project.

1.1.3 EPA GLNPO Great Lakes Legacy Act Quality Assurance Lead

Mark Loomis, EPA GLNPO Great Lakes Legacy Act (GLLA) QA lead or designee, is responsible for reviewing and approving this QAPP.

1.1.4 CH2M Program Manager

Gina Bayer, CH2M's program manager, has overall responsibility for meeting EPA's objectives and CH2M's quality standards, as well as technical QC and project oversight.

1.1.5 CH2M Quality Assurance Manager

Jewelle Keiser, CH2M's quality assurance manager (QAM), has the following responsibilities:

- Direct the QA review of the various phases of the project, as necessary.
- Direct the review of QA plans and procedures.
- Provide QA technical assistance to project staff, as necessary.
- Perform or assign appropriate technical staff to audit the sampling program.

The CH2M QAM functions independently of the project staff and has direct access to management staff to resolve QA disputes, as necessary. The CH2M QAM will remain independent of direct day-to-day operations during the investigation.

1.1.6 CH2M Project Manager

Adrienne Korpela, CH2M's project manager, is responsible for implementing the project. She is authorized to commit the resources necessary to meet project objectives and requirements. Her primary function is to achieve the technical, financial, and scheduling objectives of the project. She will report directly to the COTR and will be the main point of contact for matters concerning the project. The project manager has the following responsibilities:

- Define project objectives and develop a detailed work plan and schedule.
- Establish project policy and procedures to address the specific needs of the project as a whole and also the particular objectives of each task.
- Acquire and apply technical and corporate resources to meet budget and schedule constraints.
- Orient field leaders and support staff to the project's special considerations.
- Monitor and direct other team members.
- Develop and meet ongoing project or task staffing requirements, including mechanisms for reviewing and evaluating each task product.
- Review the work performed on each task to ensure quality, responsiveness, and timeliness.
- Review and analyze overall task performance with regard to the planned schedule and budget.
- Review external reports (deliverables) before submission to EPA.
- Represent the project team at meetings and public hearings.

1.1.7 CH2M Technical Lead

Huck Raddemann, CH2M's technical lead, will assist the project manager in producing a quality work product within the authorized schedule and budget. To accomplish that goal, the technical lead will:

- Organize, direct, and oversee personnel and resources in the absence of the project manager, and perform tasks delegated by the project manager.
- Monitor subtask progress, quality, and adherence to authorized budgets and schedules.
- Serve as the second point of communication with the EPA contract management team—the COTR, project officer, contracting officer, and the CH2M internal project management team, including the project manager, QAM, and program manager—as necessary to keep them apprised of progress.

1.1.8 CH2M Senior Technical Consultant

Frank Dillon, CH2M's senior technical consultant, will support the project manager as a technical resource throughout the duration of the project by providing senior consultation and reviewing project deliverables. The senior technical consultant will participate in ongoing work in their areas of technical expertise and will be a point of communication with the EPA team. Mr. Dillon is an expert in ecological risk assessment and contaminated sediment site assessments.

1.1.9 CH2M Field Team Leader

Kaitlin Ma, CH2M's field team leader, will be responsible for preparing for and implementing the QAPP and field procedures, coordination and oversight of the field effort, and data tracking activities after completion of the field effort. Specific responsibilities include the following:

- Verify that field staff training requirements have been met.
- Arrange for field equipment and supplies.
- Oversee CH2M staff during the field effort.
- Verify field sampling procedures daily for compliance with QAPP procedures.
- Serve as the primary point of communication with subcontractor staff and the CH2M project chemist regarding field-related logistics.
- Provide daily status updates to the CH2M project manager during the field effort.
- Verify that field documentation is appropriately maintained and tracked during and after the field effort.
- Inspect and accept field equipment.
- Initiate and implement field corrective actions.
- Responsible for preparing and updating the QAPP.

1.1.10 CH2M Health and Safety Manager

Carl Woods, CH2M's health and safety manager, will be responsible for developing the project-specific *Health and Safety Plan Munger Landing Site Sediment Characterization* (HASP; CH2M 2018b). The health and safety manager also supports the field team during field activities.

1.1.11 CH2M Site Safety Coordinator

Steve Bidga, CH2M's site safety coordinator, will be responsible for distributing the HASP (CH2M 2018b) to the field team and subcontractors and ensure implementation during fieldwork.

1.1.12 CH2M Project Chemist

Jaime Engle, CH2M's project chemist, will be responsible for tracking analytical data and overseeing the data evaluation. The project chemist's specific responsibilities include the following:

- Schedule and coordinate activities with the analytical laboratory(s).
- Oversee tracking of samples and data from the time of field collection until results are reported to GLNPO at the end of the project.
- Coordinate and oversee data verification, validation, and production of data deliverables.
- Coordinate independent validation with GLNPO and GLNPO's validation contractor.
- Evaluate usability of merged field and laboratory data.
- Prepare data usability report, incorporating the results of the independent validation.
- Compile files for the preparation of the Great Lakes Sediment Database (GLSED) deliverable.

1.1.13 CH2M Field Team Member

Raja Kaliappan, CH2M's field team member, will be responsible for completing daily tasks and ensuring work is in compliance with the *Draft Data Quality Objectives, Munger Landing Sediment Characterization* (DQO; CH2M 2018a).

1.1.14 CH2M Database Manager

Kari MacGregor, CH2M's database manager, will provide data management support, including management of the project database, upload field and analytical data, prepare the validated data set for independent validation, incorporate the results of the independent validator, prepare data tables for reporting, and prepare the GLSED electronic data deliverables (EDDs) compliant with the *Great Lakes Legacy Act Data Reporting Standard* (EPA 2010). Additional details regarding responsibilities are listed in Section 2.10.1.

1.1.15 CH2M Sample Manager

Jaime Engle, the CH2M sample manager, is responsible for entering the field- and analytical-collected data into the Scribe database in accordance with the *Great Lakes Legacy Act Data Reporting Standards* (EPA 2010). The CH2M sample manager will enter sample management data daily during the field event into Scribe, and the field data will be entered into Scribe at the conclusion of the sampling event.

1.1.16 CH2M Geographic Information System Analyst

Ann Espejo, CH2M's geographic information systems (GIS) analyst will coordinate with the project manager to set up a geodatabase before sampling and will be responsible for maintaining spatial layers and overall geodatabase integrity and accuracy, and providing GIS-related deliverables for reports.

1.1.17 CH2M Administration Assistant

Tracy Cooper, CH2M's administrative assistant, will be responsible for maintaining project documentation and assisting in deliverables for reports.

1.1.18 Cetacean Marine

Joseph Bonem, the Cetacean Marine boat captain, is responsible for coordinating and scheduling vibracoring activities for the R/V Mudpuppy II vessel. He is responsible for implementing relevant

portions of the QAPP and FSP and overseeing vibracoring activities. The boat captain is responsible for documenting GPS coordinates, reviewing and providing vibracoring measurements, such as penetration and recovery depths necessary at each sample location for logging of sediment cores, to CH2M during the field effort.

1.1.19 Analytical Laboratory Project Manager

Steve Mleczko of Pace Analytical, the laboratory project manager, is responsible for coordinating and scheduling the sample analyses, handling communications between support laboratories, accepting requirements outlined within this QAPP, and overseeing the data review and preparation of analytical reports. The laboratory project manager will conduct a final data review to check that all required analyses were performed on all samples and that all documentation is complete be responsible for releasing data to CH2M that cannot be released without the laboratory's approval.

1.1.20 Analytical Laboratory Quality Assurance Manager

Kate Verbeten of Pace Analytical, the laboratory QAM, is responsible for ensuring the quality of data received by CH2M and verifying laboratory conformance with this QAPP.

1.1.21 Analytical Laboratory Section Managers

The laboratory section managers at Pace Analytical, the subcontract laboratory, will review laboratory notebooks for accuracy, completeness, and compliance with this QAPP. The laboratory section manager will verify all entries and calculations. If all entries on the pages are correct, then the laboratory section manager will initial and date the pages. Incorrect entries will be corrected before the laboratory section manager signs.

1.1.22 Analytical Laboratory Senior Analyst

The senior analysts at Pace Analytical, the subcontract laboratory, will review 100 percent of the data for the following:

- Accuracy and compliance with calibration and QC requirements, holding-time compliance, and completeness
- Verification of analyte identification and quantitation
- Comparison of calibration and QC results with the applicable control limits
- Review of reporting limits (RLs) to see that they meet the project objectives

1.1.23 Analytical Laboratory Client Services Representative

Steve Mleczko, the laboratory manager or client services representative at Pace Analytical, the subcontract laboratory, will conduct a final data review to check that the required analyses were performed on all samples and that all documentation is complete.

1.2 Problem Definition and Background Information

The Munger Landing site located in Duluth, Minnesota, is approximately 7 miles upstream (south) of Lake Superior within the St. Louis River AOC. Munger Landing is a cutoff channel, separated from the navigation channel in the St. Louis River by an island. The Munger Landing boat launch is located on the west side of the site and serves as the nearest identifiable landmark. The site extends east across the state line into Wisconsin and across the navigation channel to a marsh on the west shore of Clough

Island. Stewart Creek and Snively Creek, located on the west bank of the channel, flow from west to east into the Stewart Creek Wetlands, which empties into the St. Louis River just south of the Munger Landing boat launch. The creeks flow along the north and south sides of a suspected upland source area, the former Westinghouse Electric Corp. repair facility. The contaminants of concern at the Munger Landing site are polychlorinated biphenyls (PCBs), dioxins and furans, and mercury.

1.2.1 Previous Investigations

A focused feasibility study (FFS) (Bay West 2018) was completed by the Minnesota Pollution Control Agency (MPCA) that developed remedial alternatives to address contaminated sediment in the St. Louis River within the Munger Landing site.

The following is a summary of investigation activities that include the Munger Landing site:

2011 MPCA Lower St. Louis River Sediment Investigation

As part of an initial sediment investigation in the Lower St. Louis River, 14 samples from 6 locations were collected within the Munger Landing area. Samples were analyzed for polycyclic aromatic hydrocarbons (PAHs), PCBs, dioxins and furans, and select metals. The investigation was performed by Somat Engineering under contract to USACE, on behalf of MPCA. (Somat Engineering 2012)

2014-2015 MPCA Munger Landing Sediment Investigation

A remedial investigation was performed by Bay West LLC for MPCA during summer of 2014 and spring 2015. Sampling was conducted to determine the nature and extend of contaminated sediment, estimate volumes, refine the list of contaminants of concern, and develop a conceptual site model. A total of 110 sediment samples were collected from 40 locations within the Munger Landing site in the St. Louis River. Samples were analyzed for select metals and total organic carbon, subsets of samples were analyzed for one or more of the following: PAHs, PCBs, dioxins and furans, grain size, and percent moisture (Bay West 2015).

2017 MPCA Munger Landing Additional Sediment Characterization

Additional sediment characterization was performed in October 2017 by Bay West, for MPCA. Fifty-two sediment samples were collected from 27 locations within the Munger Landing area of the St. Louis River to fill data gaps and refine the remedial footprint. Samples were analyzed for one or more of the following: total organic carbon (TOC), PCBs, and dioxins and furans (Bay West 2018).

2016-2018 Phase II Site Characterization and Remedial Action at the Former Westinghouse Electric Corp. Facility

Site characterization and remedial action activities were conducted at the former Westinghouse facility under the MPCA Voluntary Investigation and Cleanup Program by Nova Consulting Group, on behalf of Grand Avenue Estates of Duluth, LLP. The Phase II investigation included collection of 74 soil samples, 7 groundwater samples, and 20 soil vapor samples collected from 10 locations. Soil samples were analyzed for PCBs, RCRA metals, and diesel range organics (DRO); groundwater samples were analyzed for volatile organic compounds (VOCs), PAHs, PCBs, metals, DRO, and gasoline range organics (GRO); and soil vapor samples were analyzed for VOCs. Samples collected during remedial activities included 22 stockpile soil and 70 excavation confirmation soil samples. Analyses included one or more of the following: VOCs, semivolatile organic compounds (SVOCs), PCBs, PAHs, metals, DRO, GRO, and asbestos (Nova 2018).

1.3 Project Description and Schedule

1.3.1 Project Description

The overall objective of this site characterization is to collect data for two creeks to determine if one or both may be ongoing contaminant sources to the Munger Landing sediments, and to fill data gaps within the Munger Landing site. Data collected as part of this investigation will be used to assist MPCA and Wisconsin Department of Natural Resources (WDNR) in evaluating beneficial use impairments and refining the remedial footprint in Minnesota and Wisconsin.

Figures 1A and 1B show proposed sample locations. Table 1 shows results from the seven-step DQO process for the investigation. Table 2 summarizes proposed sample locations and analytical parameters for each proposed location. Table 3 shows analytical methods and estimated number of samples to be analyzed. The sample summary table provided by EPA (Appendix D) was used to prepare sample coordinates and parameters presented in Table 2.

This investigation will include the following:

- The sediment from 40 locations will be visually characterized and sampled for laboratory analysis. Sediment cores will be collected to refusal or a maximum depth of 10 feet and continuously sampled for delineation of recovered sediments. Sample intervals will be representative of surface and subsurface soft sediments, as well as native material (if encountered). The sampling processes are described in Section 2.
- The sediment samples collected from each location will be analyzed for one or more of the following analyses: PCB Aroclors, dioxin and furan congeners, mercury, and methyl mercury. All sample intervals will be analyzed TOC to assess the cohesion and bioavailability of contaminants to receptors.
  - Twenty-eight of the 36 sediment cores will be located within the channel near Munger Landing. Twelve locations are in Minnesota, and 16 locations are in Wisconsin.
  - Eight of the 36 sediment cores will be located along the west bank of the channel within Snively Creek and Stewart Creek.
  - At a total of four locations, a petite Ponar will be used to collect sediment surface grabs near Clough Island.
- One composite solid investigation-derived waste (IDW) sample will be collected and analyzed to characterize material for disposal. Analysis of sediment IDW will include toxicity characteristic leaching procedure (TCLP) VOCs, TCLP semivolatile organic compounds (SVOCs), TCLP Resource Conservation and Recovery Act (RCRA) metals, TCLP pesticides and TCLP herbicides, PCBs, dioxin/furan congeners, pH, and flash point.

1.3.2 Project Schedule

The field investigation activities within the Munger Landing site are expected to take 1 week beginning on October 15, 2018. The field investigation activities will be conducted by CH2M and R/V Mudpuppy II vessel, under separate contract to EPA, and include collecting sediment cores within the Munger Landing site using vibracoring methods; Ponar grab samples will be collected by CH2M and WDNR for surface sediment analysis; and manual hand-coring methods will be used for the samples along Stewart Creek and Snively Creek.

All samples (to be analyzed or place on hold) will be shipped to the laboratory. Upon receipt of samples by the laboratory, analysis will be performed within the analytical holding times for the designated “analyze”

samples. Depending on the preliminary data, the project team will decide whether to analyze the designated "hold" samples. The laboratory will submit an analytical report and EDD for each sample delivery group (SDG) within 21 calendar days of receipt of the first sample in an SDG.

The draft field site sampling technical memorandum will be submitted 14 days after receipt of laboratory data. A draft data usability report will be submitted 30 days after receipt of validated data from EPA's Quality Assurance Technical Support (QATS) contractor, APTIM. The GLSED data deliverable package, draft site characterization report and draft cultural resources survey report will be submitted 30 days after completion of the data usability report. A final site characterization report and final cultural resources survey report will be submitted 30 days after receipt of comments from EPA.

1.4 Data Quality Objectives and Criteria for Measurement Data

DQOs are qualitative and quantitative statements that define the objectives of the project. The DQOs are used to determine the most appropriate type of data, determine the appropriate procedures for data collection, and specify acceptable decision error limits that establish the quantity and quality of data needed for decision making. The technical planning team developed project-specific DQOs in accordance with *Guidance on Systematic Planning Using the Data Quality Objectives Process* (EPA 2006). Proposed additions or changes to the requirements in the approved QAPP will be documented in a QAPP addendum and submitted to EPA for review and approval. The results of the seven-step DQO process for this project are presented in Table 1.

The laboratory RLs, method detection limits (MDLs), and project screening values are presented in Table 4A. The laboratory limits should be less than the lowest screening level value for each analyte. Although it could lead to some uncertainty when laboratory limits are greater than screening values, it does not prevent conclusions from being drawn with respect to the project objectives for the following reasons:

- Even though some RLs are greater than the respective screening level, MDLs are closer to and could be less than the applicable screening level. The laboratory instrumentation would likely detect a constituent if present at a concentration greater than its MDL, and such a result would be reported as estimated because it is less than the RL.
- If a particular analyte has an RL or MDL greater that a screening level and there are sufficient other analytes in the same constituent group that would likely be detected in the event of a release with an RL or MDL less that the screening value, then determinations for further action at the site can be made with sufficient confidence.
- For dioxin and furan congener analysis, nondetected target analytes in the samples and blanks will be reported to the adjusted MDL or the estimated detection limit (EDL), whichever is greater. For target analytes with the reported "AnalyteType" of "Less_Than", the estimated maximum possible concentration (EMPC) values are treated as detect results and the EDL values are not included in the deliverables.

1.5 Instructions for Special Training Requirements and Certification

The personnel engaged in field activities will have completed the U.S. Occupational Safety and Health Administration 40-hour health and safety training that meets the requirements of 29 *Code of Federal Regulations* 1910.120. Subcontracted project personnel will read and implement the project-specific HASP

(CH2M 2018b), and documentation will be maintained to demonstrate that the requirements of the plan are followed.

Laboratories participating in analytical services will be certified as required by applicable state and/or federal agencies for the fields of testing relevant to the requirements for the project. The laboratory must have current National Environmental Laboratory Accreditation Conference certification for all of the certifiable methods performed as part of the investigation. The laboratory managers will be responsible for ensuring that all personnel have been properly trained and are qualified to perform their assigned tasks.

1.5.1 Health and Safety

CH2M and its subcontractors will abide by U.S. Occupational Safety and Health Administration regulations and the site-specific HASP (CH2M 2018b). General topics covered in the HASP include site location and scope of work, safety and health risk analysis, field team organization and responsibilities, personal protective equipment (PPE), site control measures, decontamination procedures, emergency response plan, employee training, and medical monitoring. The HASP will be kept onsite during field activities, and a copy will be maintained in the project files.

1.6 Instructions for Documentation and Records

1.6.1 Field Sampling Documentation

Field sampling activities will be recorded in field logbooks following procedures documented in the field operating procedures provided in Appendix B. Logbook entries will provide as much detail as possible so personnel going to the site can reconstruct a particular situation without reliance on memory. Modifications to field sampling protocols must be documented in the field logbook. The field team leader is responsible for verifying that modifications to sampling protocols have been documented.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to the field crew but stored in a secure location when not in use. The project name will identify each logbook, the title page of which will contain the following information:

- Name of the person to whom the logbook is assigned
- Logbook number
- Project name
- Project start date
- Project end date

At the beginning of each entry, the date, start time, weather, names of all sampling team members present, and the signature of the person making the entry will be documented. Measurements and samples collected will be recorded with a detailed description of the location of the station. The number of photographs taken also will be noted. Equipment used to make measurements will be identified, along with the date of calibration.

Entries will be made in indelible ink, and no erasures will be allowed. If an incorrect entry is made, the information will be crossed out with a single strike mark, initialed, and dated. Blank pages will be noted as being intentionally blank.

Samples will be collected following the sampling procedures documented in the field operating procedures provided in Appendix B. Sample collection equipment will be identified, along with the time of sampling, sample description, parameters being analyzed, and number of containers. Unique sample

identification (ID) will be assigned to each sample, including field duplicate samples, and will be noted in the field logbook or field forms.

Field personnel will provide comprehensive documentation of the various aspects of field sampling, field analysis, and sample chain-of-custody. This documentation constitutes a record that allows reconstruction of the field events to aid in the data review and interpretation process. Documents, records, and information relating to the performance of the fieldwork will be retained in the project file.

1.6.2 Data Reporting

Analytical data will be submitted in accordance with the laboratory contract. A data usability report will be completed and submitted as part of the project data deliverables by the project chemist. The report will include a review of the merged field and laboratory data, an assessment of field sample precision, a statement about data set completeness, and an assessment of overall usability that explains concerns about data usability for the intended purpose. Limitations of the data usability and deviations from the QAPP also will be evaluated and reported.

1.6.2.1 Field Data Reporting

Information collected in the field through visual observation, manual measurement, or field instrumentation will be recorded in field notebooks or forms and then entered into an electronic data file (Scribe database) after the completion of the field event or stored electronically (portable document format [PDF]) in the project file. The field team leader or project chemist will review the data for adherence to this QAPP and for consistency. Concerns identified as a result of the review will be discussed with the CH2M project manager and CH2M QAM, corrected if possible, and incorporated into the data evaluation process.

Field data calculations, transfers, and interpretations will be conducted by the field team and reviewed for accuracy by the field team leader, project chemist, or appropriate designee. The appropriate task manager will review field documentation, data reduction, and accuracy of data entries into the data log. The data logs and documents will be checked for the following:

- General completeness
- Readability
- Use of appropriate procedures
- Clearly stated modifications to sampling procedures
- Appropriate instrument calibration and maintenance records
- Reasonableness of data collected
- Correctness of sample locations
- Correctness of reporting units, calculations, and interpretations

Where appropriate, field data forms and calculations will be processed and included in appendixes to the report. Original field logs, documents, and data reductions will be kept in the project file.

Standard forms, such as Sediment Core Log (Appendix C) will be used in addition to the field logbooks to ensure necessary data are recorded consistently and provide a more detailed record. No blank spaces will appear on completed forms. If information requested is not applicable, the space will be marked with a dashed line or marked “N/A.” The forms are to be completed in the field and placed in the project files.

1.6.2.2 Laboratory Data Reporting

When possible, analytical data will be transferred directly from the instrument to a computerized data system. Raw data will be stored electronically. Laboratory data entry will be sufficient to document information used to arrive at reported values.

Electronic data storage will be used when possible. The electronic data will be maintained in a manner that prevents inadvertent loss, corruption, and inappropriate alteration. Electronic data will be accessible and retrievable for a period of 365 days after final acceptance of data.

Deviations from stated guidelines must be addressed through corrective action. Deviations caused by factors outside the laboratory's control, such as matrix interference, will be noted with an explanation in the report narrative. The laboratory project manager will contact the project chemist to discuss deviations before the final data are submitted. Calculations will be checked and reports reviewed for errors, oversights, or omissions. The laboratory reports for samples and analyses will contain the information necessary to perform data evaluation. The subcontract laboratory will follow the appropriate reporting requirements as specified in Section 4.1, and electronic data deliverables as specified in Section 1.6.3.

1.6.2.3 Project Document Control

CH2M is responsible for the content, distribution, and version control of the site plan documents, including this QAPP. Specifically, the project manager is responsible for implementing proper version control maintenance standards for the site plans. A memorandum will accompany site plan updates and revisions, instructing the project team to discard old versions of the plan. Current and archived site plans will be stored in the project files in the CH2M office in Milwaukee, Wisconsin, and their respective project local area network server. Project records will be stored and maintained in accordance with CH2M's data management plan, discussed in Section 2.10.

The distribution list for the QAPP is provided on pages ix and x.

1.6.3 Electronic Analytical Record Format

The field-collected data and analytical sample information will be entered into the Scribe database by the CH2M sample manager, in accordance with the *Great Lakes Legacy Act Data Reporting Standards* (EPA 2010). The CH2M sample manager will enter sample management data daily during the field event into Scribe, and the field data will be entered into Scribe at the conclusion of the sampling event.

Pace Analytical will report the batch information in the EDDs. A batch is the primary mechanism for associating QC samples with the field samples for which they were processed and analyzed. Analytical data review requires this association to assess the impact of QC sample performance to the quality of the field sample results.

1.6.3.1 Preliminary Data

Pace Analytical will provide preliminary laboratory data in the Environmental Quality Information System (EQuIS) EZEDD format for PCBs, dioxin/furan congeners, mercury, methyl mercury, and TOC.

1.6.3.2 Environmental Quality Information System

Pace Analytical will provide waste characterization data in the EPA Region 5 EQuIS EDD format. The EDD will be submitted to the project chemist by e-mail.

CH2M requests that three ASCII text files be generated as the EDDs for each batch/SDG: one for sample (SMP) data, one for tests and results with quality control (TRSQC) data, and one for test batch (BAT) data. The specifications for the custom EDD format is attached. File naming should be as follows: "*smp.txt" for SMP data, "*trs.txt" for TRSQC data, and "*bat.txt" for BAT data (where * = the SDG number).

The EPA Region 5 valid values will be used with the custom EDD format. Certain fields within each of the three files are limited to a specific range of valid values. These valid values must be used exactly as given, matching both case and spelling. If adequate values are not available from the valid value lists,

CH2M must be contacted to obtain approval for all proposed values prior to their use in generating the EDD files.

The valid values are provided by EPA and EarthSoft in an .rvf file. The Region 5 –specific .rvf file can be obtained by downloading the EQuIS Data Processor (EDP) application, which is located here: http://www.earthsoft.com/products/edp/edp-format-for-epar5/ EPA Region 5 Format File (EQuIS 6. x). In order to download the EDP checker, the laboratory needs a customized EPAR5 .xse file to run the EDD through the EDP checker program.

CH2M will provide the complete project EDD to GLNPO for entry into EPA's GLSED. The EDD will include a complete set of field and laboratory data consistent with *Great Lakes Legacy Act Data Reporting Standards* (EPA 2010) and a narrative that explains concerns about data usability for the intended purpose associated with laboratory or field data flags or anomalies.

1.6.3.3 Staged Electronic Data Deliverables

Pace Analytical will provide final laboratory data in the Staged Electronic Data Deliverable (SEDD) 5.2 Stage 2A for PCBs, dioxin/furan congeners, mercury, methyl mercury, and TOC. EDDs will comply with the most recent version of the GLLA Data Reporting Standard.

EPA GLNPO will provide laboratories with access to a Web-hosted data checker, Electronic data eXchange and Evaluation System (EXES), for self-inspection to assist in compliance checks and error checks of the data. The laboratory will submit the SEDD files through EXES using the submit data function.

Pace Analytical's test SEDD files shall be submitted through EXES prior to sample reporting for each analytical method.

1.6.4 Project Record Maintenance and Storage

Project records will be stored and maintained in accordance with CH2M's data management plan, discussed in Section 2.10. Each project team member will be responsible for filing project information or providing it to the project assistant familiar with the project filing system. Individual team members may maintain separate files or notebooks for individual tasks but must provide such materials to the project manager upon completion of each task.

The following are the general project file categories:

- Correspondence
- Original reports
- Non-laboratory project invoices and approvals by vendor
- Non-laboratory requests for proposals, bids, contracts, and SOWs
- Field data
- Data evaluation and calculations
- Site reports from others
- Photographs
- Laboratory analytical data and associated documents and memos
- Regulatory submittals, licensing, and permitting applications
- Site and reference material
- HASP
- Figures and drawings

A project-specific index of file contents is kept with the project files at all times. The project record file will be transferred to EPA as part of the closeout activities.

SECTION 2

Data Generation and Acquisition

This section describes the procedures for acquiring, collecting, handling, measuring, and managing data in support of this sampling activity. It addresses the following data generation and acquisition aspects:

- Sampling process design
- Sampling method requirements
- Sample handling and custody requirements
- Laboratory analytical method requirements
- Laboratory QC requirements
- Field and laboratory instrument calibration and frequency
- Field and laboratory instrument and equipment testing, inspection, and maintenance requirements
- Inspection and acceptance requirements for supplies and consumables
- Data acquisition requirements
- Data management

2.1 Sampling Process Design

Sediment core collection will be performed by Cetacean Marine of Bay City, Michigan, using the R/V Mudpuppy II vessel under separate contract to EPA. Sediment surface sample collection by petite Ponar will be performed by WDNR. Four CH2M staff will support the following sediment sampling activities: poling and core collection onboard the Mudpuppy, petite Ponar sampling, collection of field data (locational data, depth measurements, and observations), sediment core logging, collecting samples for laboratory analysis, and managing of IDW. Pace Analytical will send a courier to pick the samples up daily and will perform the sample analysis. PCB Aroclors, mercury, and TOC will be analyzed by Pace Analytical's laboratory in Green Bay, Wisconsin. While, dioxin and furan congeners will be analyzed by their laboratory in Minneapolis, Minnesota, and methyl mercury will be analyzed by the Duluth, Minnesota, facility.

The following FOPs describing the applicable field procedures are included in Appendix B. The FOPs are included as a supplement to the instructions provided in the QAPP. In the instances where an FOP within Appendix B is not referenced, the text of the QAPP section will act as the operating procedure for that task.

FOP Number	Title
FOP-01	Global Positioning System Procedures
FOP-02	Sediment Sampling Vessel Operation and Station Positioning
FOP-03	Recording Field Information on Mudpuppy II
FOP-04	Vibracore Boat Sediment Sampling
FOP-05	Manual Coring Methods
FOP-06	Sediment Surface Dredge (Ponar) Sampling
FOP-07	Mudpuppy II Decontamination Procedures
FOP-08	Geotechnical Field Testing
FOP-09	Field Equipment Cleaning and Decontamination Procedures
FOP-10	Sample Handling, Packaging, and Shipping
FOP-11	Documentation and Chain-of-Custody Procedure
FOP-12	Field Logbook

Field Investigation Approach

The investigation activities include collecting survey data and sediment samples for chemical and physical laboratory analyses The CH2M field team leader and field team with support from the sampling contractors are responsible for the following activities:

- Conduct mobilization and demobilization activities, including the following:
  - Review available utility maps and contact Gopher State One Call and Wisconsin's Diggers Hotline to obtain underground utility information for sampling locations and field locate utilities.
  - Identify field supplies and mobilize field equipment and supplies to the site (for example, PPE, field equipment, and sampling supplies).
  - Establish and prepare the IDW staging area at 121 Spring Street, Duluth, Minnesota 55808 (Spirit Lake Marina & RV).
  - Coordinate with MPCA and the property owner of the former Westinghouse property and the City of Duluth to gain access to the creeks for sampling.
  - Prepare field maps and load the proposed sample location and reference benchmark coordinates into global positioning system (GPS) units for navigating and surveying.
  - Confirm that analyses are scheduled through the laboratory and arrange for delivery of sample containers.
  - Upon conclusion of the field event, demobilize staff and equipment from the processing area.
- A total of 36 sediment core and 4 sediment grab sample locations are included within this investigation.
- Collect field observation data, including visual observations, geotechnical field measurements for cohesive material, if encountered (pocket penetrometer and Torvane shear strength), and photographic documentation of sample processing and field activities.
- Document field measurements at each location, including water, sediment poling, core penetration, core recovery, and refusal or native clay depths.
- Collect and document positional data (latitude and longitude coordinates) for each sample location in using differential GPS with submeter accuracy.
- Document water elevation data at the time of core or Ponar collection for each location from the National Oceanic and Atmospheric Administration gauge station #9099064 or United States Geological Survey gauge station 464646092052900, Superior Bay Duluth Ship Canal at Duluth, Minnesota.
- Conduct sediment core processing consisting of transporting cores to processing area, opening core tubes, logging the sediment description, photographing, containerizing, labeling, completing sample documentation with EPA's Scribe data management software, packing samples on ice, and shipping under proper chain of custody to the subcontracted laboratory.

Figures 1A and 1B show proposed sample locations. Table 1 summarizes the specific data use and DQOs for the sampling effort. Table 2 summarizes the sampling ID coordinates and the analytical parameters for each proposed location.

2.1.1 Utility Locating and Clearance

Before initiating intrusive subsurface activities, CH2M will contact Gopher State One Call and Wisconsin's Diggers Hotline to obtain underground utility information for sampling locations and field locate utilities. The field team will review utility maps and navigation charts for the study area to evaluate if planned activities conflict with known utilities. CH2M will verify that the locate ticket remains valid from the time the utility locate/onsite meeting is conducted through the end of the fieldwork. If utilities are identified near proposed sample locations, the locations will be modified to provide safe clearance from the identified utility.

2.1.2 Surveying

To meet the goals of the sampling event, precise positioning of sediment coring locations is required. Both accuracy (that is, ability to define position) and repeatability (that is, ability to return to a sampling station) are essential.

Positioning of the vessel and recording the horizontal position of sediment core locations will be accomplished with the use of differential GPS receivers capable of submeter accuracy. The horizontal and vertical accuracy of positional data is ±0.5 and ±0.1 foot, respectively. The units of measurement for this project are in U.S. Survey Feet (Field Operating Procedure [FOP]-01, Appendix B).

Coordinates will be recorded in the following datums:

- Latitude/longitude using the North American Datum of 1983
- Elevation in feet using the International Great Lakes Datum of 1985

Water depths less than 25 feet will be measured to the nearest 0.1 foot using a surveyor's rod outfitted with a 6-inch-diameter plate or a surveyor's tape outfitted with a sounding disc or bell anchor 6 inches in diameter and weighing between 7 and 8 pounds per the U.S. Army Corps of Engineers (USACE) guidance document (USACE 2013).

Survey equipment QA/QC checks will be performed twice daily (prior to commencing and after completing daily field surveying activities) by checking the accuracy of the GPS equipment and documented in the US EPA GLNPO Locational Data Checklist and Metadata Recording Form (Appendix C, Field Forms). The QA/QC checks will be performed by the Mudpuppy crew for the Mudpuppy's GPS and by CH2M field staff for the CH2M GPS.

2.1.3 Sediment Collection

Before advancing the core tube, manual sediment poling will be conducted at each proposed sample location to verify if available sediment is present for collection and estimate an appropriate core tube length. The sediment probe will be manually advanced into the subsurface until refusal is reached. Refusal is determined as the depth when penetration into the sediment is less than 0.1 foot after continuous pushing of the sediment probe. At refusal, the penetration depth will be measured to the water surface to the nearest 0.1 foot.

At each location, CH2M field staff will complete a Sediment Core Log (Appendix C) during sample processing at the onshore staging area. The data on the core log will include station, location coordinates, water depth, sediment thickness, sample type (vibracore, Ponar), penetration, and measured recovery. A summary of sample locations, collection type, and selected laboratory analysis is provided in the EPA Sample Summary Table (Appendix D).

2.1.3.1 Vibracore Sampling

Cetacean Marine (Bay City, Michigan) will collect sediment cores at 28 locations within the river (SD-01 through SD-28) using EPA's RV Mudpuppy II vessel under separate contract to EPA in collaboration with CH2M. Sediment sampling performed by the RV Mudpuppy II vessel will be performed in accordance with EPA's standard operating procedures, as presented in FOP-03, FOP-04, FOP-06, and FOP-07, Appendix B. Navigation of the vessel to a sampling location and final positioning will be accomplished using GPS receivers on the RV Mudpuppy II.

Sediment cores will be collected using 4-inch polycarbonate core tubes outfitted to a Rossfelder P3C vibracore unit. The vibracore unit will be advanced to refusal or a maximum depth of 10 feet. Core penetration depth will be measured for comparison against the recovered sediment thickness measurement and used to calculate percentage of recovery.

To maximize sediment recovery, vibracore liners will be outfitted with a sediment retainer. Initially, if the sediment core recovery is less than 70 percent of the core penetration depth, then the sampling position will be offset to remain within 10 feet of the proposed location, and a second sampling attempt will be made. If the recovery in the three attempts are all less than 70 percent of the core penetration depth, then the core with the greatest recovery will be used for sample processing. If no sediment is recovered after the third attempt, then the location will be abandoned, and an alternative sample location will be proposed by CH2M to the GLNPO Contracting Officer's Representative for approval prior to sampling. If, after a representative number of locations have been sampled, the site-specific core recoveries are consistently less than 70 percent, then the requirement will be revisited with the CH2M project manager and the GLNPO Contracting Officer's Representative to determine if an adjustment to the requirement is warranted.

Upon sediment core retrieval, the core bottom will be capped then sealed with duct or electrician's tape. Residual sediments on the outside of the core will be returned to the waterbody at the time of sample collection for each location. Sediment cores will be kept in an upright position on the vessel for an adequate amount of time that allows for the settling of fine-grained particles at the sediment/water interface. After allowing for settling, if a water column within the core liner exists, it will be drained to no less than 4 inches above the sediment while in a vertical position. Once excess water is drained, the top of the core will be capped and sectioned to manageable lengths, if needed. Each top of core will be labeled with the appropriate location ID, start and end depths, and stored upright in preparation for transfer to the onshore staging area for processing as described in Section 2.1.4 and in FOP-04, MP-103 Standard Operating Procedure for Using the Vibracoring System Onboard the Research Vessel Mudpuppy II.

2.1.3.2 Manual Coring

Eight locations in Stewart and Snively Creeks (SD-33 through SD-40) will be sampled by CH2M staff wading into the creek and performing manual sediment coring. Manual coring will use 3-inch-diameter polycarbonate tubing driven with a 10-pound post hammer to advance the core continuously until refusal as outlined in FOP-5, *Manual Coring Methods* included in Appendix B.

2.1.3.3 Ponar Surface Sampling

Surface sediment (0- to 0.25-foot) will be collected within the river channel by the WDNR and CH2M personnel from four locations west of Clough Island (SD-29 though SD-32) using a petite Ponar. Petite Ponar collection will be performed in accordance with EPA's standard operating procedure, outlined in FOP-06, Appendix B. The sediment will be collected in disposable aluminum pans, excess water will be decanted, and sediment will be transferred to 2-gallon airtight resealable plastic bags for transport to shore for processing.

2.1.4 Sediment Processing

Sediment cores and Ponar surface grabs will be transported at least twice daily to a temporary processing area located at Spirit Lake Marina & RV for processing by CH2M staff. Before processing sediment cores, the top core cap will be removed, and free water will be decanted by slowly tipping the core at the minimum angle needed, with care given not to pour out fine-grained soil or sediments at the interface.

Digital photographs will be taken of each Ponar sample and core. Each core will be cut open lengthwise while in a horizontal position and photographed before it is segmented into samples to document the undisturbed structure. Each photograph will include a scale (tape measure), station ID, depth interval being represented, and date of core collection. Distinct photographs will be taken of the soft sediment/native clay interface and visible nonaqueous phase liquid. Sediments will be visually characterized and logged within the Sediment Core Log (Appendix C, Field Forms) according to textural class, color, moisture content, particle size and shape, consistency, and other observations (for example, staining and odor, presence of nonaqueous phase liquid). CH2M staff will use a photoionization detector to screen the core at each sample interval for detections of organic vapor, which will be noted within Sediment Core Log (Appendix C, Field Forms). Field testing for geotechnical characteristics will be conducted on each sample interval exhibiting cohesive properties using a pocket penetrometer and miniature vane shear following ASTM International (ASTM) methods WK27337 and D4648, respectively, and as outlined in FOP-8, *Geotechnical Field Testing.*

2.1.5 Sediment Sample Collection

Sediment samples collected by petite Ponar will be representative of surface sediment (0- to 0.25-foot). Soft sediments within each core will be sampled continuously in 1-foot intervals. If native material is recovered, then the native material will be segregated into its own interval, to a maximum of 1 foot below the soft sediment/native material interface. If the last soft sediment sample interval is less than one-half the sample interval length, it will be included in the previous interval, while if it is greater than one-half the interval length, it will be processed as a separate sample interval. QA/QC samples will be collected at a 10 percent frequency for field duplicates and 5 percent frequency for matrix spike/matrix spike duplicate (MS/MSD) samples.

Rocks, twigs, leaves, and other debris will be removed from each sediment sample. Sediment samples will be thoroughly mixed until uniform texture and color is achieved while avoiding excess liquid from being decanted and placed into respective sample containers. Sample information will be entered into the Scribe sample management database. Samples will be stored on ice in coolers at 4°C (±2°C) after processing and during overnight delivery to the laboratory.

Table 2 summarizes proposed sample locations and analytical parameters for each proposed location. The sample summary table provided by EPA (Appendix D) was used to identify sample coordinates and parameters presented in Table 2. Table 3 shows the analytical methods and estimated number of samples to be analyzed, including QA/QC samples.

The top one or two sample intervals at each core location will be submitted for immediate analysis (Table 2), with the lower intervals placed on hold at the subcontract laboratory.

Samples will be picked up by the Pace Analytical sample courier. Additional requirements for sample packaging, shipment, and chain-of-custody procedures are detailed in Section 2.3. Unused sediment generated during sample processing will be containerized as IDW for characterization sampling, profiling, and proper disposal as discussed in Section 2.1.7.

2.1.6 Field Equipment Decontamination

Field equipment will be decontaminated to prevent cross contamination between sampling locations and intervals. Sampling and sample processing methods will use disposable equipment wherever possible to minimize the need for decontamination procedures.

Nondedicated and reusable equipment used during sediment sampling or processing will be decontaminated before sampling activities and between samples in accordance with FOP-09, Field Equipment Cleaning and Decontamination Procedures. Sediment coring equipment associated with vibracore and manual coring techniques will be manually brushed and/or rinsed with river water to remove residual sediments between each sample location to prevent cross contamination between locations. Equipment blanks will be collected from non-disposable equipment (for example, the Ponar sampler, sample spoons) that is used during the sample collection process, as discussed in Section 2.5.1.2

In an effort to prevent transfer of invasive species between waterways, the exteriors of vessels, trailers, vehicles, and equipment will be visually checked for vegetation prior to launching and upon retrieval of vessels. Aquatic vegetation found will be removed in accordance with FOP-07, MP-107 Standard Operating Procedure for Cleaning of Research Vessel Mudpuppy II Between Sediment Surveys to Prevent Transport of Contaminants, Invasive Species, and Waterborne Pathogens.

Sampling equipment and supplies will be decontaminated before and after use, both to prevent cross contamination of samples and to prevent the spread of invasive and exotic viruses and species. To the extent practicable, the following steps will be taken every time the equipment is moved to and from the project site to avoid transporting invasive and exotic viruses and species:

- Inspect and remove vegetation, animals or fish, and soil or sediment from equipment.
- Drain water from equipment that comes in contact with navigable waters, such as tracked vehicles, barges, boats, hoses, and pumps.
- Dispose of aquatic plants and animals in the trash. Do not release or transfer aquatic plants, animals, fish, or water from one waterbody to another.
- Wash equipment with hot water (greater than 104 degrees Fahrenheit) and/or high-pressure water or allow the equipment to dry thoroughly for 5 days before placing in another body of water.
- Use disposable equipment to prevent sample cross-contamination.

2.1.7 Investigation-Derived Waste Management

Waste characterization samples will be collected from the containers of IDW containing liquid or solid waste. Waste characterization parameters include: TCLP VOCs, TCLP SVOCs, TCLP RCRA metals, TCLP herbicides, TCLP pesticides, pH, and flash point (Table 3).

CH2M will appropriately manage and segregate IDW, including soil and sediments, and disposable sampling items such as PPE and sampling supplies generated from the field activities and sample processing. IDW is proposed to be handled in the following manner:

- Excess sediment remaining after sample processing will be treated as IDW, containerized in 5-gallon buckets at the processing area, and then transferred into new placarded 55-gallon drums with secure lids.
- Other IDW, such as polycarbonate sediment core liners, plastic sheeting, disposable sampling materials, and impacted PPE, will be disposed of as IDW and containerized in new placarded 55-gallon drums with secure lids. If these materials are not impacted by sediments, then they will be disposed of as general refuse.

Drums will be placed in a secure area at the IDW staging area at the processing area. The drum contents and condition of drums and the IDW staging area will be inspected and documented using the IDW Tracking Log – Drum Contents Log and the IDW Storage Area – Inspection Log forms (Appendix C). The IDW drums will be placarded, and appropriate waste characterization sampling will be performed for each waste stream generated. A composite sample, composed of representative material from each drum, will be collected for each type of drummed IDW generated. It is anticipated one sediment IDW sample will be collected and analyzed for the waste characterization parameters listed in Table 3. In situ PCB and dioxin/furan concentrations from sediment samples will be used for waste characterization in the waste profile. Upon receipt of analytical results from characterization sampling, a waste profile will be prepared, and CH2M will coordinate pickup and transport to a Resource Conversation and Recovery Act-permitted offsite disposal facility as soon as practicably feasible. The pickup of the IDW will be tracked using the IDW Tracking Log – Container Delivery and Pickup form (Appendix C).

2.2 Sampling Method Requirements

Sampling method requirements will be conducted in accordance with the field operating procedures (Appendix B) requirements stated in Section 2.1.

2.3 Sample Handling and Custody Requirements

Accurate records and control of samples, including their controlled custody, are necessary to provide relevant and defensible data. The chain of custody is addressed during field sample collection, data analyses in the laboratory, and through proper handling of project files. Persons will be considered to have custody of samples when samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured to prevent tampering. When samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such personnel.

Chain-of-custody forms will provide the record of responsibility for sample collection, transport, and submittal to Pace Analytical. Field personnel designated as responsible for sample custody will fill out chain-of-custody forms using the Scribe software at each sampling site, at a group of sampling sites, or at the end of each day of sampling. If the designated sampling person relinquishes samples to other sampling or field personnel, then chain-of-custody forms will be signed and dated by the appropriate personnel to document the custody transfer. Original chain-of-custody forms will accompany samples to the laboratory, and copies will be forwarded to the project files.

The sample handling, preparation, and custody will be conducted in accordance with FOP-10, *Sample Handling, Packaging, and Shipping*, and FOP-11, *Documentation and Chain-of-Custody Procedure* (Appendix B).

2.3.1 Sample Containers, Handling, and Preservation

Pace Analytical will supply the contaminant-free sample containers used for chemical analysis in this sampling effort. Sample containers for laboratory analyses will meet or exceed the requirements in *Specifications and Guidance for Obtaining Contaminant-Free Containers* (EPA 1990). Containers used for sampling will not contain target organic and inorganic contaminants exceeding the levels specified.

Specifications for the bottles will be verified by CH2M checking the manufacturer's certified statement and analytical results for each bottle lot. Containers will have been cleaned and certified as free of the analytes of concern for the project. No sample containers will be reused during collection activities for this project. Upon receipt of the samples, the laboratory will verify the adequacy of preservation and

will add preservative as necessary. Table 5 lists the containers, minimum sample quantities, required preservatives, and maximum holding times.

Corrective actions will be taken as soon as a problem is identified. Such actions may include discontinuing the use of a specific bottle lot, contacting the bottle suppliers for retesting the representative bottle from a suspect lot, resampling suspect samples, validating the data, taking into account that the contaminants could be introduced by the laboratory (for example, common laboratory solvents, sample-handling artifacts) as a bottle QC problem, and determining whether the bottles and data are usable.

Sample preservatives and sample holding times will meet the requirements set forth by EPA. Ice will be used to maintain the internal cooler temperature at approximately 4°C (±2°C) during sample collection and shipment to the laboratory.

2.3.2 Sample Identification System

CH2M will implement a sample numbering system that will identify each sample, including QA/QC samples. The sample number will provide a unique identifier for each sample, required by EQuIS site management software, which is compatible with EPA's comprehensive manual for EDD format. The unique sample numbers will be assigned sequentially.

Each sample, regardless of analytical protocol, will also be assigned a site-specific identifier, which will contain the specific location identifiers to indicate where the sample was obtained. Sediment samples will also be identified using sample interval depths. The site-specific identifier is based on the following system:

- **Study Area**—ML (Munger Landing)
  - The two-letter location code correlates to the study area.
- **Sample Location Type**—The next two letters following the study area indicate the type of sample location as follows:
  - SD = sediment sample
  - IDW = waste characterization sample – investigation-derived waste
  - EB = equipment blank sample
- **Location Number**—Sediment or soil sample locations will be sequentially numbered using 2 numeric digits:
  - Sediment: ML-SD-01
- **Sample Depth**—Depth below the sediment or soil surface from which the sample was collected will be added after the station location at the end after a forward slash (/) in a top depth, bottom depth format (0 to 0.5 foot shown as 0.0/0.5).

  For example, a soil sample collected from the 0- to 0.5-foot interval at the ML-SD-01 location would be indicated as ML-SD-01-0.0/0.5
- **QA/QC Identifier**—Field QA/QC samples will be identified using the following QA/QC identifiers:
  - Field duplicates, which are associated with the same station location as the native sample, will be identified with an "FD" (for "Field Duplicate") appended to the end of the location code.
    - ML-SD-01-0.0/0.5-FD
  - MS/MSD samples are not identified in the station location identifier but on the tag and the chain-of-custody form.

- **Equipment Blanks—**Equipment blanks will be identified using the following identifiers:
  - Equipment blanks will be taken on nondisposable equipment and will be identified with an "EB."
  - Equipment blanks will be identified with three numeric digits starting at 001 and increasing by one for each subsequent sample (ML-EB-001 is the first equipment blank used during the field event; ML-EB-002 would be the second equipment blank used during the field event).
  - The date will be added after the three-numeric digit in the "_YYYYMMDD" format where YYYY = 4-digit year, MM= 2-digit month, and DD= 2-digit day.
    - ML-EB-001_20181010
- **IDW Samples—**IDW samples will be identified using the following identifiers:
  - IDW will be identified using a series of segments: ML-IDW-[sample matrix]_[sample date]
  - Sample matrix will either be ST (solid waste) or WW (wastewater).
  - The date will be added after the three-numeric digit in the "_YYYYMMDD" format where YYYY = 4-digit year, MM= 2-digit month, and DD= 2-digit day.
    - ML-IDW-ST_20181010
    - ML-IDW-WW_20181010

2.3.3 Sample Packaging

Sample handling, packaging, and shipping procedures are described in FOP-10, *Sample Handling, Packaging, and Shipping* provided in Appendix B. Sample coolers will be shipped to arrive at Pace Analytical the morning after sampling (priority overnight) or sent by courier to arrive the same day. The laboratory will be notified of the sample shipment and the estimated date of arrival of the samples being delivered. All samples designated for either immediate analysis or hold pending analysis will be shipped to Pace Analytical. When samples are shipped, the air bill number will be documented on the chain-of-custody form accompanying the samples to the laboratory for sample tracking purposes. Completed air bills will accompany shipped samples to the laboratory and be forwarded along with data packages. The air bills will be kept as part of the project files to provide a record for sample shipment to the laboratory.

2.3.4 Sample Custody

Accurate records and control of samples, including their controlled custody, are necessary to provide relevant and defensible data. The chain-of-custody is addressed during field sample collection, data analyses in the laboratory, and through proper handling of project files. Persons will be considered to have custody of samples when samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured to prevent tampering. When samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such personnel.

Chain-of-custody forms will provide the record of responsibility for sample collection, transport, and submittal to the laboratory. Field personnel designated as responsible for sample custody will fill out chain-of-custody forms using the Scribe software at each sampling site, at a group of sampling sites, or at the end of each day of sampling. If the designated sampling person relinquishes samples to other sampling or field personnel, then chain-of-custody forms will be signed and dated by the appropriate personnel to document the custody transfer. Original chain-of-custody forms will accompany samples to the laboratory, and copies will be forwarded to the project files.

2.3.4.1 Field Custody Procedures

For samples collected for analysis, EPA chain-of-custody protocols will be followed, as described in the *National Enforcement Investigations Center (NEIC) Policies and Procedures* (EPA 1991). Chain-of-custody forms will be completed using EPA's Scribe software. The protocol for filling out the chain-of-custody form is provided in FOP-11, *Documentation and Chain-of Custody Procedure* (Appendix B).

Chain-of-custody forms are required for all samples. The sampling crew in the field will initiate chain-of-custody forms, which will contain the sample's unique ID, sample date and time, sample type, preservation (if any), and analyses required. Hard copy original chain-of-custody forms, signed by the sampling crew in the field, will accompany the samples to the laboratory. A copy of relinquished chain-of-custody forms will be retained with the field documentation. Chain-of-custody forms will remain with the samples at all times. Samples and signed chain-of-custody forms will remain in the sampling crew's possession or within view until samples are delivered to the express carrier (such as FedEx), hand-delivered to the laboratory, or placed in secure storage.

2.3.4.2 Laboratory Custody Procedures

Laboratory custody procedures will be in place for the integrity of sample and laboratory data handling.

2.3.4.3 Laboratory Sample Receipt

Upon receipt of samples, the laboratory sample custodian will verify package seals, open the packages, check temperature blanks (and record temperatures), verify sample integrity, and inspect contents against chain-of-custody forms. The laboratory project manager will contact the CH2M project chemist to resolve any discrepancies between sample containers and chain-of-custody forms. Once the shipment and chain-of-custody form are in agreement, the sample custodian will initiate an internal chain-of-custody form as well as supply the CH2M project chemist with a sample acknowledgement letter or e-mail. When applicable, sample preservation will be checked, and pH documented. If the sample temperatures are outside the required range, then the laboratory will contact the project chemist for direction on the proper course of action.

Samples will be logged into the laboratory information management system (LIMS), which will assign a unique laboratory number to each sample. The system will be used by the laboratory personnel who handle samples to ensure all sample information is captured. The required analyses will be specified by codes assigned to samples at login. Labels containing the laboratory sample number will be generated and placed on sample bottles.

2.3.4.4 Laboratory Sample Storage

After the laboratory labels the samples, they will be moved to locked or limited-access refrigerators and maintained at 4 degrees Celsius (°C; ±2°C). Access to refrigerators will be limited to members of the sample management department.

When the samples are needed, an appropriate member of the sample management department will locate the samples in the locked or secure limited-access refrigerator, sign and date the internal sample tracking form, and provide the samples to the analyst. When the analyst is finished with samples, unused portions will be returned to an appropriate member of the sample management department for replacement in a secure refrigerator.

The analyst will sign and date internal chain-of-custody forms. If entire samples are depleted during analysis, a notation of "sample depleted" or "entire sample used" will be made on the internal chain-of-custody forms.

Sample extracts will be stored in designated secure, refrigerated storage areas. Samples and sample extracts will be maintained in secure storage until disposal. No samples, extracts, or archived samples will be disposed of without prior written approval from an appropriate member of the project team. The sample custodian will note sample disposal dates in the sample ledger. The laboratory will dispose of samples in accordance with applicable regulations.

2.3.4.5 Laboratory Logbooks

Workbooks, bench sheets, instrument logbooks, and instrument printouts will be used to trace the history of samples through the analytical process and document important aspects of the work, including associated QC. Therefore, all logbooks, bench sheets, instrument logs, and instrument printouts will be part of the laboratory's permanent record. Relevant information will be entered into the LIMS at the time it is generated.

The analyst will date and initial each page or entry at the time of entry. Errors will be crossed out in indelible ink with a single stroke, corrected without obliterating or writing directly over the erroneous entry, and initialed and dated by the individual making the correction. Unused pages will be completed by lining out unused portions and initialing.

The analyst will record information about the sample, the analytical procedures performed, and the results on laboratory forms or personal notebook pages, and enter this information in the LIMS. The notes will be dated and will identify the analyst, instruments used, and instrument conditions.

Sufficient raw data records must be retained to permit reconstruction of initial instrument calibrations (for example, calibration date, test method, instrument, analysis date, each analyte name, concentrations and responses, calibration curves, response factors, or unique equations or coefficients used to reduce instrument responses into concentrations).

The laboratory group leaders will periodically review laboratory notebooks for accuracy, completeness, and compliance with this QAPP. The laboratory group leader will verify all entries and calculations. If all entries on the pages are correct, then the laboratory group leader will initial and date the pages. Incorrect entries will be corrected before the laboratory group leader signs.

2.3.4.6 Laboratory Project File

Documentation will be placed in a single, secured project file, maintained by the laboratory project manager. The file will consist of the following components, filed chronologically:

- Agreements
- Correspondence
- Memorandums
- Notes and data

Reports (including QA reports) will be filed with correspondence. Analytical laboratory documentation and field data will be filed with notes and data. Filed materials may be removed only by authorized personnel and only temporarily. The name of the person removing the file will be recorded. Laboratories will retain project files and data packages for at least 5 years, unless otherwise agreed.

2.3.4.7 General Deliverable Specifications

One copy of the analytical report in PDF shall be provided within 21 calendar days of receipt of the first sample in a SDG. In addition, one copy of the EDD must be provided within 21 calendar days of receipt of the first sample in an SDG.

2.3.4.8 Electronic Files and Hard Copy Storage

CH2M will maintain electronic files on CD-ROM (preferred media) for 10 years. Electronic files and hard copy storage should include notation of instrument-run files and calibration.

2.4 Analytical Method Requirements

Once the samples have been properly collected, documented, and successfully shipped, the subcontract laboratories will use their promulgated analytical procedures as described in the standard operating procedures (SOPs) in Appendix A to analyze the samples. Table 4A shows the quantification limits for the analyses to be performed during the investigation. The laboratories will use the methods and procedures as specified in Table 3.

The laboratory will use analytical SOPs to ensure the samples are analyzed accurately and precisely. The procedures reflect the requirements of the stated methods while including internal QC criteria.

The QC criteria used during the analyses will be those stated within the SOPs, which provide details of the corrective action plans for the analytical method requirements. Table 3 includes the complete listing of the analytical methods to be used for sample analysis on this project.

2.5 Quality Control Requirements

The analytical laboratory has a QC program to assess the reliability and validity of the analyses being performed. The purpose and creation of QC samples are discussed and summarized in the following subsections.

2.5.1 Field Quality Control Samples

QC samples will be collected to monitor accuracy, precision, and presence of field contamination. The minimum frequency for the collection of QC samples, as outlined in the following subsections, is recommended and should be reviewed and updated in accordance with the DQOs of the project. The quality (control limit acceptance or blank detections) of the QC samples will be discussed in the data usability report.

2.5.1.1 Field Duplicate Samples

A field duplicate is a split sample collected from the same interval after sample homogenization, and is used to measure heterogeneity of the matrix, analytical precision, and representativeness. Field duplicates will be collected from locations throughout the sampling area and from various depths at a minimum frequency of 10 percent. Field duplicate sample information will be documented in the chain-of-custody form, along with regular field samples, so that the laboratory can determine the duplicate–parent sample relationship. A control limit of $\pm$ 100 percent relative percent difference (RPD) will be used for native and duplicate sample values greater than or equal to five times the RL. Field duplicates will not be collected for TOC analysis or waste characterization samples.

2.5.1.2 Equipment Blanks

Two equipment blanks will be collected from nondisposable equipment that is used during the sampling process. ASTM Type II deionized water will be poured over the decontaminated equipment and collected per piece of nondisposable equipment and analyzed for the same parameters as those specified for the corresponding matrix. Disposable or dedicated equipment will be used to the extent possible for this project. TOC will not be analyzed in the equipment blanks.

2.5.1.3 Matrix Spike/Matrix Spike Duplicate

An MS/MSD consists of duplicate field sample aliquots spiked by the laboratory with analytes of concern to evaluate the effects of the matrix on the recovery of analytes. MS/MSD samples will be collected at a minimum frequency of 5 percent and designated on the chain-of-custody form for use as MS/MSD by the laboratory. The duplicate aliquots for MS/MSD analyses should be collected simultaneously or in immediate succession with the parent sample. They will be treated in exactly the same manner as the parent sample during storage and shipment. The sampling locations for the MS/MSD will be documented in the field logbook. MS/MSD samples will be collected for the applicable analytical methods. MS/MSD samples will not be collected for TOC analysis or waste characterization samples.

2.5.1.4 Temperature Blanks

A temperature blank will be included in each cooler to allow the laboratory receiving the shipment of samples to determine whether the samples have been maintained at the proper temperature. Temperature blanks will consist of an unpreserved sample container filled with distilled water. One temperature blank will accompany each sample cooler being shipped to the laboratory. Temperatures should be 4°C (±2°C).

2.5.2 Data Summation

The total PCB Aroclor concentrations will be calculated by summing the detected results; nondetected results will not be included in the sum. For results with no detectable concentrations, the total result will be reported as one-half of the highest MDL value and qualified “U” for nondetect.

Dioxin and furans will be evaluated by calculating toxicity equivalency (TEQ) associated with each of the samples. The basis for the TEQ calculations is presented in the following paragraphs.

The toxicity of each congener, indicated by a toxicity equivalency factors (TEFs), is measured with respect to the most toxic congener 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). 2,3,7,8-TCDD is assigned a TEF of 1, and the remaining congeners are assigned values of 1 or less based on their relative toxicity to 2,3,7,8-TCDD. Mammalian TEFs will be obtained from the World Health Organization (Van den Berg et al. 2006), and TEFs for fish will be obtained from Van den Berg et al. (1998).

To calculate TEQ, congener concentrations (7 dioxin congeners and 10 furan congeners) will be multiplied by their corresponding TEF to produce a congener-specific TEQ concentration. The TEQ concentrations for each of the detected congeners will be summed to determine the total TEQ concentration in the sample. Nondetected results will not be included in the sum.

2.5.3 Data Precision, Accuracy, and Completeness

Field QA/QC samples and laboratory internal QA/QC samples are collected and analyzed to assess data usability. The laboratory scope of work and analytical SOPs state acceptance criteria for precision and accuracy requirements for the QC samples. The QA/QC criteria for internal laboratory QC samples not referenced in the appropriate analytical SOPs will be those stated in the referenced methods.

PARCC parameters indicate data quality. Ideally, the intended use of the measurement data should define the necessary PARCC parameters. Both definitive and screening data will be subject to PARCC requirements. PARCC objectives for screening methods may be identical to those of definitive data as recommended in the following subsection, but the requirements may be decreased or increased depending on the project-specific objectives. The frequencies in the following subsection may vary according to the project needs.

2.5.3.1 Precision

Precision is a measure of reproducibility of analytical results. It can be defined as the degree of mutual agreement among individual measurements obtained under similar conditions. Total precision is a function of the variability associated with both the field sampling techniques as well as the laboratory analytical processes. Homogeneity of the field duplicate sample(s) will be evaluated according to the quantitation values of detected target compounds/analytes that yield relative to the values given by their associated parent samples. Field duplicate samples will be collected at a 10 percent frequency (1 field duplicate for every 10 normal samples). Precision will be evaluated as the RPD between the MS and MSD results. MS/MSD samples will be field-designated at a 5 percent frequency (1 MS and 1 MSD collected for every 20 normal samples).

2.5.3.2 Accuracy

Accuracy is the degree of agreement between a measured value and the "true" or expected value. It represents an estimate of total error from a single measurement, including both systematic or matrix error (bias) and random error that may reflect variability resulting from imprecision. Accuracy is evaluated in terms of percent recoveries determined from results of MS/MSD and laboratory control sample (LCS) analyses. Surrogate recoveries from samples analyzed for organic parameters also are used to assess accuracy.

2.5.3.3 Representativeness

Representativeness is the degree to which sample data accurately reflect the characteristics of a population of samples. It is achieved through a well-designed sampling program and by using standardized sampling strategies and techniques and analytical procedures. Factors that can affect representativeness include site homogeneity, sample homogeneity at a single point, and available information around which the sampling program is designed. Using multiple methods to measure an analyte can also result in non-representativeness of sample data.

2.5.3.4 Completeness

Completeness is the percentage of usable data (not qualified with an "R" indicating rejected during data validation) compared with the total amount generated during the sampling event. It will be determined for each method, matrix, and analyte combination. The completeness goals of each project are optimized to meet the DQOs. The goal for this project is 90 percent for sediment samples.

2.5.3.5 Comparability

Comparability is the confidence with which one data set can be compared with another. It is achieved by maintaining standard techniques and procedures for collecting and analyzing samples and reporting the analytical results in standard units. Results of performance evaluation samples and systems audits will provide additional information for assessing comparability of data among the participating subcontractor laboratory, if applicable.

2.5.3.6 Sensitivity

Sensitivity is defined as the ability of the method or instrument to detect the chemical of concern and other target compounds at the level of interest. Appropriate sampling and analytical methods will be selected that have QC acceptance limits that support the achievement of established performance criteria. Assessment of sensitivity will require thorough data validation.

2.5.4 Method Detection Limits

The MDL is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. Each participating laboratory will determine the MDL for each method, matrix, and analyte for each type of instrument that will be used during analysis. For PCBs, the laboratory performs MDL studies on each instrument, the instrument-specific MDLs are averaged, stored in the LIMS, and are maintained at acceptable criteria at or below the MDL presented in Table 4A.

MDLs initially will be determined before analyzing samples, and then determined again at least once every 12 months. The following is the procedure for determining MDL.

1. Estimate the MDL using one of the following:
   a. The concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5.
   b. The concentration equivalent of three times the standard deviation of replicate measurement of the analyte in reagent water.
   c. The region of the standard curve where there is a significant change in sensitivity (that is, a break in the slope of the standard curve).
2. Prepare (for example, extract, digest) and analyze seven samples of an MS (ASTM Type II water for aqueous methods, Ottawa sand for soil methods, glass or Teflon beads 1 millimeter in diameter or smaller for metals) containing the analyte of interest at a concentration 3 to 5 times the estimated MDL.
3. Determine the variance (S^2) for each analyte as follows:

$$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2\right] \quad (1)$$

where:

x_i = the nth measurement of the variable x

$\overline{x}$ = the average value of x

$$\overline{X} = \frac{1}{n}\sum_{i=1}^{n} x_i \quad (2)$$

4. Determine the standard deviation for each analyte as follows:

$$s = (S^2)^{1/2}$$

5. Determine the MDL for each analyte as follows:

$$MDL = 3.14(s)$$

(3.14 is the one-sided *t*-statistic at the 99 percent confidence level appropriate for determining the MDL using seven samples.)

6. If the spike level used in Step 2 is more than 10 times the calculated MDL, repeat the process using a smaller spiking level.

2.5.5 Reporting Limits

RLs should be, at a minimum, greater than two times the calculated MDL. When calibrating instruments, a standard at a concentration equal to or less than the RL must be included. The RLs specified in Table 4A were established for each analysis in order to meet the DQOs described in Table 1. RLs are highly dependent upon meeting ever-decreasing regulatory standards. Most of the RLs are set at the lowest calibration point for a particular method and follow the MDL procedures as described in 40 *Code of Federal Regulations* Part 136 Appendix B. The limits meet contractual requirements and have been determined to be attainable by the laboratory's methods.

Reporting requirements will be established as follows: the RL for the sample will be adjusted for actual sample size, moisture content, and dilutions. Results above the sample-specific RL will be reported without flags. Results between the MDL and the sample-specific RL will be reported but qualified with the "J" flag, and results for analytes not detected will be qualified "U" and reported at the MDL.

RLs and sample results will be reported to two significant figures if less than 10 and to 3 significant figures otherwise and RLs will be reported on a dry-weight basis for sediment samples for inorganics. Organics will be reported to two significant figures at any concentration.

2.6 Instrument and Equipment Testing, Inspection, and Maintenance Requirements

2.6.1 Field Instrument Maintenance

Field equipment will be calibrated daily according to the manufacturer's specifications and checked for indications of poor performance, and the results will be documented. Discrepancies will be reported immediately to the appropriate personnel for resolution. The field team will maintain a sufficient supply of spare parts to minimize downtime. Whenever possible, backup instrumentation will be on hand.

The field equipment will be maintained as stated in the operating manual.

2.6.1.1 GPS Calibration

Navigation accuracy and precision of the differential GPS equipment will be checked each morning and evening by recording the *x* and *y* coordinates of local control points. The coordinates will be recorded in the field logbook and compared daily to verify the GPS equipment is functioning consistently.

2.6.2 Laboratory Equipment and Instruments

Only qualified personnel will service instruments and equipment. Repairs, adjustments, and calibrations will be documented in the appropriate logbook or data sheet.

2.6.2.1 Instrument Maintenance

Preventive maintenance of laboratory equipment will follow guidelines recommended by the manufacturer. Malfunctioning instruments will be repaired by in-house staff or the manufacturer. The laboratory will maintain a sufficient supply of spare parts for its instruments to minimize downtime. Whenever possible, backup instrumentation will be on hand.

Whenever practical, analytical equipment should be maintained under a service contract. Such contracts allow for preventive system maintenance and repair as needed. The laboratory should have sufficiently trained staff to allow for the day-to-day maintenance of equipment. All laboratory instruments will be

maintained in accordance with manufacturer's specifications and within the requirements of the laboratory's internal QA manual.

Preventive maintenance for analyses is described in the laboratory scope of work. Maintenance activities must be documented in the logbooks to provide a history of maintenance records.

2.6.2.2 Equipment Monitoring

Operation of balances, ovens, refrigerators, and water purification systems will be checked daily and documented. Discrepancies will be reported immediately to the appropriate laboratory personnel for resolution.

Specific laboratory preventive maintenance procedures are found in the laboratory's internal QA manual.

2.7 Laboratory Quality Control/Instrument Calibration and Frequency

Laboratory QC checks indicate the state of control prevailing at the time of sample analysis and include calibrations, method blanks, and LCSs. QC checks that involve field samples, such as MS, surrogate spikes, field duplicates, and laboratory sample duplicates, provide an indication of the presence of matrix effects. Field-originated blanks provide a way to monitor for potential contamination of field samples.

All QC will be in accordance with method specifications, including but not limited to the following:

- Method blanks
- Holding time
- Initial calibrations
- Continuing calibrations
- Second source check samples
- Instrument tuning
- LCS
- MS/MSD
- Surrogate spikes
- Post-digestion spikes and serial dilutions
- Internal standards
- Retention time window studies

2.7.1 Analytical Batch

A laboratory QC batch is defined as 20 or fewer environmental samples of similar matrix that are extracted or analyzed together and contain a method blank, an LCS, an MS/MSD, or a sample duplicate, depending upon the method. For gas chromatography/mass spectrometry volatile analyses, a method blank, LCS, and MS/MSD must be analyzed in each 12-hour period, unless otherwise described in the SOW technical requirements. The number of environmental samples allowed in the laboratory QC batch is defined by the remaining time in the method-prescribed 12-hour period divided by the analytical run time. Each preparation or analytical batch should be identified in a way that allows environmental samples to be associated with the appropriate laboratory QC samples.

2.7.2 Instrument Calibration and Frequency

Laboratory instruments will be calibrated by qualified personnel before sample analysis according to the procedures specified in each method. Calibration will be verified at method-specified intervals throughout the analysis sequence. The frequency and acceptance criteria for calibration are specified for each analytical method, with supplemental requirements defined in the following subsections for methods used to determine organic compounds. When multipoint calibration is specified, the concentrations of the calibration standards should bracket those expected in the samples. Samples should be diluted, if necessary, to bring analyte responses within the calibration range. The laboratory

cannot report data that exceed the calibration range. The initial calibration curve will be verified as accurate using a standard purchased or prepared from an independent second source. The initial calibration verification involves the analysis of a standard containing all the target analytes, typically in the middle of the calibration range, each time the initial calibration is performed. Quantitation based on extrapolation is not allowed.

2.7.2.1 Initial Calibration Models for Determining Organic Compounds

Methods for determining organic compounds often provide multiple options for initial calibration curve fits and associated acceptance criteria for use. The following sections outline required good laboratory practices that will be employed by the laboratory. The hierarchy the laboratory will use when selecting the calibration curve fit for use in quantitation of sample results is outlined in the following section.

2.7.2.2 Calibration Techniques

The analyst will verify that correct instrument operating conditions and routine maintenance, as specified in the method and laboratory SOP, are employed. The laboratory must follow calibration techniques as specified in its specific SOWs and QA manual. All maintenance will be documented in a laboratory notebook for troubleshooting and scheduling of future routine, periodic maintenance.

Personnel will ensure the instrument is free of contamination before calibration and will not perform any blank subtraction.

The entire initial calibration must be performed before sample analysis. The calibration standards must be analyzed in a sequential order from lowest concentration to highest, or highest to lowest, depending on the method. If one calibration standard fails to meet criteria, it may be reanalyzed at the end of the calibration sequence. Justification for removing a calibration point from the curve fit selected includes improper purge, injection failure, nonspiked level, or other obvious failures. The failure of multiple standards suggests an instrument problem or operator error, and corrective action is required.

Only the lowest calibration point or the highest calibration point can be removed from the calibration curve without justification. If the lowest standard is removed, then the RL for that compound increases to the level of the next lowest calibration standard. Elevating the RL to greater than the project-specific objectives must be approved by the project chemist. If the highest standard is removed, then the linear range is shortened for that compound. At all times, five calibration points must be included.

The lowest standard in the calibration curve must be at or below the required RL. The other standard concentrations must define the working range of the instrument or the expected range of concentrations found in the samples.

Either external or internal standard calibration can be employed for methods not involving mass spectrometry detectors. Internal standard calibration must be used when a mass spectrometry detector is employed. The “mass spectrometry detector” includes inductively coupled plasma-mass spectrometry-type instruments, which must be used according to project requirements.

Most compounds tend to be exhibit a linear response from the instrument, and a linear approach should be favored when linearity is suggested by the calibration data. Nonlinear calibration should be considered only when a linear approach cannot be applied. It is not acceptable to use an alternate calibration procedure when a compound fails to perform in the usual manner. When this occurs, it indicates instrument issues or operator error.

If a nonlinear calibration curve fit is employed, a minimum of six calibration levels must be used for second-order (quadratic) curves, and a third-order polynomial requires at least seven calibration levels. When more than five levels of standards are analyzed in anticipation of using second- or third-order calibration curves, all calibration points must be used, regardless of the calibration option employed.

The highest or lowest calibration point may be excluded to narrow the calibration range and meet the requirements for a specific calibration option; otherwise, unjustified exclusion of calibration data is expressly forbidden.

Use of the average of all compound relative standard deviations in a calibration curve at less than the criteria is not allowed. Calibration control must be shown for each individual compound.

2.7.2.3 Calibration Options

This subsection outlines the acceptable calibration options and the hierarchy the laboratory should use when selecting a specific option. The choice of calibration option may be based on previous experience or prior knowledge of detector response and will be consistent with specific calibration requirements described in the analytical method. It is not the intent of alternate calibration models to compensate for poor instrument operating conditions or extending requirements for instrument maintenance. Possible calibration options include the following:

- Linear Calibration Using Average Calibration or Response Factors Calibration factors for external calibrations or relative response factors (RRFs) for internal calibrations must have relative standard deviations not exceeding 20 percent or 15 percent, respectively, to be used for quantitation. As a general rule, minimum response factor (RF) of 0.05 for most target analytes and 0.01 for the least responsive target analytes must be achieved to ensure detectability or the minimum RRF criteria or relative standard deviation is defined by the method requirements.
- Linear Calibration Using a Linear Regression Equation ($y = mx + b$). The correlation coefficient must equal 0.995 or more. The equation and a plot of the linear regression must be included in the raw data to be generated by the laboratory and made available in the data package upon the client's request.
- A Nonlinear Calibration. The model may be a second- or third-order polynomial. The model must be continuous without a break in the function and should *not* be forced through the origin. The coefficient of determination of the nonlinear regression should be 0.99 or greater, refer to the analytical method. The equation and a plot of the nonlinear regression must be included in the raw data to be generated by the laboratory and presented in the data package.

2.7.2.4 Continuing Calibration

Periodic verification of the initial calibration is essential in generating analytical data of known quality. The continuing calibration verification analyses ensure the instrument has not been adversely affected by the sample matrix or other instrument failures that would increase or decrease the sensitivity or accuracy of the method. The laboratory will perform continuing calibration for all methods according to the specific requirements in the method and laboratory SOP.

Use of the average of all analytes' percent drift or recovery to meet the continuing calibration requirements for the method is not allowed. If the laboratory accepts a continuing calibration as compliant, but individual compounds exceed criteria, a list of those analytes that exceeded the criteria will be provided in the laboratory report. For analyses conducted under this QAPP, notifications will be accomplished by listing in the laboratory case narrative the compounds outside the criteria and the actual values of the percent drift or recovery.

2.7.3 Method Blanks

Blanks are used to monitor each preparation or analytical batch for interference and/or contamination from glassware, reagents, and other potential contaminant sources within the laboratory. A method blank is an analyte-free matrix (laboratory reagent water for aqueous samples, Ottawa sand or sodium

sulfate for soil samples, and glass or Teflon beads 1 millimeter in diameter or smaller for metals) to which all reagents are added in the same amounts or proportions as are added to samples. The blank is run through the entire sample preparation and analytical process, along with the samples in the batch. At least one method blank should be used per preparation or analytical batch. If a target analyte is found at a concentration that exceeds the RL, corrective action must be taken to identify and eliminate the contamination source. All associated samples must be re-prepared and/or reanalyzed after the contamination source has been eliminated. No analytical data may be corrected for the concentration found in the blank.

2.7.4 Laboratory Control Sample

The LCS will consist of analyte-free matrix (laboratory reagent water for aqueous samples or Ottawa sand for soil samples) spiked with known amounts of analytes that come from a source different from that used for calibration standards. Target analytes specified in the QAPP will be spiked into the LCS. The spike levels should be less than or equal to the midpoint of the calibration range. If LCS results are outside the specified control limits, corrective action must be taken, including sample re-preparation or reanalysis, if appropriate. If more than one LCS is analyzed in a preparation or analytical batch, the results of all LCSs must be reported. Any LCS recovery outside of QC limits affects the accuracy for the entire batch and requires corrective action.

2.7.5 Surrogates

Surrogates are organic analytes that behave similarly as the analytes of interest but are not expected to occur naturally in the samples. They are spiked into the standards and into the samples and QC samples prior to sample preparation. Recoveries of surrogates are used as an indicator of accuracy, method performance, and extraction efficiency. If surrogate recoveries are outside the specified control limits, corrective action must be taken, including sample re-preparation or reanalysis, if appropriate.

2.7.6 Matrix Spike/Matrix Spike Duplicate

As described, an MS is a sample matrix fortified with known quantities of specific compounds. It is subjected to the same preparation and analytical procedures as the native sample. Target analytes specified in the QAPP are spiked into the sample. MS recoveries are used to evaluate the effect of the sample matrix on the recovery of the analytes of interest. An MSD is a second fortified sample matrix. The RPD between the results of the duplicate MSs measures the precision of sample results. Only project-specific samples designated on the chain-of-custody form will be spiked. The spike levels will be less than or equal to the midpoint of the calibration range.

2.7.7 Internal Standards

Some methods require the use of internal standards to compensate for losses during injection or purging, or losses resulting from viscosity. Internal standards are compounds that have similar properties as the analytes of interest, but are not expected to occur naturally in the samples.
A measured amount of the internal standard is added to the standards and to the samples and QC samples following preparation. When the internal standard results are outside the control limits, corrective action must be taken, including sample reanalysis, if appropriate.

2.7.8 Laboratory Sample Duplicate

A sample duplicate selected by the laboratory is called a laboratory sample duplicate. It is subjected to the same preparation and analytical procedures as the native sample. The RPD between the results of the native sample and of the laboratory sample duplicate indicates the precision of sample results.

The data collected may also yield information on whether the sample matrix is homogenous or heterogeneous.

2.7.9 Interference Check Samples

Interference check samples are used in inductively coupled plasma analyses to verify background and inter-element correction factors. They consist of two solutions. Solution A contains the interfering analytes. Solution B contains both the analytes of interest and the interfering analytes. Both solutions are analyzed at the beginning and at the end of each analytical sequence. When the interference check sample results are outside the control limits, corrective action must be taken, including sample reanalysis, if appropriate.

2.7.10 Retention Time Windows

Retention time windows for gas and liquid chromatographic analyses must be established by replicate injections of the calibration standard over multiple days as described in SW-846 8000B. The absolute retention time of the calibration verification standard at the start of each analytical sequence will be used as the centerline of the window. In order for an analyte to be reported as positive, its elution time must be within the retention time window.

2.7.11 Holding Time

The holding time requirements specified in this QAPP must be met. For methods requiring both sample preparation and analysis, the preparation holding time will be calculated from the time of sampling to the completion of preparation. The analysis holding time will be calculated from the time of completion of preparation to the time of completion of the analysis, including any required dilutions, confirmation analysis, and reanalysis. For methods requiring analysis only, the holding time is calculated from the time of sampling to completion of the analysis, including any required dilutions, confirmation analysis, and reanalysis.

2.7.12 Confirmation

Confirmation analysis must be carried out as specified for specific methods when the result is at or above the RL. Dual-column analysis will be performed for EPA SW-846 Methods 8081B, 8082A, and 8151A. The result designated as the primary result will be reported but may be reported from the confirmation column if there is a confirmed positive bias from interference on the primary column. The laboratory will follow its specific SOP on reporting confirmation data, and in all cases, confirmation data will be clearly annotated in the data package during such an occurrence. All calibration and QC requirements must be met when confirmation analysis is performed.

2.7.13 Cleanup Procedures to Minimize Matrix Effects

To maintain the lowest possible RLs, appropriate cleanup procedures should be employed when indicated by the method used to remove or minimize matrix interference. Methods for sample cleanup include gel permeation chromatography, silica gel, alumna, florisil, mercury (sulfur removal), sulfuric acid, and acid/base partitioning. Method blanks, MS/MSDs, and LCSs must be subjected to the same cleanup procedures as those performed on the samples to monitor the efficiencies of the procedures.

2.7.14 Sample Dilution

Sample dilution results in elevated RL and ultimately affects the usability of the data related to potential actions at the sampling site. It is important to minimize dilutions and maintain the lowest possible RLs. When dilutions are necessary because of high concentrations of target analytes, lesser dilutions should

also be reported to fully characterize the sample for each analyte. The level of the lesser dilution should be such that it will provide the lowest possible RLs without a lasting deleterious effect on the analytical instrumentation.

When a sample exhibits characteristics of matrix interference that are identified through analytical measurement or visual observation, appropriate cleanup procedures must be proven ineffective or inappropriate, prior to proceeding with dilution and analysis.

2.7.15 Standard Materials and Other Supplies and Consumables

Standard materials must be of known high purity and must be traceable to an approved source. Pure standards must not exceed the manufacturer's expiration date or 1 year following receipt, whichever comes first. Neat standards (used in the wet chemistry tests) allow up to 5 years before expiration. Solutions prepared by the laboratory from the pure standards must be used within the expiration date specified in the laboratory's SOP. All other supplies and consumables must be inspected before use to ensure they meet the requirements specified in the appropriate SOP. The laboratory's inventory and storage system should ensure their use within the manufacturer's expiration date and storage under proper conditions.

2.7.16 Manual Integration

The laboratory is required to train all analysts performing methods that rely on interpretation of chromatographic data on appropriate software or manual integration practices. The laboratory also must strive to minimize the use of manual integration of data. If manual integration is required to correct a software auto integration error, the manual integration will be clearly identified in the instrument data. "Before" and "after" enlargements of the region of the chromatogram where the manual integration was performed will be provided on an appropriate scale that allows an independent reviewer to evaluate the need for and quality of the manual integration.

The analyst will document the reason for the manual integration; the laboratory manager or designee will review and approve the manual integration. The initials of the analyst and reviewer will be documented in electronic format.

2.8 Inspection and Acceptance Requirements for Supplies and Consumables

It is expected that several subcontractors will provide various services to multiple project tasks. The required services must meet the task scope, specified levels of quality, and the submittal schedule. Project subcontractors or vendors should have contractual arrangements with their suppliers. Field supplies and equipment will be procured as part of the contract and maintained by the technical team.

Supplies and equipment will be acquired and initially inspected by equipment specialist personnel located at the CH2M office warehouses in Milwaukee, Wisconsin or Denver, Colorado. The R/V Mudpuppy will use its own specialized field equipment or will acquire the equipment appropriate for the task through commercial vendors. Before use at the project site, equipment will be visually inspected and tested by the field team leader upon receipt or installation to verify the correct materials and services were received and that they can meet contractual arrangements and the requirements specified in the project site-specific plans.

2.9 Data Acquisition Requirements for Nondirect Measurements

Data acquired from nondirect measurements include the following:

- Physical information, such as descriptions of sampling activities and geologic logs
- State and local environmental agency files
- Reference computer databases and literature files
- Historical reports and subjective information gathered through interviews

2.10 Data Management Plan

The data management plan outlines the procedures for storing, handling, accessing, and securing data collected during this sampling event. Data gathered during the sampling event will be consolidated and compiled into a database that can be used to evaluate site conditions and data trends. The data management plan will serve as a guide for all database users. The plan is subject to revision to allow the database management system to be modified as it is developed and maintained. The plan describes the following:

- Responsibilities of the project team for data management
- Data management system to be established for the project
- Development of the base maps onto which the data will be plotted
- Types of data to be entered into the data management system and the process of data entry

2.10.1 Team Organization and Responsibilities

CH2M team members and their responsibilities for the data management process are as follows:

- The **project manager** and **project chemist** establish the sample tracking system.
- The **project chemist** tracks the chain-of-custody forms and other sampling information. Oversees proper use of the EPA Scribe software and accuracy of the information entered. Conducts tracking of samples, forwards tracking information and received data to the database manager, and identifies the data inputs (e.g., sample numbers) to use in generating tables and plots. Reviews incoming analytical laboratory deliverables for completeness to ensure that data are present and available for further review. Oversees or performs data verification and validation. Coordinates independent validation with GLNPO and its contractor. Completes a data usability report that summarizes the field data acceptability and validation findings.
- The **database manager** is responsible for coordinating and overseeing a variety of data management tasks. These tasks include, but are not limited to, the following:
  - Setting up the data management system in consultation with the project chemist
  - Informing CH2M of missing or incorrect information in the EDD so CH2M can work with the laboratory to address such issues
  - Uploading the field data and laboratory EDDs into the project database
  - Data conversion/manual entry into the database, QC of the entered data
  - Coordinating upload of the independent validation qualifiers to the project database
  - Providing cross-tab data tables for field and laboratory data

  - Preparing the EDDs for entry of study data into the EPA's GLSED
  - Forwarding all deliverables to the project chemist, project manager, or designee

- The **GIS analyst** is responsible for coordinating with the project manager to set up a geodatabase before sampling. Maintains spatial layers and overall geodatabase integrity and accuracy. Provides GIS-related outputs for reports.

2.10.2 Sample Tracking

The project chemist or designee will be responsible for tracking samples to ensure the analytical results for all samples sent for analysis are received by the laboratory. Sample IDs, collection date, and analysis information from Scribe and the chain-of-custody forms will be used for tracking. Upon receiving a sample receipt notice from the laboratory, the project chemist will enter the date received by the laboratory and the date the deliverables are due. The project chemist also will enter the date of receipt of the data package and EDD. Upload of EDD files and entry of validation qualifiers will be tracked in the sample tracking table.

2.10.3 Data Types

Activities at the site will involve accessing the types of data collected to confirm whether project objectives were met.

Data collected during this event will be used as they become available to create a project database. The database will include field and laboratory data reviewed by CH2M and the independent validator. The data source will be noted in the database. Procedures for incorporating data into the database are presented in subsequent sections of the data management plan.

2.10.4 Data Management

2.10.4.1 Hard Copy

Measurements made during field data collection will be recorded in field logbooks or field forms. Field data will be reduced and summarized, tabulated, and stored along with the field logbooks. Raw analytical laboratory data will be stored as an original hard copy. Hard copy information includes chain-of-custody forms, analytical bench sheets, instrument printouts and chromatograms, certificates of analyses, and QA/QC report summaries. Validation reports will be stored with the data package reports.

2.10.4.2 Data Input Procedures

Sampling information, analytical results, applicable QA/QC data, data validation qualifiers, and other field-related information will be entered into the project database by the CH2M project chemist and database manager for storage and retrieval during data evaluation and report development.

The CH2M sample manager will manually enter other available field-related data collected into Scribe for loading into the project database. The entry of other field-related data will be confirmed by comparing exports from the database against the original files used to perform the data entry. The data entry confirmation procedures and results will be documented.

Pace Analytical will provide the data in the SEDD Stage 2A for PCB Aroclors, dioxin/furan congeners, mercury, methyl mercury and TOC. The SEDD files will be submitted directly to the EPA Analytical Services Branch by Web-based Sample Management Office portal. The data undergoes an initial electronic assessment in EXES, and verification and validation by EPA's QATS contractor (refer to Section 4 for details).

The validated data will be exported from EXES into EQuIS EDDs or contract laboratory program universal EDDs, and CH2M will upload the EDDs to the project database.

2.10.5 Computer Database

The technical data, including sample location information, laboratory analytical results, and analytical data validation, will be managed using EQuIS 6, a third-party database system by EarthSoft, Inc., that is used to store and analyze project data submissions. The core EQuIS applications are its chemistry and geology modules, each of which is associated with its own underlying Microsoft SQL Server database. CH2M owns licenses for the geology and chemistry modules. The EQuIS database system is based on a relational model in which independent tables, each containing a certain type or entity of data, can be linked through selected fields that are common to two or more tables. The database design allows for the inclusion of historical data and allows users to effectively conduct trend analysis and generate a variety of data reports to aid in data interpretation.

The CH2M project chemist will evaluate the field data in Scribe and the laboratory submittal for completeness and compliance. Once it is determined that the data are complete and finalized, they will be imported into the project database. Field and laboratory data will be merged, and each record evaluated for successful and complete merging.

The database will be protected from unauthorized access, tampering, accidental deletions or additions, and data or program loss that can result from power outages or hardware failure. The following procedures will be adopted to ensure protection:

- The master database, hosted by EarthSoft, Inc., will be stored on a network file server with Web access from a local server to the installation of the EQuIS data management system and access via EQuIS Enterprise Web interface. Members of the data management team involved in loading, modifying, or querying the database will be given access through EQuIS user accounts and passwords, as well as the appropriate network server permissions.
- EQuIS Enterprise provides users with a Web-based interface that allows for data reporting in standard formats. Where required, data exports from copies of the master database will be stored on the local area network for access by project staff through custom reporting tools developed to minimize possible database corruption by users. Whenever the master database is updated or modified, the data will be recopied exported to the local area network to ensure that the current copy data set is available to users.
- Daily backups of the master database and its copies will be made to ensure the data will not be lost due to problems with the network. Each night a daily differential backup will be performed by EarthSoft, Inc. Then, each week a full backup will be completed by EarthSoft, Inc. The backups are stored on a SAN device located in Utah and are then transferred to an offsite data center.

2.10.6 Geographic Information System

Workflow for creating, maintaining, and organizing geospatial data will follow the spatial data standard format for projects whenever possible.

An ArcView project or extension will be used providing the following functionality: load and display project site base maps; display sampling station locations and associated sampling data (date, media, results); and perform ad hoc queries to highlight sampling locations meeting user-entered criteria for sampling (such as data by date, sample type, analyte, depth/elevation, result value, or any combination thereof).

2.10.7 Documentation

Documentation of data management activities is critical because it provides the following:

- A record of project data management activities
- Reference information critical for database users
- Evidence that the activities have been properly planned, executed, and verified
- Continuity of data management operations when personnel changes occur

The data management plan is the initial general documentation of the project data management efforts. Additional documentation will be maintained to document specific issues, such as database structure definitions, database inventories, database maintenance, user requests, database issues and problems, and client contact.

2.10.8 Project Record File

The final project record file will be the central repository for documents that constitute evidence relevant to sampling and analysis activities. CH2M will be the custodian of the file and will maintain the contents of the file for the project, including relevant records, reports, logs, field notebooks, pictures, contractor reports, and data reviews, in a secured area with limited access during the project duration.

CH2M will keep records until project completion and closeout at which time the project data contained within the project record file will be transferred to EPA.

As necessary before closeout, records may be transferred to a records storage facility. The records storage facility must provide secure, controlled-access records storage.

Records of raw analytical laboratory data, QA data, and reports will be kept by the subcontract laboratory for at least 5 years.

2.10.9 Presentation of Investigation Data

Depending on the data user's needs, data presentation may consist of any of the following formats:

- Tabulated results of data summaries
- Figures showing location-specific analytical results

Other types of data elements may be added as the field investigation needs and activities evolve.

SECTION 3

Assessment and Oversight

This section describes the activities for assessing compliance of QA/QC activities.

3.1 Assessments and Response Actions

Field and laboratory activities will be assessed for technical and procedural compliance with this QAPP. Performance and system audits are key factors for verifying compliance. The following are the purposes of the audits:

- Confirm that appropriate documents are properly completed and kept current and organized.
- Ensure measurement systems are accurate.
- Identify nonconformance or deficiencies and initiate necessary corrective actions.
- Verify that field and laboratory QA procedures called for are properly followed and executed.

The CH2M project manager, CH2M QAM, and the laboratory QAM are responsible for ensuring conformance with SOPs. Activities selected for audit will be evaluated against specified requirements, and the audit will include evaluation of the method, procedures, and instructions. Documents and records will be examined as necessary to evaluate whether the QA program is effective and properly implemented. Reports and recommendations must be prepared on all audits and submitted to the CH2M QAM for retention in the project files.

The CH2M project manager is responsible for overseeing CH2M project personnel and ensuring that staff members follow proper protocol for field activities, project support activities, and the execution of the project-related tasks. The CH2M project manager will assign qualified personnel to conduct specific project activities appropriate to their qualifications. The CH2M project manager will request regular feedback from lower-level management personnel and individuals directly involved with project activities to gauge effectiveness. The CH2M project manager is responsible for implementing corrective activities as needed on this project.

The laboratory project manager is responsible for coordinating and scheduling the laboratory analyses, supervising the in-house chain-of-custody, accepting requirements outlined within the QAPP, overseeing data review, and ensuring that the laboratory QA requirements are met and that laboratory QA procedures are properly followed, and analytical reports are correctly prepared.

3.1.1 Field Audits

Planning, scheduling, and conducting QA audits and surveillance are required to verify that site activities are being performed efficiently in conformance with approved plans, standards, federal and state regulatory requirements, sound scientific practices, and contractual requirements. Planned and scheduled audits may be performed to verify compliance with aspects of the QA program and to evaluate the effectiveness of the QA program. An audit performed by project manager, QAM, or designee of the field event may include the following:

- Objective examination of work areas, activities, and processes
- Review of documents and records
- Interviews with project personnel
- Review of plans and standards

The field team leader will conduct a daily internal review of the sampling program during the project and will pay particular attention to the sampling program with respect to representativeness, comparability, and completeness of the specific measurement parameters involved. Problems identified through the review will be documented in the logbook and appropriate corrective actions implemented. The field team leader or a designee will review field documentation (chain-of-custody forms, field daily sheets, and logbooks) daily for accuracy, completeness, and compliance with QAPP requirements. The field team leader will also audit field sampling procedures daily for compliance with QAPP procedures to check for the following:

- Sampling protocols are followed.
- Samples are placed in proper containers.
- Samples are stored and transported properly.
- Field documentation is completed.

EPA may also perform scheduled or non-scheduled field audits during sampling activities.

3.1.1.1 Field Corrective Action

Any project team member may initiate a field corrective action process, which consists of identifying a problem, acting to eliminate it, monitoring the effectiveness of the corrective action, verifying that the problem has been eliminated, and documenting the corrective action in the logbook.

Corrective actions include correcting chain-of-custody forms; addressing problems associated with sample collection, packaging, shipping, and field record keeping; and providing additional training in sampling and analysis. Additional approaches may include resampling or evaluating and amending sampling procedures. The field team leader will summarize the problem, establish possible causes, and designate the person responsible for a corrective action. The field team leader will verify that the initial action has been taken and appears effective and will follow up to verify that the problem has been resolved.

Technical staff and project personnel will be responsible for reporting suspected technical or QA nonconformance or suspected deficiencies to the field team leader, who will be responsible for assessing suspected problems in consultation with the CH2M QAM, laboratory QAM, and the CH2M project manager. Based on the situation's potential to affect data quality, the project manager will notify the COTR to discuss the issue before a decision is made. If a reportable nonconformance is found to require corrective action, the field team leader will initiate a nonconformance report and submit it to the CH2M project manager.

The field team leader will be responsible for ensuring corrective actions for nonconformance are initiated by the following method:

- Evaluating reported nonconformance
- Controlling additional work on nonconforming items
- Determining disposition or action to be taken
- Maintaining a log of nonconformance
- Reviewing nonconformance reports and corrective actions taken
- Ensuring nonconformance reports and corrective actions are replayed to the CH2M management team and documented in the project files

3.1.2 Laboratory Quality Assurance Program

The laboratory will maintain a QA manual or equivalent document. The laboratory QAM will define the laboratory's internal procedures for QA/QC as follows:

- QA policies, objectives, and requirements
- Organization and personnel
- Document control
- SOPs (analytical methodology and administrative)
- Data generation
- Software verification
- QA
- QC
- Nonconformance/corrective action procedures
- Data review

3.1.3 Laboratory Audits

The laboratory QAM may conduct internal system audits, which are qualitative evaluations of all components of the laboratory QC measurement system. The audit will serve to determine whether all measurement systems were used appropriately. System audits will be conducted to evaluate the following:

- Sample handling procedures
- Calibration procedures
- Analytical procedures
- QC results
- Safety procedures
- Record keeping procedures
- Timeliness of analysis and reporting

Laboratories may also be subject to external audits, which focus on assessing general laboratory practices and conformance to this QAPP. Laboratory audits may be performed before the analyses begin and at any time during the course of the project, as deemed appropriate.

The laboratory QAM will review internal laboratory performance. The laboratory QAM will evaluate laboratory precision and accuracy by comparing the results of duplicate samples, QC samples, spikes, and blanks. The laboratory QAM or other client services individual will check the analytical results prior to distribution when a beyond-control-limit situation is encountered.

External laboratory performance reviews may be conducted based on evaluation of the results of check samples analyzed as part of EPA or state certification requirements. They also may be conducted by sending "double-blind" performance evaluation samples (those not discernible from routine field samples) to the analytical laboratory. EPA GLNPO may conduct external audits.

3.1.3.1 Laboratory Corrective Action

Corrective actions may be required for analytical/equipment problems or for noncompliance problems. Analytical/equipment problems may occur during sampling, sample handling, sample preparation, laboratory instrumental analysis, or data review.

A corrective action program will be determined and implemented when a noncompliance problem is identified. The person identifying the problem will be responsible for notifying the proper project member. If the problem is analytical in nature, information on the problem will be communicated to the laboratory QAM and the CH2M project chemist, who will in turn direct information to proper project members. Implementation of corrective actions will be confirmed through similar channels.

Corrective actions will be documented. No staff member will initiate a corrective action without prior communication about the action that needs correction and the proposed corrective action through the proper channels. If corrective actions are insufficient, the CH2M project manager or the CH2M QAM may issue a stop work order.

Corrective actions are required whenever an actual or potential out-of-control situation is noted. The investigative action taken depends somewhat on the analysis and the event. Laboratory personnel are alerted that corrective actions may be necessary if the following are found:

- QC data are outside the warning or acceptable windows for precision and accuracy
- Blanks contain target analytes above acceptable levels
- Undesirable trends are detected in spike recoveries or RPD between duplicates
- Unusual changes in detection limits occur
- Inquiries concerning data quality are received
- Deficiencies are detected by the laboratory QAM during internal or external audits or from results of performance evaluation samples

Corrective action procedures are often handled at the bench level by the analyst. The analyst will review preparation or extraction procedures for possible errors and check instrument calibrations, spike and calibration mixes, and instrument sensitivity. If problems persist or cannot be identified, matters will be referred to the laboratory supervisor, laboratory project manager, or laboratory QAM for further investigation. Once the issue is resolved, full documentation of the corrective action procedures will be filed with the CH2M QAM and laboratory QAM after approval by CH2M. Corrective actions may include the following:

- Resampling and analyzing
- Evaluating and amending sampling procedures
- Evaluating and amending analytical procedures
- Accepting data and acknowledging the level of uncertainty
- Reanalyzing the samples, if sample or extract volume is adequate and holding-time criteria permit

If resampling is necessary because of laboratory problems, the CH2M project manager must identify the appropriate approach, including cost recovery from the laboratory for the additional sampling effort.

3.1.3.2 Laboratory Standard Operating Procedures

The laboratory will maintain SOPs for all analytical methods and laboratory operations. The format for the procedures will conform to the following references:

- *Test Methods for Evaluating Solid Waste, Physical and Chemical Methods* (EPA 2008)
- "Good Laboratory Practices" in *Principles and Guidance to Regulations for Ensuring Data Integrity in Automated Laboratory Operations* (EPA 1995)

All SOPs must have a unique ID number that is traceable to previous revisions of the same document.

3.1.3.3 Demonstration of Capability

Personnel in the laboratory QA department will maintain records documenting the ability of each analyst to perform applicable method protocols. Documentation will include annual checks for each method and analyst. Internal, blind performance evaluation samples for each method and matrix demonstrating overall laboratory performance must be submitted annually. The laboratory may receive additional blind performance evaluation samples in conjunction with the program.

3.1.4 Corrective Action

Corrective action may be required as a result of deviations from field or analytical procedures. Deficiencies identified in audits and data quality evaluations may also call for corrective action. All project personnel have the responsibility, as part of their normal work duties, to identify, report, and solicit approval of corrective actions for conditions adverse to data quality.

Field and laboratory staff may encounter conditions that require immediate corrective action. Personnel will document conditions and the results of corrective actions in a field logbook or laboratory nonconformance report and communicate their actions as soon as possible to the field team leader, laboratory supervisor, and if necessary, the project chemist for immediate input. The Corrective Action Preventive Action system is in place to allow for supervisory review or client input for all deviations or deficiencies. The corrective action reporting system requires immediate documentation of deviations or deficiencies and for supervisory review of the actions taken to correct them. At a minimum, the corrective action report should include the following:

- Type of deviation or deficiency
- Date of occurrence
- Impact of the deviation or deficiency, such as samples affected
- Corrective action taken
- Documentation that the process has been returned to control

The only time a corrective action report may be waived is when a deviation or deficiency is immediately corrected, and its impact is precluded. An example would be an unacceptable initial calibration that is repeated before samples are analyzed.

A core program or project team member can initiate a corrective action preventive action but will consult with the CH2M QAM prior to submittal. The CH2M QAM will be responsible for reviewing corrective action preventive actions, assigning them to the appropriate action owners, and monitoring completion of both short- and long-term actions. The ultimate responsibility for the laboratory corrective action process is the laboratory QAM, who must ensure that proper documentation, approval, and closeout of all out-of-control or nonconformance events are performed. A nonconformance report will summarize each nonconformance condition. Corrective action reports that could affect data quality must be brought to the attention of the project chemist. Report disposition will be the responsibility of the project chemist. The CH2M project manager may be notified about a particular report at the project chemist's discretion. Copies of corrective action reports must be maintained in the laboratory or field project files and will be submitted with the associated data package.

3.2 Reports to Management

In addition to audit reports submitted to the CH2M project manager in accordance with the QAPP, a monthly progress report will be prepared by the CH2M project manager and submitted to the COTR.

After the sample results received from the laboratory are evaluated, reduced, and tabulated, and the results of the independent validation are received, a data evaluation package documenting the field investigation will be submitted to the COTR. The data evaluation package will include an electronic file containing the final laboratory and field data, including coordinates and copies of field notes and sediment core logs, and raw laboratory data.

SECTION 4

Data Validation and Usability

This section describes QA activities associated with data management and reporting.

4.1 Field and Laboratory Data Management

Data will be reduced manually or by using appropriate application software. Quantitation procedures specified for each method must be followed. If data are reduced manually, the documentation must include the formulas used. Any application software used for data reduction must have been previously verified by the laboratory for accuracy. Documentation of the software's verification must be maintained on file in the laboratory. Documentation of data reduction must allow recreation of the calculations.

Analytical data will undergo at least four levels of review at the laboratory before release. The following four steps will be followed:

- The analyst performing the tests initially will review 100 percent of the data to check for the following:
  - Sample preparation information is correct and complete.
  - Sample analysis information is correct and complete.
  - Appropriate analytical procedures were followed.
  - Analytical results and reporting units are correct and complete.
  - QC samples are within established control limits or qualified when outside limits.
  - Documentation is complete.
- The senior analyst or the section supervisor will review 100 percent of the data for the following:
  - Accuracy and compliance with calibration and QC requirements, holding-time compliance, and completeness
  - Verification of analyte identification and quantitation
  - Comparison of calibration and QC results with the applicable control limits
  - Review of RLs to see that they meet the project objectives
- The laboratory QAM will review at least 10 percent of data or deliverables generated for the program against the project-specific requirements.
- The laboratory manager or client services representative will conduct a final data review to check that all required analyses were performed on all samples and that all documentation is complete.

Data will be generated in the field during sample collection and in the laboratory during sample analysis. CH2M is ultimately responsible for overseeing data management for the project both in the field and in the laboratory.

In support of data review, verification, and validation, a suite of procedures has been established and includes the following:

- Field data will be recorded and reported using Scribe. Scribe export files for the project field data will be submitted to the database manager for review and will be incorporated into the project database. The database manager will review the files for completeness, and the CH2M project chemist will check compliance with the QAPP and the GLLA data reporting standard. Deviations and nonconformance issues will be documented and potential impact on sample results will be evaluated and detailed in the CH2M data usability report.

- Laboratories will submit the laboratory data in the GLNPO SEDD format directly to the EXES database. Waste characterization will be submitted to the CH2M project chemist in the EQuIS EDD 3-file format or excel file.
- Laboratory data will be checked for completeness and compliance by CH2M. The EPA Mission Support contractor, General Dynamics Information Technology performs completeness and compliance checks of the SEDD files. The data will then be verified and validated by EPA's QATS contractor, APTIM.
- Data verification and validation findings will be reviewed by CH2M. Usability of the project data will be evaluated by CH2M based on the data assessment findings and documented in the data usability report, and findings by the validator will be incorporated into the final data set.
- The laboratory and field data will be merged into a single database for the project.
- A final deliverable for GLSED will be submitted to EPA with the data usability report and the supporting data assessment documentation.

4.1.1 Laboratory Report Description

Laboratory reports (PDF), in summary format, provided by the subcontract laboratory will be consistent with the deliverable requirements using either contract laboratory program equivalent forms or internal laboratory standardized versions. The laboratory will provide a Level 4 data package for all analytical fractions as appropriate by method for this project. The laboratory data report should be organized in a consistent and logical format that facilitates data identification and retrieval.

Laboratory reports for all samples and analyses will contain the information necessary to perform data evaluation. Reports will be designed logically to permit the validator and other reviewers ease of access and ability to navigate the reported data.

Results of multiple dilutions should be reviewed for consistency. The laboratory must resolve and correct discrepancies. Laboratory qualifiers will be applied when there is a condition of nonconformance that could potentially affect data usability. The qualifiers must be properly defined as part of the deliverables. Issues relevant to data quality must be addressed in a case narrative.

A **Level 1 report** will include at least the following information (when applicable):

- Cover letter complete with the following information:
  - Title of report and unique report identification (sample delivery group number)
  - Project name and site location
  - Name and location of laboratory and second-site or subcontracted laboratory
  - Client name and address
  - Statement of authenticity and official signature and title of person authorizing report release
- Table of contents
- Summary of samples received that correlates field sample IDs with the laboratory IDs
- Laboratory qualifier flags and definitions
- Field ID number
- Date received
- Date prepared
- Date analyzed (and time of analysis if the holding time is less than or equal to 48 hours)
- Preparation and analytical methods

- Result for each analyte (dry-weight basis for sediments)
- Percent solids results for sediment samples
- Dilution factor (provide both diluted and undiluted results when available)
- Sample-specific RL adjusted for sample size, dilution/concentration
- Sample-specific MDL adjusted for sample size, dilution/concentration (when project objectives require reporting less than the RL)
- Units

A **Level 2 report** will consist of all the elements included in a Level 1 deliverable, plus the following:

- Case narrative that addresses at least the following information:
  - Sample receipt discrepancies, such as bubbles in volatile organic analysis samples and temperature exceedances
  - Descriptions of all nonconformances in the sample receipt, handling, preparation, and analytical and reporting processes, and the corrective action taken in each occurrence
  - ID and justification for sample dilution
- Surrogate percent recoveries
- MS/MSD and LCS spike concentrations, native sample results, spiked sample results, percent recoveries, and RPDs between the MS and MSD results; associated QC limits must also be provided
- Method blank results
- Analytical batch reference number that cross-references samples to QC sample analyses
- Executed chain-of-custody and sample receipt checklist

A **Level 3 report** will consist of all the elements in Level 1 and Level 2 reports, plus the following:

- Analytical sequence or laboratory run log that contains sufficient information to correlate samples reported in the summary results to the associated method QC information, such as initial and continuing calibration analyses
- Confirmation results
- Internal standard recovery and retention time information, as applicable
- Initial calibration summary, including standard concentrations, RFs, average RFs, relative standard deviations or correlation coefficients, and calibration plots or equations, if applicable
- Continuing calibration verification summary, including expected and recovered concentrations and percent differences
- Instrument tuning and mass calibration information for gas chromatography/mass spectrometry and inductively coupled plasma/mass spectrometry analyses
- Any other method-specific QC sample results

A **Level 4 report** will include all elements outlined above for the Level 1 through Level 3 reports and all the associated raw data (Table 6). It is imperative that the relative scale used for chromatographic and other instrument data be supplied in a scale that facilitates review. Complex areas of sample chromatograms will

be sufficiently enlarged to facilitate viewing, and the enlargements will be provided. The following information also will be supplied:

- Sample preparation logs that include the following:
  - Preparation start and end times
  - Beginning and ending temperatures of water baths and digestion blocks
- Example calculation (and algorithm) for obtaining numerical results from at least one sample for each matrix analyzed
- Reconstructed ion chromatograms or selected ion current profiles for each sample (and blank) analyzed and mass spectra for each compound identified, including the following:
  - Raw compound spectra
  - Enhanced or background spectra
  - Laboratory-generated library spectra (for tentatively identified compounds provide the reference mass spectra from software spectra library)

4.2 Data Review, Verification, and Validation

Data validation is the process of reviewing project data against the data QA/QC requirements. The data are evaluated for precision and accuracy against the analytical protocol requirements stated in the laboratory scope of work. Nonconformance issues or deficiencies that could affect the reported result's precision or accuracy are identified and considered when assessing whether the result is sufficient to achieve DQOs.

The data collected as part of the field investigation must be consistent with this QAPP. EPA National Functional Guidelines will be used as guidance on data validation procedures. QC requirements are as specified in the analytical methods, laboratory SOWs, and laboratory SOPs. QC requirements specified in the laboratory SOWs will take precedence over the National Functional Guidelines requirements when listed.

4.2.1 Completeness and Compliance

The CH2M project chemist will check the laboratory deliverable for completeness and compliance with the contract and QAPP requirements. The data are verified to assess whether the EDDs and the laboratory report data deliverables are consistent with one another to ensure an accurate database. The data will be evaluated in such a way as to determine whether the results make sense if compared with anticipated results. If the data are consistent with anticipated results, no corrective action will be deemed necessary. However, if the data obtained from the laboratory are not consistent with the anticipated results, an in-depth evaluation of the results may be necessary to interpret the deviation.

Field data will be reviewed for completeness and usability by CH2M. Waste characterization data will not be validated.

4.2.2 Independent Data Verification and Validation

The analytical laboratory data for sediment investigation samples (excluding waste characterization) will be provided to EPA's QATS contractor, APTIM, for data verification and validation. APTIM will conduct Tier 1 validation on 100 percent of the data and Tier 2 on 20 percent of the data for mercury, methyl mercury, TOC, and dioxin/furan congeners. Tier 1 and Tier 2 validation will be performed on 100 percent of the PCB data. CH2M will provide the QAPP, and laboratory SOPs to the QATS contractor for reference.
The laboratory data packages and EDDs will be submitted through the SMO Portal and made available to the

QATS contractor. The results of the QATS contractor validation will be documented in a data validation narrative and by data qualifiers in the EDD files generated in EXES and provided to CH2M.

4.2.3 Validation Review

The CH2M project chemist will review the independent third-party data validation results and check that qualifiers were applied correctly to the sample results in the EDD files. Findings by the independent validator will be incorporated into the data set, which will be submitted to GLNPO for entry into GLSED.

The project chemist will evaluate and assess how the data, as qualified, can be used for the project.

4.3 Validation and Verification Methods

Data validation is conducted to assess the effect of the overall sampling and analysis process on the usability of data. There are two areas of review: laboratory performance evaluation, and the effect of matrix and sampling interference. The laboratory performance evaluation is a check for compliance with the method requirements. The laboratory either did or did not analyze the samples within the QC limits of the analytical method and according to protocol requirements. Potential matrix and sampling effects are assessed by a QC evaluation of the analytical results and by an examination of the results of testing blank, duplicate, and MS samples; and then by determining how, if at all, it could affect the usability of the data.

The analytical data will be supported by a data package. The data package will contain the supporting QC data for the associated field samples (see Section 4.1.1 for the data package content requirements). Before the laboratory will release each data package, the laboratory QAM (or the analytical section supervisor) must carefully review the sample and laboratory performance QC data to verify sample identity, the completeness and accuracy of the sample and QC data, and compliance with method specifications.

The verification/validation process will be performed by a combination of electronic and manual methods.

The analytical laboratory data will undergo an initial electronic assessment in EXES, and validation by EPA's QATS contractor. The electronic assessment includes data flagging for issues related to method blanks, laboratory control samples, MS/MSD samples, field duplicates, surrogate recoveries, holding time, and reconciliation of dilutions and re-extractions. The remaining validation checks will be performed manually, and qualifiers will be entered by APTIM using EXES.

If, during the data review and verification process, a systematic problem or other issue with the data set is identified, the CH2M project chemist will contact the laboratory's project manager or QA manager. Additional evaluation of the data may be performed, including an in-depth review of the raw data to verify accuracy followed by analysis and interpretation of the data in the context of the project objectives and end-use as part of the usability assessment.

The CH2M project chemist will evaluate the data validation results. The evaluation will assess how the data, as qualified by the data validator, can be used for project decision making once discrepancies or anomalies have been resolved.

The data validation reports prepared by APTIM will be provided as an attachment to the data usability report prepared by CH2M.

4.3.1 Field Data

Scribe will be used to generate sample numbers, labels, and chain-of-custody forms. Field records will be generated in hard copy field logs and included as an appendix to the final data summary. The field data to be incorporated in the project database will be entered into Scribe by CH2M team members. The CH2M project

chemist or field team leader will forward the complete field database file to the CH2M data manager who will import the field data into the project database.

The field data will be assessed for completeness, compliance, and accuracy in accordance with the requirements stated in this QAPP. The data entry in electronic files will be checked by comparing hard copy data contained in the logbooks or forms to a printout of the electronic file. Data entry confirmation procedures and results will be documented.

Locational data will be plotted and assessed against the proposed locations provided in the Table 2 and discrepancies will be documented. The deviations from the QAPP will be evaluated for the impact to the usability of the data and decision making and documented in the data usability report.

4.3.2 Laboratory Data

The subcontract laboratories will generate chemical analytical data supporting the project. Data will be generated and managed at the laboratories according to the laboratory SOPs (Appendix A). As detailed in the laboratory SOW, all analytical data are to be checked and reviewed at the laboratory by the analyst generating the data and an experienced data reviewer before being released to CH2M.

Discrepancies must be resolved and corrected at the time of discovery. Laboratory qualifiers will be applied when there is nonconformance that could potentially affect data usability. The laboratory qualifiers will be defined as part of the deliverables. Issues relevant to the quality of the data will be addressed in the laboratory case narrative.

Analytical results will be submitted as an EDD and will be accompanied by an analytical report in an electronic (PDF) format. SDG data reports will be generated by the laboratories consistent with the formats identified in the laboratory SOWs.

For the data package, each analytical report must contain the information specified in the SOW and a case narrative that includes, but is not limited to, the following information:

- Sample summary, cross referencing the field and laboratory sample identification, matrix, the date that the sample was collected in the field, and the date the laboratory received the sample
- Project summary referencing the analytical methodology
- Discussion of protocol deviations that may have occurred during sample testing
- Discussion of QC sample questions and the corrective measures taken
- Summary and discussion of samples that were diluted by the presence of an interference or target analyte

For electronic data submittal, laboratories will report analytical data in the GLNPO SEDD format and load directly to EXES, or in the EQuIS or Excel file format, as previously outlined. Data packages (EDD and narrative) and full reports (PDF) will be provided to CH2M.

4.4 Reconciliation with Data Quality Objectives

The final activity of the data validation process is to assess whether the data fulfill the objectives for the project. The project chemist will check final results, as adjusted for the findings of any data validation/data evaluation, against the DQOs. The data acquired from the sediment characterization investigation should fulfill the project objectives.

The CH2M project manager or designee will evaluate investigation results to assess whether the project objectives have been met. The objectives will be met if all scheduled samples and data readings documented in the QAPP are obtained and all data are deemed usable after sufficient validation and

evaluation. If the objectives are not met, the reasons for not meeting them will be identified and examined to determine data insufficiency. A corrective action will be implemented.

SECTION 5

General Field Operations

This section describes general field operations and procedures to be executed to ensure the safety of personnel onsite during field activities, as well as the quality of field data collection and field documentation. It also references FOP-12 in Appendix B that provides step-by-step procedures for conducting field data documentation.

5.1 Health and Safety Plan

CH2M staff and entities directly subcontracted to CH2M will abide by U.S. Occupational Safety and Health Administration regulations and the site-specific HASP (CH2M 2018b). General topics covered in the HASP include site location and scope of work, safety and health risk analysis, field team organization and responsibilities, PPE, site control measures, decontamination procedures, emergency response plan, employee training, and medical monitoring. The HASP will be developed prior to mobilization and kept onsite during field activities, and a copy will be maintained in the project files.

5.2 Field Data Documentation Procedures

Consistent procedures will be implemented by CH2M to document the location, media, and the physical parameters collected in the field. The procedures include recording the sample location information, photographs, maintaining a file of parameter data generated as a result of field activities, and recording field sampling location survey data. Field notes at each location may include the following information (if applicable): date, time, personnel, weather conditions, station identification, *x*- and *y*-coordinates, *z* elevations (top of water, top of sediment), water depth, core penetration depth, sediment recovery thickness, and media descriptions. The following subsections describe the documentation methods that will be used.

5.2.1 Field Logbook

A field logbook will be initiated at the start of the first onsite activity to document field activities throughout the field effort in accordance with CH2M FOP-12, Field Logbook (Appendix B).

5.2.2 Field Forms

Standard forms may be used in addition to the field logbooks to ensure necessary data are recorded consistently and provide a more detailed record of field data. No blank spaces will appear on completed forms. If information requested is not applicable, then the space will be marked with a dashed line or marked “N/A.” The forms are to be completed in the field and placed in the project files. Field forms will provide information necessary to document sample location ID, sediment core descriptions and measurements, survey information (*x, y* coordinates and *z* elevations), observations (for example, staining or odor), and IDW tracking information. Field forms to be implemented by CH2M for this project include Sediment Core Logs, Geographic Information System Metadata Forms, PID Calibration Form, IDW Inspection Log, and an IDW Tracking Form located in Appendix C.

5.2.3 Photographic Documentation

The CH2M field team leader or designee will selectively photograph field activities and field conditions to complement descriptions of field activities in the field logbook. The following information will be recorded in the logbook when photographs are taken:

- Date and time
- Location and compass direction of the photograph
- Description and identification of the subject
- Initials of the person who took the photograph

CH2M will maintain digital picture files for reference during the project and develop a photographic log for subsequent reporting.

5.3 Field Data Quality Control Procedures

Information collected in the field through visual observation, manual measurement, and/or field instrumentation will be recorded in field logbooks and/or on data forms. The field team leader will review the data for consistency and adherence to this QAPP. Concerns identified will be corrected and incorporated into the data evaluation process.

Field data calculations, transfers, and interpretations conducted by the field team will also be reviewed by the CH2M field team leader. Original field documents will be kept in the project file.

Field documents will be checked for the following:

- General completeness
- Readability
- Clearly stated use of appropriate procedures and modifications to probing and sediment sampling procedures
- Appropriate instrument calibration and maintenance records (as appropriate)
- Reasonableness of data collected
- Correctness of sample locations
- Correctness of reporting units, calculations, and interpretations

SECTION 6

References

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Tables

Table 1. Data Quality Objectives Development for Site Characterization

Munger Landing Sediment Characterization, St. Louis AOC, Minnesota and Wisconsin

State the Problem	Goal of the Study	Information Inputs	Study Boundaries	Analytic Approach	Performance or Acceptance Criteria	Plan for Obtaining Data
The data in this study are being collected in support of site characterization activities for Munger Landing in the St. Louis Area of Concern. Specifically, this evaluation is being conducted to study the two creeks and determine if one or both may be an ongoing source of contaminants to Munger Landing, and to fill data gaps within the Munger Landing site. Data collected as part of this investigation will be used to assist MPCA and WDNR.	The purpose of the sediment sampling activities is to collect chemical and physical data for sediments within the Munger Landing site to support the following evaluations: Fill data gaps, assist MPCA and WNDR in evaluating beneficial use impairments and refining the remedial footprint. Sediment thickness, water depth, and water elevation data. Description of physical sediment characteristics and photographs of in situ sediment conditions from sediment cores. Sediment characteristics needed to establish a waste profile for disposal in a landfill.	New Data: Sediment poling will be conducted to obtain sediment thickness measurements. Sediment cores will be collected and visually characterized for sediment type, particle size, color, moisture, consistency, as well as odors and staining. Samples will be collected as described under "Plan for Obtaining Data" will be submitted for laboratory analysis of the following: Sediment samples: polychlorinated biphenyl (PCB) Aroclors, dioxins and furans, mercury, methyl mercury, and total organic carbon (TOC). Waste characterization samples: toxicity characteristic leaching procedure (TCLP) volatile organic compounds, TCLP semivolatile organic compounds, TCLP pesticides, TCLP herbicides, TCLP metals, pH, and flash point. Equipment blank samples: PCB Aroclors, dioxins and furans, mercury, and methyl mercury. Additional field data collection for sample locations: global positioning system data (x, y coordinates), water depth, water elevation, sediment elevation, sediment poling thickness, core penetration, and core recovery. Water elevation data (*z* elevation) will be collected at the nearest staff gauge, and geotechnical field measurements. Sample information: chain of custody, unique sample ID, date, and time. See attached Field Forms in Appendix C.	Munger landing is in West Duluth, Minnesota. Located approximately 7 miles upstream of Lake Superior. The southern portion of the site straddles Minnesota and extends across the state line into Wisconsin. See Figures 1A and 1B. Sampling is scheduled to occur during the week of October 15, 2018. Data evaluation and reporting of the data will occur in November through February 2018.	Descriptive and analytical summaries of the data collected during the field investigation will be prepared to support potential future management decisions and activities at the site. Performance Evaluation Samples will be submitted to the subcontract laboratory by the EPA GLNPO QATS contractor, APTIM. Sediment data, specifically mercury, total PCBs, and total Dioxin/Furan Toxicity Equivalency Quotients (TEQs) will be screened against Minnesota Pollution Control Agency Sediment Quality Targets (MPCA SQTs). The following will be presented in the site characterization report: Summary of field sampling activities, notes, observations, and field collected data. Data tables presenting analytical results from the investigation and statistical summaries. Assessment of surface versus subsurface contamination and identification of spatial trends in the data. Figures depicting sample locations and analytical results.	Performance criteria for analytical chemistry data are established within the EPA-approved methods and laboratory standard operating procedures. Most potential decision errors typically will be associated with field sample variability and sample collection procedures. Analytical error usually is a much smaller portion of the total error associated with an environmental measurement. Locational information will be obtained using differential global positioning system receivers capable of submeter accuracy attached to the R/V Mudpuppy II and handheld Trimble GPS units. Water depth will be measured to the nearest 0.1 foot from the water surface to the top of sediment. The surface water elevation will be obtained from National Oceanic and Atmospheric Administration gauge station #9099064 at the Duluth vessel yard or United States Geological Survey gauge station 464646092052900, Superior Bay Duluth Ship Canal at Duluth, Minnesota. Probed sediment thickness measurements will be collected to the nearest 0.1 foot. The water depth will be subtracted from the probe refusal depths to determine the sediment thickness. Core penetration thickness measurements will be collected to the nearest 0.1 foot. The water depth will be subtracted from the overall penetration depth to determine sediment core penetration thickness. Sediment core recovery measurements will be collected to the nearest 0.1 foot and compared to respective sediment core penetration thickness measurements to determine the percent of recovery. Location data will be in latitude/longitude North American Datum 1983, and elevation data will be in International Great Lakes Datum of 1985.	Sediment poling will be conducted prior to coring activities at each proposed sample location. Sediment poling will serve to gauge sediment thickness available for sampling as well as to aid in selecting an appropriate length of sediment core liner for sampling. At each proposed location, the following data will be collected: • Water depth will be measured using a surveyor's tape measure outfitted with a sounding disc or bell anchor 6 inches in diameter and weighing between 7 and 8 pounds following Appendix B of the USACE Hydrographic Surveying Manual (USACE 2013). A sediment probe will be manually advanced into the subsurface until refusal is reached. Refusal is defined as the depth at which penetration through the sediment layer is less than 0.1 foot after continuous manual advancement. • Sediment cores will be collected from 36 proposed locations (Figure 1A). Twenty-eight of the 36 locations proposed within the river were determined by targeting areas that required further delineation. Eight of the 36 locations are proposed within Snively Creek and Steward Creek to determine if one or both creeks are an ongoing source of contamination to Munger Landing. • Each sediment core will be collected to a maximum 10-foot push and sampled continuously in 1-foot intervals to the native sediment interface (if encountered). The top one or two sample intervals at each core location (Table 2) will be submitted for immediate analysis, with the lower intervals placed on hold at the subcontract laboratory. If native sediment is recovered, the material will be segregated into its own interval to a maximum of 1 foot below the native sediment interface. In addition, QA/QC samples will be collected at a 10 percent frequency for field duplicates and 5 percent frequency for matrix spike/matrix spike duplicate samples collected within the Munger Landing project area. • Surface sediment samples (0- to 0.25-foot) will be collected by petite Ponar from 4 locations west of Clough Island (ML-SD-29 through ML-SD-32). • Field data will be documented on the field form for each location.

Table 2. Sample Locations and Parameters Summary

Munger Landing Sediment Characterization, St. Louis AOC, Minnesota and Wisconsin

						Parameter Summary				
Proposed Location ID	**Sampling Vessel**	**Proposed Latitude[1]**	**Proposed Longitude[1]**	**State**	**Analyze Top Intervals[2]**	**PCB Aroclors**	**Dioxin/ Furan**	**Mercury**	**Methyl Mercury**	**TOC**
ML-SD-01	Mudpuppy[3]	46 42.32127270N	092 12.16717963W	WI	2	X	X	X	X	X
ML-SD-02	Mudpuppy[3]	46 42.31358970N	092 12.16322623W	WI	2	X	X	X	X	X
ML-SD-03	Mudpuppy[3]	46 42.28558711N	092 12.16162483W	WI	2	X	X	X	X	X
ML-SD-04	Mudpuppy[3]	46 42.31625551N	092 12.22934561W	MN	2		X			X
ML-SD-05	Mudpuppy[3]	46 42.28701871N	092 12.22553741W	WI	2	X	X			X
ML-SD-06	Mudpuppy[3]	46 42.28752871N	092 12.26030080W	MN	2		X			X
ML-SD-07	Mudpuppy[3]	46 42.27069152N	092 12.30264099W	MN	2		X	X		X
ML-SD-08	Mudpuppy[3]	46 42.24136292N	092 12.26643821W	WI	2	X	X	X	X	X
ML-SD-09	Mudpuppy[3]	46 42.23649632N	092 12.31823439W	MN	2		X	X		X
ML-SD-10	Mudpuppy[3]	46 42.21565832N	092 12.33905019W	MN	2	X	X	X		X
ML-SD-11	Mudpuppy[3]	46 42.20730993N	092 12.38046998W	MN	2	X	X	X		X
ML-SD-12	Mudpuppy[3]	46 42.17512353N	092 12.31348180W	WI	2	X	X	X	X	X
ML-SD-13	Mudpuppy[3]	46 42.17639794N	092 12.38360378W	MN	2	X	X			X
ML-SD-14	Mudpuppy[3]	46 42.13316914N	092 12.38548899W	MN	2	X	X			X
ML-SD-15	Mudpuppy[3]	46 42.13572874N	092 12.32923600W	WI	2	X	X			X
ML-SD-16	Mudpuppy[3]	46 42.09056194N	092 12.34572281W	WI	2	X	X	X	X	X
ML-SD-17	Mudpuppy[3]	46 42.02603976N	092 12.42444580W	MN	2	X	X			X
ML-SD-18	Mudpuppy[3]	46 42.04120355N	092 12.32534142W	WI	2	X	X	X	X	X
ML-SD-19	Mudpuppy[3]	46 41.98761275N	092 12.30528643W	WI	2	X	X	X	X	X
ML-SD-20	Mudpuppy[3]	46 42.13678954N	092 12.30534341W	WI	2	X	X			X
ML-SD-21	Mudpuppy[3]	46 42.09198994N	092 12.30842742W	WI	2	X	X	X	X	X
ML-SD-22	Mudpuppy[3]	46 42.03912755N	092 12.29226283W	WI	2	X	X	X	X	X
ML-SD-23	Mudpuppy[3]	46 41.91237697N	092 12.26870206W	WI	2	X	X			X
ML-SD-24	Mudpuppy[3]	46 41.89000117N	092 12.28603846W	WI	2	X	X			X
ML-SD-25	Mudpuppy[3]	46 41.93139937N	092 12.33214783W	MN	2	X	X			X
ML-SD-26	Mudpuppy[3]	46 41.91256117N	092 12.30457844W	WI	2	X	X			X
ML-SD-27	Mudpuppy[3]	46 41.80401998N	092 12.36584684W	MN	1	X	X			X
ML-SD-28	Mudpuppy[3]	46 41.79957038N	092 12.31013926W	MN	1	X	X			X
ML-SD-29	Ponar[4]	46 42.01226971N	092 11.68407361W	WI	1		X			X
ML-SD-30	Ponar[4]	46 41.92848632N	092 11.66541303W	WI	1		X			X
ML-SD-31	Ponar[4]	46 41.88126332N	092 11.67607624W	WI	1		X			X
ML-SD-32	Ponar[4]	46 41.87212352N	092 11.62009385W	WI	1		X			X
ML-SD-33	Manual[5]	46 41.95339498N	092 12.83881282W	MN	2	X	X	X		X
ML-SD-34	Manual[5]	46 41.95299993N	092 12.70632368W	MN	2	X	X	X		X
ML-SD-35	Manual[5]	46 41.97321908N	092 12.64475554W	MN	2	X	X	X		X
ML-SD-36	Manual[5]	46 41.95057820N	092 12.58079064W	MN	2	X	X	X		X
ML-SD-37	Manual[5]	46 41.87034090N	092 12.95365610W	MN	2	X	X	X		X
ML-SD-38	Manual[5]	46 41.87183159N	092 12.91627155W	MN	2	X	X	X		X
ML-SD-39	Manual[5]	46 41.86339145N	092 12.85306649W	MN	2	X	X	X		X
ML-SD-40	Manual[5]	46 41.85553012N	092 12.66021431W	MN	2	X	X	X		X

Notes:

[1]Coordinates are in North American Datum of 1983 (NAD83) StatePlane Minnesota North FIPS 2201 Feet in degrees, decimals, minutes

[2]Interval numbers (top most intervals) to be analyzed immediataly, all other lower interval samples to be placed on hold

[3]Collect sediment cores using EPA's RV Mudpuppy II vessel, maximum depth of 10 ft, sample intervals of 1ft

[4]Surface sample only, petite Ponar sampling to be performed by WDNR; 0.0-0.25 ft interval

[5]Manual coring methods within Stewart Creek and Snively Creek

Abbreviations: PCB = polychlorinated biphenyl; TOC = Total Organic Carbon; ft = feet; WI = Wisconsin; MN = Minnesota

Table 3. Sediment Sample Summary

Munger Landing Sediment Characterization, St. Louis AOC, Minnesota and Wisconsin

Analysis	Extraction and Analysis Methods	Estimated Field Analysis Samples	Estimated Field Hold Samples	QA/QC Analysis Samples			QA/QC Hold Samples		Total No. of Samples
				FD	MS/MSD	PES	FD	MS/ MSD	
Sediment									
PCB Aroclors	SW-846 3541/8082	62	32	8	4/4	1	2	1/1	115
Dioxin/Furan	EPA 1613B	74	40	10	5/5	1	2	1/1	139
Mercury	SW-846 7471B	44	21	5	3/3	1	2	1/1	81
Methyl Mercury	EPA 1630	20	-	2	1/1	-	-	-	24
TOC	Lloyd Kahn[a]	74	40	10	-	-	2	-	126
Equipment Blank									
PCB Aroclors	SW-846 8082A	2	-	-	-	-	-	-	2
Dioxin/Furan	EPA 1613B	2	-	-	-	-	-	-	2
Mercury	SW-846 7470A	2	-	-	-	-	-	-	2
Methyl Mercury	EPA 1630	2	-	-	-	-	-	-	2
Waste Characterization (Sediment)									
TCLP VOC	SW-846 1311/8260B	1	-	-	-	-	-	-	1
TCLP SVOC	SW-846 1311/8270C	1	-	-	-	-	-	-	1
TCLP pesticides	SW-846 1311/8081B	1	-	-	-	-	-	-	1
TCLP herbicides	SW-846 1311/8151A	1	-	-	-	-	-	-	1
TCLP metals	SW-846 1311/6010C/7470A	1	-	-	-	-	-	-	1
pH	SW-846 9045D	1	-	-	-	-	-	-	1
Flash point	SW-846 1020	1	-	-	-	-	-	-	1

Notes:

Sediment sample counts are estimated based on sediment thickness estimates documented in the Bay West focused feasibility study (2018) but are likely to change based on field conditions and recoveries.

[a] Recommend the use of a high temperature, automated, dry combustion technique after pretesting and pretreatment to remove inorganic carbonates.

[b] Hold samples will either be analyzed or disposed of by the lab after review of preliminary data, if analyzed hold sample data will be submitted on a 28-day turnaround time.

FD = field duplicate sample; MS/MSD = matrix spike matrix spike duplicate sample; PES = performance evaluation sample; PCB = polychlorinated biphenyl; TOC = total organic carbon; TCLP = toxicity characteristic leaching procedure; VOC = volatile organic compound; SVOC = semivolatile organic compound

Table 4A. Measurement Quality Objectives for Sediment Samples

Munger Landing Sediment Characterization, St. Louis AOC, Minnesota and Wisconsin

Method	Analyte	CAS	Laboratory Location	MDL	RL	Units	MPCA SQT[a]			LCS Low	LCS High	MS/MSD Low	MS/MSD High	MS/MSD RPD
							Level I	Midpoint[b]	Level II					
Metals														
SW-846 7471B	Mercury	7439-97-6	Green Bay, WI	0.011	0.037	mg/kg	0.18	0.64	1.1	85	115	85	115	20
EPA 1630	Methyl Mercury	22967-92-6	Duluth, MN	0.611	3.1	mg/kg	-	-	-	67	133	65	135	35
General Chemistry														
Lloyd Kahn	Total Organic Carbon	-	Green Bay, WI	33.88	100	mg/kg	-	-	-	80	120	80	120	20
PCB Aroclors														
SW-846 8082	Aroclor 1016	12674-11-2	Green Bay, WI	25	50	µg/kg	-	-	-	61	105	35	125	20
SW-846 8082	Aroclor 1221	11104-28-2	Green Bay, WI	25	50	µg/kg	-	-	-	61	105	35	125	20
SW-846 8082	Aroclor 1232	11141-16-5	Green Bay, WI	25	50	µg/kg	-	-	-	61	105	35	125	20
SW-846 8082	Aroclor 1242	53469-21-9	Green Bay, WI	25	50	µg/kg	-	-	-	61	105	35	125	20
SW-846 8082	Aroclor 1248	12672-29-6	Green Bay, WI	25	50	µg/kg	-	-	-	61	105	35	125	20
SW-846 8082	Aroclor 1254	11097-69-1	Green Bay, WI	25	50	µg/kg	-	-	-	61	105	35	125	20
SW-846 8082	Aroclor 1260	11096-82-5	Green Bay, WI	25	50	µg/kg	-	-	-	61	105	35	125	20
SW-846 8082	Aroclor 1262	37324-23-5	Green Bay, WI	25	50	µg/kg	-	-	-	61	105	35	125	20
SW-846 8082	Aroclor 1268	11100-14-4	Green Bay, WI	25	50	µg/kg	-	-	-	61	105	35	125	20
SW-846 8082	Total PCBs	-	Green Bay, WI	25	50	µg/kg	60	370	680	-	-	-	-	-
Dioxin/Furan Congeners														
EPA 1613B	2,3,7,8-TCDD	1746-01-6	Minneapolis, MN	0.311	1	ng/kg	-	-	-	6.7	15.8	6.7	15.8	20
EPA 1613B	2,3,7,8-TCDF	51207-31-9	Minneapolis, MN	0.140	1	ng/kg	-	-	-	7.5	15.8	7.5	15.8	20
EPA 1613B	1,2,3,7,8-PeCDD	40321-76-4	Minneapolis, MN	0.156	5	ng/kg	-	-	-	35	71	35	71	20
EPA 1613B	1,2,3,7,8-PeCDF	57117-41-6	Minneapolis, MN	0.190	5	ng/kg	-	-	-	40	67	40	67	20
EPA 1613B	2,3,4,7,8-PeCDF	57117-31-4	Minneapolis, MN	0.145	5	ng/kg	-	-	-	34	80	34	80	20
EPA 1613B	1,2,3,4,7,8-HxCDD	39227-28-6	Minneapolis, MN	0.356	5	ng/kg	-	-	-	35	82	35	82	20
EPA 1613B	1,2,3,6,7,8-HxCDD	57653-85-7	Minneapolis, MN	0.226	5	ng/kg	-	-	-	38	67	38	67	20
EPA 1613B	1,2,3,7,8,9-HxCDD	19408-74-3	Minneapolis, MN	0.472	5	ng/kg	-	-	-	32	81	32	81	20

Table 4A. Measurement Quality Objectives for Sediment Samples

Munger Landing Sediment Characterization, St. Louis AOC, Minnesota and Wisconsin

Method	Analyte	CAS	Laboratory Location	MDL	RL	Units	MPCA SQT[a]			LCS Low	LCS High	MS/MSD Low	MS/MSD High	MS/MSD RPD
							Level I	Midpoint[b]	Level II					
EPA 1613B	1,2,3,4,7,8-HxCDF	70648-26-9	Minneapolis, MN	0.198	5	ng/kg	-	-	-	36	67	36	67	20
EPA 1613B	1,2,3,6,7,8-HxCDF	57117-44-9	Minneapolis, MN	0.209	5	ng/kg	-	-	-	42	65	42	65	20
EPA 1613B	1,2,3,7,8,9-HxCDF	72918-21-9	Minneapolis, MN	0.261	5	ng/kg	-	-	-	39	65	39	65	20
EPA 1613B	2,3,4,6,7,8-HxCDF	60851-34-5	Minneapolis, MN	0.273	5	ng/kg	-	-	-	35	78	35	78	20
EPA 1613B	1,2,3,4,6,7,8-HpCDD	35822-46-9	Minneapolis, MN	0.457	5	ng/kg	-	-	-	35	70	35	70	20
EPA 1613B	1,2,3,4,6,7,8-HpCDF	67562-39-4	Minneapolis, MN	0.336	5	ng/kg	-	-	-	41	61	41	61	20
EPA 1613B	1,2,3,4,7,8,9-HpCDF	55673-89-7	Minneapolis, MN	0.442	5	ng/kg	-	-	-	39	69	39	69	20
EPA 1613B	OCDD	3268-87-9	Minneapolis, MN	0.730	10	ng/kg	-	-	-	78	144	78	144	20
EPA 1613B	OCDF	39001-02-0	Minneapolis, MN	1.140	10	ng/kg	-	-	-	63	170	63	170	20
EPA 1613B	Total TCDD	-	Minneapolis, MN	0.311	1	ng/kg	-	-	-	-	-	-	-	20
EPA 1613B	Total TCDF	-	Minneapolis, MN	0.140	1	ng/kg	-	-	-	-	-	-	-	20
EPA 1613B	Total PeCDD	-	Minneapolis, MN	0.156	5	ng/kg	-	-	-	-	-	-	-	20
EPA 1613B	Total PeCDF	-	Minneapolis, MN	0.335	10	ng/kg	-	-	-	-	-	-	-	20
EPA 1613B	Total HxCDD	-	Minneapolis, MN	1.050	15	ng/kg	-	-	-	-	-	-	-	20
EPA 1613B	Total HxCDF	-	Minneapolis, MN	0.940	20	ng/kg	-	-	-	-	-	-	-	20
EPA 1613B	Total HpCDD	-	Minneapolis, MN	0.457	5	ng/kg	-	-	-	-	-	-	-	20
EPA 1613B	Total HpCDF	-	Minneapolis, MN	0.780	10	ng/kg	-	-	-	-	-	-	-	20
-	Dioxin/Furan TEQ	-	-	-	-	ng/kg	0.85	11.2	21.5	-	-	-	-	-

Notes:

[a]Guidance for the Use and Application of Sediment Quality Targets (SQT) for the Protection of Sediment-Dwelling Organisms in Minnesota (MPCA 2007).

[b]The midpoint between the Level I and Level II SQT is equal to the cleanup levels presented in the Munger Landing FFS (Bay West 2018).

MDL = method detection limit; RL = reporting limit; PAL = project action limit; LCS = laboratory control sample; MS/MSD = matrix spike/matrix spike duplicate; RPD = relative percent difference; mg/kg = milligrams per kilogram; µg/kg = microgram per kilogram; ng/kg = nanograms per kilogram; TEQ = toxicity equivalency

Table 4B. Project Action Limits for Investigation-Derived Waste Characterization

Munger Landing Sediment Characterization, St. Louis AOC, Minnesota and Wisconsin

Analyte	CAS Number	Project Action Limit (mg/L)	Analyte	CAS Number	Project Action Limit (mg/L)
TCLP Metals			***TCLP VOCs***		
Arsenic	7440-38-2	5.0	1,1-Dichloroethene	75-35-4	0.7
Barium	7440-39-3	100.0	1,2-Dichloroethane	107-06-2	0.5
Cadmium	7440-43-9	1.0	1,4-Dichlorobenzene	106-46-7	7.5
Chromium	7440-47-3	5.0	2-Butanone (MEK)	78-93-3	200.0
Lead	7439-92-1	5.0	Benzene	71-43-2	0.5
Selenium	7782-49-2	1.0	Carbon tetrachloride	56-23-5	0.5
Silver	7440-22-4	5.0	Chlorobenzene	108-90-7	100.0
Mercury	7439-97-6	0.2	Chloroform	67-66-3	6.0
TCLP Pesticides			Trichloroethene	79-01-6	0.5
Gamma-BHC (Lindane)	58-89-9	0.4	Tetrachloroethene	127-18-4	0.7
Alpha-Chlordane	5103-71-9	N/A	Vinyl Chloride	75-01-4	0.2
Gamma-Chlordane	5103-74-2	N/A	***TCLP SVOCs***		
Chlordane	57-74-9	0.03	2,4-Dinitrotoluene	121-14-2	0.13
Endrin	72-20-8	0.02	Hexachlorobenzene	118-74-1	0.13
Heptachlor	76-44-8	0.008	Hexachlorobutadiene	87-68-3	0.5
Heptachlor Epoxide	1024-57-3	0.008	Hexachloroethane	67-72-1	3.0
Methoxychlor	72-43-5	10.0	Nitrobenzene	98-95-3	2.0
Toxaphene	8001-35-2	0.5	Pyridine	110-86-1	5.0
Total PCBs			2,4,5-Trichlorophenol	95-95-4	400.0
Aroclor 1016	12674-11-2	1 mg/kg	2,4,6-Trichlorophenol	88-06-2	2.0
Aroclor 1221	11104-28-2	1 mg/kg	2-Methylphenol (o-cresol)	95-48-7	200.0
Aroclor 1232	11141-16-5	1 mg/kg	3-Methylphenol (m-cresol)	108-39-4	200.0
Aroclor 1242	53469-21-9	1 mg/kg	4-Methylphenol (p-cresol)	106-44-5	200.0
Aroclor 1248	12672-29-6	1 mg/kg	Pentachlorophenol	87-86-5	100.0
Aroclor 1254	11097-69-1	1 mg/kg	***TCLP Herbicides***		
Aroclor 1260	11096-82-5	1 mg/kg	2,4-D	94-75-7	10.0
Aroclor 1262	37324-23-5	1 mg/kg	Silvex (2,4,5-TP)	93-72-1	1.0
Aroclor 1268	11100-14-4	1 mg/kg	***pH***	-	-
-	-	-	***Ignitability***	-	-

mg/L = milligrams per liter; ppm = parts per million

Table 5. Sample Containers, Preservatives, and Holding Times

Munger Landing Sediment Characterization, St. Louis River Area of Concern, Minnesota and Wisconsin

Analysis	Method	Sample Container*	Preservation	Holding Times
Sediment				
PCB Aroclors	SW-846 3541/8082	1 × 4-oz G-TLC	≤6˚C	1 year to extraction, 1 year to analysis
Dioxin/Furan	EPA 1613B	1 × 4-oz G-TLC	≤6˚C, stored in the dark	1 year
Mercury	SW-846 7471B	1 × 4-oz G-TLC	≤6˚C	28 days
Methyl Mercury	EPA 1630	1 × 4-oz G-TLC	≤6˚C	28 days
TOC	Lloyd Kahn	1 × 4-oz G-TLC	≤6˚C	14 days
Equipment Blanks				
PCB Aroclors	SW-846 8082A	2 x 1 L amber	≤6˚C	7 days to extraction, 40 days to analysis
Dioxin/Furan	EPA 1613B	2 x 1 L amber	≤6˚C	1 year
Mercury	SW-846 7470A	1 x 250 ml HDPE	HNO3 to pH <2, ≤6˚C	28 days
Methyl Mercury	EPA 1630	1 x 250 ml HDPE	HCl to pH <2, ≤6˚C	6 months
Waste Characterization (Sediment)				
TCLP VOC	SW-846 1311/8260B	6 x 4-oz G-TLC	≤6˚C	14 days to TCLP extraction, 14 days to analysis
TCLP SVOC	SW-846 1311/8270C			14 days to TCLP extraction, 7 days to extraction, 40 days to analysis
TCLP Pesticides	SW-846 1311/8081B			14 days to TCLP extraction, 7 days to extraction, 40 days to analysis
TCLP Herbicides	SW-846 1311/8151A			14 days to TCLP extraction, 7 days to extraction, 40 days to analysis
TCLP Metals	SW-846 1311/6010C/7470A			180 days (28 days Hg) to TCLP extraction, 180 days (28 days Hg) to analysis
pH	SW-846 9045D			7 days
Flash Point	SW-846 1020			10 days

* Container and quantity requirements may be adjusted pending laboratory procurement.
Holding times are from the time of sample collection.

G-TLC = glass with Teflon-lined cap; HDPE = high-density polyethylene

Table 6. Data Package Deliverables (Pace Analytical)

Munger Landing Sediment Characterization, St. Louis River Area of Concern, Minnesota and Wisconsin

All Analytical Fractions

Case Narrative—A detailed case narrative per analytical fraction is required and will include explanation of any noncompliance and/or exceptions and corrective action. Exceptions will be noted for receipt, holding times, methods, preparation, calibration, blanks, spikes, surrogates (if applicable), and sample exceptions.

Sample ID Cross-Reference Sheet (Laboratory IDs and Client IDs)

Completed chain-of-custody and any sample receipt information

Sample preparation (extraction/digestion/dilution) logs

Copies of nonconformance memorandums and corrective actions

Form[a]	Organic Fractions	Level III	Level IV
1	Sample results with laboratory sample ID, client sample ID, and station ID	●	● + raw
2	Surrogate recovery summary (with applicable control limits)	●	●
3	MS/MSD accuracy and precision summary[b] (including spike added, percent recovery, and applicable control limits)	●	● + raw
3	LCS accuracy summary (including spike added, percent recovery, and applicable control limits)	●	● + raw
4	Method blank summary	●	● + raw
5	Instrument tuning summary (including tuning summary for applicable initial calibrations)	●	●
6	Initial calibration summary (including concentration levels of standards)	●	● + raw
6	Initial calibration summary (retention times [RT], response or calibration factors, and linearity demonstration)	●	● + raw
7	Continuing calibration summary	●	● + raw
7	Continuing calibration summary (unique instrument/column ID, RTs, RT windows, calibration or response factors, percent difference or drift—as appropriate to method)	●	● + raw
8	Internal standard summary (including applicable initial calibrations and analytical sequence)	●	●
8	Analytical sequence—For every analysis associated with a particular analytical sequence starting with the initial calibration, enter the client sample identification, laboratory sample identifier, and date and time of analysis. Each sample analyzed as part of the sequence shall be reported on Form 8, even if it is not associated with the batch/SDG. The laboratory shall use ZZZZZ as the client sample identification to distinguish all samples that are not part of the batch/SDG being reported.	●	● + raw
10	Compound identification summary (where confirmation is required), including RT, RT windows, concentrations for detected compounds on both columns, and percent difference between results	●	● + raw
11	Complete raw data associated with each SDG		●

Table 6. Data Package Deliverables (Pace Analytical)

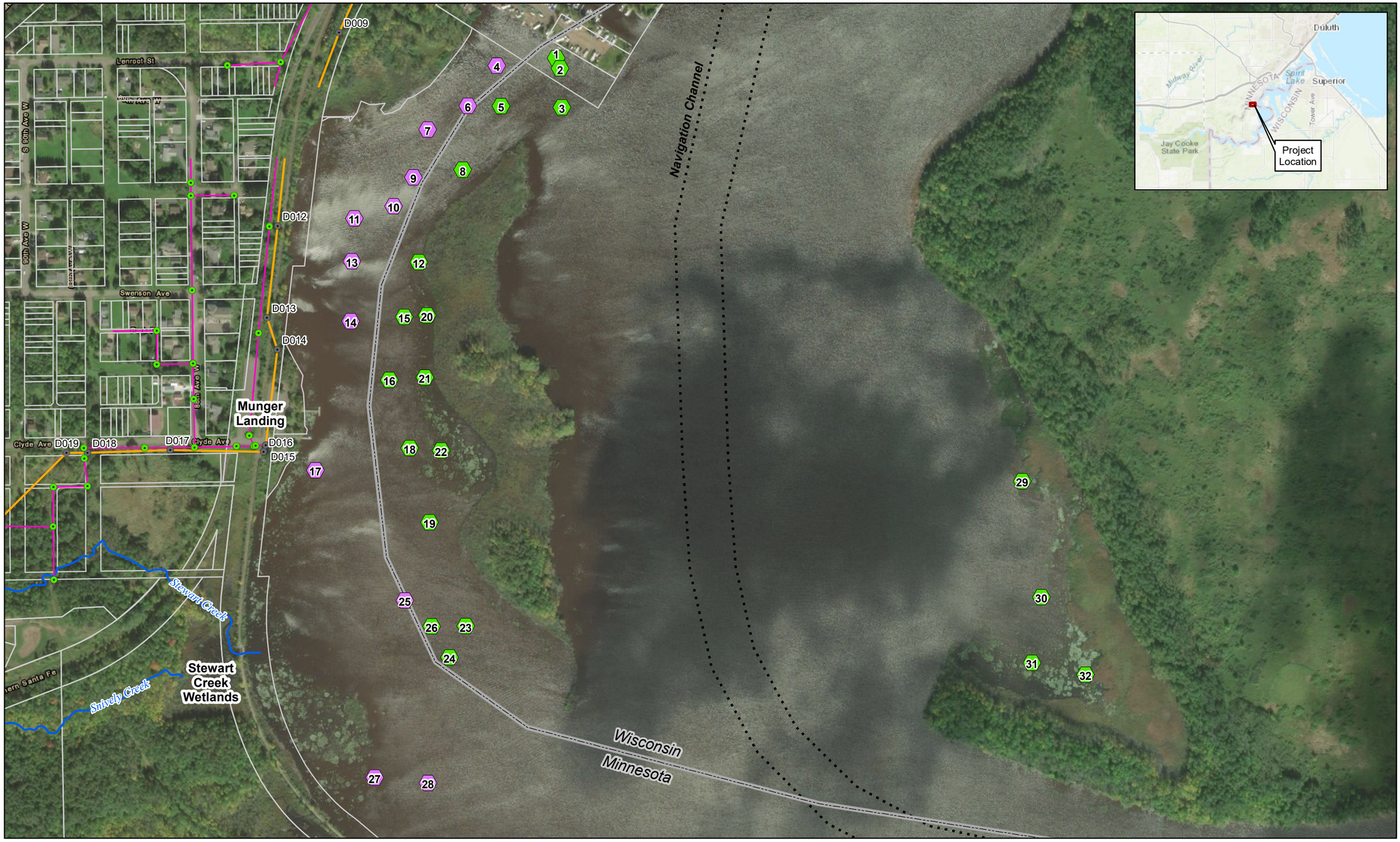
Munger Landing Sediment Characterization, St. Louis River Area of Concern, Minnesota and Wisconsin

Form[a]	Inorganic Fractions	Level III	Level IV
1	Sample results (with laboratory ID, sample ID, and station ID)	●	● + raw
2A	Initial and continuing calibration summary	●	● + raw
3	Initial and continuing calibration blanks and method blanks summary	●	● + raw
5A	Predigestion matrix spike recoveries summary	●	● + raw
6	Native duplicate or MS/MSD precision summary	●	● + raw
7	Laboratory control sample recovery summary	●	● + raw
10	Instrument or method detection limit summary	●	●
13	Preparation log summary	●	● + raw
14	Analytical run sequence and GFAA post-spike recovery summary (as appropriate to method)	●	● + raw
15	Complete raw data associated with each sample delivery group		●

[a] Contract laboratory program form or summary form with equivalent information.

[b] With RPD calculated according to method specifications (contract laboratory program using % recovery, SW-846 using concentration)

Figures



Legend

2018 Proposed Sample Locations by State
- Minnesota
- Wisconsin

- City Manhole
- City Sewer

WLSSD Manholes
- Drop
- Standard

WLSSD Collection System
- Gravity

- Creek
- State Boundary
- Navigation Channel
- Parcel Boundary

Note:
WLSSD = Western Lake Superior Sanitary District

N

0 400 800
Feet

Figure 1A
2018 Proposed Sample Locations
Munger Landing
St. Louis County, Minnesota

ch2m

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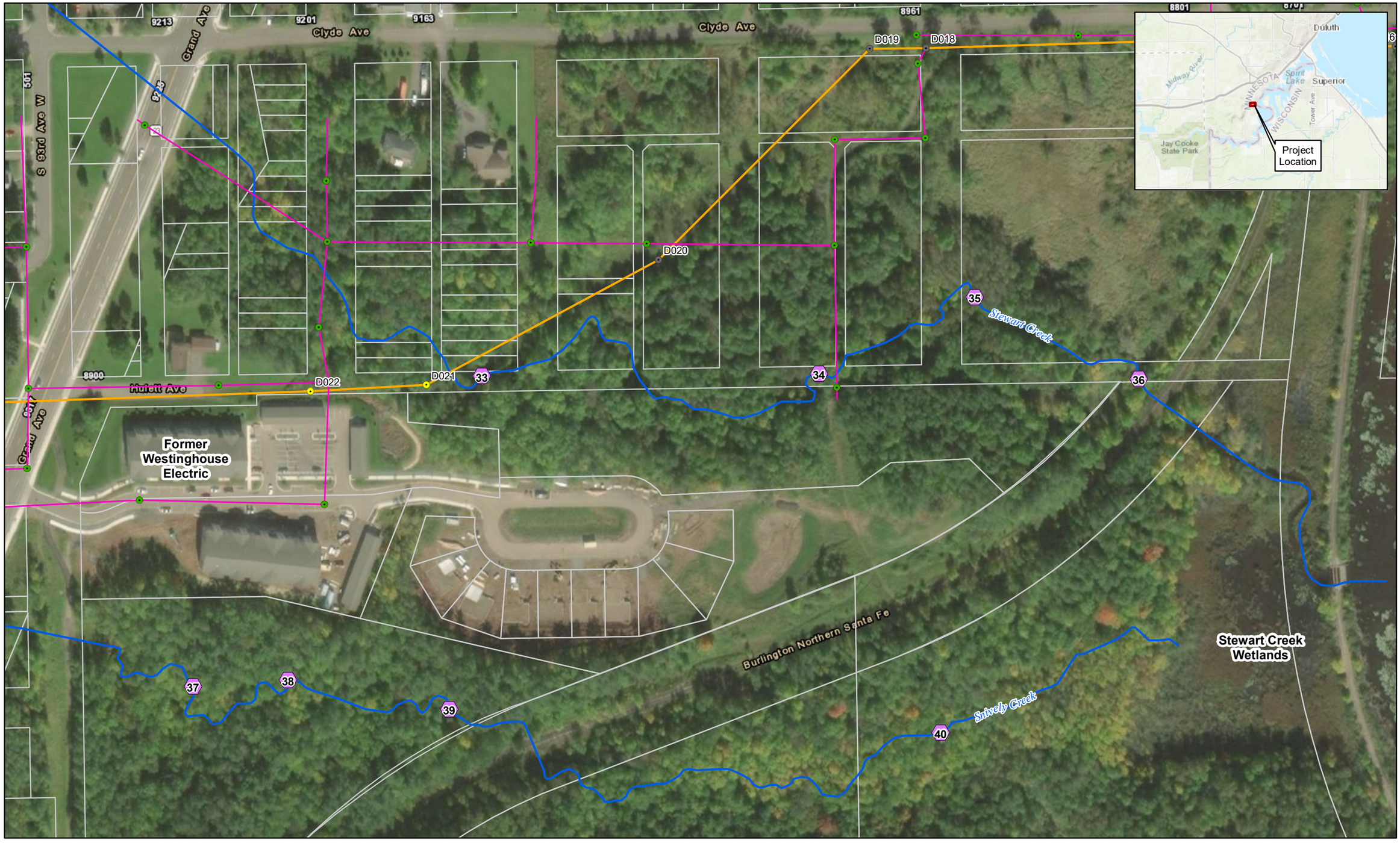

Legend

- Proposed Sample Location
- City Manhole
- City Sewer

WLSSD Manholes

- Drop
- Standard

WLSSD Collection System

- Gravity
- Creek
- Parcel Boundary

Note:
WLSSD = Western Lake Superior Sanitary District

N

0 150 300
Feet

Figure 1B
2018 Proposed Sample Locations
Munger Landing
St. Louis County, Minnesota

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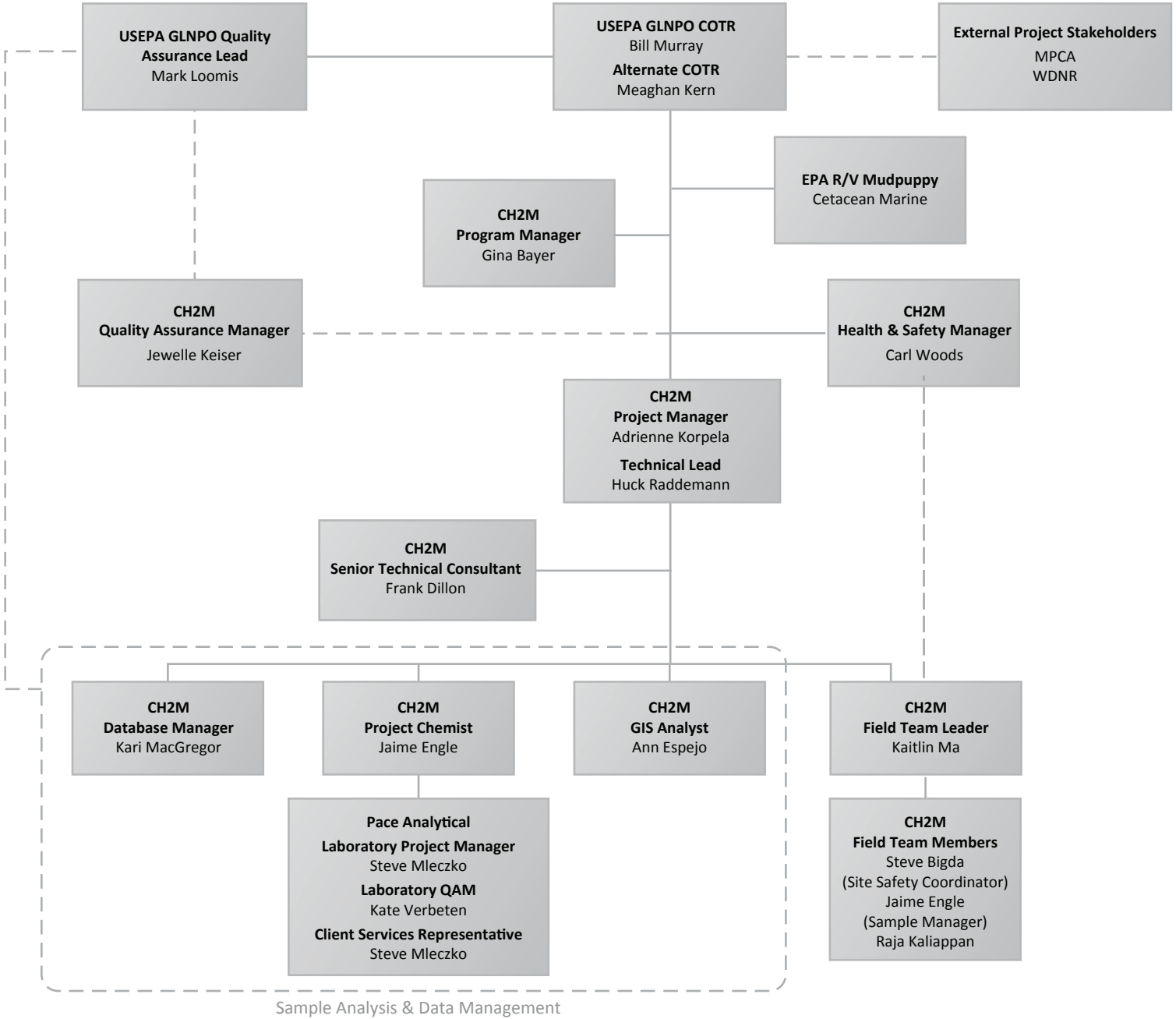

Figure 2
Project Organizational Structure
Munger Landing, St. Louis River AOC

Appendix A
Analytical Laboratory
Standard Operating Procedures

Standard Operating Procedure

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TITLE: CHLORINATED HERBICIDE ACIDS BY GAS CHROMATOGRAPHY (EPA METHODS 8151A, 615 & 1658)

Reviewed by: Blake Judge, Steve Miller

Department Manager *QA Department*

1.0 SCOPE AND APPLICATION

STATE NOTE: For samples analyzed in conjunction with the Ohio Voluntary Action Program (VAP) please utilize SOP# 330320OH.

1.1 This standard operating procedure describes a gas chromatographic method for the determination of chlorinated herbicides. It is used for waste samples, waters, soils, sediments, and other solid samples as per EPA methods 8151A, 615 and 1658. Compounds analyzed by this method and their typical reporting limits are found below (subject to change).

Analyte	Soil mg/kg	Water mg/L
Dalapon	0.8	0.002
Dicamba	0.07	0.002
MCPP	6.5	0.05
MCPA	6.5	0.05
Dichloroprop	0.07	0.002
2,4-D	0.07	0.002
2,4,5-TP (Silvex)	0.07	0.002
2,4,5-T	0.07	0.002
2,4-DB	0.07	0.002
Dinoseb	0.07	0.002
Pentachlorophenol	-	0.001

1.2 An MDL study must be completed at least annually or more frequently if major instrumentation changes occur. Method Detection Limits (MDLs) are performed based on ESC SOP #030206. Updated MDL records are filed and stored on ESC's intranet.

1.2.1 Limit of Detection (LOD) and Limit of Quantitation (LOQ) studies are completed at the frequency required by the TNI standard per the procedure identified in the ESC SOP #030206, *Method Detection Limits (MDL), Limits of Detection (LOD) and Limits of Quantitation (LOQ).* Should the procedure be utilized for DOD support; then the frequency of these studies must meet the requirements of the current DOD QSM (see Attachment II).

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Standard Operating Procedure

TITLE: CHLORINATED HERBICIDE ACIDS BY GAS CHROMATOGRAPHY (EPA METHODS 8151A, 615 & 1658)

1.3 Only experienced analysts are permitted to work with diazomethane generation due to the potential hazards linked with its use (explosive and carcinogenic).

2.0 METHOD SUMMARY AND DEFINITIONS

2.1 This procedure provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides in water, soil, and waste samples.

2.2 Samples are extracted with diethyl ether and converted to methyl esters using diazomethane. The derivatized esters are determined by gas chromatography using an electron capture detector.

2.3 Derivative – A compound that can be created from another compound, if one atom is replaced with another atom or group of atoms.

2.4 Ester – An organic compound in which an organic group replaces a hydrogen atom (or more than one) in a hydroxyl group. This is usually a condensation reaction of an acid and an alcohol, but may also be produced in other ways.

2.5 Esterification – the general name for a chemical reaction in which two chemicals form an ester as the reaction product.

2.6 Hydrolysis – A chemical reaction or process in which a chemical compound reacts with water. In organic chemistry this is the opposite of condensation.

2.7 See the current Quality Assurance Manual for other definitions associated with terms found in this document.

3.0 HEALTH AND SAFETY

3.1 The toxicity or carcinogenicity of each reagent used in the laboratory has not been fully established. Each chemical must be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of safety data sheets (SDSs) is made available on ESC's intranet to all personnel. Use hazardous reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing protocols.

3.2 Use safety glasses and gloves when handling acids, bases and when generating diazomethane. Diazomethane is a carcinogen and can explode under certain conditions.

3.3 IMPORTANT - When using diazomethane:

- Use a safety screen
- Perform all possible operations in a well-ventilated hood.
- Use pipette bulbs
- Do not heat above 90^{o} C
- Avoid grinding surfaces, ground glass joints, and glass stirrers – prevent scratching/etching of glassware
- Store away from alkali metals

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Standard Operating Procedure

TITLE: CHLORINATED HERBICIDE ACIDS BY GAS CHROMATOGRAPHY (EPA METHODS 8151A, 615 & 1658)

3.4 Ethyl ether is an extremely flammable solvent. If a mechanical device is used for sample preparation, the device must be equipped with an explosion-proof motor and placed in a hood to avoid possible damage and injury due to an explosion.

3.5 Waste generated from the procedure needs to be disposed according to ESC policy and by local, state and federal law.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

4.1 All samples must have been collected using a sampling plan that addresses the considerations of this method.

4.2 The holding time for soils, sludge and waste samples is 14 days from collection to extraction then analyzed within 28 days of extraction. The holding time for waters is 7 days of collection to extraction then analyzed within 28 days of extraction. Extracts must be stored under refrigeration at $4 \pm 2^{o}C$.

4.3 Collect water samples in a 1L amber glass container with a Teflon lined lid. If residual chlorine is suspected to be present, add 3mL of 10% sodium thiosulfate per gallon of sample collected. Soils/Sediments and sludge samples should be collected in a 250mL wide-mouth glass container with a Teflon lined lid. Concentrated waste should be collected in a 125mL wide-mouth glass container with a Teflon lined lid.

4.4 Samples submitted for analysis that do not meet the requirements contained within this section must be addressed before performing the logging process within the laboratory. In some cases, exceeding the appropriate preservation and storage criteria can cause significant bias in the resulting data. Clients may need to resubmit samples where the conditions during shipment cause uncertainty regarding sample integrity. If samples do not meet the requirements for preservation, sampling, shipment and storage and the client approves the completion of the analytical process, sample results can be qualified per the ESC SOP #030201, *Data Handling and Reporting*.

5.0 INTERFERENCES

5.1 Method interferences can be caused by contaminants in solvents, reagents, laboratory glassware, or sampling equipment. These materials must be demonstrated to be free of interferences under analytical conditions by routine analysis of reagent blanks.

5.2 Glassware must be scrupulously cleaned. All glassware must be cleaned per EPA protocol, as stated in SOP #030701, *Glassware Cleaning*. Since herbicides are strong organic acids, they react with alkaline substances and this can result in analyte losses during analysis. Glassware used for herbicide sample preparation must be acid-rinsed and then rinsed with organic-free reagent water to remove the potential for alkaline interference. Sodium sulfate and glass wool, if utilized, must also be acidified.

5.3 Organic acids, especially chlorinated acids and phenols, including chlorophenols, can interfere with the methylation process.

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Standard Operating Procedure

TITLE: CHLORINATED HERBICIDE ACIDS BY GAS CHROMATOGRAPHY (EPA METHODS 8151A, 615 & 1658)

5.4 Matrix interferences can also be caused by contaminants that are co-extracted and the extent of matrix interferences differ significantly from sample to sample, depending upon the nature of sample.

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation (or equivalents):

Instrument name:	SVGC #11
Use (method #'s):	8151A;
Model #:	Agilent 6890
Column (type, brand, size):	RTX–CLPesticides 30m x 0.32mm x 0.5um, RTX-CLPesticides II 30m x 0.32mm x 0.25um
Detector:	Dual Micro ECD
Software name and version:	EnviroQuant Chemstation G1701CA
Software version:	C.01.00
Sample introduction system:	Dual HP 7683 AS
Computer name:	SVCOMPN
Computer brand, and model #:	HP Vectra
Gases used (grade and supplier):	N2 – Zero Grade UHP: H_2 or He (carrier)

6.2 Erlenmeyer flasks - 250 and 500mL Pyrex with 24/40 ground glass joint

6.3 Various sizes of beakers

6.4 Separatory funnel - 2000mL with Teflon stopcock

6.5 Vials 10-15mL with Teflon lined screw caps

6.6 Funnels and glass wool

6.7 Buchi automatic concentrator or equivalent

6.8 Syringes - Hamilton Gastight or equivalent: 1mL, 250uL, 100uL, 10uL

6.9 8, 16, and 40mL vials with Teflon lined caps

6.10 Sonicator - Tekmar Model 600, Model 400, or equivalent.

6.11 9" VWR Disposable Pasteur Pipette or equivalent

6.12 10mL Pyrex Disposable Pipette or equivalent

6.13 1.8mL Wheaton ABC Vials with Teflon rubber lined caps or equivalent

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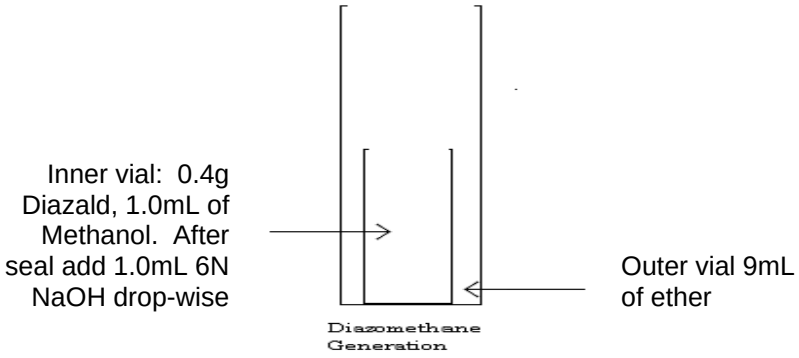
6.14 10mL Pyrex Volumetric Flasks - Class "A" or equivalent.

6.15 Acidified glass wool – place glass wool into breaker, rinse three times with $MeCl_2$, fill breaker with sufficient diethyl ether to cover glass wool, add one drop of sulfuric acid. Mix and allow ether to evaporate.

6.16 Diazomethane generator:



7.0 REAGENTS AND STANDARDS

7.1 All reagents and standards must be recorded in the appropriate preparation log and assigned a unique number. See SOP #030230, *Standards Logger – Tree Operation*. Additional information regarding reagent preparation can be found in the Standards Logger (Tree) digital archive system. All spiking solutions and surrogate standard solutions should be replaced at least every 6 months or sooner if a problem is detected unless otherwise noted.

7.2 Concentrated sulfuric acid (H_2S0_4) - VWR VW6840-3 reagent grade or equivalent

7.3 Concentrated hydrochloric acid (HCl) - EM Science reagent grade or equivalent

7.4 Hydrochloric Acid 1:3 (HCl) - Add 1 volume of HCl to 3 volumes of deionized water. This is used for acid rinsing of glassware

7.5 Potassium Hydroxide 37% (KOH) – Dissolve 37g KOH pellets in deionized water and dilute to 100mL

7.6 Diazald – Aldrich Chemical Co.,

7.7 Diazomethane – ACROS 2M solution (or equivalent)

7.8 Diethyl ether - VWR #VW2142-5 pesticide quality or equivalent (must be peroxide free).

NOTE: Diethyl ether used for this procedure must be stabilized with BHT, not ethanol, as ethanol-stabilized ether can lead to inefficient methylation and low recoveries for target analytes.

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7.9 Acetone - VWR #EM-AX0116-1 pesticide quality or equivalent

7.10 Hexane - VWR #EM-HX0298-1 pesticide quality or equivalent

7.11 Methanol - VWR #EM-MX0480-1 pesticide quality or equivalent

7.12 Methylene Chloride – VWR #EM-DX0831-1 pesticide quality or equivalent

7.13 Isooctane - VWR #EM-TX1389-1 pesticide quality or equivalent

7.14 Sodium Sulfate (anhydrous) (Na_2S0_4) – Bake at 400^oC or pre-clean with $MeCl_2$. Prepare an acidified diethyl ether solution by adding 3-4mL of concentrated sulfuric acid to approximately 800mL of diethyl ether. Slurry 2kg of sodium sulfate by adding the acidified diethyl ether to the Na_2SO_4 in a large baking dish and mix thoroughly using glass rod or glass pipette. Allow ether to evaporate or evaporate under vacuum. Mix 1g of the acidified sodium sulfate with 5mL reagent water and measure the pH. It must be below a pH of 4. If not, re-acidify; if the pH is less than 4, 7.14 Stock standards of acids and esters are ordered from a commercial vendor at a concentration of 100ppm for all target analytes except MCPP and MCPA which are at 1000ppm. Standards must be placed in vials with Teflon lined screw caps and stored at 4^oC. Stock standards must be replaced after six months or sooner if comparison to check standards indicates a problem

7.15 Stock Surrogate Standard - 2,4-Dichlorophenyl acetic acid (DCAA) –Store the stock solution at room temperature and replace the solution after six months or sooner if comparison to check standards indicate a problem. This standard is ordered from a commercial vendor at the concentration of 1000 ppm.

7.16 Calibration Standards – NSI Custom Herbicide Mix in acetonitrile – a minimum of five calibration standards for each parameter of interest must be prepared through the esterification of the target analyte and surrogate stock standards.

Prepare a 10ug/mL intermediate standard with 2mL of custom herbicide mix and 100uL of surrogate stock solution adjusted to 10mL with hexane. (2mL of custom herbicide mix can be combined with 2-3mL acetone before adjusting to final volume of 10mL with hexane since acetonitrile and hexane are not miscible solvents.) 5mL of the 10ug/mL standard is then esterified and adjusted to 10mL by the process described in section 8.4. The concentration of the analytes and surrogate in the esterified intermediate is 5ug/mL. The esterified standard must be given a unique standard number in the Tree Standards Logger to document the esterification process.

Use this solution to produce a minimum of 5 calibration standards at levels that may include but are not limited to 0.02ug/mL, 0.05ug/mL, 0.10ug/mL, 0.20ug/mL, 0.5ug/mL and 1.0ug/mL. These standards are created to have a final volume of 10mL in hexane. The lowest level of the calibration curve must be at or below the RL.

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Standard Concentration (ug/mL)	Intermediate Stock Used
0.02	4.0uL
0.05	10.0uL
0.10	20.0uL
0.20	40.0uL
0.50	100.0uL
1.00	200.0uL

STATE NOTE: For all Minnesota sample analyses, the RL level standard is re-injected and quantitated against the newly updated calibration curve and is evaluated for the ±40% deviation criterion.

7.17 Working Surrogate Spike Solution - 5.0ug/mL in methanol or acetone. Use 1mL of solution for soil and water samples with a final extracted volume of 10mL.

7.18 Working Target Analyte Spike Solution (MS/MSD/LCS/LCSD) - 5.0ug/mL in methanol or acetone. Use 1mL of solution for soil and water samples with a final extracted volume of 10mL.

7.19 10N Sodium hydroxide - Dissolve 400g sodium hydroxide in 1L DI Water.

7.20 Sulfuric Acid 1:3 (H_2SO_4) - Add 1 volume of H_2SO_4 to 3 volumes of deionized water. This is used for adjusting pH.

7.21 Silicic Acid, H_2SiO_5 – 100 mesh powder.

8.0 PROCEDURE

8.1 Preparation of Waste Samples

8.1.1 Transfer 1.0g of sample to a 16mL vial.

8.1.2 Add 1mL of surrogate standard (5ug/mL) and adjust to final volume of 10mL with diethyl ether.

8.1.3 Add 2 grams of acidified sodium sulfate. Cap and shake for 2 minutes. Let sit for 2hrs

8.1.4 Make a funnel with filter paper and acidified Na_2SO_4 and filter samples into concentration vessel. Rinse with ether.

8.1.5 Concentrate to 1mL at 50-60 degrees and then esterify by adding 1mL 2,2,4-T (isooctane) and 0.5mL MeOH and diazomethane up to a final volume of 10mL with Hexane.

8.1.6 Minimum QC for this matrix is 1 blank and LCS/LCSD per batch. All QC must be prepped concurrently with the field samples and be performed using the same procedures.

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8.2 Preparation of soil, sediment, and other solid samples

8.2.1 Extraction:

8.2.1.1 To a 250mL beaker, add 15g of each well mixed sample. Select one sample to be utilized for the MS/MSD pair and prepare 2 additional beakers containing 15g each of this sample.

8.2.1.2 Adjust the pH of each soil sample to <2 by adding 1.0-2.0mL concentrated HCl to each beaker and then mixing with a glass-stirring rod.

8.2.1.3 Prepare blank, LCS and LCSD using 15g of sand to a 250mL beaker for each QC sample.

8.2.1.4 Add acidified sodium sulfate to the field samples in order to obtain a free flowing mixture.

8.2.1.5 Add 0.5mL of surrogate (concentration 5ug/mL) to each sample, including all QC.

8.2.1.6 Add 0.5mL (concentration 5ug/mL) of target analyte spiking solution to each of the LCS, LCSD, MS and MSD samples.

8.2.1.7 Add 50mL of methylene chloride/acetone (1:1 v/v) to each beaker.

8.2.1.8 Sonicate each field and QC sample for 3 minutes on pulse at 50% and output sufficient to mix sample. Rinse probe between samples with methylene chloride.

8.2.1.9 Following sonication, allow the solids to settle then filter the solvent layer through #41 filter paper containing acidified sodium sulfate. Collect the extract in a Buchi vessel.

8.2.1.10 Sonicate the sample two additional times using 50mL of methylene chloride. Filter and combine each additional extract with the original in the Buchi vessel and concentrate to 1-5mL.

8.2.1.11 If concentration and esterification are not done immediately, the extract, at this stage, can be stored in the hood overnight.

8.2.2 Cleanup of non-hydrolyzed herbicides if the analysis is for acids only.

8.2.2.1 Transfer the methylene chloride extracts (from section 8.2.1.13) to clean separatory funnels and extract the organic phase solution 3 times with 15mL each of diluted KOH solution prepared using 30mL reagent water and 15mL of 37% KOH. Rotate for 3-5mins each and drain $MeCl_2$ into waste container after the 3rd rotation. Combine the 3 aqueous fractions. At this point the basic aqueous solution contains the herbicide salts.

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8.2.2.2 Add 10-12mL of cold (4°C) 3:1 sulfuric acid to each sample, seal, and shake to mix. Check the pH of the sample with pH paper. If the sample does not have a pH less than or equal to 2, adjust the pH by adding additional 2mL increments until the pH is less than 2.0.

8.2.2.3 Add 40mL of ethyl ether to the sample extract and rotate for 3-5 mins. Repeat twice more with 20mL portions of ethyl ether. Drain the water layer into waste after the 3rd rotation. Combine the solvent layers from each rotation into washed flask containing 10g of acidified anhydrous sodium sulfate.

8.2.2.4 Allow the extract and the acidified sodium sulfate to remain in contact for minimum of 2 hours, with periodic shaking, to sufficiently dry the sample. This drying step is critical to ensure complete esterification. Any moisture remaining in the ether can result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask.

8.2.2.5 If concentration is not performed immediately, the extract, at this stage, can be stored in the refrigerator overnight or in a hood.

8.2.3 Extract concentration

8.2.3.1 Transfer each ether extract into a Buchi vessel. If water appears present, filter the extract through acidified sodium sulfate in a gravity funnel plugged with acid washed glass wool. Use a glass rod to crush caked sodium sulfate during the transfer.

8.2.3.2 Rinse each flask with 20-30mL of ether and pour into the appropriate Buchi vessel.

8.2.3.3 Concentrate each sample 1mL of ether and proceed to section 8.4. Please see SOP #330708, *Buchi Syncore Concentration System*.

8.3 Preparation of Aqueous Samples

8.3.1 Extraction

8.3.1.1 Pour 1000mL of each sample into a clean 2 liter separatory funnel. A smaller volume of sample can be used and diluted to one liter with DI water if necessary. If sufficient sample volume is provided by the client, one sample can be prepared in triplicate, with one aliquot acting as the actual sample and the remaining two as the MS/MSD pair.

If preparing a TCLP sample, use 100mL of sample and bring to a final volume of 1000mL with DI water. Additional TCLP Blank and MS/D is added to WG.

8.3.1.2 Pour 1000mL of reagent water to each of 3 separatory funnels for use as the blank, LCS and LCSD samples.

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8.3.1.3 Add 1mL of surrogate to each field and QC sample.

8.3.1.4 Add 1mL of target analyte spiking solution to each funnel containing the LCS, LCSD, MS and MSD, if available.

8.3.1.5 Add 250g of NaCl to each funnel, seal, and shake to dissolve the salt.

8.3.1.6 Add 10-12mL of cold (4°C) 3:1 sulfuric acid to each sample, seal, and shake to mix. Check the pH of the sample with pH paper. If the sample does not have a pH less than or equal to 2, adjust the pH by adding additional 2mL increments until the pH is less than 2.0.

8.3.1.7 Add 120mL diethyl ether to each sample, seal and rotate for 3-5 minutes with periodic venting to release pressure.

8.3.1.8 Allow the organic layer to separate from the water phase. If the emulsion interface between the two layers is more than one-third the volume of the solvent layer, employ mechanical techniques to complete the separation.

8.3.1.9 Drain the (lower layer) aqueous layer into the original sample bottle or other container and collect the ether phase (top layer) in an acid washed 500mL Erlenmeyer flask containing approximately 10g of acidified sodium sulfate. Periodically swirl the flask and drying agent. Foil may be used to cap the flask.

8.3.1.10 Repeat this extraction procedure twice more with 60mL portions of ethyl ether. Combine all collected ether fractions in the 500mL Erlenmeyer flask.

8.3.1.11 Allow the extract and the sodium sulfate to remain in contact for minimum of 2 hours, with periodic shaking, to sufficiently dry the sample. This drying step is critical to ensure complete esterification. Any moisture remaining in the ether can result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask.

8.3.1.12 If concentration is not performed immediately, the extract, at this stage, can be stored in the refrigerator/hood overnight.

8.3.1.13 Transfer and concentrate the extract as found in 8.2.3.

8.4 Esterification

8.4.1 To each sample extract, add 0.5mL of methanol and 1mL of 2,2,4-Trimethylpentane (Isooctane).

8.4.2 Prepare the diazomethane generator (figure, 6.16) by adding 9mL of diethyl ether to a clean, dry, unscratched 40mL vial.

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8.4.3 Add 0.38-0.42g of Diazald to an 8mL vial; place the tube into the large vial containing the ether. Using a syringe/pipetter, add 1.0mL methanol to Diazald, then seal the vial.

8.4.4 Place the apparatus in hood. DO NOT ALLOW EXPOSURE TO GENERATED TOXIC GASES.

8.4.5 Using a syringe, puncture the septum and slowly add 1mL 10N NaOH drop wise into the reagent tube. Gas evolution is obvious. Note pressure in the vial could eject the plunger from the syringe. Remove the syringe and check for leaks. (A drop of water placed at the puncture point can verify re-sealing of the vial.

8.4.6 Allow at least 20 minutes to complete: then carefully – under the hood remove the vial cap. There should be some pressure in the vial. The ether should be yellow from the diazomethane present. Remove the inner reaction tube. Place inner tube into water to destroy remaining Diazald and add silicic acid. Diazald reagent is good for only 7 days and must be stored in freezer.

8.4.7 If generating more than one vial of diazomethane, combine the all the vials contents prior to use. Add at least 2.0mL of diazomethane reagent to extracts or enough to turn extract yellow – sample may need to be blown down again. Allow 10 minutes for the reaction to complete.

8.4.8 Alternatively to steps 8.4.2-8.4.7, 0.5ml-2.0ml aliquots of premade 2M Diazomethane can be added to each extract for esterification.

8.4.9 After esterification, ~ 0.1 to 0.2grams of Silicic acid may be added to each extract to destroy any un-reacted diazomethane in the sample. This causes the generation of nitrogen gas in the extract. Allow the extracts to stand until the evolution of nitrogen gas has stopped.

8.4.10 Adjust each water sample extract in a volumetric flask to 10mL with hexane. Adjust each soil sample extract in a volumetric flask to 5mL with hexane. Sample is now ready for analysis.

8.5 Gas Chromatographic Conditions

8.5.1 Column used for this analysis is an RTX - CL Pesticides, 30m x 0.32mm ID, 0.5um film thickness or a SPB-608 or RTX – CL Pesticides 2, 30m x 0.32mm ID, 0.25um film thickness may also be utilized. Any equivalent column can be used that can provide adequate sensitivity and performance.

8.5.2 Column conditions used include the following, but can be altered to improve method performance or better meet project requirements; See Cyberlab and/or maintenance log for specifics:

- Initial temperature - 80°C, hold 1.0 minute
- Temperature program - Final 260°C, 10°C/min
- Injector - 200°C

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- Detector - 300°C

STATE NOTE: For all Minnesota sample analyses, the RL level standard will be re-injected and quantitated against the newly updated calibration curve and is evaluated for the ±40% deviation criterion with the exception of the listed poor performers in this procedure. 8.6 Initial Calibration: Instrument maintenance must be performed routinely to optimize instrument performance and improve chromatography. Commonly performed maintenance includes changing of the injection port liner and clipping the column at the injection port end to eliminate active sites. A new calibration curve may be analyzed following any major maintenance performed on the analytical system if validation of most current calibration does not confirm within method criteria.

8.6.1 The calibration standards prepared in section 7.15 are injected into the optimized GC. The computer program generates a calibration curve using either calibration factors or linear regression. If the percent relative standard deviation (% RSD) of the calibration factors for each analyte is less than 20%, the average calibration factor can be used in place of a curve regression model for quantitation. If the %RSD exceeds 20%, a calibration curve using linear regression is employed. The linear regression calibration curve must have a correlation factor of 0.990 or greater (USACE requires 0.995 or better) using equal or inverse weighting. The origin may not be used as a point in the calibration curve and the curve must not be forced through zero.

8.6.2 The deletion of the highest point is acceptable when necessary, with the analyst noting that the high end of the calibration has been lowered. The deletion of the lowest calibration point is acceptable, when necessary, provided that the analyst notes the deletion on the injection log and raises the reporting limit, if necessary, for that compound.

8.6.3 Second Column Confirmation: Any sample that shows a detectable concentration of any compound above the method detection limit must be confirmed on a second column or by GC/MS. (MCPA/MCPP is recommended to be confirmed by GCMS for positive detection). Calibration criteria must be met on both columns for positive confirmation of target analytes. The result from the primary column and the confirmation column should agree within 40% RPD.

8.6.4 Second Source Calibration Verification (SSCV): The initial calibration curve generated must be verified using a source that is different from the stock solutions used to prepare the calibration curve. This source can be a separate manufacturer or separate lot number from the same manufacturer, if available. The second source verification is performed at the mid-range of the calibration curve, but the concentration may be altered to better reflect client/project needs. The calibration factor for the SSCV is calculated using the equation found in section 9.1 and the difference from the initial calibration curve can be determined using the equation found in section 9.3.

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8.6.5 A retention time window for each compound in the calibration mix must be established. To determine the retention time window, make three injections of the calibration standard mix solution over a 72-hour period. The retention time window shall be defined as +/- three standard deviations of the mean absolute retention time established during the 72-hour period for each component in the calibration mix. The typical default retention times are set at +0.05 minutes. The experience of the analyst should weigh heavily on the interpretation of chromatograms. If the standard deviation for a component is zero, the standard deviation of a closely eluting compound should be used to determine a valid retention time window. Retention time windows should be recalculated whenever a new column is installed or major instrument maintenance is performed.

8.7 Initial and Continuing Calibration Verification: The initial calibration of the analytical system must be verified at least once for every 12 hour shift when an initial calibration curve is not analyzed. A calibration standard is injected initially, then after every 10 samples and at the conclusion of the analytical sequence.

8.7.1 The calibration factor for the (ICV/CCV) is determined using the calculation found in section 9.1 and then the percent difference from the initial calibration curve is determined using the calculation in section 9.3.

8.7.2 The ICV/CCV is routinely at the mid-level concentration of the calibration standard; however other concentrations may be used to better meet client or regulatory requirements.

8.8 For acceptance criteria and corrective actions, see sections 10.0 & 11.0.

9.0 DATA ANALYSIS AND CALCULATIONS

See the current Quality Assurance Manual for equations associated with common calculations.

10.0 QUALITY CONTROL AND METHOD PERFORMANCE

10.1 All analysts must meet the qualifications specified in SOP #030205, *Technical Training and Personnel Qualifications* before approval to perform this method. Analysts must complete an initial demonstration of proficiency before being approved to perform this method. Continuing proficiency must be demonstrated using proficiency testing, laboratory control sample analysis and/or proficiency testing (PT) studies. Method performance is assessed per analyst. Updated method performance records are filed and stored on ESC's intranet.

10.2 Use the designated Run log to record batch order and standards/reagents used during analysis. See SOP #030201, *Data Handling and Reporting*.

10.3 Batches:

Batches are defined as sets of 1 - 20 samples. Batch analysis must include the following: 1 method blank, 1 Initial Calibration Verification (ICV), 1 Laboratory Control

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Sample/Laboratory Control Sample Duplicate pair (LCS/LCSD), 1 Matrix Spike/Spike Duplicate (MS/MSD) pair, 1 Continuing Calibration Verification (CCV) every 10 samples, 1 CCV at end of run. Exceptions are made for waste dilution samples where the minimum batch QC must include a blank, an LCS/LCSD pair, 1 Continuing Calibration Verification (CCV) every 10 samples, 1 CCV at end of run.

10.4 Initial Calibration – For EPA Methods 8151A and EPA 1658, if the percent relative standard deviation (% RSD) of the calibration factors for each analyte is less than 20%, the average calibration factor can be used in place of a curve regression model for quantitation. For EPA Methods 615, if the percent relative standard deviation (% RSD) of the calibration factors for each analyte is less than 10%, the average calibration factor can be used in place of a curve regression model for quantitation. If the %RSD exceeds the previous acceptance ranges, a calibration curve using linear regression is employed. The linear regression calibration curve must have a correlation factor of 0.990 or greater with equal or inverse weighting. The origin may not be used as a point in the calibration curve and the curve must not be forced through zero.

10.5 Second Source Calibration Verification - A second source calibration verification standard (SSCV) is analyzed after each calibration and must meet criteria of +/- 20% of the expected concentration for each analyte.

10.6 Initial/Calibration Check Standard (ICV/CCV) - On days when a full calibration is not needed, an ICV must be analyzed prior to the analysis of any QC or field samples. Additionally, a CCV must be analyzed following every 10 sample extracts and at the end of the analytical sequence.

- The CF for EPA 8151A and EPA 1658, the ICV/CCV must be within 15% of the initial calibration.
- The CF for EPA 615, the ICV/CCV must be within 10% of the initial calibration.

10.7 Method Blank - A method blank must be extracted and analyzed with each set of samples. The blank must be carried through the same procedure as the samples and must not contain target analytes above the method detection limit.

10.8 Matrix Spike (MS) And Matrix Spike Duplicate (MSD) - must be performed with each batch of samples, where sufficient volume is submitted by the client. The spike and spike duplicate must meet ESC acceptance criteria.

10.9 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD) - must be extracted with each batch of samples. The control must be within current ESC acceptance criteria presented in the LIMS.

10.10 Confirmation - Any sample that shows a detectable concentration of any compound above the method detection limit must be confirmed on a second column or by GC/MS. Acceptable calibration criteria must be met on both primary and secondary columns. The results from the primary column and the confirmation column should agree within 40% RPD. If agreement is not achieved within acceptable criteria, the judgment of the analyst

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must be used to determine the source of the discrepancy (i.e. co-elution, interference on either column, etc.). Generally, results from the primary column are used for reporting.

10.11 Surrogate Recovery - Calculate the surrogate recovery on all samples, blanks, and spikes. Determine if the recovery is within acceptable limits.

10.12 QC Limits – See the LIMS (limits subject to change – based on historical data)

10.13 RLV – The reporting limit verification when analyzed must recover within ±50% of the target concentration for the standard.

STATE NOTE: For all samples analyzed from Minnesota, the reporting limit must be verified at least monthly. The reporting limit verification (RLV) must recovery within ±40% of the expected concentration. If these criteria are not met, the RLV may be re-analyzed once, instrument maintenance can be performed or a higher concentration standard can be analyzed. If a higher concentration standard is utilized, the reporting limit must be raised to the higher level verified.

10.14 Any sample analyte responses that are beyond the linear range of the calibration curve must be diluted and re-analyzed.

10.15 Manual Integration – All manual integrations must comply with the requirements found in ESC SOP #030215, *Manual Integration Procedure*. Before and after integrations must be available for review by the secondary data reviewer.

10.16 For corrective actions, see section 11.0.

11.0 DATA VALIDATION AND CORRECTIVE ACTION

11.1 The analyst must verify that all reported results are derived from analytical results that are above the reporting limit and below the highest standard of the initial calibration. Verify the results are reported as follows:

Sample concentrations that have been analyzed using the maximum amount of sample and are below the reporting limit, are reported as <RL. The reporting limit must be appropriately compensated for any dilutions performed.

11.2 All data must undergo a second analyst review. The analyst checking the data must check the performance of the initial calibration, mid-point check standard and continuing calibrations to ensure that they meet the criteria of the method.

11.2.1 The analyst should must review any sample that has quantifiable compounds and make sure that they have been confirmed.

11.2.2 All calculations must be checked.

11.2.3 All surrogate recoveries must be checked to ensure that they are within limits or that corrective action has occurred.

11.2.4 Blanks must be free of all interfering peaks above 1/2RL.

11.2.5 Quality control criteria must be checked for the LCS, LCSD, MS, and MSD.

11.2.6 Data must be checked to determine the need for appropriate flags. Comments are noted when results are flagged.

11.2.7 The reviewer must verify all reported results are derived from analytical results that are above the reporting limit and below the highest standard of the initial calibration curve.

11.2.8 All manual integrations must be verified through checking the before/after shot of the sample and/or QC.

11.2.9 All multipliers/dilutions must be verified on the quant report and must agree with the information provided on the injection log.

11.2.10 Retention times of the samples must be compared to that of the calibration standard. Random spot checking of 10% of the data should be sufficient.

11.2.11 Verify linear regression by reviewing the calibration curve printout.

11.2.12 See SOP #030201, *Data Handling and Reporting*.

11.3 Method Blank - If the blank shows any detectable amount greater than the RL, the laboratory performance is assumed to be out of control and the problem must be corrected. Corrective actions include: re-analysis once. If the failure persists, re-extract the entire batch of samples, if submitted sample volume permits, or, if acceptable to the client, the data may be flagged with a "B".

General guidelines for qualifying sample results with regard to method blank quality are as follows:

- If the method blank concentration is less than the MDL and sample results are greater than the RL, then no qualification is required.
- No qualification is necessary when an analyte is detected in the method blank but not in the associated samples.
- If the concentration in a sample is more than ten times the concentration in the method blank, then no qualification is required.
- If the method blank concentration is greater than the MDL but less than the RL and sample results are greater than the MDL, then qualify associated sample results to indicate that analyte was detected in the method blank.
- If the method blank concentration is greater than the RL, further corrective action and qualification is required. An analyst should consult their supervisor for further instruction.

11.4 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD) - If the control does not perform within current ESC limits, the laboratory performance is assumed to be out of control and the problem must be corrected, if the failures occur in target analytes of interest. No LCS failures are permitted with this analysis. LCS or LCSD samples that do not pass the acceptable QC criteria must be re-analyzed.

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Corrective action can include re-analysis, if instrument malfunction is suspected, or re-preparation and re-analysis of the entire batch, if the failure is suspected as either extraction or sample related.

STATE NOTE: For all samples analyzed from South Carolina, the LCS/LCSD recovery must be evaluated within 70-130% for both soil and water matrices with an RPD of <20%.

11.5 Initial/Calibration Check Standard (ICV/CCV) - When the initial or continuing calibration verification is out of the acceptance criteria and analysis of a second consecutive (immediate) calibration verification fails to produce results within acceptance criteria, corrective actions shall be performed. The laboratory shall demonstrate acceptable performance after the final round of corrective action with two consecutive calibration verifications, or a new initial instrument calibration shall be performed.

11.5.1 The value of the CCV can exceed acceptance criteria for a single compound provided that all samples in the analytical batch are BDL (below detection limit). Where failures occur above the criteria, the instrument must be evaluated to determine the cause and corrective action taken. If the CCV is below the acceptance criteria, all samples from the last passing CCV through the failed CCV must be reanalyzed. A new calibration curve must be analyzed if corrective action does not result in a passing calibration standard.

11.6 Confirmation - If the relative percent difference of the results exceeds 40% and one result is significantly higher (e.g., >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or operator) during peak integration. If re-integration is necessary, ESC manual integration procedures must be followed and documented. When confirmation is not within the 40% criteria, unless otherwise specified in an approved project plan, the primary column quantitation is reported, as this is a consistent approach, unless the experience of the analyst or obvious interference is otherwise noted.

11.7 Surrogates - If the recovery is not within ESC current control limits, confirm that there are no errors in the calculations, surrogate solutions and standards. Check the instrument performance. Examine the chromatograms for interfering peaks and integrated areas. Re-calculate the data and/or re-analyze the extract if any of the above checks reveal a problem. Re-extract and re-analyze the sample if none of the above is a problem or flag the data "J1" (surrogate high) or “J2” (surrogate low).

11.7.1 If the sample surrogate is above the acceptable QC range, but the samples are non-detected for all target analytes, flag the sample with a J1 and report. If the surrogate is below the acceptable QC range, re-analyze the sample if the surrogate still fails, re-extract and re-analyze or flag data, if insufficient sample volume was submitted by the client.

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11.8 Second Source Calibration Verification - The SSCV must recover within ±20% (unless stated otherwise). If the acceptance criteria are not met, re-analyze once, if the SSCV fails again, re-prepare the SSCV and/or initial calibration curve.

11.9 Matrix Spike (MS) And Matrix Spike Duplicate (MSD) - If the spike and spike duplicate do not meet current ESC limits, the sample must be flagged as possible matrix interference. When required, matrix spike failures must be flagged with "J5" (high) or "J6" (low), when QC limits are exceeded. If there is an RPD failure, the data is flagged with a "J3".

11.10 Method Reporting Limit – When analyzed, if the MRL does not meet the acceptance criteria, the MRL may be re-analyzed once, instrument maintenance can be performed, a higher concentration standard can be injected, or a new calibration curve must be generated. If a higher concentration standard is utilized, the reporting limit for the field samples must be elevated to the higher level verified. BDL samples may be reported if a high bias is seen in MRL evaluation.

11.11 Due to the large number of compounds being analyzed in many of the EPA methods, there is a likelihood that failures can occur in LCS/LCSD samples. NELAP recognizes this likelihood and adopted the concept of allowable marginal exceedances to account for random failures that can occur; however, in the case of the methods contained in this procedure, marginal exceedances do not apply since the total number of analytes is <11 and no marginal exceedance is allowed by NELAC policy guidelines.

11.12 Data that does not meet acceptable QC criteria may be acceptable for use in certain circumstances.

11.12.1 If a method blank contains an amount of target analyte, but all samples are non-detected, the data may be reported with a "B" flag. If a method blank contains an amount of target analyte, but the samples contain analyte at a level that is 10 times the level present in the method blanks, the data may be reported with a "B" flag.

11.12.2 If the MS/MSD fails in an initial analysis and again upon re-analysis, the data is released with an appropriate qualifier as the failure is accepted as matrix related.

11.12.3 If a calibration verification standard at any level (ICV/CCV/SSCV/MRL etc.) is above the acceptable QC criteria and all samples being bracketed are below the reporting limit, the data is acceptable based on a high calibration bias with undetectable levels in the field samples. Any positive samples require re-analysis.

11.12.4 If the surrogate exhibits high recovery in the field samples and the target analytes in the field samples are below the reporting limit, the data may be released with a J1 qualifier indicating the high bias. If the QC samples (LCS, LCSD, MS, MSD) exhibit a high bias in the surrogate and the field samples are below the reporting limit for the target analyte, the data may be released with a J1 qualifier.

11.12.5 If the target analyte spiked in the quality control samples (LCS, LCSD, MS, MSD) exhibits high recovery and the target analytes in the field samples are below the reporting limit, the data may be released with a J4 qualifier indicating the high bias.

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11.12.6 If the target analyte spiked into the QC pair (LCS/LCSD, MS/MSD) exhibit acceptable recoveries, but high calculated RPD values for precision, and the target analytes in the field sample are flagged with a J3 for the precision beyond acceptable quality control limits.

11.12.7 Sample results can be qualified and possible bias is narrated per the ESC SOP #030201, *Data Handling and Reporting*.

STATE NOTE: Drinking water samples analyzed using this procedure for compliance cannot be qualified.

12.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

12.1 The EPA requires that laboratory waste management practice to be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner. See *ESC Waste Management Plan.*

12.2 See SOP #030302, *Environmental Sustainability & Pollution Prevention*.

13.0 METHOD MODIFICATIONS/CLARIFICATIONS

13.1 Modifications to this method are noted in the body of the text as state notes. Compliance analyses performed in conjunction with specific state requirements must be performed as noted within the specific state(s) listed.

13.2 Adjustments to the concentrations of standards/spiking solutions, standards providers, and quality control are subject to change to better meet client/project/regulatory needs or to improve laboratory method performance.

13.3 Soil samples are sonicated twice. This modification is technically justified via acceptable results for performance evaluation samples, DOCs, MDLs, etc.

14.0 REFERENCES

14.1 *Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivitization*, SW846 Method 8151A, Revision 1, December 1996.

14.2 *The Determination of Chlorinated Herbicides in Municipal and Industrial Wastewater*, EPA Method 615, August 1993.

14.3 *The Determination of Phenoxy-Acid Herbicides in Municipal and Industrial Wastewater*, EPA Method 1658, 1993

14.4 *Determinative Chromatographic Separations*, SW846 Method 8000B, Revision 2, December 1996.

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Attachment I: Revision History

Current Version:

Version	Date	Description of Revisions
18	11/29/2017	Updated per 2017 A2LA audit finding in CAR2872. Changed ESC logo. Revised Attachment II Table 5.

Superseded Versions:

This document supersedes the following:

Version	Date	Description of Revisions
0	8/23/94	Origination
1	8/15/96	
2	2/11/00	
3	8/22/00	
4	10/16/01	
5	4/02/02	
6	7/09/03	
7	7/27/04	
8	12/17/04	
9	5/16/07	Revision to incorporate diazomethane generation and to clarify procedures.
10	2/19/09	Technical and Quality Review and update. Clarified use of ICV/CCV, included state notes, removed redundant information, revised sections 12.0 & 13.0.
11	5/11/12	Technical and Quality Review and update. Revised Attachment II and sections 7.1, 7.16, 8.6.3, 9.2, 10.8, and 12.1; Added state note in sections 1.0, 10.13, and 11.12; Added sections 1.2.1, 2.19 through 2.24, 4.4, 8.6.2, 10.13 through 10.15, 11.10, 11.12 and 13.3; Removed state note in sections 8.6.2 and 11.6.
12	9/24/14	Technical and Quality Review and update. Revised title, state note before section 1.1; Revised sections 1.1, 3.3, 6.1, 6.9, 8.6, 7.1, 7.13, 7.19, 8.1, 8.2.1, 8.2.3, 8.3.1, 8.4, 8.6, 10.4, 10.6, 10.10, 11.5.1, 11.6, 14.2 and 14.3; Added section 8.3.1.1; Removed sections 8.2.1.11, 8.2.2, 8.2.3.2, 8.3.1.6, 8.3.1.11 through 8.3.1.13, 13.1 and 14.4; Removed Attachments II and III and Ohio VAP State Notes.
13	8/19/15	Technical and Quality Review and update. Revised Sections 4.4, 7.1, 7.7, 7.13, 8.2.1.7, 8.2.1.9, 8.2.2.2, 8.2.3.3, 8.4.6, 12.2, and 13.3.
14	11/3/2015	Technical and quality review and revision. Header and signature block revision. Revised Sections 1.2.1, 2.16, 8.2.1.10, 8.2.1.12, 8.6.5, 10.7, 10.8, 10.9, 10.10, 10.11, 10.12, 11.3, 11.4, 11.7, 11.9, and Attachment II. Removed Section 5.5.
15	3/31/2016	Technical and quality review and update. Revised Sections 1.0, 1.1, 1.2.1, 2.4, 2.5, 2.6, 2.7, 6.1, 8.1.5, 8.4.9, 8.6.3, 8.7, 10.13, 11.5, 11.10, 11.11, 11.and 12.7. Deleted Sections 2.8 through 2.25 and 9.1 through 9.8. Added Sections 7.7 and 8.4.8.
16	4/17/2017	Technical and quality review and update. Header and signature block re-formatting. Revised Sections 3.1, 7.14, 8.1.1, 8.1.5, 8.5.1, 8.5.2, 11.5, 14.1, 14.2, 14.3, 14.4, and Attachment II Table 2. Deleted Section 8.3.1.3. Added Section 8.3.1.5.

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Version	Date	Description of Revisions
17	6/12/2017	Technical and quality review and update. Revised Sections 1.2, 8.2.1.1, 8.2.1.3, 8.2.1.5, 8.2.1.6, 8.2.1.7, 8.2.1.1, 8.2.2.1, 8.2.2.2, 8.2.2.3, 8.3.1.7, 8.3.1.9, 8.4.10, and 10.1. Deleted Section 8.2.1.12. Added Section 8.3.1.10 and re-numbered remaining subsections.

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Attachment II: DoD Requirements

1.0 Equipment/Instrument Maintenance

Instrument maintenance must be performed routinely to optimize instrument performance and improve chromatography. Commonly performed maintenance includes cleaning/repairing detector, column clipping/replacement, injector port cleaning/changing liner, etc. A new calibration curve must be analyzed following any major maintenance performed on the analytical system.

2.0 Computer Hardware and Software

Software name and version: HP Chemstation G1701DA or equivalent

3.0 Troubleshooting

Table 1. GC Troubleshooting Guide

Problem	Cause	Treatment
No Peaks	Syringe clogged	Clean or replace syringe
	Detector/Software/Computer failure	Check cables. Restart computer.
	Column Leaks	Use new ferrules.
	Broken Column	If at ends, clip column. If in the middle or multiple sites, replace column.
Peaks too Small	Split too high	Reduce split
	Column connection leaks	Check column installation. Search for leaks. Replace ferrules.
	Injector temperature too low	Check temperature program. Increase injector temperature.
	Dirty ECD	Clean ECD.
Retention Times Change	Gas flow too low or too high	Replace septum. Check gas regulator.
	Oven temperature unstable	Check temperature program. Check temperature with external thermometer.
	Column blocked	Compare flow at column entrance to outlet. Replace column.
Constantly Rising Baseline	Leak at column entrance or injection septum.	Check column installation; search for leaks; replace ferrules.
	Injector contaminated.	Make a run at lower injector temperature; if the baseline improves, replace liner, use low bleed or high temperature septa.
	Column contaminated.	Cut two turns from column entrance; rinse column with solvent (only chemically bonded phases); otherwise replace column or use guard column.
	Detector contaminated.	Clean detector.
	Increase of temperature too fast.	Decrease temperature gradient and end temperature.

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Table 1. GC Troubleshooting Guide

Problem	Cause	Treatment
	Poor gas quality.	Use gas grades recommended for GC; for longer supply lines from gas source to GC use gas purification cartridges directly connected to the GC.
Increasing Baseline at High Temperatures	Decomposition of the stationary phase.	Check for leaks; matrix check for compatibility with the column.
	Column contaminated.	Cut two turns from column entrance; rinse column with solvent (only chemically bonded phases); otherwise replace column or use guard column.
	Increase of temperature too fast / end temperature too high.	Decrease temperature gradient and end temperature.
	Column not properly conditioned.	Condition column according to manufacturers' instructions (while column is not connected to the detector).
	Detector contaminated	Clean detector according to manufacturers' instructions.
	Poor gas quality.	Use gas grades recommended for GC; for longer supply lines from gas source to GC use gas purification cartridges directly connected to the GC.
Plateaus at Certain Temperatures	Steps in temperature program too drastic.	Avoid very short and strong heating periods.
Fronting	Column overload.	Decrease injection volume; dilute sample.
	Sample vaporizes too slowly, not evenly or condenses.	Increase injector temperature (consider max. temperature limits of the column).
	Analytes coelute.	Change temperature program or use column with different selectivity.
	Sample decomposes.	Check temperature program, oven temperature (external thermometer); if analytes are not temperature-stable, reduce injector temperature; replace liner.
	Column absorbs or decomposes analytes.	Check capillary ends; check intact deactivation using the test mixture; for poor results shorten both column ends by about 10 cm; or replace column; if column test does not show any defects: a) use a column with thicker film b) use phase with better deactivation c) use column with special selectivity.

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Table 1. GC Troubleshooting Guide

Problem	Cause	Treatment
Tailing	Sample vaporizes too slowly, not evenly or condenses.	Increase injector temperature (consider max. temperature limits of the column).
	System leaks.	Check column installation; search for leaks; replace ferrules.
	Analytes coelute.	Change temperature program or use column with different selectivity.
	Sample decomposes.	Check temperature program, oven temperature (external thermometer); if analytes are not temperature-stable, reduce injector temperature; replace liner by a deactivated one.
	Column absorbs or decomposes analytes.	Check capillary ends; check intact deactivation using the test mixture; for poor results shorten both column ends by about 10 cm; or replace column; if column test does not show any defects: a) use a column with thicker film b) use phase with better deactivation c) use column with special selectivity.
	Split rate too low.	Increase split rate.
	Column overload.	Decrease injection volume; dilute sample.
Split Peaks	Solvent and column not compatible.	Change solvent or use guard column.
	Solvent mixtures with large differences in boiling point and polarity.	Use just one solvent.
	Sample decomposes.	Check temperature program, oven temperature (external thermometer); if analytes are not temperature-stable, reduce injector temperature; replace liner by a deactivated one.
	Analytes coelute.	Modify temperature program or use longer column; possibly change column polarity.
	Detector overload.	Inject less; control make-up flow.

4.0 Other Requirements

4.1 All hardcopy laboratory notebooks must be reviewed by the Supervisor, or their designee, on a monthly basis.

4.2 If not self-explanatory (e.g., a typo or transposed number), corrections to technical and quality records shall also include a justification for the change.

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4.3 A person performing a manual integration must sign and date each manually integrated chromatogram and record the rationale for performing manual integration. Electronic signatures are acceptable.

4.4 The results of calibration and verification of support equipment must be within the specifications required of the application for which this equipment is used or the equipment must be removed from service until repaired. Calibration and verification records, including those of established correction factors, must be maintained. In the absence of method-specific requirements, the minimum requirements are as follows:

Table 2. Support Equipment Checks

Performance Check	Frequency	Acceptance Criteria
Balance calibration check [Using two standard weights that bracket the expected mass]	Daily prior to use	Top-loading balance: ±2% or ±0.02g, whichever is greater Analytical balance: ±0.1% or ±0.5 mg, whichever is greater
Verification of standard mass [Using weights traceable to the International System of Units (SI) through a NMI	Every 5 years	Certificate of Calibration from ISO/IEC 17025 accredited calibration laboratory
Monitoring of refrigerator/freezer temperatures	Daily (i.e. 7 days per week) [use MIN/MAX thermometers or data loggers equipped with notification of out of control event capabilities if personnel not available to record daily]	Refrigerators: 0˚C to 6˚C Freezers: ≤-10˚C
Thermometer verification check [Using a thermometer traceable to the SI through an NMI] [Performed at two temperatures that bracket the target temperature(s). Assume linearity between the two bracketing temperatures.] [If only a single temperature is used, at the temperature of use]	Liquid in glass: Before first use and annually Electronic: Before first use and quarterly	Apply correction factors or replace thermometer
Volumetric labware	Class B: By lot before first use Class A and B: Upon evidence of deterioration	Bias: Mean within ±2% of nominal volume Precision: RSD ≤1% of nominal volume (based on 10 replicate measurements)
Non-volumetric labware [Applicable only when used for measuring initial sample volume and final extract/ digestates volume]	By lot before first use or upon evidence of deterioration	Bias: Mean within ±3% of nominal volume Precision: RSD ≤3% of nominal volume (based on 10 replicate measurements)

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Table 2. Support Equipment Checks

Performance Check	Frequency	Acceptance Criteria
Mechanical volumetric pipette	Quarterly	Bias: Mean within ±2% of nominal volume Precision: RSD ≤1% of nominal volume (based on minimum of 3 replicate measurements) [Note: for variable volume pipettes, the nominal volume is the volume of use]
Glass microliter syringe	Upon receipt and upon evidence of deterioration	General Certificate of Bias & Precision upon receipt Replace if deterioration is evident
Drying oven temperature check	Daily prior to and after use	Within ±5% of set temperature
Water purification system	Daily prior to use	See method blank criteria given in Section 4.20 of this addendum

4.5 The expiration date of the prepared standard shall not exceed the expiration date of the primary standard. All containers must bear a preparation date.

4.6 To avoid preparing non-representative samples, the laboratory shall not "target" within a relatively small mass range (e.g., 1.00 ± 0.01g) because such targeting will produce non-representative subsamples if the sample has high heterogeneity. The laboratory shall not manipulate the sample material so the sample aliquot weighs exactly 1.00g ± 0.01g, as an example.

4.7 In the absence of project-specific requirements, the minimum standard data qualifiers to be used are:

U Analyte was not detected and is reported as less than the LOD or as defined by the customer. The LOD has been adjusted for any dilution or concentration of the sample.

J The reported result is an estimated value (e.g., matrix interference was observed or the analyte was detected at a concentration outside the quantitation range).

B Blank contamination. The recorded result is associated with a contaminated blank.

N Non-target analyte. The analyte is a tentatively identified compound using mass spectrometry or any non-customer requested compounds that are tentatively identified.

Q One or more quality control criteria failed (e.g., LCS recovery, surrogate spike recovery, or CCV recovery).

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Additional data qualifiers may be used, or different letters or symbols to denote the qualifiers listed above, as long as they are appropriately defined and their use is consistent with project-specific requirements (e.g., QSM 5.0, the contract, and project-planning documents).

4.8 If the time of the sample collection is not provided, assume the most conservative time of day. For the purpose of batch processing, the start and stop dates and times of the batch preparation shall be recorded.

4.9 Each preparation method listed on the scope of accreditation must have quarterly LOD/LOQ verifications. However, not all possible combinations of preparation and cleanup techniques are required to have LOD/LOQ verifications. If LOD/LOQ verifications are not performed on all combinations, the laboratory must base the LOD/LOQ verifications on the worst case basis (preparation method with all applicable cleanup steps).

4.10 After each MDL determination, the laboratory must establish the LOD by spiking a quality system matrix at a concentration of at least 2 times but no greater than four times the MDL. This spike concentration establishes the LOD and the concentration at which the LOD shall be verified. It is specific to each suite of analyte, matrix, and method (including sample preparation). The following requirements apply to the initial LOD establishment and to the LOD verifications:

- The apparent signal to noise (S/N) ratio at the LOD must be at least three and the results must meet all method requirements for analyte identification (e.g., ion abundance, second column confirmation, or pattern recognition). For data systems that do not provide a measure of noise, the signal produced by the verification sample must produce a result that is at least three standard deviations greater than the mean method blank concentration. This is initially estimated based on a minimum of four method blank analyses and later established with a minimum of 20 method blank results.
- If the LOD verification fails, then the laboratory must repeat the MDL determination and LOD verification or perform and pass two consecutive LOD verifications at a higher spike concentration and set the LOD at the higher concentration.
- The laboratory shall maintain documentation for all MDL determinations and LOD verifications.
- The DL and LOD must be reported for all analyte-matrix-methods suites, unless it is not applicable to the test or specifically excluded by project requirements.

4.11 The LOD shall be verified quarterly. In situations where methods are setup and used on an infrequent basis, the laboratory may choose to perform LOD verifications on a one per batch basis. All verification data will be in compliance, reported, and available for review.

4.12 For DoD, at a minimum, the LOQ shall be verified quarterly. In situations where methods are setup and used on an infrequent basis, the laboratory may choose to perform LOQ verifications on a one per batch basis.

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4.13 All initial instrument calibrations must be verified with a standard obtained from a second manufacturer prior to analyzing any samples. The use of a standard from a second lot obtained from the same manufacturer (independently prepared from different source materials) is acceptable for use as a second source standard. The concentration of the second source standard shall be at or near the midpoint of the calibration range. The acceptance criteria for the initial calibration verification must be at least as stringent as those for the continuing calibration verification.

4.14 Exclusion of calibration points without documented scientifically valid technical justification is not permitted.

4.15 The concentration of the CCV standard shall be greater than the low calibration standard and less than or equal to the midpoint of the calibration range.

4.16 All CCVs analyzed must be evaluated and reported. If a CCV fails, reanalysis or corrective actions must be taken.

- If a CCV fails, the laboratory can immediately analyze two additional consecutive CCVs (immediately is defined as starting a consecutive pair within one hour; no samples can be run between the failed CCV and the two additional CCVs). This approach allows for spurious failures of analytes to be reported without reanalysis of samples. Any corrective actions that change the dynamics of the system (e.g., clip column, clean injection port, run blanks) requires that all samples since the last acceptable CCV be reanalyzed.
- Both of these CCVs must meet acceptance criteria in order for the samples to be reported without reanalysis.
- If either of these two CCVs fail or if the laboratory cannot immediately analyze two CCVs, the associated samples cannot be reported and must be reanalyzed.
- Corrective action(s) and recalibration must occur if the above scenario fails. All affected samples since the last acceptable CCV must be reanalyzed.
- Flagging of data for a failed CCV is only appropriate when the affected samples cannot be reanalyzed. The laboratory must notify the client prior to reporting data associated with a failed CCV.

4.17 The results of all MS/MSDs must be evaluated using the same acceptance criteria used for the DoD LCS limits (see Addendum Tables 3 and 4) or project limits, if specified. If the specific analyte(s) are not available in the Addendum Tables 3 and 4, the laboratory shall use their LCS in-house limits (see the LIMS) as a means of evaluating MS/MSDs. The MS and MSD must be spiked with all reported analytes.

4.19 Surrogate spike results shall be compared with DoD LCS limits (see Addendum Tables 3 and 4) or acceptance criteria specified by the client. If these criteria are not available, the laboratory shall compare the results with its in-house statistically established LCS criteria (see the LIMS).

4.20 The method blank shall be considered to be contaminated if:

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- The concentration of any target analyte (chemical of concern) in the blank exceeds 1/2 the LOQ and is greater than 1/10th the amount measured in any associated sample, or 1/0th the regulatory limit, whichever is greater;
- The concentration of any common laboratory contaminant in the blank exceeds the LOQ;
- If a method blank is contaminated as described above, then the laboratory shall reprocess affected samples in a subsequent preparation batch, except when sample results are below the LOD. If insufficient sample volume remains for reprocessing, the results shall be reported with appropriate data qualifiers.

4.21 Sporadic Marginal Exceedances are not allowed for target analytes (chemicals of concern as identified by a project) without project-specific approval. Target analytes are considered those few analytes that are critical for the success of a project (such as risk drivers) where sporadic marginal exceedances cannot be allowed. Laboratories should consult with clients whenever long lists of analytes are requested for analysis to determine if marginal exceedances will not be allowed.

4.22 DoD considers the same analyte exceeding the LCS control limit two (2) out of three (3) consecutive LCS to be indicative of non-random behavior, which requires corrective action and reanalysis of the LCS.

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Table 3. LCS Control Limits – Method 8151 Solid Matrix

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
93-76-5	2,4,5-T	1106	84.6	17.7	31	138
93-72-1	2,4,5-TP [Silvex]	1179	86.1	14.3	43	129
94-75-7	2,4-D	1256	86	19.3	28	144
94-82-6	2,4-DB	1030	88.2	17.9	34	142
19719-28-9	2,4-Dichlorophenylacetic Acid	1041	74	15.9	27	122
100-02-7	4-Nitrophenol	208	76.7	20	17	137
50594-66-6	Acifluorfen	206	79.8	18	26	134
1861-32-1	Dacthal (DCPA)	147	72.5	15.6	26	119
1918-00-9	Dicamba	1070	85.2	15.7	38	132
120-36-5	Dichloroprop	1033	91.4	21	28	155
94-74-6	MCPA	935	81.5	17.8	28	135
93-65-2	MCPP	807	88.7	18	35	143

Table 4. LCS Control Limits – Method 8151 Water Matrix

CAS ID	Analyte	N Records	Mean	Standard Deviation	Lower Control Limit	Upper Control Limit
93-76-5	2,4,5-T	1758	94.8	17.5	42	147
93-72-1	2,4,5-TP [Silvex]	2289	92.9	13.8	51	134
94-75-7	2,4-D	2396	98.4	17.7	45	152
94-82-6	2,4-DB	1427	94.1	19.7	35	153
19719-28-9	2,4-Dichlorophenylacetic Acid	905	85	17.7	32	138
100-02-7	4-Nitrophenol	245	89.8	17.4	38	142
50594-66-6	Acifluorfen	262	95.5	16.2	47	144
133-90-4	Chloramben	230	79.5	18.5	24	135
1861-32-1	Dacthal (DCPA)	160	76.2	13.6	36	117
75-99-0	Dalapon	1220	79	20	19	139
1918-00-9	Dicamba	1434	95.3	15.2	50	141
120-36-5	Dichloroprop	1404	102	18.8	46	159
94-74-6	MCPA	1284	89.2	18.2	35	144
93-65-2	MCPP	1137	95.2	20.7	33	157
7085-19-0	Mecoprop	126	97.4	21.2	34	161
87-86-5	Pentachlorophenol	1149	97.5	13.8	56	139

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TITLE: CHLORINATED HERBICIDE ACIDS BY GAS CHROMATOGRAPHY (EPA METHODS 8151A, 615 & 1658)

Table 5. Quality Control Requirements – Organic Analysis by Gas Chromatography

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Breakdown check (Endrin/DDT 8081 only)	Before sample analysis and at the beginning of each 12-hour shift.	Degradation of DDT and Endrin must each be ≤15%.	Correct problem, then repeat breakdown checks.	Flagging is not appropriate.	No samples shall be run until degradation of DDT and Endrin is each ≤15%.
Initial Calibration (ICAL) for all analytes (including surrogates)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	ICAL must meet one of the three options below: **Option 1:** RSD for each analyte ≤ 20%; **Option 2:** linear least squares regression for each analyte: r2 ≥ 0.99; **Option 3:** non-linear least squares regression (quadratic) for each analyte: r2 ≥ 0.99.	Correct problem then repeat ICAL.	Flagging is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic. Quantitation for multicomponent analytes such as chlordane, toxaphene, and Aroclors must be performed using a 5-point calibration. Results may not be quantitated using a single point. No samples shall be analyzed until ICAL has passed.
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA	NA	Calculated for each analyte and surrogate.

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TITLE: CHLORINATED HERBICIDE ACIDS BY GAS CHROMATOGRAPHY (EPA METHODS 8151A, 615 & 1658)

Table 5. Quality Control Requirements – Organic Analysis by Gas Chromatography

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Retention Time (RT) window width	At method set-up and after major maintenance (e.g., column change).	RT width is ± 3 times standard deviation for each analyte RT from the 72-hour study or 0.03 minutes, whichever is greater.	NA	NA	Calculated for each analyte and surrogate. Only applicable if internal standard calibration is not used.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes within established RT windows. All reported analytes within ± 20% of true value.	Correct problem, rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.

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TITLE: CHLORINATED HERBICIDE ACIDS BY GAS CHROMATOGRAPHY (EPA METHODS 8151A, 615 & 1658)

Table 5. Quality Control Requirements – Organic Analysis by Gas Chromatography

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Continuing Calibration Verification (CCV)	Before sample analysis, after every 10 field samples, and at the end of the analysis sequence with the exception of CCVs for Pesticides multi-component analytes (i.e., Toxaphene, Chlordane), which are only required before sample analysis.	All reported analytes and surrogates within established RT windows. All reported analytes and surrogates within ± 20% of true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat the CCV and all associated samples since the last successful CCV. Alternately, recalibrate if necessary; then reanalyze a; associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

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TITLE: CHLORINATED HERBICIDE ACIDS BY GAS CHROMATOGRAPHY (EPA METHODS 8151A, 615 & 1658)

Table 5. Quality Control Requirements – Organic Analysis by Gas Chromatography

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Internal Standards (IS)	If employed, every field sample, standard, and QC sample.	Retention time within ± 0.06 RRT UNITS from retention time of the midpoint standard in the ICAL; Internal standard signal (area or height) within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	Inspect GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the Case Narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging is not appropriate for failed standards.	NA
Method Blank (MB)	One per preparatory batch.	No analytes detected >1/2 LOQ or > 1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater.	Correct problem. If required, reprep and reanalyze MB and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

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TITLE: CHLORINATED HERBICIDE ACIDS BY GAS CHROMATOGRAPHY (EPA METHODS 8151A, 615 & 1658)

Table 5. Quality Control Requirements – Organic Analysis by Gas Chromatography

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use Table 3 and 4 limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits (see the LIMS) if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use Table 3 and 4 limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits (see the LIMS) if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error).
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use Table 3 and 4 limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits (see the LIMS) if project limits are not specified. RPD ≤ 30% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.

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TITLE: CHLORINATED HERBICIDE ACIDS BY GAS CHROMATOGRAPHY (EPA METHODS 8151A, 615 & 1658)

Table 5. Quality Control Requirements – Organic Analysis by Gas Chromatography

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Surrogate Spike	All field and QC samples.	QC acceptance criteria specified by the project, if available; otherwise use Table 3 and 4 limits or in-house LCS limits (see the LIMS) if analyte(s) are not listed.	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.
Confirmation of positive results (second column)	All results > the DL must be confirmed (except for single column methods such as TPH by Method 8015 where confirmation is not an option or requirement).	Calibration and QC criteria for second column are the same as for initial or primary column analysis. Results between primary and secondary column RPD ≤ 40%.	NA	Apply J-flag if RPD >40%. Discuss in the case narrative.	Use project-specific reporting requirements if available; otherwise, use method requirements if available; otherwise report the result from the primary column.

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SOP Minor Revision Summary

SOP:			
Title -	SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (EPA METHODS 3510C & 625)		
Number -	330702	**Department -**	Org Prep
Revision -	17	**Rev. Date -**	2/12/2018

This Standard Operating Procedure has been amended to include changes required during normal business operations. These changes as defined by SOP 010103 (Document Control and Distribution) are routine modifications that will be incorporated into the SOP upon the next scheduled review.

Rev.	Date	Section	Brief Description
a	8/9/18	8.3 First Note	Replace neutral extraction with a third acid extraction

Standard Operating Procedure

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TITLE: SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (EPA METHODS 3510C & 625)

Reviewed by: Blake Judge, Steve Miller, Mike Jones, Kandy Kaul

Department Manager *QA Department*

1.0 SCOPE AND APPLICATION

STATE NOTE: For samples analyzed in conjunction with the Ohio Voluntary Action Program (VAP) please utilize SOP #330702OH.

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods. Determinative methods include the following: Base/neutral & Acid Extractables (BNAs) (SOP #330345), Chlorinated pesticides (SOP #330344), Polychlorinated Biphenyls (PCBs) (SOP #330343), Diesel Range Organics (SOP #330350), Organonitrogen & Organophosphorous Pesticides (SOP #330318), Polynuclear Aromatic Hydrocarbons (PAHs) (SOP #330322), Extractable Petroleum Hydrocarbons (various procedures).

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.4 An MDL study must be completed at least annually or more frequently if major instrumentation changes occur. Method Detection Limits (MDLs) are performed based on ESC SOP #030206. Updated MDL records are filed and stored in a central location within the department.

1.4.1 Limit of Detection (LOD) and Limit of Quantitation (LOQ) studies are completed at the frequency required by the TNI standard per the procedure identified in the ESC SOP #030206, *Method Detection Limits (MDL), Limits of Detection (LOD) and Limits of Quantitation (LOQ).* Should the procedure be utilized for DOD support; then the frequency of these studies must meet the requirements of the current DOD QSM.

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TITLE: SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (EPA METHODS 3510C & 625)

2.0 METHOD SUMMARY AND DEFINITIONS

2.1 A measured volume of sample, usually 1L, at a specified pH (see Attachment II), is serially extracted with methylene chloride using a separatory funnel. The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used. See Controlled Document SEM-02 *Prep Extraction.com* for appropriate exchange solvents.

2.2 ESC has found that a neutral extraction, in addition to the basic and acidic extractions, is beneficial to obtaining optimum recovery of key compounds for BNA analysis.

2.3 Sample Extraction - A sample of a known volume or weight is prepared for analysis by removing soluble substances using solvent.

2.4 See the current Quality Assurance Manual for other definitions associated with terms found in this document.

3.0 HEALTH AND SAFETY

3.1 The toxicity or carcinogenicity of each reagent used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of safety data sheets (SDSs) are made available on ESC's intranet to all personnel. Use hazardous reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing protocols.

3.2 **CAUTION:** Be careful when diluting and mixing acids. ALWAYS pour acid slowly into water when mixing.

3.3 This procedure requires the handling of samples containing corrosive acid. Prior to performing this procedure, the analyst must be familiar with the proper use of corrosive liquid spill kits and contaminant procedures.

3.4 **SOLVENTS** - This method requires the use of Dichloromethane, also called Methylene Chloride. Gloves that are specifically manufactured for protection against Methylene Chloride are required PPE. The Lab is equipped with "Purple Nitrile" gloves for sample handling. The breakthrough time for Methylene chloride is six minutes, when totally immersed. Every analyst is required to review the SDS sheet for ALL SOLVENTS used in the extraction lab. It is extremely important to handle the solvents under a hood limiting personal exposure.

3.5 Büchi tubes (or equivalent concentration tubes) must be covered and crimped with aluminum foil when outside of the hood to minimize solvent exposure.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

4.1 All samples must have been collected using a sampling plan that addresses the considerations of this method.

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4.2 Holding times for samples prepared using this method can be found in the appropriate determinative methods. In general, holding times for aqueous samples submitted for organic analysis is a maximum of seven days from the time of collection to extract preparation, with some exceptions (i.e. 365 days for PCB analysis). Holding times for extracts are 40 days following extraction to analysis.

STATE NOTE: All samples from North Carolina must be extracted within 14 days of collection. There are no exceptions.

4.3 The container for aqueous samples and liquid sludge should be 1L amber glass bottles with 0.008% $Na_2S_2O_3$ per liter, if residual chlorine is present or suspected.

4.4 All field samples and extracts must be stored in accordance with the determinative method requirements. Generally, field samples must be stored at <6°C from collection to extraction. Extracts must be stored at <6°C from preparation to analysis. Extracts must be allowed to equilibrate to room temperature prior to injection, as some compounds (surrogates, spiked compounds, target analytes, etc.) may not quantitate accurately at cooler temperatures.

5.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510C. Method 3510C is preferred over Method 3520 for the analysis of these classes of compounds. However, the recovery of phenols may be optimized by using Method 3520 or performing the initial extraction, in this method, at the acid pH.

6.0 EQUIPMENT AND SUPPLIES

6.1 Separatory funnel – Teflon 2L, with screw on cap

6.2 Büchi Syncore Automatic Concentrator or equivalent

6.3 175mL glass Büchi tubes with 300-500µL tips or equivalent

6.4 WKL3200 Lauda chiller unit

6.5 Pasteur pipettes and pipette bulbs

6.6 2.0mL, 8.0mL, 12mL, 16mL, and 40mL vials with Teflon®- lined screw caps or crimp tops

6.7 pH indicator paper - pH range including the desired extraction pH

6.8 Syringe – 10µL, 25µL, 50µL, 100µL, 250µL, and 1.0mL

Certified syringes available for DOD projects.

6.9 Graduated cylinder – 1L

6.10 Funnels with glass wool plug – fill 1/3 full with Na_2SO_4

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6.11 ATR Automatic Liquid Extractor

6.12 Bottle top dispensers – each bottle top dispenser is numbered and checked quarterly to ensure proper volume is dispersed

7.0 REAGENTS AND STANDARDS

7.1 All reagents and standards must be recorded in the appropriate preparation log and assigned a unique number. See SOP #030230, *Standard Logger – Tree Operation*. Additional information regarding reagent preparation can be found in the Standards Logger (Tree) digital archive system. All spiking solutions and surrogate standard solutions should be replaced at least every six months or sooner if a problem is detected unless otherwise noted.

7.2 Solvents and Salts/Sands

Table 7.2.1 Solvents

Solvent	Purity (or equivalent)	Vendor (or equivalent)	Catalog Number (or equivalent)
Acetone	Omni Solv	VWR	EM-AX0116-1
Acetonitrile	High purity	VWR	BJ 015-4
Dichloromethane	HPLC grade	VWR	BJ 300-4
Ethyl Ether	Omni Solv	VWR	EM-EX0182-1
Hexane	Omni Solv	VWR	EM-HX0296-1
Methanol	Omni Solv	VWR	EM-MX0480-1
Methyl t-Butyl Ether	Omni Solv	VWR	EM-MX0826-6
Pentane	HPLC grade	Fox Scientific	9331-03
Stock Sulfuric Acid		VWR	

Table 7.2.2 Salts & Sands

Product	Product Information (or equivalent)	Vendor (or equivalent)	Catalog Number (or equivalent)
Silica Gel	60-200 Mesh	VWR	3405-05
Sodium Chloride	Max. impurities & spec.	VWR	VW6430-7
Sodium Hydroxide		VWR	
Sodium Sulfate	Trace pure, 10-60 Mesh	VWR	EM-SX0760E3

7.3 Organic-free reagent water - For semivolatile and nonvolatile samples, all references to water in the methods refer to water in which an interferent is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about one pound of activated carbon. A water purification system may be used to generate organic-free deionized water. (As defined in Chapter One of SW-846)

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7.4 Sodium hydroxide solution (10N), NaOH. Dissolve 400g NaOH in 1.0L of organic-free water. Allow to equilibrate to room temperature before use.

7.5 Sodium sulfate (granular, anhydrous), Na_2SO_4, baked at 400°C for four hours and allowed to cool to room temperature before use.

7.6 Sulfuric acid solution (1:1 v/v), H_2SO_4. Slowly add 500mL of H_2SO_4 to 500mL of organic-free reagent water. Allow to equilibrate to room temperature before use.

7.7 Document the date opened for surrogates, spikes, acids, solvents, solids, and gels.

7.8 Information on surrogate and spiking standards can be found in the appropriate determinative method.

8.0 PROCEDURE

8.1 **Water** – Mark the meniscus of the sample in the sample container. Add surrogate to the sample container. Pour samples into 2L separatory funnels). For volume determination of the sample, the container is refilled with DI water to the mark and poured into a 1L graduated cylinder. For samples containing sediment, the graduated cylinder is filled to 1L with DI water and the sample container is filled to the marked line. The volume is determined from the difference from the remaining volume in the graduated cylinder compared to 1L. Sample volume is measured to the closest 10mL mark. For some 8270, 8081, 8082, 608, and 625 samples, smaller volumes may be used along with required quality control samples.

8.1.1 For the method blank, LCS and LCSD samples, use three aliquots of reagent water in separate 2L separatory funnels.

8.2 Add the surrogate standards to all samples, spikes, and method blanks. See Attachment II for additional guidance.

NOTE: Surrogate may be added to samples after transfer if sample contains heavy amounts of sediment or if headspace does not allow for surrogate addition without loss of sample volume.

8.2.1 For the sample in each analytical batch selected for the MS/MSD and LCS/LCSD, add the matrix spiking standard. (See Controlled Document SEM-02 *Prep Extraction.doc*)

8.3 Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH using 1:1(v/v) sulfuric acid or 10N sodium hydroxide, assuring that there is not a significant change in volume (less than 1%) of the sample being extracted. When checking pH, use a clean disposable pipette for each sample then dip into the middle of the sample, removing a couple of drops, and drip onto the pH strip.

NOTE: For BNA 8270 & 625 - Adjust the sample to a neutral pH. Perform steps 8.4 through 8.6. Adjust the pH with 10N NaOH to a pH >11. Perform steps 8.4 through 8.6 (twice). Adjust the pH with 1:1 H_2SO_4 to a pH of <2.0. Using a 2nd Büchi tube, perform steps 8.4 through 8.6 (three times). Combine all extracts into the Büchi tube and skip to 8.9.

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NOTE: For BNA 8270D analyzed for samples originating from South Carolina - Adjust the sample to a neutral pH. Perform steps 8.4 through 8.6. Adjust the pH with 10N NaOH to a pH >11. Perform steps 8.4 through 8.6 (three times). Adjust the pH with 1:1 H_2SO_4 to a pH of <2.0. Using a 2nd Büchi tube, perform steps 8.4 through 8.6 (three times). Combine all extracts into the Büchi tube and skip to 8.9.

NOTE: For method 8015 and other state specific petroleum methods where the pH is required at <2. Samples are qualified if above two and not adjusted.

8.4 Add a scoop of salt (NaCl) as needed per method to improve conditions for target recoveries – "salting out" technique.

8.5 Dispense 60mL of methylene chloride from a 4L container with bottle top pump into the client sample bottle, rinse and pour into separatory funnel. If a heavy amount of sediment is left in the container the aliquot of MeCl2 may be added to a beaker or Erlenmeyer flask that has been pre-rinsed with methylene chloride and add to the separatory funnel. Document presence of sediment and adjusted volume of sample used for extraction.

8.6 Seal and shake the separatory funnel vigorously for at least two minutes (with the automatic extractor) with periodic venting to release excess pressure.

NOTE: The automatic extractor should always remain at proper control which equals 50rpm.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting must be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel must be vented into a hood to avoid exposure of the analyst to solvent vapors.

8.7 Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ optimum techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, or other physical methods. Collect the solvent extract through $NaSO_4$ funnel in a Büchi tube.

STATE NOTE: For EPHTN samples only: If the emulsion cannot be broken, recovery of <80% of the methylene chloride, analyst must see supervisor. If solvent recovery is less than 80%, initial sample volume must be altered in order to reflect the low solvent recovery. Therefore, if a 1L sample is to be extracted with a total volume of 150mL of solvent and 75mL is recovered at the end of the extraction, the initial volume of the sample extracted would be 500mL.

8.8 Add 50mL of methylene chloride to the separatory funnel by the same method as 8.4. Repeat steps 8.5 and 8.6.

8.9 Add 40mL of methylene chloride to the separatory funnel by the same method as 8.4. Repeat steps 8.5 and 8.6.

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8.10 If necessary, perform the concentration and solvent exchange using the Büchi concentrator or bring to final volume for analysis. Concentration volumes and exchange solvents, if necessary, are included in Attachment II.

8.10.1 Büchi Syncore Concentrator Technique - For instructions on the use of the Büchi Syncore Concentrator, refer to SOP #330708

8.11 The extract may now be analyzed for the target analyte using the appropriate determinative technique(s). If analysis of the extract is not being performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than two days, it must be transferred to a vial with a Teflon®-lined screw-cap or crimp top, and labeled appropriately. Prior to analysis, sample extracts must be kept at the determinative method-specified temperature and must be analyzed within the holding time of the determinative method.

8.12 TCLP and SPLP Extracts and Liquid Sludge

8.12.1 Use 100mL of TCLP EXTRACT for methods 8270, 8151, 8081, and 8082 and the sample is brought to a volume of 1000mL with DI water. For TCLP, a method blank must also be extracted with each batch of TCLP leachates. For sludge, choose a volume depending on the amount of solids in the sample (typically 100mL).

8.12.2 Use 1000mL of SPLP EXTRACT. A SPLP method blank must also be analyzed with each batch of SPLP leachates.

8.12.3 A Matrix Spike must be extracted for each TCLP matrix.

8.12.4 Extract according to the above procedure, with the exception of the afore-mentioned volumes.

9.0 DATA ANALYSIS AND CALCULATIONS

See Determinative Method.

10.0 QUALITY CONTROL AND METHOD PERFORMANCE

10.1 All analysts must meet the qualifications specified in SOP #030205, *Technical Training and Personnel Qualifications* before approval to perform this method. Analysts must complete an initial demonstration of proficiency before being approved to perform this method. Continuing proficiency must be demonstrated using proficiency testing, laboratory control sample analysis and/or MDL studies. Method performance is assessed per analyst. Updated method performance records are filed and stored in a central location within the department.

10.2 Use the designated Run log to record batch order and standards/reagents used during analysis. See SOP #030201, *Data Handling and Reporting*.

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10.3 Batches

Batches are defined as sets of 1 - 20 samples. Batch analysis must include the following: 1 method blank, 1 Laboratory Control Sample (LCS)/1 Laboratory Control Sample Duplicate (LCSD) pair, 1 Matrix Spike/Spike Duplicate (MS/MSD) pair, if sample volume permits. All batch information must be maintained in the preparation documentation assigned to the department.

10.4 Method Blank - A method blank must be extracted and analyzed with each set of samples. The method blank must be carried through the same procedure as the samples and must not contain target analytes above the method detection limit. For more specific information regarding acceptable blank criteria, please see the appropriate determinative procedure for the target analytes requested in the field samples.

10.5 Surrogate – A surrogate spiking solution is added to each sample and method blank being prepared for analysis. The surrogate is selected to be similar in chemical nature to the target analytes for each method, but generally not a compound that occurs naturally in samples. The surrogate is spiked at a known concentration and then the recovery is assessed following extract analysis to determine extraction efficiency for each sample and blank. Acceptance criteria for the surrogate spike can be found in the specific determinative procedure.

10.6 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD) - must be extracted and analyzed with each batch of samples. An LCS/LCSD pair is two aliquots of a clean matrix spiked with target analytes and carried through the entire extraction process to determine the effect of the sample preparation and analysis on the target analytes with no effect of the sample matrix. The control must be within the acceptance criteria listed in the determinative methods.

10.7 Matrix Spike Sample/Matrix Spike Sample Duplicate (MS/MSD) - must be extracted and analyzed with each batch of samples when sufficient field sample volume is available. An MS/MSD pair is two aliquots of a field sample matrix spiked with target analytes and carried through the entire extraction process to determine the effect of the sample preparation and analysis on the target analytes with no effect of the sample matrix. The control must be within the acceptance criteria listed in the determinative methods.

10.8 Method performance criteria can be found in each determinative SOP.

11.0 DATA VALIDATION AND CORRECTIVE ACTION

11.1 Second analyst review must be performed according to SOP #030201, *Data Handling and Reporting.*

11.2 Any method blanks, matrix spike, and replicate samples must be subjected to exactly the same analytical procedures as those used on actual samples.

11.3 Additional corrective actions can be found in each determinative method.

12.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

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Standard Operating Procedure

TITLE: SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (EPA METHODS 3510C & 625)

12.1 The EPA requires that a laboratory waste management practice be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner. See *ESC Waste Management Plan.*

12.2 See SOP #030302, *Environmental Sustainability & Pollution Prevention*.

13.0 METHOD MODIFICATIONS/CLARIFICATIONS

13.1 Extractions are performed using solvent volumes of 60mL, then 50mL and then 40mL, rather than using 60mL of solvent three times to better accommodate concentrator tube volumes.

13.2 Modifications to this method are noted in the body of the text as state notes. Compliance analyses performed in conjunction with specific state requirements must be performed as noted within the specific state(s) note listed.

13.3 Adjustments to the concentrations of standards/spiking solutions, standards providers, and quality control are subject to change to better meet client/project/regulatory needs or to improve laboratory method performance.

13.4 Sections 8.1 through 8.3 are based on the extraction process from EPA Method 625 which may vary slightly from that found in EPA Method 3510C.

14.0 REFERENCES

14.1 *Separatory Funnel Liquid-Liquid Extraction*, SW-846 Method 3510C, Revision 3, December 1996.

14.2 *Organic Analytes*, SW-846 Chapter 4, Revision 4, February 2007.

14.3 *Organic Extraction and Sample Preparation*, SW-846 Method 3500C, Revision 3, February 2007.

14.4 *Base/Neutral and Acids,* Method 625, 40 CFR §136, Appendix A.

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Standard Operating Procedure

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TITLE: SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (EPA METHODS 3510C & 625)

Attachment I: Revision History

Current Version:

Version	Date	Description of Revisions
17	2/5/2018	Technical and Quality Review and update. Changed ESC logo. Revised sections 2.1, 3.1, 3.4, 4.2, 6.6, 6.9, 6.10, 7.1, 7.2, 7.3, 7.5, 7.6, 8.1, 8.1.1, 8.2, 8.2.1, 8.3, 8.4, 8.6, 8.7, 8.10, 8.10.1, 8.11, 10.3, 11.1, 12.1, 14.1, 14.2, 14.3 and 14.4. Revised titles of Tables 7.2.1 and 7.2.2. Added NOTE to section 8.2.

Superseded Versions:

This document supersedes the following:

Version	Date	Description of Revisions
0	7/1/94	Origination
1	3/1/95	
2	5/3/95	
3	7/1/8	
4	7/31/99	
5	8/21/00	
6	10/16/01	
7	1/8/03	
8	11/18/03	
9	9/21/05	Added Methods 8151A & 8310; Added information on Buchi; Added information on bottle-top dispensers; Added documentation on reagents; Corrected numbering sequences; Added information on the auto-extractor RPM value; Deleted TurboVap use; Added Butachlor, Metolachlor and Metribuzin to 507 analysis; Added Tech Notes
10	1/29/09	Technical and Quality Review and update. Added sections 12.1-12.2, 13.2; Updated Attachments II, III, V; Clarified holding times; Added state notes. Ohio VAP approved 1/29/09.
11	10/01/10	Technical and Quality Review and update. Added sections 2.3 through 2.12, 13.3, state note following sections 1.4 and 10.3 and attachment VI; Revised sections 3.4, 7.1, 7.5, 7.6, 8.1, 8.2, 8.3, 8.4, 8.10, 12.1 and attachments II through V; Removed sections 6.7, 8.10. Ohio VAP approved 9/30/10.
12	12/23/11	Technical and Quality Review and update. Revised sections 1.1, 4.2, 7.4, 7.6, 8.11, 12.1 Tables 7.2.1 & 7.2.2 and Attachments IV, V and VII; Added sections 1.4.1, 2.13, 2.14, 8.11.2, 13.4, and 14.4.
13	5/23/13	Technical and Quality Review and update. Revised Attachments V, VI, VII, and sections 7.1 and 10.3; Added sections 10.4 through 10.8 and added state note to section 1.0

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TITLE: SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (EPA METHODS 3510C & 625)

Version	Date	Description of Revisions
14	11/13/14	Technical and Quality Review and update. Revised Attachments V and VII, and Sections 8.3, 8.5 and 8.6; Added section 8.4: Deleted section 8.2.2.
15	11/17/2015	Technical and quality review and update. Header and signature bar re-formatting. Revised Sections 1.0, 1.4.1, 6.3, 7.1, 8.1, 8.3, 8.5, 8.7, 8.10, 10.4, and 12.2. Deleted Attachment II through Attachment IV, Attachment VI, and Attachment VII.
16	10/14/2016	Technical and quality review and update. Header and signature block re-formatting. Revised Sections 2.3, 2.4, Table 7.2.1, and Table 7.2.2. Deleted Sections 2.3 through 2.9 and 2.11 through 2.14.

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TITLE: SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (EPA METHODS 3510C & 625)

Attachment II: Specific Extraction Conditions for Various Determinative Methods

Determinative Method	Initial Extraction pH	Secondary Extraction pH	Exchange Solvent req. for analysis
8015	varies	none	none
8081	5-9	none	hexane
8082	5-9	none	hexane
8141	as received	none	hexane
8270	([c,d]) <2	>11	none
8310	as received	none	acetonitrile

(c) The specificity of GC/MS may make cleanup of the extracts unnecessary.

Refer to Method 3600 for guidance on the cleanup procedures available if required.

(d) Extraction pH sequence may be reversed to better separate acid and neutral components. Excessive pH adjustments may result in the loss of some analytes (see Sec. 3.2).

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Environmental Science Corporation
SOP MINOR REVISION FORM

SOP/DOC# 330702 Current revision date & number: 2/12/2018 R17

Procedure/Method : SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (EPA METHODS 3510C & 625)

Date	Requested By	Section	Revision	Reason*	Approvals	
					Supervisor	QA
8/9/18	SCM	8.3 NOTE	Change the 1st Note to read: "**For BNA 8270 & 625** - Adjust the pH with 10N NaOH to a pH >11. Perform steps 8.4 through 8.6 (three times). Adjust the pH with 1:1 H2SO4 to a pH of <2.0. Using a 2nd Büchi tube, perform steps 8.4 through 8.6 (three times). Combine all extracts into the Büchi tube and skip to 8.9."	CAR3171		

*Comments:

Standard Operating Procedure

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TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE (EPA METHOD 1311)

Reviewed by: Jeremy Gupton, Kandy Kaul, Jim Brownfield

Department Manager *QA Department*

1.0 SCOPE AND APPLICATION

1.1 This method applies to any sample type (solid, liquid, and multi-phasic waste samples).

1.2 The Toxicity Characteristic Leaching Procedure (TCLP) is designed to determine the environmental mobility of both organic and inorganic contaminants present in liquid, solid, and multi-phasic wastes.

1.3 If a total analysis of the waste demonstrates that individual contaminants are not present in the waste or that they are present but at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, the TCLP need not be analyzed.

1.4 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

2.0 METHOD SUMMARY AND DEFINITIONS

2.1 For liquid wastes (<0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8µm glass fiber filter, is defined as the TCLP extract. All solid determinations must be performed.

2.2 For wastes containing ≥ 0.5% dry solids, the liquid, if any, is separated from the solid phase and stored for later analysis. The particle size of the solid reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. A special extractor vessel is used when testing for volatile analytes.

2.3 Following extraction the liquid extract is separated from the solid phase by filtration through 0.6 to 0.8µm glass fiber filter. If compatible (multiple phases will not form upon combination), the initial liquid phase of the waste is added to the liquid extract and analyzed together. If they are not compatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

2.4 TCLP – The Toxicity Characteristic Leaching Procedure is a method designed to imitate the leaching process that occurs in landfills.

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2.5 Liquid phase - The liquid component of the sample that passes through the filter during the initial determination of solids present in the field sample.

2.6 Solid phase - The component of the sample that does not pass through the filter during the initial determination of solids present in the field sample.

2.7 See the current Quality Assurance Manual for other definitions associated with terms found in this document.

3.0 HEALTH AND SAFETY

3.1 The toxicity or carcinogenicity of each reagent used in the laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of safety data sheets (SDSs) is made available on ESC's intranet to all personnel. Use hazardous reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing protocols.

3.2 Samples should be placed in a fume hood if they emit vapors, or are known or suspected to be particularly hazardous.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

4.1 All samples must have been collected using a sampling plan that addresses the considerations of this method.

4.2 Sampling

4.2.1 All samples should be collected in glass or Teflon jars. Minimally, a 105g aliquot of solid material should be collected for each analysis needed (It is always wise to collect extra sample in the event that additional extract preparation is required).

4.2.2 A separate aliquot is needed for extraction of volatiles and should be collected with minimal headspace.

4.3 Preservation

4.3.1 Preservatives should not be added to the field sample. The sample should be refrigerated at ≤ 6°C (not frozen) unless it causes physical change to the sample (i.e., precipitation).

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4.4 Holding times:

	From Field Collection To TCLP Extraction	From TCLP Extraction To Preparative Extraction	From Preparative Extraction To Determinative Analysis	Total Elapsed Time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except Hg	180	NA	180	360

NA = not applicable

5.0 INTERFERENCES

5.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

6.0 EQUIPMENT AND SUPPLIES

6.1 Tumbling apparatus capable of rotating the vessel in an end over end fashion at 30 ± 2rpm

6.2 Bottle Extraction Vessel. When the waste is being evaluated using the non-volatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel. The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste. It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than PTFE, shall not be used if organics are to be analyzed.

6.3 Zero Headspace Extraction (ZHE) vessel. This device is for use only when the waste is being tested for the mobility of volatile analytes. The ZHE allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel. The vessels have an internal volume of 500-600mL, and are equipped to accommodate a 90-110mm filter. The devices contain O-rings, which should be replaced frequently. For the ZHE to be acceptable for use, the piston within the ZHE should move with approximately 15 psi of pressure or less. If it takes more pressure to move the piston, the O-rings need to be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses. The ZHE should be checked for leaks after every extraction. Pressurize the device to 40 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Re-test the device. If leakage problems cannot be solved, the ZHE is unacceptable for TCLP analyses.

6.4 Borosilicate glass fiber filters must be used and have an effective pore size of 0.6 to 0.8µm, or equivalent. When evaluating the mobility of metals, filters must be acid washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with DI

water. Alternatively, pre-acid washed filters can be purchased. Glass fiber filters are fragile and should be handled with care.

6.5 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. The type of filter holder used depends on the properties of the material to be filtered. These devices shall have a minimum internal volume of 300mL and be equipped to accommodate a minimum filter size of approximately 47mm (filter holders having an internal capacity of 1.5L or greater, and equipped to accommodate a filter approximately 142mm diameter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid containing wastes. All other types of wastes should be filtered using positive pressure filtration.

NOTE: Record "vacuum" in the filtration device column in Prep Data when a vacuum device is used to filter samples.

6.6 Hazard Waste Pressure Filter System – Millipore (Fisher # YT30 142 HM) or equivalent

NOTE: Record the letter associated with the positive pressure vacuum device in the filtration device column in Prep Data when a positive pressure device is used to filter samples.

6.7 Laboratory Balance and Weigh Boats: Any laboratory balance accurate to within ± 0.01 grams may be used.

6.8 pH Meter: The meter must be accurate to ± 0.05 units at 23 ± 2°C.

6.9 200mL beakers used for initial and adjusted pH

6.10 Magnetic stir plate and stir bars

6.11 Hot plate

6.12 Spatulas (wood and metal)

6.13 Mortar/Pestle

6.14 9.5mm and 1.0mm sieve

6.15 ZHE plunger

6.16 Tin snips and hammer

6.17 Homogenizer

6.18 Tedlar® bags

7.0 REAGENTS AND STANDARDS

7.1 All reagents and standards must be recorded in the appropriate preparation log and assigned a unique number. See SOP #030230, *Standards Logger – Tree Operation.* Additional information regarding reagent preparation can be found in the Standards

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Logger (Tree) digital archive system. All spiking solutions and surrogate standard solutions should be replaced at least every six months or sooner if a problem is detected unless otherwise noted.

7.2 Reagent grade water

7.3 1N HCl made from ACS reagent grade HCl. Slowly add 83mL of concentrated hydrochloric acid to approximately 500mL of reagent water and then adjust to 1 liter with reagent water. Note: This is an exothermic reaction and should be performed carefully. Always add acid to a larger volume of water; never add water to a larger volume of acid.

7.4 6N NaOH made from ACS reagent grade NaOH. Slowly add 240g of NaOH pellets to approximately 800mL of reagent water, stirring continuously (*do not add the water to the NaOH pellets)*. When the pellets have dissolved completely, adjust the volume to 1 liter with reagent water. Do this twice to obtain 2 liters. Note: This is a highly exothermic reaction and should be performed carefully.

7.5 Glacial Acetic Acid - ACS reagent grade

7.6 TCLP Extraction Fluids:

7.6.1 #1 Extraction Fluid: Add about 120 liters of DI water to a 180L drum. Add 1929mL of 6N NaOH and 1026mL of Glacial Acetic Acid. Bring to a volume of 180L with DI water. The pH of this fluid should be 4.93 $\pm$ 0.05.

7.6.2 #2 Extraction Fluid: Add about 80L of DI water to a 100L drum. Add 570mL of Glacial Acetic Acid. Bring to a volume to 100L. The pH of this fluid should be 2.88 $\pm$ 0.05.

7.6.3 Upon preparation, if the fluid is $\pm$0.05pH units outside of the acceptable range the fluid must be discarded and re-prepared before use. Also, the fluid must be checked daily prior to preparing samples for tumbling and if the pH of the extraction fluid is beyond the acceptable range, the fluid must be discarded and re-prepared before use.

NOTE: Always check the slope of the pH meter and re-calibrate and re-test the solution, if the fluid is initially determined to be outside the method required pH range.

7.7 pH meter calibration buffers at pH values of 2, 4, 7 and 10 are used to calibrate the pH meter daily. Buffers are used fresh daily then discarded. The slope of the pH meter following calibration must be 98-102. The pH 7 buffer is then re-analyzed and the reading must be 7.0 $\pm$ 0.05su.

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8.0 PROCEDURE

8.1 Preliminary Evaluation – Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. These preliminary evaluations include:

- Determination of the percent solids
- Determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration
- Determination of whether the solid portion of the waste requires particle size reduction
- Determination of which of the two extraction fluids are to be used for the non-volatile TCLP extraction of the waste

8.2 Determination Of Percent Solid

8.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (100% solids), then skip this step and proceed to particle size reduction if needed.

8.2.2 If the sample is liquid, semi-liquid, or contains liquid; determination of percent solids is required.

8.2.3 Pre-weigh the filter paper and the container that will receive the filtrate.

8.2.4 Assemble the filter holder.

8.2.5 Homogenize the sample in the original container before a portion of the sample is transferred to a secondary container.

8.2.6 Weigh out a sub-sample of the waste (100 gram minimum) and record the weight of the sample plus the weighing container.

8.2.7 Transfer the sample to the filter holder (liquid and solid phases) and spread the sample evenly over the surface of the filter.

NOTE: Vacuum filtration can be used when samples contain <10% solid and for highly granular liquid containing wastes. Pressure filtration is used in any other case.

8.2.8 Weigh and record the weight of the weighing container that contained the subsample of waste. This weight includes the weight of the container plus any sample residue adhered to it.

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8.2.9 Slowly apply pressure of 1-10psi to the filter apparatus until gas moves through the filter. If this point is not reached under 10psi, and if no additional liquid has passed through the filter in any two minute interval, slowly increase the pressure in 10psi increments to a maximum of 50psi. After each incremental increase of 10psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any two minute interval, proceed to the next 10psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50psi (i.e., filtration does not result in any additional filtrate within any two minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

NOTE: Some wastes, such as oils and paints, will contain liquid material that does not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

8.2.10 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Store the filtrate at ≤ 6°C (not frozen) until the TCLP extraction is completed.

8.2.11 Determine the weight of the liquid phase by subtracting the weight of the filtrate container from the total weight of the filtrate filled container.

Weight of liquid phase = (Filtrate + Container) – (Container)

8.2.12 Determine the total weight of sample that was filtered by subtracting the container and residue weight from the total weight of the sample filled container.

Weight of sample filtered= (Sample + Container)–(Container + Residue)

8.2.13 Determine Percent Wet Solids:

$$\text{Percent wet solids} = \frac{\text{Weight of sample filtered (8.2.12)} - \text{Weight of filtrate (8.2.11)}}{\text{Weight of waste filtered (8.2.12)}} \times 100$$

8.2.14 If the percent wet solid is ≥ 5%, then proceed to particle size reduction below if needed.

8.2.15 If the percent wet solids is <0.5% and non-volatile analyses (semivolatiles, pesticides, herbicides, or metals) are required, then the filtrate obtained is considered to be the TCLP extract, so it can be processed accordingly.

8.2.16 If the percent wet solids is <0.5% and volatile analysis is required, then proceed to section 8.6 using a fresh aliquot of sample.

8.2.17 If the percent wet solids is ≥0.5% and <5% **and** some liquid is entrapped in the filter, then determine Percent Dry Solids as follows below.

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NOTE: If it is obvious that very little liquid is entrapped in the filter, do not dry filter; proceed to Particle Size Determination. Once the solid phase has been oven-dried, it cannot be used for the Particle Size, Extraction Fluid Determinations, or the TCLP Extraction.

NOTE: If obviously oily (non-aqueous) material is entrained on the filter, do not dry the filter; proceed to Particle Size Determination. Once the solid phase has been oven-dried, it cannot be used for the Particle Size, Extraction Fluid Determinations, or the TCLP Extraction.

8.2.18 Dry the filter paper and solid phase at 100 ± 20°C to constant weight (two consecutive stable weights with ±1%) in a drying oven.

8.2.19 Determine Percent Dry Solids:

$$\text{Percent Dry Solids} = \frac{\text{Dried filter and solid phase (8.2.18)} - \text{Filter (8.2.3)}}{\text{Waste filtered (8.2.12)}} \times 100$$

8.2.20 If the Percent Dry Solids is <0.5%, and non-volatile analyses (semivolatiles, pesticides, herbicides, or metals) are required, then the filtrate obtained is considered to be the TCLP extract, so it can be processed accordingly.

8.2.21 If the Percent Dry Solids is <0.5% and volatile analysis is required, then proceed to section 8.6 using a fresh aliquot of sample.

8.2.22 If the Percent Dry Solids is ≥0.5% and the sample will be analyzed for non-volatile constituents, return to the beginning of this section and re-filter a fresh portion of the waste to separate the liquid and solid phases. Once the solid phase has been oven-dried it cannot be used for the Particle Size, Extraction Fluid Determinations, or the TCLP extraction.

8.2.23 If the Percent Dry Solids is ≥0.5% and volatile analysis is required, then proceed to section 8.6 using a fresh aliquot of sample.

8.3 Determination of Particle Size Reduction

8.3.1 Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1cm^2, or is smaller than 1cm in its narrowest dimension (i.e., is capable of passing through a 9.5mm (0.375 inch) standard sieve).

8.3.2 If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are being prepared for organic volatiles extraction, special precautions must be taken (see Section 8.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended.

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8.3.3 If all the solid phase will obviously pass through the 9.5mm sieve particle size reduction is not needed and go to section 8.4.

8.4 Determination of Type of Extraction Fluid

8.4.1 If the percent solids content of the sample is ≥0.5% and if the sample will be extracted for non-volatile analytes, determine the appropriate extraction fluid.

8.4.2 Reduce a subsample of the solid phase (if necessary) to a particle size of approximately 1mm in diameter or less and transfer 5.0g of the solid into a beaker. (If sample is multiphasic, filter out the solids and weigh out 5.0g of the solid phase into a beaker.)

NOTE: If a sample is not conducive to particle size reduction down to approximately 1mm diameter, then the reasoning and/or the matrix should be recorded. Examples of material which is not conducive to particle size reduction of approximately 1mm diameter includes (but is not limited to) filters, rags, rocks, and oily materials.

8.4.3 Add 96.5mL of reagent water to the beaker, cover with a watch glass, and stir vigorously until the pH stabilizes or for up to five minutes using a magnetic stirrer. Measure and record the pH.

8.4.4 If the pH ≤5.0, extraction fluid #1 is used.

8.4.5 If the pH>5.0, add 3.5mL 1.0N HCl, slurry briefly, cover with a watch glass, heat to 50°C and hold for 10 minutes. Allow the solution cool to room temperature and record the pH. If the pH is ≤5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2.

8.5 Non-Volatile TCLP Extraction

8.5.1 A minimum sample size of 100 grams (solid and liquid phases) is required. In some cases, a larger sample size may be appropriate, depending on the dry solids content of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern.

NOTE: A smaller sample amount (<100g) is allowed when a sample volume is sent from customer that is <100g and the customer approves the qualification prior to the leaching and allows the lab to proceed with a short sample.

8.5.2 Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required.

8.5.3 If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

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8.5.4 If the sample will obviously yield no liquid when subjected to pressure filtration (100% solid), weigh out a subsample of the waste (100g minimum) and proceed to Section 8.5.6.

8.5.5 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device and filtration procedures described in Section 8.2.

8.5.5.1 After liquid/solid phase separation, store the liquid phase at ≤ 6°C (not frozen) until the TCLP extraction is completed.

8.5.5.2 Transfer the solid phase into the extraction vessel and include the filter used for the phase separation.

8.5.6 Determine the amount of extraction fluid needed:

Volume of Extraction Fluid (mL) = 20 × Solid Phase Weight (g)

8.5.7 Slowly add this amount of appropriate extraction fluid to the extractor vessel.

NOTE: The pH of the extraction fluids needs to be verified each day the fluid is used. Close the extractor bottle tightly, secure in rotary extractor device, and rotate at 30 ± 2 rpm for 18 ± 2 hours.

8.5.8 Check and record the rotation speed in the speed of the tumbler (rpm).

8.5.9 Ambient temperature (temperature of room in which extraction is to take place) shall be maintained at 23 ± 2°C during extraction period. Monitor and record the minimum and maximum room temperature of the extraction during the 18 ± 2 hours extraction time.

8.5.10 After the 18 ± 2 hours extraction is complete, remove the samples from the tumbler and allow the samples to settle.

8.5.11 Separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter. For final filtration of the TCLP leachate, the glass fiber filter may be changed, if necessary, to facilitate filtration.

NOTE: The blank which was tumbled must be filtered as well.

8.5.12 If the sample contained no initial liquid phase (100% solids), the filtered liquid leachate obtained is defined as the TCLP extract.

8.5.13 If compatible (multiple phases will not result on combination), combine the filtered liquid leachate with the initial liquid phase of the sample. This combined liquid is defined as the TCLP extract.

8.5.14 If the initial liquid phase of the sample is not or may not be compatible with the filtered liquid leachate, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically.

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8.5.15 Following collection of the TCLP extract, the pH of the extract is recorded. The preparatory method should be applied as soon as possible. For organic analysis, extracts are refrigerated at ≤6°C (not frozen) until the extraction. For metal analysis, extracts are typically digested right after they are collected. If digestion of the extracts needs to be delayed, then preserve all samples and blanks with nitric acid to pH <2. If the individual phases are to be analyzed separately, determine the volume of the individual phases, conduct the appropriate analyses, and combine the results mathematically by using a simple volume weighted average calculation found in section 9.1.

8.6 Volatile TCLP Extraction

8.6.1 Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold to minimize loss of volatiles. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

8.6.2 Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

8.6.3 Assembling the ZHE

8.6.3.1 Place clean O-rings on the piston, top plate, and bottom plate.

8.6.3.2 Place the top plate upside down on a counter. Place one 90mm screen inside the top plate. Insert one 90mm, glass fiber, 0.7µm filter on top of the screen and cover them with a second 90mm screen. Insert an O-ring on top of the screen/filter sandwich.

8.6.3.3 Wet the piston O-rings with reagent water. Place the barrel right side up and force the piston down to the bottom of the barrel, making sure that the wiper blade side is up. If the sample to be extracted contains free liquid; therefore, must be filtered, do not force the piston to the bottom but only partway down so that it can be filtered.

8.6.3.4 For the ZHE to be acceptable for use, the piston within the ZHE should move with approximately 15psi of pressure or less. If it takes more pressure to move the piston, the O-rings need to be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses. The ZHE should be checked for leaks. Pressurize the device to 40psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Re-test the device. If leakage problems cannot be solved, the ZHE is unacceptable for TCLP analyses.

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8.6.4 Place the ZHE piston within the body of the ZHE. Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample. Secure the gas inlet/outlet flange onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange aside.

8.6.5 If the waste is 100% solid, weigh out a sub-sample (25 gram maximum) of the waste. Record the weight.

8.6.6 If the waste contains <0.5% dry solids, the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required.

8.6.7 For wastes containing ≥0.5% dry solids, use the percent solids information to determine the sample size to charge in the ZHE. The recommended sample size is as follows:

8.6.7.1 For wastes containing ≥0.5% and <5% solids, weigh out a 500 gram sample of waste and record the weight.

8.6.7.2 For wastes containing ≥5% solids, determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge the ZHE (g)} = \frac{25}{\text{Percent solids}} \times 100$$

8.6.7.3 Weigh out a sub-sample of the waste of the appropriate size and record the weight.

8.6.8 If necessary, prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to the appropriate surface area or particle size. Samples and appropriate reduction equipment should be handled cold. Samples should not be exposed to the atmosphere for any more time than is absolutely necessary.

8.6.9 Quantitatively transfer the sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position. Do not attach the extract collection device to the top plate.

8.6.10 Attach a gas line to the gas inlet/outlet valve and, with the liquid inlet/outlet valve open, begin applying gentle pressure of 1-10psi to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure.

8.6.11 If the sample is 100% solid, slowly increase the pressure to a maximum of 50psi to force the headspace out of the device.

8.6.12 If the sample is <100% solid, then attach a pre-weighed filtrate collection container (Tedlar® bag) to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10psi to force the liquid phase of the sample into the Tedlar® bag. If no additional liquid has passed through the filter in any two minute interval, slowly increase the pressure in 10psi increments to a maximum of 50psi. After each incremental increase of 10psi, if no additional liquid has passed through the filter in any two minute interval, proceed to the next 10psi increment. When liquid flow has ceased such that continued pressure filtration at 50psi does not result in any additional filtrate within a two minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

8.6.13 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

8.6.14 The liquid phase may now be either analyzed immediately or stored at ≤6°C (not frozen) under minimal headspace conditions until time of analysis.

8.6.15 Determine the appropriate amount of Extraction Fluid #1 to add to the ZHE:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{Percent solids} \times W_s}{100}$$

where: W_s = Weight of sample used (liquid and solid phases)

8.6.16 The following sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases for leaching volatile components.

8.6.16.1 With the ZHE in the vertical position, attach a line from the extraction fluid to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be pre flushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston, open the liquid inlet/outlet valve, and begin transferring extraction fluid into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of the fluid has been introduced into the device.

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8.6.16.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion two or three times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10psi and slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with about 30psi and check all ZHE fittings to ensure that they are closed.

8.6.17 Place the ZHE in the rotary agitation apparatus and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature must be maintained at 23 ± 2°C during agitation.

8.6.18 Following the 18 ± 2 hour agitation period, check and record the pressure from the ZHE gauge. If the pressure has not been maintained, the device is leaking. Check the ZHE for leaking as specified in Section 6.3, and repeat again with new sample.

STATE NOTE: A specific criteria for the amount of loss is required when preparing and analyzing samples from Wisconsin. If more than 10% (4-5psi) of the charged pressure is lost, the sample must be re-extracted. When significant loss is observed, the O-rings are replaced as a part of the corrective action process.

8.6.19 If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. Filter through the glass fiber filter, using the ZHE device. The sample is filtered into VOA vials using needles to ensure that loss of volatile analytes is minimized.

8.6.20 If the original waste contained no initial liquid phase, the filtered liquid material obtained is defined as the TCLP extract.

8.6.21 If the waste contained an initial liquid phase, the filtered liquid material obtained and the initial liquid phase are collectively defined as the TCLP extract. Recombination – The initial liquid filtered from the sample is kept in a Tedlar® bag for later recombination. The filtrate after rotation is then added to the Tedlar® bag containing the initial liquid filtrate. Once mixed the sample can be transferred to a VOA vial for analysis.

8.6.22 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at ≤6°C (not frozen) until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using the simple volume weighted average equation found in Section 9.1.

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8.7 Spikes - For every sample type, for every parameter being tested there must be sufficient sample for a spike and a duplicate spike. This will be triple the amount that would be normally be provided to analytical personnel. The spike is added at the bench during analytical preparation, not during TCLP extraction.

8.8 Determination of Leachate Needed

Metals - a minimum of 50mL
Mercury - a minimum of 50mL
Pesticides and PCB's - a minimum of 250mL
BNA and PAH - a minimum of 250mL
Herbicides - minimum of 250mL
All volatiles – (1) 40mL vial

STATE NOTE: The State of South Carolina's Bureau of Land & Waste Management may require drinking water detection limits. These low limits may also require a sample volume of 1 liter. For those samples that fail to meet the above criteria for these specific samples a narrative needs to accompany the samples explaining the samples extraction and why it failed to meet the required limits.

8.9 Clean up – All Lab ware must be clean and dry before use. Extraction vessels and volumetric ware are washed in Miele lab dishwashers using the preprogramed wash cycle and a combination of ProCare Lab 10AP Detergent and ProCare Lab 30C Neutralizer or equivalent.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Mathematical combination of incompatible liquid phase/leachate:

$$\text{Final Analyte Concentration} = \frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$$

where:

V1 = The volume of the first phases (L).
C1 = The concentration of the analyte of concern in the first phase (mg/L).
V2 = The volume of the second phase (L).
C2 = The concentration of the analyte of concern in the second phase (mg/L).

9.2 Percent Dry Solid= $\frac{(\text{wt of dry waste \& filter- wt of filter} \bullet 100)}{\text{wt of sample}}$

9.3 Percent Solid = $\frac{\text{solid phase weight} \bullet 100\%}{\text{Weight of sample}}$

9.4 PPF (Percent Pass Filter) = 100 – %Solids (Section 9.2) See section 13.4

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10.0 QUALITY CONTROL AND METHOD PERFORMANCE

10.1 All analysts must meet the qualifications specified in SOP #030205, *Technical Training and Personnel Qualifications* before approval to perform this method. Analysts must complete an initial demonstration of proficiency before being approved to perform this method. Continuing proficiency must be demonstrated using proficiency testing and/or laboratory control sample analyses. Method performance is assessed per analyst. Updated method performance records are filed and stored in a central location within the department.

10.2 Use the designated Run log to record batch order and standards/reagents used during analysis. See SOP #030201, *Data Handling and Reporting*.

10.3 Extraction Batches: Extraction batches are defined as sets of 1 - 20 samples. Extraction batches must include the following: 1 method blank, 1 Matrix Spike/Spike Duplicate (MS/MSD) pair (if enough sample is available) and Duplicate (Dup). Exceptions are made for waste dilution samples where the minimum batch QC must include a blank, and LCS/LCSD pair.

10.4 Instrument maintenance should be performed routinely to optimize instrument performance.

10.5 A minimum of one blank (using the same extraction fluid as used for the samples) for every 20 extractions that have been conducted in an extraction vessel.

NOTE: Be sure to preserve metals blanks.

10.6 A matrix spike, matrix spike duplicate and sample duplicate shall be performed for each waste type. At a minimum, follow the matrix spike addition guidance provided in each analytical method.

10.7 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP leaching of the sample.

10.8 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist.

11.0 DATA VALIDATION AND CORRECTIVE ACTION

11.1 All data must undergo a second analyst review.

11.1.1 The analyst should look at any sample that has quantifiable compounds and make sure that they have been confirmed.

11.1.2 All calculations must be checked.

11.1.3 Data must be checked for the presence or absence of appropriate flags. Comments should be noted when data is flagged.

11.1.4 See SOP #030201, *Data Handling and Reporting*.

11.2 Refer to SOP #030208, *Corrective and Preventive Action.*

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12.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

12.1 The EPA requires that a laboratory waste management practice be conducted consistent with all applicable federal and state laws and regulations. Excess reagents, samples and method process wastes must be characterized and disposed of in an acceptable manner. See *ESC Waste Management Plan.*

12.2 Refer to SOP #030302, *Environmental Sustainability & Pollution Prevention*.

13.0 METHOD MODIFICATIONS/CLARIFICATIONS

13.1 In Section 7.3, NaOH solution is made up at 6N rather than 1N due to the large volume of Extraction Fluid #1 that is made up at a time.

13.2 Modifications to this method are noted in the body of the text as state notes. Compliance analyses performed in conjunction with specific state requirements must be performed as noted within the specific state(s) note listed.

13.3 Pressurizing the ZHE device during tumbling at 20psi instead of the method defined 5-10psi is performed due to the limitations of the pressure gauges on the extractors. The pressure at 30psi was found to not have a significant impact on the results of the analysis by the published method authors (Section 9.1.2, EPA Method 1311).

13.4 Samples that have a matrix that is incompatible with the ZHE apparatus (such as solvents which degrade the piston seals) may be tumbled in glass containers paying particular attention to keeping the headspace of the container to a minimum. These samples shall be clearly marked on the bench sheet with an explanation and also clearly qualified on the final test report.

13.5 Per specific client request, a variation of the solids determination in this procedure can be performed and reported. When TCLP_PPF is requested by a client, the percent of liquid that passes through the filter during the Sections 8.2 and 9.4 is reported to the client.

14.0 REFERENCES

14.1 Federal Register Part V Friday June 29, 1990 (Federal register/vol.51, No.216/Friday, November 7, 1986 Rules and Regulations Appendix 1 to Part 268--Toxicity Characteristic Leaching Procedure (TCLP)).

14.2 *Toxicity Characteristic Leaching Procedure*, SW-846 Method 1311, Revision 0, July 1992.

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Standard Operating Procedure

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TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE (EPA METHOD 1311)

Attachment I: Revision History

Current Version:

Version	Date	Description of Revisions
16	7/14/2018	Replaced logo. Technical and quality review and update. Changed ESC logo. Revised sections 2.2, 2.9, 4.3.1, 6.4, 6.5, 6.6, 6.9, 6.14, 6.16, 6.18, 7.1, 7.3, 7.4, 7.5, 7.6, 7.6.1, 7.6.3, 7.7, 8.1, 8.2, 8.2.1, 8.2.3, 8.2.4, 8.2.5, 8.2.7, 8.2.6.1, 8.2.8, 8.2.12, 8.3, 8.4.2, 8.5, 8.7, 8.8, 8.9, 9.1, 10.3, 11.2, 12.1, 13.3, 14.1 and 14.2. Deleted sections 2.3, 2.4, 2.5, 2.7, 4.5, 4.6, 5.1 through 5.8, 8.1.1, 8.2.6, 8.2.9 through 8.2.13, 8.4.1, and renumbered as necessary. Deleted and replaced section 8.5 and all subsections. Added sections 2.3, 5.1, 8.2.1, 8.2.2, 8.2.7.1, 8.2.6, 8.2.8, 8.2.9, 8.2.14 through 8.2.23, 8.3.1, 8.3.2, 8.3.3, 8.4.1, 8.4.2 and renumbered as necessary. Deleted Attachments II and III. Major revision of section 8.6 and all subsections included: Deleted sections 8.6, 8.6.1. Added sections 8.6, 8.6.1, 8.6.2, 8.6.3, 8.6.3.1, 8.6.3.2, 8.6.3.3, 8.6.3.4 and renumbered remainder of section as needed. Then split newly numbered 8.6.6 and renumbered into 8.6.7, 8.6.7.1, 8.6.7.2 and 8.6.7.3. Revised 8.6.8, 8.6.9, split 8.6.10 to make 8.6.11, revised 8.6.12, 8.6.14 and added section 8.6.15 then renumbered remainder of section. Revised 8.6.16.2, split and added State Note to section 8.6.18 to make 8.6.19. Revised sections 8.6.21 and 8.6.22.

Superseded Versions:

This document supersedes the following:

Version	Date	Description of Revisions
0	12/04/95	Origination
1	8/23/00	
2	4/30/01	
3	2/4/04	
4	10/15/05	
5	11/06/05	Technical and Quality Review and update.
6	10/2/07	Technical and Quality Review and update.
7	1/23/09	Incorporation of Minor Revision. Format correction. Technical and Quality Review.
8	9/18/09	Technical and Quality Review and update. Revised attachments II, Revised sections 2.2, 2.4, 3.1, 4.1, 4.2.1, 6.3, 7.1, 7.6, 8.3.1, 8.4.2, 8.5.1, 8.6.7, 8.6.12, 8.6.14, 8.7, 8.8, 12.1. Reformatted sections 10 & 11 to agree with current format convention.
9	10/22/10	Technical and Quality Review and update. Added Attachment III, Revised sections 1.1, 2.2, 2.4, 4.3, 6.8, 6.14, 8.2.10, 8.2.14, 8.3.1, 8.5.5, 8.6.16, 8.8, 9.1, 10.7, and 12.1
10	10/21/11	Technical and Quality Review and update. Added state note following section 8.7, Revised sections 7.7
11	5/2/12	Technical and Quality Review and update. Revised sections 8.6.6 and

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Standard Operating Procedure

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TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE (EPA METHOD 1311)

		8.6.12; Added section 13.3.
	6/11/13	Reviewed with no changes per L. Layne/D. Marlin
12	11/20/14	Technical and Quality Review and update. Revised Attachments II and III and sections 7.1; Added section 13.4 & 13.5.
13	10/27/2015	Technical and Quality review and update. Header and signature block revision. Revised Sections 1.2, 5.7, 6.3, 6.18, 7.1, 8.6, 8.6.17, and 10.7.
14	8/17/2016	Technical and quality review and update. Header re-formatting. Revised Sections 2.2, 2.5, 2.10, 7.7, and 8.6.7. Deleted Sections 2.7 and 2.11.
15	8/3/2017	Technical and quality review and update. Revised logo. Signature block re-formatted. Revised Section 3.1, 8.3, 10.1, and 14.2.

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STANDARD OPERATING PROCEDURE

METHYL MERCURY BY COLD-VAPOR ATOMIC FLUORESCENCE SPECTROMETRY
Reference Methods: EPA 1630

SOP Number:	S-DUL-M-001-rev.02
Effective Date:	Date of Final Signature
Supersedes:	S-DUL-M-001-rev.01

APPROVALS

Laboratory General Manager — Date: 12/18/17

Laboratory Quality Manager — Date: 12/11/17

PERIODIC REVIEW

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

Signature	Title	Date

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TABLE OF CONTENTS

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to describe the determination of methyl mercury (MeHg or CH3Hg) in water, tissue, and solids.

2. Summary of Method

2.1. EPA 1630 method is primarily intended for the environmental methyl mercury analysis of water matrices, either filtered through a 0.45 micron filter, or unfiltered at trace levels. Water samples are preserved by adding 4 ml/L 11.6 M HCl. Tissue samples are collected unpreserved. The water method involves distillation, derivatization, purge and trap, GC separation and atomic fluorescence detection procedures. The tissue/solid method prep involves weighing out a portion of sample, adding 25% KOH/MeOH solution, heating, then adding more methanol. The procedure for analysis involves the same aspects as water. The method embraces various techniques from metals, wet chemistry and volatiles disciplines: i.e., distillation, pH adjustment, ethylation, purging ethylated sample, capturing analyte on carbotrap (BRL Tenax trap), heating trap to elute the analyte into a GC column for separation of peaks, converting vapor to inorganic form and detection on an atomic fluorescence detector.

2.1.1. Distillation of the sample (water only):Distillation procedure is intended to eliminate potential interferences during the ethylation and analysis procedure and it is critical to have the pH of the distillate adjusted to 4.5-5 using acetate buffer; attention should also be paid to flow rates of carrier gas, temperature of distillation and iced receiver vials, as well as the extent of distillation.

2.1.2. Preparation of the sample (tissue/solid only): Approximately 1 gram of sample is weighed out, then 10 mL of 25% w/v KOH/MeOH is added to the sample vial. This is heated for 3-4 hours at 65 degrees C, then is brought up to a total volume of 25.6mL with MeOH. This sits for a minimum of day before analysis.

2.1.3. Derivatization of the distillate: The distillate is ethylated using sodium tetraethyl borate ($NaBEt_4$) and reacted for 15 minutes, then purged with grade 5 Nitrogen gas (N_2) for 5 minutes. The ethylated distillate and ethylated mercury species are collected onto a carbotrap. Then the mercury is desorbed / eluted out of the trap with heat and gas flow into the GC column for separation.

2.1.4. Separation in GC column: Mercury vapor is heated in a pyrolytic column, reducing organic mercury to elemental mercury vapor, carried to cold vapor atomic fluorescence detector and species are identified by retention time and elution order.

2.2. Some critical factors to be aware of in order to conduct successful analysis for this sensitive method include distillation rate, final pH, ethylation agent quality and freshness, scrupulously clean glassware or Teflonware, temperature of thedesorption coil, condition of the trap and column, and lamp stability. Large amounts of water vapor absorbed onto the Tenax traps during purge will cause an instrument response in excess of system sensitivity which will mask the response from the ethylated mercury species in the sample, resulting in loss of the sample. Extreme caution and specific environmental controls are required to be used throughout all procedures to avoid contamination.

2.3. This SOP is tailored for Brooks Rand MERX Mercury/Methyl Mercury Analysis System and is based on EPA 1630 methodology utilizing advances in analytical technology. The method is performance based and performance criteria specified in EPA Method 1630, Section 9.1.2 must be met. Any changes considered necessary by the analyst, should be recorded and submitted to quality management department for evaluation and approval.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method or non-analytical process.

3.2. **Parameters**: Method 1630isfordeterminationof methyl mercuryintherange of0.06- 6.25 ng/L (ppt).This range may be extended using sample dilution or extending the calibration range.

4. Applicable Matrices

4.1. This SOP is applicable to samplesincludingdrinking,surface,andgroundwaters,as wellasdomesticandindustrialwastewaters, tissue, and solids.

5. Limits of Detection and Quantitation

5.1. The reporting limit (LOQ) for water samples is 0.06 ng/L. The reporting limit (LOQ) for tissue/solid samples is 3.1 ng/L. All current MDLs can be found in the LIMS and is accessible through the Quality Department.

6. Interferences

6.1. Contaminationby carryover–contaminationmayoccurwhena samplecontaininga low concentrationof mercuryisprocessedimmediatelyaftera samplecontaininga high concentrationofMeHg.When an unusually concentrated sample is encountered, an ethylation blank should be analyzed immediately following the sample to check for carryover.Samplesanalyzedfollowinga samplethathasbeendeterminedto resultincarryovermustbe reanalyzed.Samplesthatarethought tocontainthelowest concentrationofMeHgshouldbeanalyzedfirst.

6.2. Contaminationcontrol– thismustbe maintainedbyusinga cleanenvironment, minimizingexposuretoanuncontrolledenvironment,cleanworksurfaces,wearingnon-talc gloves,usingmetalfreeapparatus,andnumberingeachpieceoftheapparatusto identifypotentialproblemcomponents.All samplesmustbeprocessedintheclean room/hood.Thecleanroom/hoodisa positivepressureroom/areawithits ownairhandlingsystem. Distillation vials and tubing are precleaned according to the procedure and prevented from coming in contact with possible contamination sources, such as dirty tubing/vials/bags. The Autosampler vials must meet cleanliness requirements. Sample bottle lots supplied to sample collectors are pretested prior to use.

6.3. Whenthis methodisproperlyapplied,nosignificantinterferenceshavebeenobservedin theanalysisofambientwaters.

6.4. Thefluorescentintensityisstronglydependentuponthepresenceof molecularspeciesin thecarriergasthatcancause“quenching”oftheexcitedatoms.TheTenax trap eliminatesquenchingduetotracegases,butitstill remainstheanalyst’sresponsibilityto ensurehighpurityinertcarriergasina leak-freeanalyticaltrain.Insomerarecases(suchasoilpollutedwater)lowmolecularweightorganiccompoundsmaypurg ewiththe methylethylmercuryandcollectontheTenaxtrap,subsequentlyresultinginsignal quenchingduringelution.Suchcasesarebesttreatedby sampledilutionpriorto distillation.

6.5. Investigationshaveshownthatapositiveartifactispossiblewiththedistillation procedureincaseswherehighinorganicHgconcentrationsarepresent.Innaturalwaters,

approximately0.01to0.05%ofambientinorganicHginsolutionmaybemethylatedbyambientorganicmatterdurin gthedistillationstep.In mostwaters,wherethepercentMeHgis1-30%ofthetotal,thiseffectis minor.However,theanalystshould be aware that in inorganic Hg contaminated waters, the fraction MeHg can be <1% of the total, and so flagging of the data (as representing a maximum estimate of MeHg concentration) may be warranted. **In samples with high levels of divalent mercury (Hg(II)), solvent extraction may be preferred.**

7. Sample Collection, Preservation, Shipment and Storage

7.1. For water, pre-certified Teflon/ fluoropolymer sample containers with fluoropolymer or fluoropolymer-lined caps are double bagged in new plastic zip-lock bags, and labeled with the unique container ID and date. It is recommended that samplers follow sampling procedures in the most recent approved revision of EPA Method 1669. It is critical that the bottles have tight sealing caps to avoid diffusion of atmospheric Hg through the threads. Polyethylene sample bottles are unacceptable.Tissue/solid samples can be collected in 2-4oz jars.

7.2. Water sample collection bottles will be preserved with 4 mL/L HCl for fresh water samples and 2 ml/L H_2SO_4 for saline samples (containers for saline samples are prepared in the laboratory per client request). Samples should be collected with no headspace. Samples are transported in an ice containing cooler to keep them cold and in the dark (to prevent photo degradation of methyl mercury). Due to the potential for contamination in the field, filtration and preservation of samples is recommended to be performed in the clean room/hood at the laboratory.Samples that require lab filtration are collected in non-preserved containers, filled with no headspace, capped tightly and maintained at 0-6^{0}C. These samples must be processed and preserved within 48 hours of sampling.

7.3. Upon receipt of the samples, a standard log-in procedure is followed in which a unique identifier ID is assigned to each sample for tracking purposes in the laboratory and LIMS. Once the samples arrive at the Duluth laboratory, water samples are individually checked to ensure that the pH is < 2. To do this, a small aliquot is taken from the sample container using a clean pipet tip, and then placed on a pH strip. If the sample is not at the correct pH, additional HCl must be added, and the sample must be re-checked for correct acidity. Once the correct acidity is shown, samples are stored in a cool (0-6^{0}C) dark refrigerator which is kept separated from potential contamination sources to await distillation and analysis.

7.4. Properly preserved samples may be held for 6 months at the laboratory. Ethylated distillate should be analyzed within 48 hours. Tissue/solid samples should be analyzed within 28 days after sample collection date.

8. Definitions

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

8.2. **Dissolvedmethylmercury**:AlldistillableMeHg (CH_3Hg) formsandspeciesfoundinthefiltrateof anaqueoussolutionthathasbeenfilteredthrougha0.45-micronfilter.

8.3. **Methyl Mercury**: All acid-distillable Hg, which, upon reaction with $NaBEt_4$ yields methylethylmercury.Thisincludes,butisnotlimitedto,CH_3Hg^+,stronglyorgano-complexed CH_3Hgcompounds,adsorbedparticulateCH_3Hg,andCH_3Hgboundin microorganisms.Infreshlycollectedsamples,dimethylmercury($(CH_3)_2Hg$)willnotbe

recoveredasCH_3Hg,butinsampleswhichhavebeenacidifiedforseveraldays,most $(CH_3)_2Hg$hasbrokendowntoCH3Hg.Inthismethod,CH_3Hgandtotal recoverable CH_3Hgaresynonymous.

8.4. **CalibrationBlanks** – see also Ethylation Blanks below: The calibration blank(s) result isutilizedtocorrectthecalibrationcoefficient. Since there are three traps utilized in the BRL Merx system, three Calibration blanks are analyzed and the mean of these blanks represents the calibration blank result.

8.5. **EthylationBlank**:Usedtodemonstratethatthereagentsusedtopreparesamplesfor Hg analysesarefreefromcontamination.Thepresenceof CH_3Hgintheethylationblankindicatesaproblemwithoneormoreofthereagent solutions.Purgingtheacetatebufferwithmercury-freenitrogen to make sure CH_3Hgtoacceptablelevels.Ifcontaminationstill remains then use a new lot of the buffer andverify itscleanliness.

Note: Ethylation Blanks are used as the Calibration Blank set, Rinse and CCB, none of which are distilled.

8.6. **MethodBlank:**Usedtodemonstratethattheentireanalyticalsystemisfreefrom contaminationthatcouldotherwisecompromisesampleresults.Methodblanksare preparedandanalyzedusingsamplecontainers,labware,reagents,andprocedures identicaltothoseusedtoprepareandanalyzethesamples.Aminimumofthreemethod blanksisrequired to evaluate all three analytical traps.Themeanmethodblankfinalresultisusedforthecorrection of thefinalresultforsamples.Iftheresultforanymethodblankisfoundtocontain >0.06ng/L, or the variation is >0.015ng/LHgthesystemis outofcontrol.Samplesassociatedwitha contaminated methodblanksmustbereanalyzed.

8.7. **Field Blanks:** The representative Field Blanks shall be batched, prepared, and analyzed with the associated samples whenever possible. If Field Blanks are greater than the reporting level, the associated samples are qualified. If samples are filtered in the field, these filter / equipment blanks are treated similar to the field blank.

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

9.1. Table 9.1: Equipment and Supplies

Supply	Description	Vendor/Item #
DI Water System	Water Purification System	Barnstead D464I
Mercury Analyzer	Cold Vapor Atomic Fluorescence	Brooks Rand Model III
Autosampler		Brooks Rand PS
Total Hg Purge and Trap		Brooks Rand Merx
Hg Speciation Purge and Trap		Brooks Rand Merx
Distillation Block		Brooks Rand
Flow Meter		Brooks Rand
Refrigerator D-1		Admiral

Refrigerator D-2		Estate/Whirlpool
Oven		Thermo-Lindberg Blue M
Hood DB-1		ESCO
Hood DB-2		ESCO
Hood 3 DE-1		Labconco
Balance	Capable of measuring to 0.001 g	Sartorius ME 14145
Amber Glass Vials	40 ml	Brooks Rand Certified
Teflon Vials	For distillation	Fisher Scientific or equivalent
Pipettors	10-200µL, 100-1000µL, 1-10 ml	Finnpipette or equivalent
Nitrogen Gas		Praxair or equivalent
LIMS	Data reporting software	See master list for current version
Mercury Guru 4.1		
XPRO Systems		

10. Reagents and Standards

10.1. All reagents and/or drychemicals usedto makereagentsmust beofthe highestpurityavailablefromthevendor andshowntobelowin mercury. Uponreceipt atthelaboratory,containerswill be markedwiththedateof receipt andstoredintheappropriateareas.Whenreagents are mixedfor use inthismethod,thepersonwho mixesthemwill initial anddatethereagent container according to the Pace SOP for Reagents and Standards.

10.2. Uponreceipt atthelaboratoryor onthedayofpreparation,standardsshould belabeledwiththedatereceivedor madeandtheinitials oftheperson preparing them. Highlyconcentratedstocksolutionsshouldbestoredaway fromthe mainworkingareastopreventcontaminationofthecleanlab. All standardsmust beassignedauniqueidentificationcodeandbeenteredintothelaboratorydatabase system.

10.3. Table 10.3: Reagents and Standards

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Reagent water	Ultra-pure reagent grade water shown to be 18 MΩ minimum starting from pre-purified reverse osmosis source. The water is delivered through a 0.2 um filter. All water is obtained from a Barnstead water purification system.	

Acetate Buffer	2M, contains antifoaming agent	Brooks Rand Stored at Room Temperature
Ethylating Reagent Sodium Tetraethyl Borate($NaBEt_4$)	Pour the $NaBEt_4$ (part A) into 40mL of 2.0% KOH solution (part B) that has beenchilled to 0 ^{0}C (stored in the freezer) to producethe workingsolution. Thissolutionis thentransferredintoindividual4.0mL amber glass vials, and capped. Thissolutionis thentransferredintoindividual4.0mL amber glass vials, capped and stored at <-10^{0}C in the freezer and is mostly thawed just prior to use. The solution expires in about 3 hoursaftertheinitialthaw.	Brooks Rand **$NaBEt_4$solutions shouldnot be used iftheyshowanydiscoloration** ThefrozenNaBEt$_4$hasbeen proven tobestablefor 6 monthsif stored in the freezer.
H_2SO_4	9M To prepare a 200 mL solution, slowly add 100 mL concentrated H_2SO_4 into 100 mL DI water	
20% KCl in 0.2% L-Cysteine	To prepare a 200 mL solution, dissolve 0.4 g of L-Cysteine and 40 g of KCl into 159.6 mL DI water, shake well to dissolve	Expires in 6 month or when crystals form
Trace Metal Grade HCl		Fisher brand or equivalent
Methanol		Fisher or equivalent
25% w/v KOH/MeOH		To prepare a 100 mL solution, dissolve 25 g of KOH in 100 mL of MeOH
Methyl mercury stock solution used for Calibration	MeHgCl = 1 mg/L MeHg as Hg, (also contains 0.5% acetic acid and 0.2% HCl) are stored in the standard refrigerator. The MeHgCl is for calibration	
Methyl mercury stock solution used for second source verification	MeHgOH = 1 mg/L MeHg as Hg, are purchased from Brooks Rand and stored in the standard refrigerator. The MeHgOH is for calibration verification, i.e. ICV/IPR standard	
Methyl mercury working standard #1 (1 ng/mL MeHgCl with 0.5% acetic acid and 0.2% HCl)	Dispense approximately 50 mLof reagent grade water into a 100 mL mercury clean class A volumetric flask. Pipette 100 uL of the stock standard (1 ppm) to the volumetric flask, add 0.2 mL	This solution should be stored in an amber glass vial in dark place at room temperature and prepared every month.

	conc. HCl, 0.5 mL of conc. glacial acetic acid and dilute to 100 mL with DI water. It is recommended the working standard be compared to the previous working standard and agree within 5%.	
Methyl mercury working standard #2 (0.01 ng/mL MeHg)	Dispense approximately 9.9 mL of reagent grade water into a 40 mL pre-certified mercury clean glass vial. Pipette 100 uL of the standard 1 to the vial, cap it and invert a few times.	This solution should be used within 2 hours.
Methyl mercury standard for ICV	following the same procedure of the above working standard#1 using MeHgOH instead of MeHgCl	
Grade 5 Ultra High Purity Nitrogen	For distillation and UHP grade Argon and Nitrogen for analysis	

11. Calibration and Standardization

11.1. Table 11.1: Calibration and Standardization

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average response factor	≤15%	If it is not met, review for any standard preparation or analysis errors. Perform any necessary maintenance prior to recalibrating the instrument. The initial calibration must pass prior to sample analysis.
Reporting Limit Standard	Calculate the recovery of the reporting limit standard following each daily calibration	60-140%	Evaluate the source of error. Remake the standard if it is considered the source of error. If the reanalysis does not meet criteria, recalibrate the instrument prior to proceeding with analysis.
Second Source Verification Standard (ICV)	Immediately after each initial calibration	69-131%	If the requirements for initial calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back
Continuing Calibration Verification (CCV)	After every 10 samples, samples must be bracketed with a closing CCV standard.	67-133%	If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the

			same standard are permitted back to back.
Calibration Blanks	3 system blanks – One on each of the 3 traps	< 0.06ng/L for each individual blank; standard deviation of the three blanks must be ≤ 0.1 ng/L.	If the requirement is not met, evaluate the source of the detections. Re-prepare the blanks and reanalyze. If it is still not met, stop analysis, perform and document all maintenance performed and recalibrate the instrument.

Note: Details of the preparation of the calibration standard series are listed in Attachment VI.

Note: The Initial Calibration Verification (ICV) isevaluated toassess the accuracy of the initial calibration standards.TheICV must be from independent source; MeHgCl is for calibration and MeHgOH is for verification.

12. Procedure

12.1. Distillation and Sample Preparation Procedure (Waters):The Brooks Rand Methyl Mercury Distillation System (MDS) is used for distillation. It is a standalone distillation system which has 2 major units, the distillation unit and receiving unit. The distillation unit integrates with gas flow control, heating block temperature control, heating block, etc. The receiving unit is an aluminum block in ice-bath (cooler). The MDS has 2 identical sets, each set can handle up to 10 distillations simultaneously. Thedistillation procedureoutlinedhereisrequired to remove matrices thatmay interfere withthe ethylation process. The samplesaredistilled at138^{0}Cwith the additionof 0.2 mL of 20% KCl/0.2% L-Cysteine and 0.5 mL 9M H_2SO_4 solution. It takes two to three hours to complete the distillation. The distillation step requires organization and experience; it is a time consuming step when compared to ethylation, purge & trap, and analysis steps.

12.2. Sample Preparation Procedure (Tissue/Solid):Weigh about one gram of solid or homogeneous biological material (0.5 g if using freeze-dried material) into a 30 mL Teflon vial. Add 10 mL of 25% (w/v) KOH/methanol solution and cap the vial tightly. Digest the sample in an oven or hot block at 65º C for 3-4 hours. Avoid heating overnight, as recoveries drop sharply; recoveries may return to expected levels after sitting for several hours at room temperature. After digestion, bring the final volume to 25.6 mL with methanol, invert to mix, and let sit a minimum of one day prior to analysis. Analyze an appropriate aliquot, depending on the sample's expected concentration of MeHg and Hg (II). A maximum of 30 µL of the sample digestate may be analyzed due to the methanol content.

12.3. DistillationBlank (Method Blank): A distillationblankispreparedbydispensing50 mL ultra-pure DI water comparable to thatof samplesintoa distillation vialthat contains0.2mL of 20% KCl/0.2% L-Cysteine,and0.5mL 9M H_2SO_4. They are used to verify acceptable background levelsandcalculatedetectionlimits during analysis.

12.4. MatrixSpike/Matrix Spike Duplicate: A matrix spike and a matrix spike duplicate are preparedbyadding 100 pg MeHgCl standard each toa 50ml split of the source sample. They are usedtoevaluateproceduralaccuracy and presence of matrixinterferences.

12.5. Methyl MercuryDistillation:Aqueoussamplesareaddedtopre-weighedTeflon vialsinapproximately50mL aliquots and weights recorded.Capsareplacedonthe distillation vials with the inletattached to aN_2source, andthe outlet attachedtoa Teflon receiving vial. The distillation vials are heated

to approximately 138 ^{0}C andallowedtodistill until10–20%of the total volume remains. Three distillationblanks,one set of spikedduplicates, andnine othersamples aredistilledforatotal of 10individualfield samplesperdistillation block(up to 20distillations).

12.5.1. Organization and detailed record keeping is imperative. Sample ID, distillation vial# and receiving vial# should be linked to each other with a traceable pattern.

12.6. Distillation Set-up:

12.6.1. Turnonthe distillation heating block, use the “Up” and "down" arrow button to adjust the temperature to138°C and save the setting by pushing set button.The 1st row of the LED display is the current actual temperature reading(in red color), the 2nd row is the pre-set temperature of 138 degree (in green). Turn it off. **This is for the initial use, next time you use it, just turn it on and off.**

12.6.2. Weigh each distillation vialandrecord the tareweightandthe vial number (engraved on the vial).

12.6.3. To prepare samples,shakeeach acidified sample bottle to homogenize the contentsbeforetransferring ~ 50 mLof sample aliquotintothe distillation vials.Setup 10% of samples (one or twosamples minimum) in triplicate forthe duplicate spike analysis.To prepare MS/MSD, 100 uL of MeHgCl working standard at a concentration of 1.0 ng/Lis addedto eachoneof twovials containingsimilar volumesof the same sample.Record the sample ID, vial ID, tareweightandvialplussample weightalongsidethe appropriate distillationvialnumber.

12.6.4. Pipette 0.5mL 9M $H_2SO_4$and 0.2 mL 20% KCl/ 0.2% L-Cysteine mixture intoeachdistillationvial, including method blank and quality control standards mentioned in the following paragraph. Atotalof 10 vials peraluminumblock areprepared.

Note: Make sure the KCl/L-Cys solution is not crystallized, asthis could cause low recoveries on distillation. If it is crystalized, prepare fresh one to use.

12.6.5. Preparethe 3distillationblanks by dispensing 50mL DI water intoeach of threevials and add 0.2mL of tracemetalgrade concentrated HCl to each of them to acidify.

- Preparethe two low level LCS/LCSD (3pg)by dispensing 50mL DI water intoeach of twovials and adding 0.2mL of tracemetalgrade concentrated HCl and 300 uL of fresh made 0.01 ng/mL MeHgCl standard.

- Prepareanother set of higher level LCS/LCSD (100pg)by dispensing 50mL DI water intoeach of twovials and adding 0.2mL of tracemetalgrade conc. HCl as well as 100 uL of 1 ng/mL MeHgCl standard to each.

- Recordvial ID, vialpluswaterweight,andblock position.

12.6.6. Fiteach ofthevials with the distillation cap/transfer tubing corresponding to the blockpositiontobe occupied by thatvial (eachcaphasbeenengraved witha numberbetween1 and 10). Cappedvials shouldbeplacedinan acrylic rack topreventtipping.

12.6.7. Weigh each of 10cleanvialstobe usedasreceivingvials. Record the tare weight of eachvialand itsunique ID. Dispense 15mL of ultra-pure DI water toeach of the receivingvials.Record vialID vialpluswater weight,andblockposition. In an ordered manner, thread the transfer tubes through the Teflon ports in the side of the cooler and cap each receiving vials accordingly. Placethedistillationvials

intheir corresponding positionsinthedistillation block.

12.6.8. Turnonthe N_2flowto the flowmetersandconnect the gas lines to the inletportsof the distillation vialcaps.

12.6.9. Immediately connect the tubing from the distillation vials to the inlet ports of the receiving vial caps. Check for bubbling in the receiving vial water (which indicates N_2 flow through the system, the system is not blocked or leaked) and place the receiving vial into the cooling block either pre-frozen or filled with ice.

12.6.10. Adjust the flowonthe flow meters to 50mL/min and turn on heating.

12.7. Distillation: Allow the distillation to proceed until 80% of the original volume has been distilled (usually about 2-3 hours). Throughout the distillation, periodically check the receiving vial to ensure unrestricted N_2 flow, no leakage, and the block temperature.

12.8. Shutdown: As individual distillations reach completion, the distillation vial can be removed from the block and receiving vials can be removed from the cooler. Weigh the receiving vials and record the full weight. Add 3 mLs DI water to bring thevolume of distillates to 58 mLs. The receiving vials are cappedand placed in the refrigerator overnight to await analysis. The distillation vials are rinsed with tap water and placed in the holding bin for the acid cleaning process.

12.8.1. Clean up. See the cleaning procedure in Section 12.18.

12.8.2. After the last distillation vial has been removed from the block, the N_2flow and the hotplates should be turned off.

Note: It is strongly recommended to analyze distillates within 1weekof distillation.

Note: TurnonN_2before makinganyconnections, this will flushthe flow metersandlines with cleanN_2andprevent the samplesfrombacking up into the flow meters.

12.9. Ethylation and Sample Analysis Procedure:

12.9.1. After thedistillation, the sample distillates (in sealed receiving vials)are stored in the dark at room temperature for up to 48 hours before analysis.

12.9.2. Obtaining good resultsfromtheMERX systemrequires following theexact steps below. Itisnecessarytofollowthepreparationmethodexactly,otherwisethe variationinresults maynotbeaproductoftheMERXsystem,butinsteadit maybedue to thepreparation of thesample.

12.9.3. The following criticalstepsthatmust be taken prior toloading the sample ontotheMERX system: vial preparation, calibration, buffering, ethylation, sealing the vial, and analyzingthe sample.

12.10. VialPreparation:TheMERXsystemisdesignedtoanalyzesamplesprepared ina40mL amberglass vialwhichissealedusingathreadedcapcontainingaseptum.Thevialandlid shouldbetriplerinsedtoensurecleanlinesspriortoanysamplebeingaddedto the vial. It is recommended that precleaned certified vessels are used.

12.11. Calibration: See Section 11.

12.12. Buffering: AsperEPA Method1630,add0.300mLof2MAcetateBuffertothesampleinthe vial. Usethis in everyvial that gets processed bytheMERXincluding all blanks.Forthe MERX tofunction properly, it is important that all samples maintain apH of 4.5-5.
Ifthe0.300mLofbufferisnotadequatetostabilizethepH,more can be added tothe vial. pH can be taken by pipetting trace amount of buffered sample onto a pH strip paper.

12.13. Ethylation: Asper EPA1630, add0.04mL of$NaBEt_4$toeachvial thatgetsprocessed by the MERXincludingall blanks, excessive amounts will sharply decrease the distillation efficiency**.**

12.14. Sealing the vial:

12.14.1. Afteraddingthesample,theacetatebuffer,andtheethylationreagentintothe vial;thevial mustbetoppedoffwithDI water.Ensurethat therearenoairbubbles inthevial, similar to VOC samplepreparation. Carefully seal the vial such that no sample spills over thesides. Twist the cap to makethelidtight, vigorously shake the bottle sothat the sample in the bottle mixes well with the ethylating reagent and buffer. Look for any bubbles that may have been introduced to the vial while it is being sealed. Should this occur, re-open the vial and removethe bubble. Any trapped air in the vial will lead to the methyl ethyl mercury becoming unstable and low recoveries will result.

12.14.2. The sealed vial is stable for 2 days; however, it is strongly advised to analyze the sample as soon as possible. Typical degradation in responsedue to aging is on the order of 0.2% per hour.

12.14.3. The preparation of water sample vials for methyl mercury analysis onMERX is summarized below:

1. Add sample to vial (record exact amount of sample added)

2.Add 0.3 mL of acetate buffer (or appropriate amount for samples)

3. Add 0.04 mL of $NaBEt_4$

4. Fill vial completely (no headspace) with reagent water (use a squirt bottle)

5. Cap tightly

6. Invert rapidly to mix contents

12.15. AnalyzingtheSample: AnalyzingthesamplewillrequiretheuseofMercuryGURU4.1software. Refer to Section 12.16 for the operation details.

12.16. OperatingtheMERXSystem:TheMERXsystemcomescompletewithanAutosampler,a Methyl Hg Purge& Trapmodule,aMethylHg GC&Pyrolysismodule, andaModel III CVAFS(ColdVaporAtomicFluorescence Spectrometry)detector. WiththehelpofMercury GURU 4.1software, these4unitsallowforhighturnout ofMethyl Mercurysampleanalysis. The Purge& Trapmodule has a triple collecting trap design to improve efficiency, i.e. the 1st trap is dried while another trap collects ethylated Hg species from the next vial. After drying, another vial is purged onto a 3rd trap, while the 2nd is dried, and the 1st trap now dry, which is instantly IR heated to thermally release the Hg species in an Argon carrier gas stream.

12.16.1. Start GURU 4.1, locate the Integration Mode menu in roughly the middle ofthe screen. Using the pull down list, choose Auto Methyl Hg, Peak Height as Integration type.

12.16.2. Open “MeHg”template which was previously created with the typical setting and calibration curve information.

12.16.3. SaveasData(File/Save AsData), either in“.brd” or “.brt” format.

12.16.4. Turninstrumentsoniftheyhavebeenoff.

Note: the detector should stay on all of the time or be turned on 24-48 hours before using the instrument.

12.16.5. Connectinstrumentstocomputer(Instrument□Connect;thenpressAccept)

12.16.6. Turn gases on at regulator if they have been off. In the Automation tab, there is aset of 3 check boxes to turn the gases on, click those boxes. It should be at your typical settings or a default of: (a)Purge: 50(b) Dry: 30(c) GC:40Turn the knobs on the faceplate of the Purge & Trap module to make the gaugereadings (gas flow) correct.

12.16.7. If the detector is not in Auto Methyl Mercury mode then switch it to Auto Methyl Mercury mode by adjusting the PMT setting, finding COM ports*andautozeroingthedetector. Make sure N_2, Ar lines are connected to Purge & Trap module and Stainless steel needle is used for Auto sampler.

Note: When switching between Auto Total Mercury and Auto Methyl Mercury, you may disconnect COM ports by going to Instrument tab and choosing “Disconnect”, otherwise GURU may not able to locate the communication port(s) automatically, especially for the Purge & Trap module, manually reconnect as needed. Reset the CableMax serial-to-USB adaptor box, restart Guru and/or reboot computer may be required.

12.16.8. MeasureNoise(Instrument□MeasureNoise)

12.16.9. Set run duration to 5 min, purge duration to 5 min, drying duration to 3 min,and heating time to 9.9 seconds instead of the default 9.2 seconds. In the Batch Information tab, typical times are listed.

12.16.10. Set thenumberofvialstobeanalyzed(thiscanbeadjustedwhilethesystemisanalyzing).Also ensurethatthefirstvialpositionnumberiscorrect(defaultisposition1).

12.16.11. Put thepreparedvialsontotheauto sampler rack.

12.16.12. PressStartBatch button. TheMERXsystem willmakea seriesofclickingnoises,it mustfirstgothroughaseriesofprocesses (self-diagnosis and trapconditioning) beforeit can start to process vials. There is an approximately 9 minutedelaybeforethe auto sampler moves to the location of the first vial.

12.16.13. Atthispointyou cancontinuetopreparesamplestoputontheauto samplerorupdate the Run Information in Guru, such as Batch Number, Analyst Name, etc.

12.16.14. Mercury Gurusoftwareintegrates thedetectorsignal strength andcalculatesresultsbasedon calibration (with method blank correction)andsamplevolumeinformation. The calibrationdata,distillationblankvalues,matrixspike recovery,andRPDs forduplicate are automatically evaluated and QCresultsare automaticallyflaggedbasedonpre-defined criteria.The analyst should review all the peaks for their correctness for methylmercury.

Note: Guru lacks the capability to manually adjusting peak baseline.

Note: Guru calculations are based on default parameters, i.e. analysis volume is 40 mL, 50 mL for sample volume (for distillation) and 58 mL for dilution volume (distillate collected, including 18 mL DI added), adjustment should be made if the actual parameters are different. Run types are different for calibration, blank, QC and samples, make sure choose the correct volumes when set up a batch sequence.

12.17. Trouble Shooting MERX.

12.17.1. FluctuatingSignal/IncreasedNoise.

- Mercury Lamp Age.Most often a fluctuating signal is caused by a flickering lamp. This mayhappen as the lamp ages.Replace thelamp.

12.17.2. IncreasedBackground Noise.

- Mercury Contamination. Asuddenincreasein backgroundis oftenaresultofHg contaminationinthecarrier gas tubingandfluorescencecell. AmassofHgassmallas100ngcancauseatemporary increaseinthebackground. Allowingthedetectortositidleforseveralminutesand continuingtoflowcarriergasthroughthetubingandcellwilleventuallyresultina returntonormalbackgroundlevel. Formoreextremecases,replacingtheFEPtubing forthecarriergas, includingtheinternaltubingoftheACMandCVAFSModel III,is required inorder torestore tothe normal background in the short term.

- Alternatively, thecause may becontaminationonthetraps. Toremove anysuchcontamination,runaseries ofblanksoneachtrap. Itisoftenpossibletoclear out contamination carryover by doing this, however in the caseof extremecontamination, it may be necessarytouse new traps for future analysis.

12.17.3. Scatter

- Smallparticlesofdustcanenterandremainin thecellover time. Thiswillusuallycause an insignificant increase in thebackground level, i.e., thesensitivitycan still beadjusted suchthat the lowest level peaks are discernible from the noise.

- Itispossibleforacontaminanttoprecipitateinor‘fog’thefluorescencecellsuddenly, orslowlyovertime. Thismaybecausedbyaproblematicsample. Ifthisissuspected, followthefluorescencecellcleaningprocedure.Also replacetheFEPtubingforthecarriergas,includingtheinternaltubing oftheACM and CVAFS Model III.

12.17.4. DecreasedSensitivity Over Time

- Mostdecreasesinsensitivityare eithermethodrelated oraresultofdetection equipment otherthantheCVAFSModelIII. Examplesofmethodrelated causes may be contaminatedorpoorqualityreagentsorinadvertentlyomittingreagent. Theageof systemcomponents such astheGC Columnor Speciation Trapsmay contribute to decreaseinsensitivity.

12.18. Distillation Equipment CleaningProcedures

12.18.1. All opening/capping of vials are done in the laminar flow hoods and all the plastic containers used for the extra caps or other solutions/reagents shall be rinsed with 2% HCl three times and DI water three times prior to use. The oven is cleaned using 409 spray before use.

12.18.2. Distillation Equipment (Initial Cleaning):

- A 33% HCl solution is added to the vials. The vials are then placed in the oven (55-60 ^{0}C) overnight.
- The next day, the receiving vials are rinsed at least 3 times with DI water, then a 1% HCl solution is added, and they are put back in the oven overnight.
- The vials are taken out the next day, rinsed at least 3 times with DI water, and stored with 0.5% HCl solution, just enough to cover the bottom of the vials. The vials are then triple bagged and put back in the oven the day before vials are to be used. Rinse multiple times with DI water before use.
- The regular caps are soaked, and double bagged once dry. The distillationcaps (with tubing) are kept separate from the regular caps. These are rinsed, with water rinsing through the tubing. The water is shaken out and they are laid in the Laminar flow hood to dry. Once dry, they can be double bagged.

12.18.3. Distillation Equipment (After Each Use): Teflon distillation and receiving vials, tubing and caps used for distillation of water samples are cleaned as follows:

- For vials, tubing, and caps used to distill any MeHg sample: Rinse with DI water, fill with 2% HCl. Tubing and caps are also injected through pipette or dispenser with 2% HCl in fume hood. The vials are capped with the tubing firmly in place, triple zip-lock bagged and are heated in the oven overnight at 57^{0}C. Record date cleaned.
- When out of the oven, vials are triple-rinsed with DI water and placed in room temperature 10% HCl for storage until use. Initially test the solution by total Hg method. The result should be less than 1.00 ng/L. The HCl solution can be used for a month and the container should remain closed at all times except loading or unloading vials, tubing and caps. Rinse vials well with DI water before use.
- The tubing is rinsed with a stream of DI water.
- Caps with tubing are rinsed with DI water, shaken out, and laid out in the Laminar Flow Hood to dry. They are then double bagged

13. Quality Control

13.1. Table 13.1 Quality Control

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Ethylated Blank	3ethylationblanks arepreparedbyadding approximately40 mLofreagentgradewater, 300µLofacetate buffer, and 40µLofNaBEt$_4$toeachvial.	3 per batch of 20	Ifanyoneethylation blank exceedsthe criteria, another set ofethylationblanksshouldberunto ensurenooperator error.Ifthissecondset ofblanksis alsoout ofcontrol theanalystmustisolateandcorrecttheproblembeforecontinuing.	Ifanyoneethylation blank exceedsthe criteria, another set ofethylationblanksshouldberunto ensurenooperator error.Ifthissecondset ofblanksis alsoout ofcontrol theanalystmustisolateandcorrecttheproblembeforecontinuing.
Method Blank (MB)	DI water with reagents used for samples (boiling stones forsolids, ground chicken for tissue along with reagents)	3 per batch of 20	The maximumacceptableabsoluteconcentrationfor anyone methodblankmust not exceed 0.06 ng/L.	Ifthedistillationblanksfail to meet either oftheacceptancecriteria,theentirebatchofsamplesmust bedistilledandanalyzedagainor flaggedaccordingly.If there is insufficient sample volume report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	DI water spiked with all target compounds. Boiling stones added for solids, ground chicken for tissue.	One per 20 samples	67-133%	Analyze a new LCS; If problem persists, check spike solution; Perform system maintenance prior to new LCS run ***Exceptions:*** If LCS recovery is > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Client sample spiked with all target compounds	One per 10 samples	65-135%	If LCS and MBs are acceptable, the MS/MSD should be reviewed. Per method requirements the sample is diluted until the matrix spike recovery is within method criteria.
MSD	MS Duplicate	One per 10 samples.	RPD< 35%	Report results with an appropriate footnote.

13.2. QC Samples

13.2.1. Standards:Createastandardcurvebyaddingvaryingamounts of workingstandardtocover theexpectedconcentrations rangeintheanalytical batch. To approximately40 mLofreagentwater ineachofthereactionvials. Pipette300µLofacetatebuffer and40µLofNaBEt$_4$toeachofthe reactionvials.Checkstandards areanalyzedthroughouttherunto verifythat noinstrument drift exists.

- Acceptancecriteria: Peak heights obtainedfor thestandards duringthe calibrationarecorrectedfor CH_3Hg^+intheacetate buffer andtheNaBEt$_4$ bysubtractingtheaverage peak areaoftheethylationblanks. Simplelinear regressionwhileforcingzerointerceptis appliedto thepeak area/masscombinationstodeterminethe best-fitline(DQOis r^2equal toor greater than0.995) andestablishtheequationusedtodeterminethe mass ofthesamplealiquotfromitsresultingpeak area.

Note:EPA 1630 method **DOES NOT** specify to use surrogate to monitor the efficiency of the distillation and purge-and-trap processes, however n-propyl mercury may be used as surrogate per client's request.

13.3. Instrument Calibration and Frequency

13.3.1. TheMERXMeHg detectoriscalibratedonadaily basis.Standards and blanks are analyzed at the frequency of each ten samples, from the beginning to the end of the analysis day. The instrumentresponse fromthe standardsisused to calculateameanresponse factor(RF)in nanograms perpeakarea. Ethylationblanksare used to measureandcorrect formercury in the system during the reactionandanalysis processes.

13.4. Reporting of Results:

13.4.1. Reporting units: Methyl Mercury in ng/L as Hg.Reporting levels and significant figures:

Report to the nearest 0.01 ng/L for values less than 10 ng/L;

Report to three (3) significant figures for values exceeding 10 ng/L.

13.4.2. The distillation procedure is not 100% efficient in recovering CH3Hg because not all of the sample volume can be distilled, to avoid co-distillation of HCl. The laboratory specific efficiency of the distillation is determined by the running mean of the last 30 recoveries calculated for LCSs, excluding any values that are more than two standard deviations from the mean. Since the distillation technique is inherently and reproducibly non quantitative, all results should be recovery corrected by an empirically derived factor. See Equation in Section 14.

13.5. Documentation and Data Management:

13.5.1. Allraw data produced in the laboratory should be archived. Hard copies of EXCEL spreadsheets and data reports are archived with raw data. All electronic data is archived and backed up on regular basis.

13.5.2. Allvariablesinvolvedin any analytical procedure such as distillationsetup, operation,andshut down are written downondistillationbench sheets. Thedistillation benchsheets are then enteredinto Microsoft Excelspreadsheets. Afterthe Excel sheetshave beencheckedtheyare enteredintothe database program. Theprogramperformsalldata sorting,assimilation and calculations.

13.5.3. Data review and authorization: data should go through peer review for any possible error during analysis and transcription and get QA approval before being released to client.

13.5.4. All the following information should be documented :

- Name of analyst and Date of analysis.
- Type and date prepared for reagents and standards used
- Summary statistics of blanks, standards, distillation blanks, and matrix spikes.
- Identification of vial contents, volume analyzed, instrument response, and sampletrap identification for each analysis performed.
- Identification of all equipment used in analysis, such as pipettor IDs.
- Percent recoveries of matrix spikes and percent difference of duplicates
- All invalid data and incorrectly entered data.
- Concentrations, total mass, and detection limits of MeHg in the samples.
- Comments pertaining to special samples run, problematic samples, corrective actions taken, and results of any calculations performed to ensure acceptance criteria are being met.

13.5.5. Guru software are capable to generate reports with most of the information except the sample chain of custody, standard prep log, distillation log and vial cleaning log. There is space to make comments on the printed Guru report.

14. Data Analysis and Calculations

14.1. Calibration Factor for each non-zero Calibration Standard:

CF = (Astd – Asb) / Cstd

CF = standard's Calibration Factor

Astd = peak area of the Calibration Standard analyzed

Asb = average peak area of the 3 Calibration Blanks

Cstd = concentration of the Calibration Standard analyzed

14.2. Thecheckstandards areevaluatedwiththefollowing formulafor percentrecovery:

%R = ((PHC - PHEB)/M)/(VS*CS) * 100

%R =Percentrecovery

PHC=Peak heightofcheckstandard

PHEB =Averagepeak heightofethylationblanks

M =Slopeofcalibrationline

VS=Volumeofstandardadded

CS=Concentrationofstandardadded

14.3. Thefollowingformulais usedtocalculatethe absoluteMBconcentration.

[MB]= (PHMB/M)/D

[MB]= absoluteconcentrationoftheMBinng

PHMB= peak heightoftheMB

M = slopeofcalibrationline D=fractiondistilled

14.4. AbsoluteMBconcentrations areusedtocalculatean absolutedetectionlimitfor thedayusingthefollowing formula.

[DL]= 3xσ[MB]

[DL]=absolutedetectionlimit

σ[MB]=standarddeviationamongabsolute method blanks

14.5. A dailydetectionlimit(DDL) iscalculatedfor each samplefromtheabsolutedetectionlimitinasample batchbythefollowingformula:

DDL= (([DL]/D) x(VD/ VA))/VS

DDL= daily detectionlimit

D = fractiondistilled

VD = total volumeof distillate,inliters

VA= volumeof distillateanalyzed,inliters

VS= volumeofsample,inliters

14.6. Matrix Spike/Matrix Spike Duplicate Percentrecoveryiscalculatedasfollows:

%R = (MS–(Sx(VMS/ VS)) /STD

%R =percentrecovery

MS=mass ofmethylmercuryinspikedsample

S=mass ofmethylmercuryinunspikedsample

VMS=volumeofspikedsample

VS=volumeof unspikedsample

STD=mass ofmethylmercury addedtosample

14.7. The following calculation can be used to calculate the LCS percent recovery:

% Recovery = (LCS Concentration/True Value) X 100

14.8. ng/L to ng/g conversion

$$\frac{EV \times R \times PV}{IV \times DW} \times \frac{1L}{1000\ mL} = R'$$

R= Result (ng/L)

IV= Injected volume (mL)

DW = Weight of solid/tissue (g)

PV= Total Volume

EV= Sample+MeOH Volume

R'= Result (ng/g)

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See table in section 13.

16. Corrective Actions for Out-of-Control Data

16.1. See table in section 13.

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

17.1. If not specified by the table in section 13, the contingencies are as follows. If there is no additional sample volume to perform re-analyses, all data will be reported as final with applicable qualifiers. If necessary, an official case narrative will be prepared by the Quality Manager or Project Manager.

18. Method Performance

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

18.2. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually (per the method) per S-MN-Q-269 – Determination of Limit of Detection and Limit of Quantitation (or equivalent replacement) for each matrix per instrument**.**

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020 - Training Procedures (or equivalent replacement).

18.4. **Periodic performance evaluation (PE)** samples are analyzed to demonstrate continuing competence per SOP S-MN-Q-258 – Proficiency Testing Program (or equivalent replacement). Results are stored in the QA office.

19. Method Modifications

19.1. The method was modified to perform analysis on tissue/solid matrices.

20. Instrument/Equipment Maintenance

20.1. Please refer to instrument manual for maintenance procedures performed by the lab.

20.2. All maintenance activities are listed in maintenance logs that are assigned to each separate instrument.

21. Troubleshooting

21.1. Troubleshooting the instrument is based on recommendations provided by instrument manufacturer. These can be located in the maintenance logs.

22. Safety

22.1. **Standards and Reagents**: The toxicity or carcinogenicity of each reagent used in thismethod has not been fully established. Each chemical should be regarded as a potentialhealth hazard and exposure should be as low as reasonably achievable. Cautions areincluded for known extremely hazardous materials.

22.2. The laboratory is responsible for maintaining a current awareness file of OSHAregulations regarding the safe handling of the chemicals specified in this method. A reference file of Safety Data Sheets (SDS) and a formal safety plan is made available to all personnel involved in chemical analysis.

22.3. A reference file of SDS is maintained by the lab and available to all personnel to review at any time needed.

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

22.5. Before beginning any of the procedures involved in this method, each individual must read and sign the Chemical Hygiene Plan developed for the lab. Specific safety concerns for each chemical can be found in the Material Safety Data Sheets for that chemical, all of which are located in the laboratory.

22.6. Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability and nervousness. ForfurtherinformationonwastemanagementconsultWasteHandling (S-VM-S-001), or equivalent replacement. Mercury may require treatment as Hazardous Waste.

22.7. Due to the toxicological and physical properties of Hg, only highly trained personnel using extremely cautionary procedures should handle high concentration standards. These cautionary measures include use of vinyl gloves and high volume hoods when preparing standards.

22.8. Strong acid solutions are employed in the cleaning of equipment and preparation of reagents. Proper acid handling techniques should be employed whenever acids are being used. These techniques include the use of acid resistant clothing and the utilization of high volume fume hoods.

22.9. $NaBEt_4$ is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. Any $NaBEt_4$ use should take place in a high volume fume hood. To discard unused portions of ethylating reagent, in a high volume fume hood empty bottles into a large beaker of 6N hydrochloric acid (HCl). Place beaker on a hotplate and boil down to ½ volume then discard remaining solution as an acid waste. Triethylboron will bubble off to the air where it is oxidized to harmless boric acid

22.10. Methylmercury is regarded as highly toxic which can cause adverse effect neuro-development as well as coronary heart disease, plus it is highly bioaccumulative. Due to its toxicological and physical properties, only highly trained personnel using extremely cautionary procedures should handle high concentration standards. These cautionary measures include use of latex and polyethylene gloves and high volume fume hoods when preparing standards.

22.11. Hydrochloric Acid (HCl) can cause severe burns. Fumes can cause severe respiratory damage. Flush affected areas with large amounts of water. Always work with concentrated HCl under a fume hood.

22.12. Sulfuric Acid (H_2SO_4) is a strong oxidizer, poison, chronic exposure to mists can cause cancer, and it reacts violently with water. Flush affected areas with large amounts of water.

22.13. Potassium Chloride (KOH) is a moderate irritant, eye irritant, irritant to skin and respiratory tract. Avoid contact, wash thoroughly with soap after contact. Flush affected areas with large amounts of water.

22.14. Compressed gases in tanks can cause bodily harm if discharged. Compressed gases discharged in confined spaces or rooms (such as clean labs) can displace oxygen and cause asphyxiation.

22.15. Direct contact with aluminum block should be avoided as serious burns could result. Also, the aluminum block is part of a distillation system in which steam emission is possible. Care should be taken when adjusting distillation vials to avoid burns from steam.

23. Waste Management

23.1. The quantity of chemicals purchased is based on expected usage during its shelf lifeand disposal cost of unused material. Actual reagent preparation volumes reflectanticipated usage and reagent stability.

23.2. Excess reagents, samples and method process wastes are characterized and disposed of inan acceptable manner. For further information on waste management, refer to SOPS-VM-S-001 Waste Handling, or equivalent replacement.

24. Pollution Prevention

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

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. US EPAMethod1630: "Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry" August, 1998. US. Environmental Protection Agency Office of Water. Office of Science and Technology Engineering and Analysis Division (4303) 401 M Street SW Washington, D.C. 20460.

25.3. Brooks Rand MERX User Manuals: "MERX Automated Methyl Mercury Analytical System Users Guide".

25.4. For Distillation: "Methyl Mercury Distillation System Users Guide".

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. AttachmentI:MERXMethylMercury Analysis System Diagram

26.2. AttachmentII:MERXMethylMercury Distillation System Diagram

26.3. AttachmentIII:MERX System Typical Instrument Setting

26.4. AttachmentIV:MERX/GURU Sample Run Example

26.5. AttachmentV:Mercury Species GC Elution Order

26.6. AttachmentVI:Calibration and Sample Prep Quick Guide

26.7. Attachment VII: MeHg Distillation Prep Log

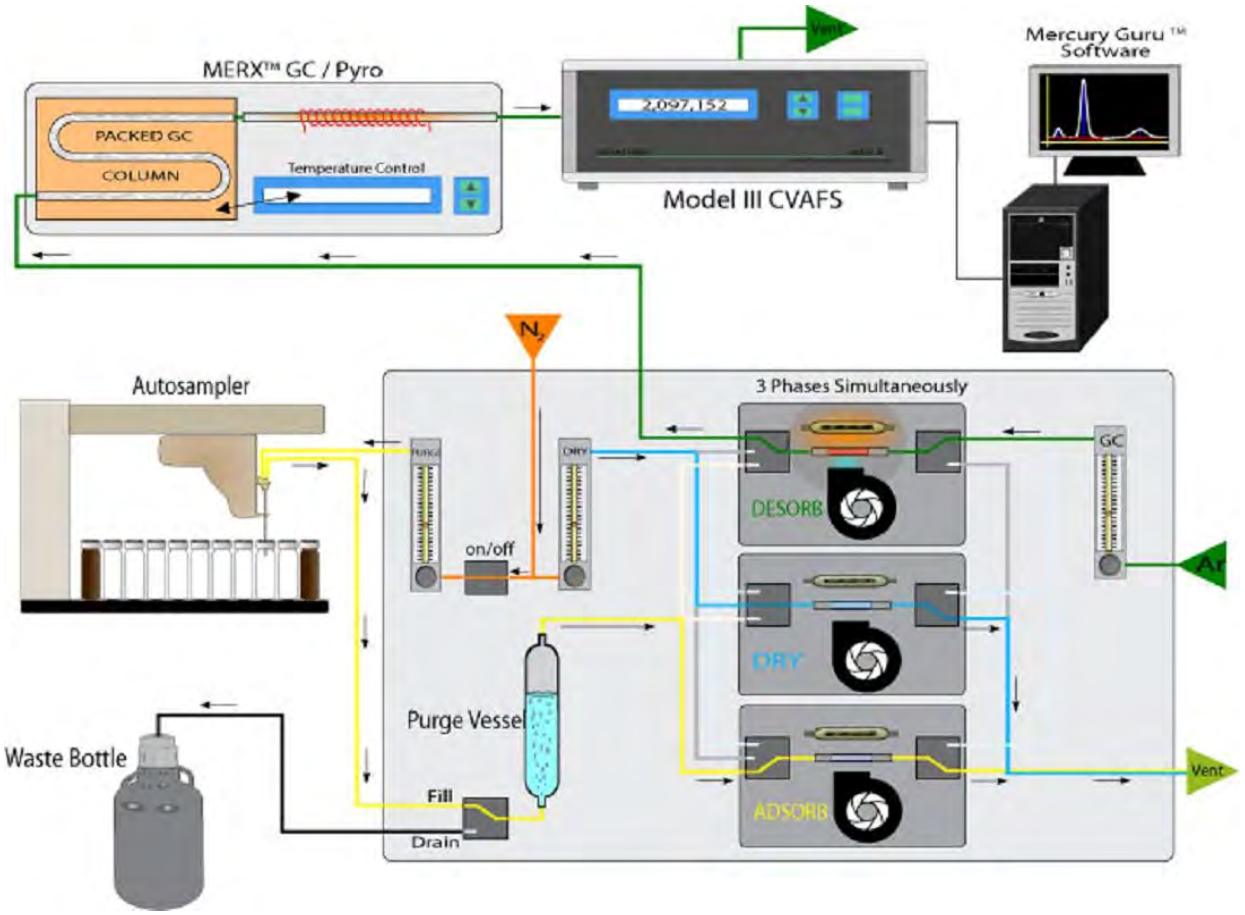
26.8. Attachment VIII: MeHg Sample Prep and Loading Guidelines

26.9. Attachment IX: Data Review Checklist

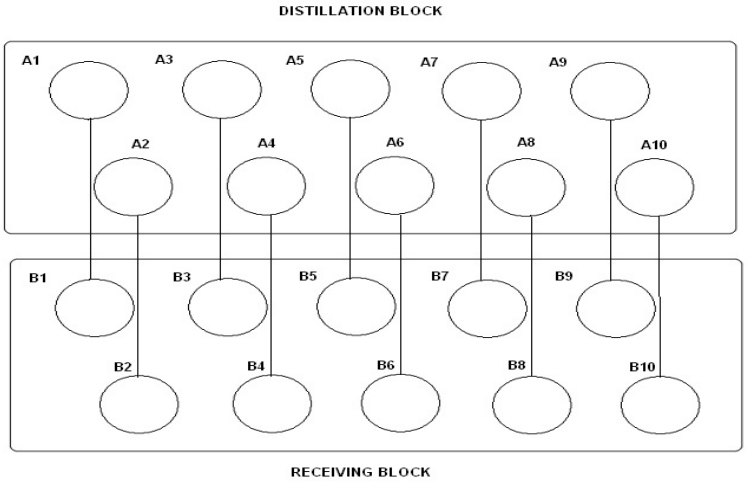
27. Revisions

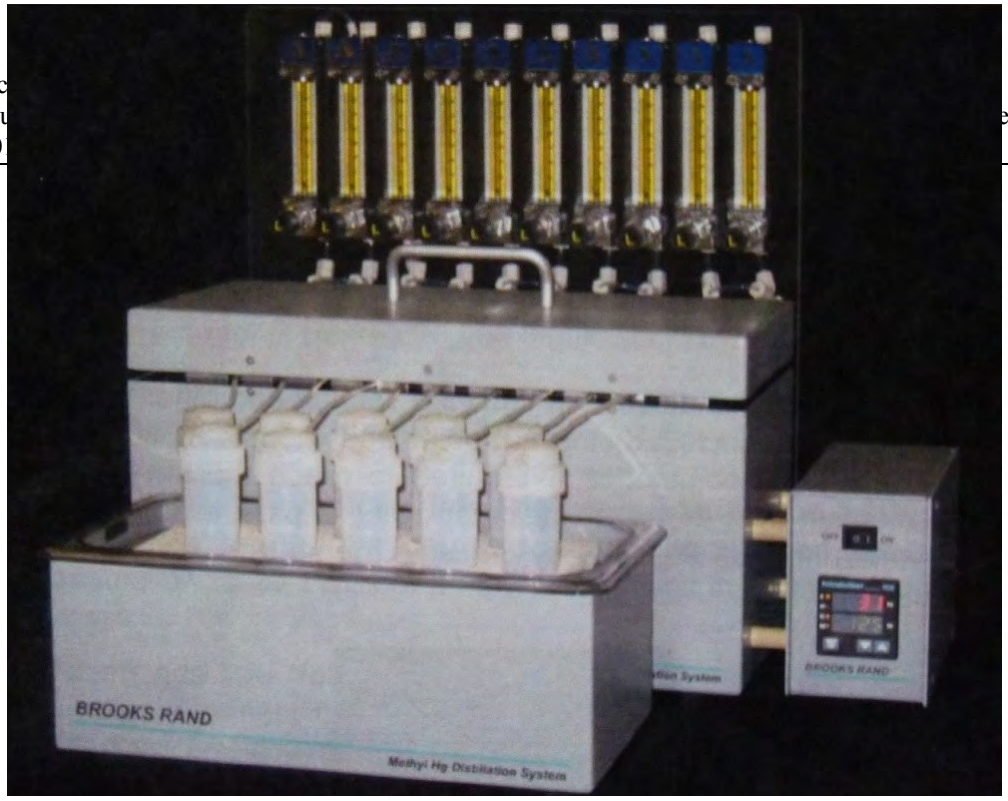
Document Number	Reason for Change	Date
S-DUL-M-001-rev.02	Updated to LLC throughout General formatting on cover page Removed "Assistant" from the GM signature line on the cover page 1.1 removed extra space Updated attachment VI	11Dec2017

ATTACHMENT I:MERX Methyl Mercury Analysis System Scheme

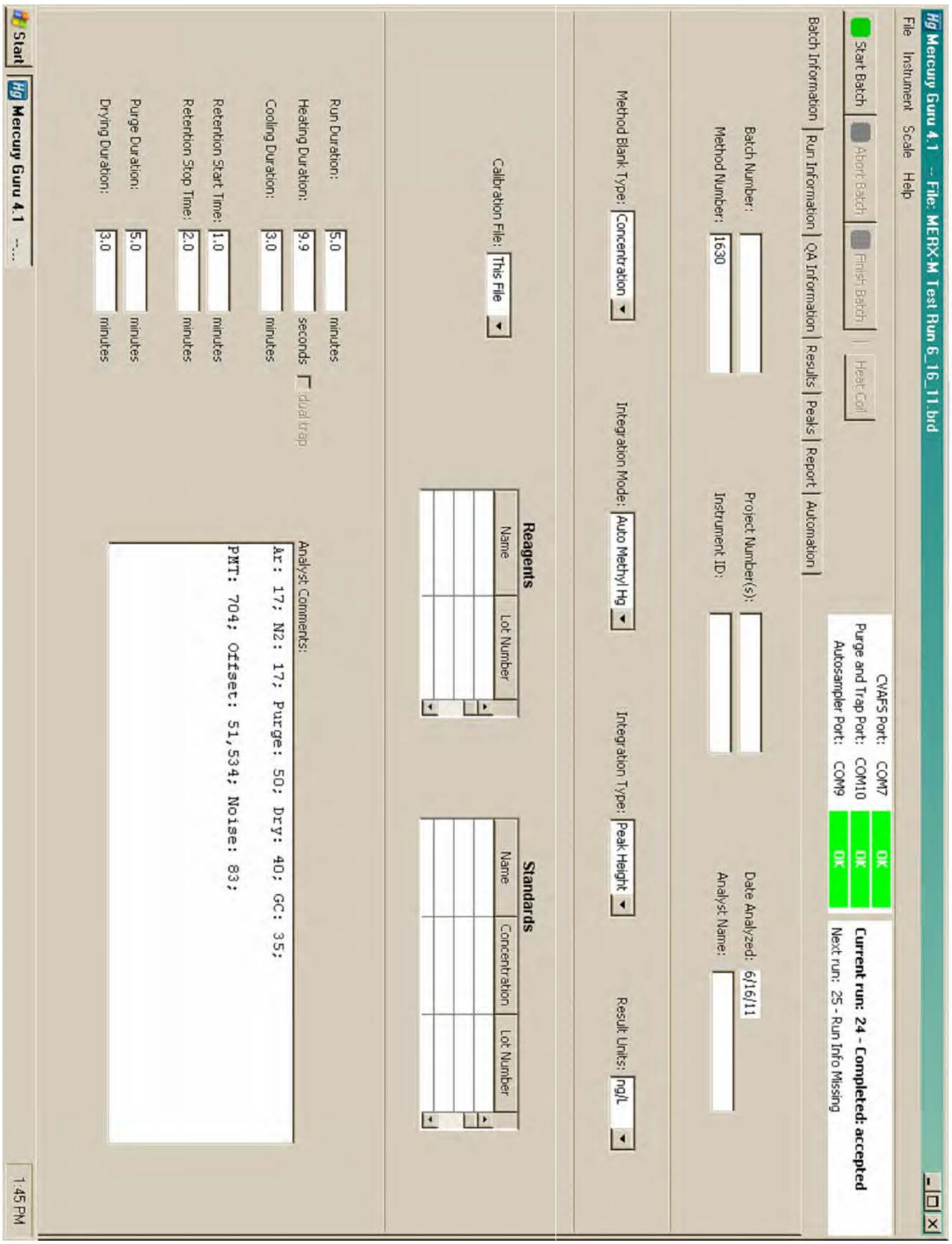


ATTACHMENT II:MERX Methyl Mercury Distillation System Diagram





ATTACHMENT III: MERX Typical Instrument Setting



ATTACHMENT IV: Sample Run Example

QA Information Report

Batch Number:
Method Number: 1630

Project Number(s):
Instrument ID: MERX

Date Analyzed: 10/13/14
Analyst Name: CK

Type	Abbr	Criteria	Units	Use	Cal. Blank Corr.	Meth. Blank Corr.	Rec. Correction
Sample	S	< Highest Standard Peak Height		yes	yes	yes	
Ethylation Blank	CB	< 2.4	pg	yes	no	no	
Calibration Standard	STD	75-125	% Recovery	yes	yes	no	
Continuing Calibration Blank	CCB	< 2.4	pg	yes	yes	no	
Rinse	EB	< 0.06	ng/L	yes	yes	yes	
Field Blank	FB	< 0.06	ng/L	yes	yes	yes	
Initial Precision and Recovery	IPR	80-121	% Recovery	yes	yes	no	
Matrix Spike	MS	65-135	% Recovery	yes	yes	yes	
Matrix Spike Duplicate	MSD	65-135	% Recovery	yes	yes	yes	
Method Blank A	MBA	< 0.06	ng/L	yes	no	no	
Method Blank B	MBB	< 0.7	ng/L	no	no	no	
Method Blank C	MBC	< 0.1	ng/L	no	no	no	
Method Blank D	MBD	< 2.3	ng/L	no	no	no	
Method Duplicate	MD	< 35	RPD	no	yes	no	
Ongoing Precision and Recovery	OPR	87-133	% Recovery	yes	yes	yes	
Quality Control Sample	QCS	69-140	% Recovery	yes	yes	yes	
Reagent Blank	RB	< 2.4	pg	no	yes	no	
Trip Blank	TB	< 0.06	ng/L	no	yes	yes	

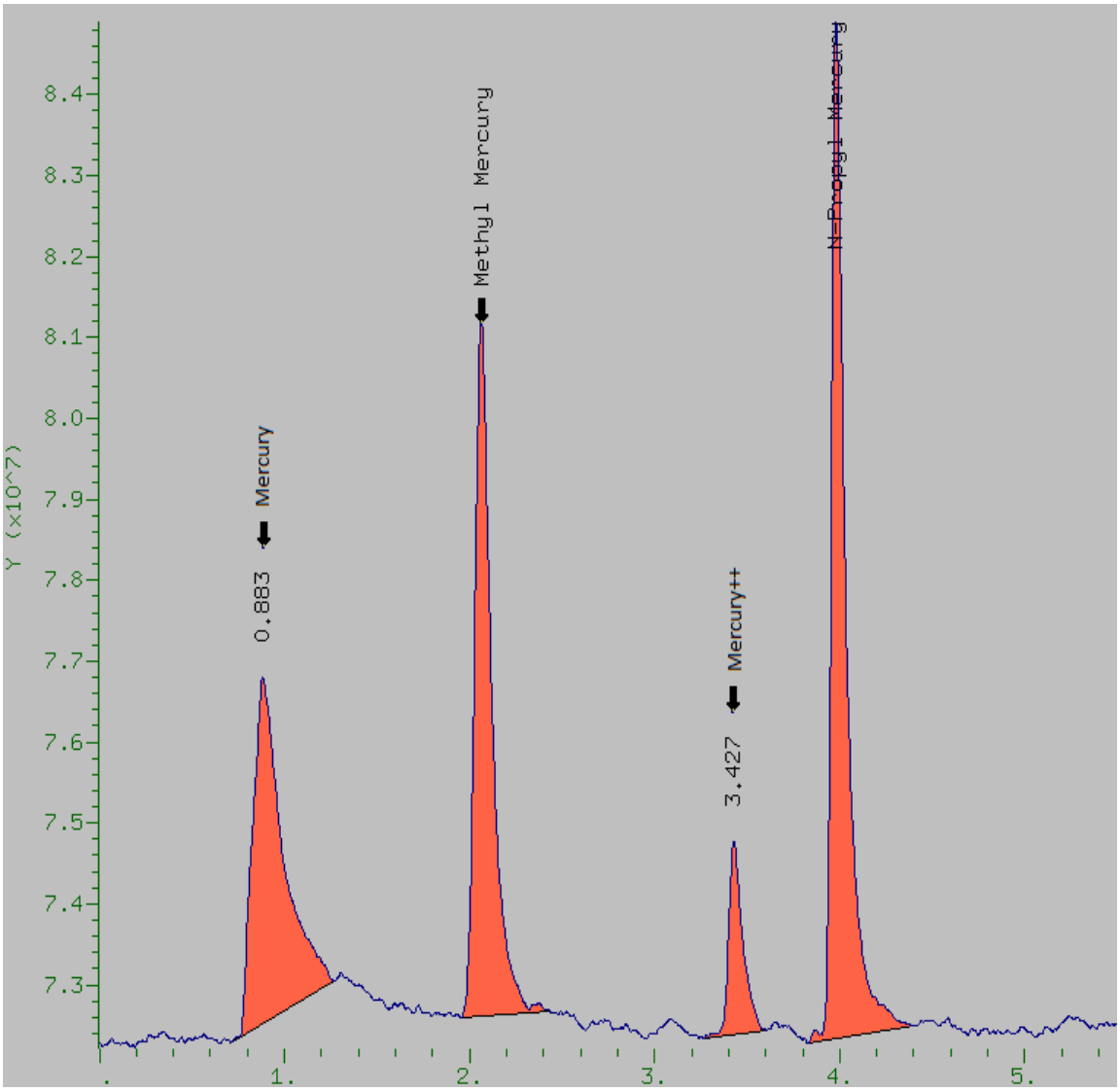
QA Reported Parameters	Criteria	Units
Average Calibration Coefficient		
RSD of Calibration Coefficients	< 15	% RSD
Average Calibration Bubbler Blank	< 2.4	pg
SD of Calibration Bubbler Blanks	< 2	
MS/MSD Precision	< 35	% RPD

QA Comments:

Page 1 of 1 (QA Information Report)

Mercury Suite ver 4.1 © 1998-2009 Brooks Rand LLC

ATTACHMENT V: Mercury Species GC Elution Order



ATTACHMENT VI: Calibration and Sample Prep Quick Guide

F-DUL-M-008 (Use most current version)

Pace Analytical	Document Name: MeHg Prep Guide	Document Revised: 11Dec2017 Page 1 of 1
	Document No.: F-DUL-M-008-rev.01	Issuing Authority: Pace Duluth Minnesota Quality Office

Calibration Prep Formula

Calib Level	Mass	Conc.	Vol (mL)	Std Conc.	Std Vol
1	1 pg	0.025 ppt	40	0.01 ng/mL	100 uL
2	2 pg	0.05 ppt	40	0.01 ng/mL	200 uL
3	2.4 pg	0.06 ppt	40	0.01 ng/mL	240 uL
4	10 pg	0.25 ppt	40	0.01 ng/mL	1000 uL
5	20 pg	0.5 ppt	40	1 ng/mL	20 uL
6	50 pg	1.25 ppt	40	1 ng/mL	50 uL
7	250 pg	6.25 ppt	40	1 ng/mL	250 uL
8	1000 pg	25 ppt	40	1 ng/mL	1000 uL

1 ng/mL MeHgCl/MeHgOH Prep Method:

100 uL of 1ppm stock MeHgCl or MeHgOH soln, 0.2 mL HCl, 0.5 mL acetic acid to 100 mL

0.01 ng/mL MeHgCl Prep Method:

add 100 uL 1 ng/mL std into 9.9 mL water, **good for 2 hours ONLY!**

(No HCl needed for all calibration levels)

(add acetate buffer 300 uL and Ethylation Reagent 50 uL)

(all calibration samples do not need distillation)

Sample/QC Prep Guide

	Vol (mL)	Conc.	Std Conc.	Std Vol	Std Mass
Sample	~50/actual				
Sample MS	~50/actual		1 ng/mL	100 uL	
Sample MSD	~50/actual		1 ng/mL	100 uL	
MB (X3)	~50/actual				
LCS	~50/actual	2 ng/L	1 ng/mL	100 uL	100 pg
MDL (X8)	~50/actual	0.06 ng/L	0.01 ng/mL	300 uL	3 pg

Distillation:	add 200 uL conc. HCl, 200 uL 20% KCl/0.2% L-Cys, 500 uL 9M H2SO4
	(HCl is for MB and LCS only, not for samples and MS/MSD)
Ethylation:	add acetate buffer (300 uL) and Ethylation Reagent (50 uL)

(20% KCl/0.2%L-Cys Prep: 40g KCl, 0.4 g L-Cys to 159.60 g water)

(9M H2SO4 Prep: 1:1 from conc. H2SO4)

(25% KOH/MeOH Prep: 25 g KOH per 100 mL MeOH)

(1 mg/L=1 ppm=1 ug/mL 1 ug/L=1 ppb=1 ng/mL 1 ng/L=1 ppt=1 pg/mL)

ATTACHMENT VII: Methyl Mercury Distillation Log

F-DUL-M-005 (Use most current version)

Pace Analytical	Document Name: MeHg Distillation Logbook	Document Revised: 03Aug2016 Page 1 of 25
	Document No.: F-DUL-M-005-rev.00	Issuing Authority: Pace Duluth Minnesota Quality Office

MeHg Distillation Log

Date		Analyst		Method: EPA 1630

Rack A						Rack B					
Sample ID	Vial ID	Position	Distillation Tare	Distl Tare + 50mL	Sample Volume	Vial ID	Position	Receiving w/15mL DI	Receiving + Distillate	Dilution Volume	pH Check

Rack C						Rack D					
Sample ID	Vial ID	Position	Distillation Tare	Distl Tare + 50mL	Sample Volume	Vial ID	Position	Receiving w/15mL DI	Receiving + Distillate	Dilution Volume	pH Check

(Assume: 1 mL sample/water= 1 gram at 20°C) ("Dilution Volume"="Receiving+Distillate"-"Receiving w/ 15 mL DI"+18)

Reagents prep date: KCl/L-Cys _____ H2SO4_____ HCl _____ NaBEt4_____ MeHgCl Std#1_____ MeHgCl Std#2_____

MeHgOH Std _____ Acetate Buffer _____

Vials/Tubings cleaned date: Sample distillates analyzed date:

Comments:

Reviewed by: _____ Date:_____

ATTACHMENT VIII: MeHg Sample Prep and Loading Guideline

F-DUL-M-007 (Use most current version)

Pace Analytical	Document Name: MeHg Sample Prep & Loading Guideline Form	Document Revised: 03Aug2016 Page 1 of 1
	Document No.: F-DUL-M-007-rev.00	Issuing Authority: Pace Duluth Minnesota Quality Office

MeHg Sample Prep and Loading Guideline

Timeline*	Hour 1	Hour 2	Hour 3	Hour 4	Hour 5	Hour 6
Run Count*	#1-6	#7-12	#13-20	#21-27	#28-36	#37-End
Prep Step	Prep 1	Prep 2	Prep 3	Prep 4	Prep 5	Prep 6
Details	• 3 Rinses • 3 Calib Blanks • Start Instrument • Load these 6 blanks • Prep 0.01 ng/mL std	• Cal Level 0.5/1/2/2.4/10/20 (using 0.01ng/mL standard)	• Cal Level 50/250 and ICV 50 (using 1 ng/mL std) • RLV 2.4 (using fresh 0.01 ng/mL standard) • Rinses and MBs	• LCS 3 X2 • LCS 100 X2 • Sample #1 • Sample MS/MSD	• Sample #2~10 • CCV • Rinses If less samples, adjust accordingly.	• Extra samples • Extra MS/MSD • Ending CCV • Rinses
Ethylation	Ethylation Reagent Aliquot 1			Ethylation Reagent Aliquot 2		
Loading	Loading 1	Loading 2	Loading 3	Loading 4	Loading 5	Loading 6
Analysis	Analysis1	Analysis2	Analysis3	Analysis4	Analysis5	Analysis6

Notes:

1. Middle CCV and Ending CCV should always be prepared fresh, **NOT** few hours in advance.
2. Allow 15 minutes to have the ethylation done and vials loaded on autosampler should be analyzed within 1~1.5 hours, which means the Next Loading should be loaded roughly 5 minutes before the finish of the analysis of the previous load and the Next Prep should be prepared roughly 20 minutes before the finish of the analysis of the previous load.
3. Check pH of all distillates (incl. MB/LCSs/Samples/MS/MSD) before ethylation.
4. Frequencies of each aliquot of ethylation reagent uses: thaw/refreeze no more than 3 times, otherwise open a new one.
5. Use the same Acetate Buffer for the whole batch.
6. Replace immediately with new reagents/standards if suspecting being contaminated by misuse of pipette tips.
7. If Cal between 0.5~20 need some re-runs, it's better to remake a new 0.01ng/mL standard for use, same for RLV 2.4.

*Timescale and run count are approximate.

ATTACHMENT IX: Data Review Checklist

F-DUL-Q-038 (Use most current version)

Pace Analytical	Document Name: Methyl Mercury Data Review Checklist	Document Revised: 03Aug2016 Page 1 of 1
	Document No.: F-DUL-Q-038-rev.00	Issuing Authority: Pace Duluth Minnesota Quality Office

Methyl Mercury (1630) Data Review Checklist

Batch #: _____
Date of Analysis: _____

Criteria	Yes	No	See Comments
Initial OPR (ICV) analyzed before proceeding?			
Did ICV pass 69-131% recovery criteria?			
3 Method Blanks analyzed per each run?			
Were all Method Blanks <0.06 ng/L?			
Was an OPR (CCV) analyzed every 10 samples?			
Did all OPRs (CCV) pass 67-133% criteria?			
Did all LCS pass 67-133% criteria?			
Was a MS/MSD set analyzed for every 10 samples?			
Did both the MS/MSD pass 65-135% criteria?			
Did the MS/MSD RPD pass the ≤35% criteria?			
Are samples requiring qualification designated properly?			
Were only QC bracketed samples reported?			

Calibration Review (if performed) or NA	Yes	No	See Comments
3 System (calibration) blanks analyzed?			
Was the SD on the system blanks <0.1 ng/L?			
Was the recovery of the lowest standard 75-125%?			
Was the RSD of the Calibration Factor (CF) <15%?			
Was the carryover check of the highest standard analyzed?			
Did the ICV (OPR) pass 69-131%?			
Did Reporting Limit Verification Std (RLV) pass 60-140%?			

Comments

"To the best of my knowledge, all the above information is correct and the supporting documentation has been provided."

Analyst: _____ Date: _____

Reviewer: _____ Date: _____

Pace Analytical Services, LLC – Green Bay WI
1241 Bellevue Street, Suite 9
Green Bay, WI 54302
Phone: 920.469.2436
Fax: 920.469.8827

STANDARD OPERATING PROCEDURE

MEASUREMENT OF pH IN WATER, SOIL, AND WASTE

REFERENCE METHODS: SM 4500-H^+ AND SW-846 METHODS 9040C AND 9045D

LOCAL SOP NUMBER:	S-GB-I-071-REV.03
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S -GB-I-071-REV.02

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 06/27/17

Kate Verbeten, Laboratory Quality Manager — Date: 6/26/17

Chad Rusch, Department Manager — Date: 06/26/2017

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

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1. Purpose

The purpose of this SOP is to provide a laboratory specific procedure to measure pH in water, soil, and waste samples while meeting the requirements of SM 4500-H^+ and SW846 Methods 9040C and 9045D.

2. Summary of Method

2.1. Water samples and wastes containing at least 20% water are measured electrometrically using a combination pH electrode with temperature compensation. The method for analyzing this type of sample is either SM Method 4500-H^+ or SW846 9040C and must be reported referencing one of these methods.

2.2. Soils and solids containing less than 20% water are mixed with reagent water and the pH of the resulting aqueous suspension is measured in the same manner as a water sample. The method for analyzing this type of sample is SW846 9045D and must be reported referencing this method.

3. Scope and Application

3.1. Since pH measurement requires some water content, concentrated acids and bases and concentrated acids and bases mixed with inert substances cannot be measured.

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

4. Applicable Matrices

4.1. This method is applicable to water samples (including drinking water, surface water, groundwater, saline water, and domestic and industrial wastewaters), soils, sludges, and solid wastes.

5. Limits of Detection and Quantitation

5.1. The reporting limit (LOQ) for all analytes is 0.1 standard units for this method. MDLs are not determined for this method.

6. Interferences

6.1. The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.

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

6.3. Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or washing with detergent, then rinsing with distilled water. An additional treatment with hydrochloric acid (1:9) may be necessary to remove any remaining film.

6.4. Sample temperature can cause variations in electrometric measurement of pH in two ways, by causing a change in electrode output and by actually altering the sample pH. Since both variation sources cannot be fully controlled, measurements should be made using a temperature compensating electrode and the sample temperature at the time of analysis should be reported with the pH result.

7. Sample Collection, Preservation, Shipment and Storage

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

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Glass or Plastic container of at least 200mL.	If samples cannot be analyzed immediately, they must be stored at ≤6 °C	If samples cannot be analyzed immediately, they must be stored at ≤6 °C	Samples should be analyzed as soon as possible following collection, preferably at the collection site.(1)
Soil	Glass or Plastic container of at least 80g.	If samples cannot be analyzed immediately, they must be stored at ≤6 °C	If samples cannot be analyzed immediately, they must be stored at ≤6°C	Samples should be analyzed as soon as possible following collection, preferably at the collection site.(1)

(1) Pace observes a 15 minute hold time. Results must qualify as exceeding the recommended hold time for this ***field parameter,*** when analysis occurs beyond this time frame.

8. Definitions

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

9. Equipment and Supplies

9.1. Equipment

Equipment	Manufacturer	Model / Version
pH Meter	Orion	Orion 720A
Glass Combination Electrode with Automatic Temperature Compensation (ATC)	Orion	9157BN
Analytical Balance	Mettler	PJ 480

9.2. Supplies

Item	Manufacturer	Catalog #
Disposable Beakers (1oz, 5.5oz)	Dart (Webraunt)	1oz-1148619, 5.5oz-1161677
Magnetic Stirrer	DataPlate	PMC 730 Series
Magnetic Stir Bars	Fisherbrand	14-513-93
Wash Bottle	Fisherbrand	11-865-162
Kimwipes	Fisher	06-666A

10. Reagents and Standards

10.1. Stock Standards and Reagents

Standard/Reagent	Alias	Purchased From	Catalog Number	Concentration /Purity	Expiration	Storage
NanoPure® Water	Water	In House	NA	ASTM Type I, ≥18 Mega ohm	Generated for use	Room Temp
Electrode Filling Solution		Orion /Fisher	900011	4M KCl	Manufacturer's expiration date	Room Temp
Primary Calibration Buffer, pH 2.00	1°-2.00	Fisher Scientific	SB96-1	± 0.02	Manufacturer's expiration date	Room Temp
Primary Calibration Buffer, pH 4.00	1°-4.00	Radiometer	S11M002	± 0.01	Manufacturer's expiration date	Room Temp
Primary Calibration Buffer, pH 7.00	1°-7.00	Oakton	05942-42	± 0.01	Manufacturer's expiration date	Room Temp
Primary Calibration Buffer, pH 10.00	1°-10.00	Fisher Scientific	SB115-4	± 0.02	Manufacturer's expiration date	Room Temp
Primary Calibration Buffer, pH 12.45	1°-12.45	RICCA	1618-16	± 0.01	Manufacturer's expiration date	Room Temp
Secondary Source Calibration Buffer, pH 4.00	2°-4.00	Fisher Scientific	SB101-4	± 0.01	Manufacturer's expiration date	Room Temp
Secondary Source Calibration Buffer, pH 7.00	2°-7.00	Fisher Scientific	SB107-4	± 0.01	Manufacturer's expiration date	Room Temp

Or Equivalent

11. Calibration

11.1. The meter must be calibrated daily prior to use with five calibration buffer solutions prior to analyzing samples. These solutions must bracket the expected range of pH values measured.

11.2. Press ***power*** to turn the meter on. Press **2nd/channel** until the correct input channel is selected.

11.3. Press the **mode** key until the pH mode indicator is displayed.

11.4. Press **calibrate;** CALIBRATE is displayed. The time and date of the last calibration is displayed.

11.5. After a few seconds ENTER NO; BUFFERS is displayed. Use the numeric keys to enter the number of buffers to be used and then press **yes**. Enter five for the number of buffers to be used.

11.6. Place a stir bar in the beaker, put the beaker on the stirrer, and adjust the stirrer to a moderate speed. When the BUFFER 1 prompt appears place electrode(s) in first buffer.

11.7. When the electrode signal has stabilized, the prompt READY CAL AS will appear. Use the numeric keys to enter the value of the buffer. Press **yes** to enter the value.

11.8. Rinse the electrode with DI water and gently wipe with a tissue. Repeat the last two steps for each buffer.

11.9. The average electrode slope is displayed at the SLOPE prompt.

11.10. The meter automatically proceeds to MEASURE mode.

11.11. Record the slope in the pH logbook.

11.12. Re-read each calibration buffer and record the readings and temperature. The readings should be within ± 0.05 pH units of the buffer solution value.

11.13. If any calibration buffer is not within criteria, rinse and read it again to verify the failure.

11.13.2. If it passes, document and proceed with analysis of samples.

11.13.3. If it fails, repeat adjustments on successive portions of the calibration buffer solutions until readings are within ± 0.05 pH units of the buffer solution value.

12. Procedure

12.1. Multiphasic Samples

12.1.1. As per SW846 9045D If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. Add a sample comment stating the oily phase of the sample was not included in the analysis.

12.2. Water Samples

12.2.1. Allow samples to warm to room temperature. Samples must be within ±2°C of the standard buffer solutions used for calibration.

12.2.2. Place the sample in a 50-mL disposable beaker, using sufficient volume to cover the sensing elements of the electrode and provide adequate clearance for the magnetic stirring bar. Place a magnetic stirring bar in the beaker and place the beaker on the stirrer. Turn on the stirrer to a moderate speed. The sample should be noticeably mixing but should not develop a vortex.

12.2.3. Rinse the electrode with DI water and gently wipe with a tissue. Place the pH electrode into the sample beaker, taking care to provide adequate clearance for the stirring bar.

12.2.4. Wait for the meter reading to stabilize and record the pH result, temperature, and time analyzed. Record the results to 0.1 pH units. Correct the temperature using the temperature correction on the meter.

12.2.5. When following EPA 9040C, repeat measurement on successive aliquots of sample until values differ by <0.1 pH units. Report the first result of the two measurements that agree within 0.1 pH units.

12.3. Soil and Solid Samples

12.3.1. Place 20g of sample into a 50-mL disposable beaker. Add 20mL DI water and a stirring bar to the beaker and place it on the stirrer. Turn the stirrer to a moderate speed and continuously stir the suspension for 5 minutes.

12.3.2. If the matrix is hydroscopic and has absorbed all the water leaving no remaining free liquid for analysis, repeat the preparation using 20g of sample and 40mL DI water.

12.3.3. Turn off the stirrer and allow the sample to sit, permitting the suspended particulates an opportunity to settle to the bottom of the container. Samples may be allowed to sit for up to one hour prior to analysis. Excessive solids in suspension may speed the clogging of the frit between the electrodes.

12.3.4. Rinse the electrode with DI water and gently wipe with a tissue. Place the pH electrode into the sample beaker.

12.3.5. Wait for the meter reading to stabilize and record the pH result, temperature, and time analyzed. Record the results to 0.1 pH units. Correct the temperature using the temperature correction on the meter.

12.3.6. When following EPA 9040C, repeat measurement on successive aliquots of sample until values differ by <0.1 pH units. Report the first result of the two measurements that agree within 0.1 pH units.

13. Quality Control

13.1. pH Probe Calibration

13.1.1. Calibrate the temperature function of the pH probe on an annual basis as per the current revision of Pace Analytical Services – Green Bay WI SOP S-GB-Q-030, Support Equipment. Record the calibration in the thermometer calibration logbook and label the probe with the date of calibration.

13.1.2. Calibrate the pH meter/probe daily prior to use.

13.1.3. Repeat adjustments on successive portions of the calibration buffer solutions until readings are within ± 0.05 pH units of the buffer solution value.

13.2. ICV Secondary Source Checks

13.2.1. Buffers of pH 4.00 and 7.00, from a source different than the calibration.

13.2.2. Analyzed after calibration and prior to samples.

13.2.3. Acceptance criteria of ± 0.1 pH units from the buffer solution value.

13.2.4. If outside of control limits, reanalyze with a fresh aliquot of buffer. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. No samples may be analyzed or reported.

13.3. CCV Buffer

13.3.1. Buffer of 7.00 pH

13.3.2. One after every 10 samples and at the end of the batch of samples.

13.3.3. Acceptance criteria of ± 0.1 pH units from the buffer solution value.

13.3.4. If outside of control limits, reanalyze with a fresh aliquot of buffer. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.

13.4. Duplicate

13.4.1. A duplicate aliquot of a sample to be analyzed along with the original sample. Duplicate analyses indicate the precision associated with the laboratory procedures.

13.4.2. One per batch of 20 or fewer samples.

13.4.3. Acceptance criteria of ± 0.1 pH units from the parent sample.

13.4.4. If outside of control limits, qualify the DUP and the parent sample.

14. Data Analysis and Calculation

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

Preparation Method ⇨ Quality Control Measure ⇩	**SW846 9040C, 9045D, and SM 4500 H+B** **Frequency**	**Acceptance Criteria**
pH Probe Calibration	Daily calibration	± 0.05 pH Units
Secondary Source Checks	Daily after calibration	± 0.1 pH Units
CCV Buffer	One after every 10 samples and at the end of the batch of samples.	± 0.1 pH Units
Duplicate Sample	One per batch of 20 or fewer samples.	± 0.1 pH Units

16. Corrective Actions for Out-of-Control Data

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**pH If these conditions are not achieved ⇒**
pH Probe Calibration	• 1
Secondary Source Checks	• 2
CCV Buffer	• 3
Duplicate Sample	• 4

1. If outside of control limits, perform maintenance and recalibrate.

2. If outside of control limits, reanalyze with a fresh aliquot of buffer. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.

3. If outside of control limits, reanalyze with a fresh aliquot of buffer. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.

4. If outside of control limits, qualify the DUP and the parent sample.

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

17.1. See section 16.

18. Method Performance

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

18.2. Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, *Orientation and Training Procedures* (most current revision or replacement). All results must be in control to qualify the analyst for reporting sample results (within 0.1 pH units of the true value). Results of DOC studies for each analyst shall be retained in the lab quality assurance office. DOCs must be repeated annually. For SM 4500H+B and SW846 9040C four analysis of the second source pH 7 buffer within ± 0.1 pH Units of the true value will serve as the DOCs. For SW846 9045D four analysis of a solid sample that are within ± 0.1 pH Units of the average will serve as the DOCs.

18.3. Periodic performance evaluation (PE) samples are analyzed per the most recent version of S-GB-Q-021 *PE/PT Program* (most current revision or replacement), to demonstrate continuing competence. All results are stored in the QA office. These are performed twice a year per matrix.

19. Method Modifications

19.1. If the matrix is hydroscopic and has absorbed all the water leaving no remaining free liquid for analysis, repeat the preparation using 20g of sample and 40mL DI water. This is a method modification of 9045C. Method 9045C requires a 1:1 ratio, but since this would not be possible with a sample of this nature the noted procedure will be followed and the sample qualified as such.

19.2. Both EPA 9040C Revision 3, November 2004 and EPA 9045D Revision 4, November 2004 specify in 7.1.2 for the calibration to have a minimum of two calibration points that bracket the expected pH of the samples and are approximately three pH units apart. Pace Analytical Inc. Green Bay, WI uses a range of 5 buffers from 2.00 to 12.45 pH units. The last two buffers are not separated by 3 or more pH units.

19.3. EPA 9040C Revision 3, November 2004, EPA 9045D Revision 4, November 2004, and SM 4500 H+B, Editorial Revision 2011 do not specify sample container, preservation, or storage requirements. This is a result of the pH test being a field parameter with the sample hold being samples should be analyzed as soon as possible. This is specified in section 6.0 of both of the EPA methods. As a result, Pace Analytical Inc. Green Bay, WI observes a 15 minute hold on all pH samples. The lab also observes thermal preservation at $<6^{o}C$. This is based on 40CFR Part 136, Table II. While pH is not specified in the table, the lab follows the strictest temperature guidelines of $\leq 6^{o}C$ listed in the table for sample storage and containers made for polyethylene or glass.

19.4. EPA 9040C Revision 3, November 2004, EPA 9045D Revision 4, November 2004, and SM 4500 H+B, Editorial Revision 2011 all specify buffers being made from primary standard buffer salts. Since preparation of reference solutions from these salts requires special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas; certified premade buffers are purchased pre-made and the manufacturer's expiration dates are followed.

20. Instrument/Equipment Maintenance

20.1. See pH Meter operator's manual for information.

21. Troubleshooting

21.1. See pH Meter operator's manual for information.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel involved in the chemical analysis, and is located at the following link: https://msdsmanagement.msdsonline.com/c0ce0b0a-17d3-4f3c-afc6-25352729b299/ebinder/?nas=True. A formal safety plan has been prepared and is distributed to all personnel with documented training. Standard solutions should be prepared in a hood whenever possible.

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

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-GB-W-001, Waste Handling and Management (most current revision or replacement).

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

24. Pollution Prevention

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

25. References

25.1. Method 4500-H^+ B-2011., Standard Methods for the Examination of Water and Wastewater.

25.2. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods"; EPA SW-846, latest revision. Method 9040C Revision 3 November 2004 "pH Electrometric Measurement".

25.3. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods"; EPA SW-846, latest revision. Method 9045D Revision 3 November 2004 "Soil and Waste pH".

25.4. EPA 40CFR Part 136 / Vol. 77, No. 97 / Friday, May 18, 2012 Rules and Regulations

25.5. Pace Analytical Quality Manual; latest revision.

25.6. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

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

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-GB-I-071-Rev.02	Throughout document: Removed Method References for SW846 7196. Updated formatting following current revision of SOP: S-GB-Q-017 *Preparation of SOPs*, and updated to current method references. Section 7.2: Changed temperature to ≤6°C. Table 13.1: Added pH Meter calibration information. Attachment A: Updated to current pH Logbook Benchsheet.	19Nov2014
S-GB-I-071-Rev.03	Throughout Document: Changed from Inc to LLC., updated all font to TNR 11pt. General: made administrative edits that do not affect the policies or procedures within the document. Section 19: Added method modifications. Section 22: Added link for SDS documentation. Section 27: Removed previous reason for change which can be found in prior SOP.	26Jun2017

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STANDARD OPERATING PROCEDURE

The Determination of Total Organic Carbon Using the Multi EA4000 Instrument

Reference Method: Lloyd Kahn

SOP NUMBER:	S-GB-I-076-REV.02
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-I-076-REV.01

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 04/27/17

Kate Verbeten, Laboratory Quality Manager — Date: 4/26/17

Chad Rusch, Department Manager — Date: 04/26/2017

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

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Table of Contents

1. PURPOSE/IDENTIFICATION OF METHOD

The purpose of this Standard Operating Procedure (SOP) is to describe the procedures used to determine the concentration of Total Organic Carbon (TOC) in solid and soil samples using the Multi EA4000 Instrument by the Lloyd Kahn Method.

2. SUMMARY OF METHOD

2.1 Inorganic carbon forms from carbonates and bicarbonates are removed by acid treatment and heating.

2.2 The sample is placed in a combustion furnace where it heats up to 1000^{o}C. The product of the decomposed by pyrolysis is CO_2 gas.

2.3 The CO_2 that is formed is determined by direct non-dispersive infrared detection (NDIR). This measurement is proportional to the carbon in the sample.

3. SCOPE AND APPLICATION

3.1 Personnel: The policies and procedures contained in this SOP are applicable to all personnel involved in the analysis of Lloyd Kahn.

3.2 Parameters: This SOP is applicable the analysis of Total Organic Carbon (TOC) in soils and solids.

4. APPLICABLE MATRICES

4.1 This SOP is applicable to solid samples.

5. LIMITS OF DETECTION AND QUANTITATION

5.1 Current LOD and LOQ can be found in the Laboratory Information Management System (LIMS) - EpicPro.

5.2 Level of Detection (LOD): The LOD is determined by the 40CFR Part 136B MDL study. Once the 40CFR Part 136B MDL is determined it may be elevated, if deemed unrealistic as demonstrated using method blank evaluations.

5.3 Level of Quantitation (LOQ): The LOQ is calculated as 3 times the LOD. A realistic LOQ is typically near the lowest non-zero calibration point and higher than typical blank measurements.

6. INTERFERENCES

6.1 Carbonate and bicarbonate carbon represent interferences under the terms of this test and must be removed or accounted for in the final calculation.

6.2 Volatile organics in the samples may be lost in the de-carbonation step, resulting in a low bias.

6.3 This SOP is applicable only to those samples that can be adequately represented with no more than 1g.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

Table A: Sample Collection, Preservation, Shipment, and Storage

Matrix	Method	Container(s)	Preservation	Hold Time	Shipment Conditions	Lab Storage Conditions
Solid	Lloyd Kahn	Clean Amber Glass, minimum of 4 oz	None	14 days	On ice, $\leq 6^0$C	$\leq 6^0$C

8. DEFINITIONS

8.1 Total Carbon (TC): The measurement of all the carbon in the sample, both inorganic and organic.

8.2 Total Organic Carbon (TOC): All carbon atoms covalently bonded in organic molecules. To measure TOC, all the inorganic carbon is removed by addition of acid and heating: The result is that only organic carbon is left.

8.3 Total Inorganic Carbon (TIC): The measurement of the total inorganic carbon is found by subtracting the Total Organic Carbon from the Total Carbon. TIC = TC – TOC.

8.4 Additional definitions can be found in Section 10 of the Pace Analytical Services Quality Manual.

9. EQUIPMENT AND SUPPLIES

9.1 Equipment

Equipment	Manufacturer*	Model(s)/Catalog number *
TOC Analyzer	Analytikjena	EA4000 with NDIR detector
Auto-sampler	Analytikjena	TIC Solid Module
Top loading Analytical Balance	Mettler	BA310P
Vented Fume Hood	Hamilton	Fisher
Mortar and Pestle (500mL)	Fisher	S337641
Drying Oven	Yamato	DKN600

*Or equivalent

9.2 Supplies

Supplies	Manufacturer*	Catalog number *
Ceramic Sampling Boats	Analytikjena	886.130
Volumetric Flasks	Fisher	Various
Disposable Transfer pipettes	Eppendorf	Various
Spoonula (Lab Spoon)	Fisher	Various
Gloves – Heat Resistant		

*Or equivalent

10. STANDARDS AND REAGENTS

10.1 Stock Standards and Reagents

Standard / Reagent	Alias	Purchased From	Catalog Number	Concentration / Purity	Expiration	Storage
NanoPure® Water	Water	In House	NA	ASTM Type I, ≥18 Mega ohm	Generated for use	Room Temp
Hydrochloric Acid	Conc. HCl	JT Baker	9530-33	36-38%	1 year from open	
Compressed Oxygen	O_2	Airgas	UN1072	Ultra High Purity (UHP)		
Primary Stock Standard	1° $CaCO_3$	Ricca Chemical	RDCC0050-500B1	120 g/kg C	5 years from receipt	
Secondary Stock Standard	2° $CaCO_3$	Fisher Scientific	C64-500	120 g/kg C		
Potassium Hydrogen Phthalate	KHP	EMD	PX1476-3	470.5 g/kg C		
Sand - SiO_2	Sigma	Sigma-Aldrich	S5631-1KG	0.0 g/kg C		
Sand - SiO_2	Acros	Acros Organics	37094-0050	0.0 g/kg C		

*Or equivalent

10.2 Working Standards and Reagents

Standard / Reagent	Alias	Stock or Intermediate	Amount Used	Final Volume (W/Diluent)	Diluent	Final Concentration	Expiration	Storage
10% Hydrochloric Acid	10% HCl	Conc. HCl	20mL	80mL	Water	10%	6 month	Room Temp
Primary Source CaCO3/SiO2 Blend **	1°	1° $CaCO_3$	1.000g	6.000g	Sigma - SiO_2	20 g/kg TOC	1 year	Desiccator
Secondary CaCO3/SiO2 Blend**	2°	2° $CaCO_3$	1.000g	6.000g	Sigma - SiO_2	20 g/kg TOC		
$KHP/CaCO_3/SiO_2$ Blend	Secondary Spike	KHP	0.0425g	10.000g	5.9g of Sigma	2.944 g/Kg TC 2.0 g/Kg OC 0.944 g/Kg IC		
		$CaCO_3$	0.0787g		3.9788g of Acros			
Level 0 Calibration Standard, Initial Calibration Blank, Continuing Calibration Blank, Method Blank	CAL0 ICB CCB MB	1°	0.0mg	1,000mg	Ceramic Boat	0 mg/kg	5 years from receipt	
Level 1 Calibration Standard and Reporting Limit Verification Standard	CAL1 CRDL	1°	5.0mg	1,000mg		100 mg/kg		
Level 2 Calibration Standard	CAL2	1°	10mg	1,000mg		200 mg/kg		
Level 3 Calibration Standard	CAL3	1°	50mg	1,000mg		1,000 mg/kg		
Level 4 Calibration Standard and Continuing Calibration Verification Standard	CAL4 CCV	1°	100mg	1,000mg		2,000 mg/kg		
Level 5 Calibration Standard	CAL5	1°	200mg	1,000mg		4,000 mg/kg		
Initial Calibration Verification Standard	ICV	2°	100mg	1,000mg		2,000 mg/kg		
Laboratory Control Spike	LCS	Secondary Spike	500mg	1,000mg		1,000 mg/kg	1 year	
Matrix Control Spike/Matrix Control Spike Duplicate	MS MSD	Secondary Spike	250mg	1,000mg		500 mg/kg		
IC Check (acidified)	IC Check	2°	50mg	1,000mg		0 mg/kg	5 years from receipt	

11. CALIBRATION AND STANDARDIZATION

11.1 A new calibration curve should be prepared yearly at minimum or whenever the continuing calibration standard does not pass control criteria.

11.2 KHP is ground with mortar and pestle and passed through a 60M sieve. Neat standards are dried in oven at 75°C for 1 hour prior to blending/storing in desiccator.

11.3 Turn on the Furnace unit, main power switch and the **Compressed Oxygen.**

11.4 Enter MultiWin software through the **MultiWin** icon and log in.

11.5 *Activating the instrument.* After software open, initialize analyzer to start furnace.

11.6 *Setting up a new curve.* First select the method being used by going to **Method >Method-Activate** if desired method not already in use. Then go to **Sequence > Calibration-Sequence > New.** Click "Next" on method showing, change Sequence Name if desired and hit "Next." Hit "Next to leave Rack selection and first position at defaults, Change calibration points to 5 with constant concentration, hit "Next." Select the box to measure Boat Blank, hit "Next." Change nominal value to 120 g/Kg, then hit "OK." Enter in the exact weights for corresponding ID's, set the boats in the matching number slots on the auto sampler, and hit the icon on the top with the green checkmark to activate the samples, then hit "OK." When the temperature is within 50 points of method requirements, the pump will kick in allowing you to hit the S**tart** button to begin. Create the following curve:

11.7 Calibration Information

Standard ID	Volume (mg)	Concentration (g/kg C)	Method ID	µg C (m-Nominal)
CAL0	0	20	TC	0
CAL1	5	20	TC	100
CAL2	10	20	TC	200
CAL3	50	20	TC	1,000
CAL4	100	20	TC	2,000
CAL5	200	20	TC	4,000

11.8 *Activating the New Curve*. When finished, the window will pop up showing results for each point. Select the points to be used and verify the linear regression for the µg C has a corresponding correlation coefficient > 0.995. The software plots the CAL1 through CAL5 standards using µg C (m-Nominal) versus Integral (I-Net in Area Units (AU)) minus the CAL0. Under the Parameter tab for the calibration run, select the **Link with Method** button, when prompted "Link with the calibration method?" select "Yes" Hit "Accept" at the bottom of the next screen. Hit close, the calibration is saved and active. If previous calibration range still showing to be part of the new calibration, go to Method > Edit. Hit the Plus sign on the top, then select the CalibrationData tab. Click on "Edit" and then delete the portions of this curve that are from the previous curve. Finish by clicking "Accept" on the bottom.

11.9 *Running the New Curve*. To run the curve desired, go to by to **Method > Load** and select the method. The new curve should already be linked.

11.10 *Initial Calibration QC*. Select Start **Measurement box on main screen.** Click the Plus sign icon on top and type in a name for the AnalysisGroup, click OK. Select Analysis Group that was created in the right hand column and select OK box at the bottom. Enter the Sample names in the "Name" box, & enter the weights in mg in the "Sequence entry" tab on the bottom. After all samples are entered, hit the checkmark icon on top to activate samples & hit OK. When prompted to save under different name, hit "Yes" and enter in a name. To load samples, return to Sequence > Analysis sequence > edit to be able to rotate auto-sampler. To rotate auto-sampler, use the blue arrow icons on the top right of toolbar. When the temperature is within range, the pump will start. Hit the **Start Measurement** button to begin. To edit sequence at any time, return to Analysis Sequence edit screen and adjust accordingly.

11.11 The calibration report and all analyses should be printed to the paperless drive (40WTAA) with all standards traced back to COA.

12. PROCEDURE

12.1 Soil samples that are collected in regulated domestic areas or that are of foreign origin must be handled in accordance with the Pace SOP: S-GB-S-001, Regulated Soil Handling (most current revision or replacement).

12.2 No injections can be used if they are above the calibration curve. If a sample exceeds the upper end of the calibration curve, a smaller volume of sample must be used and the analysis re-performed. All quality control and samples are single replicate analysis with the exception of the precision control sample which is analyzed with four replicates.

12.3 Soil Sample Preparation

12.3.1 Weigh the sample directly into a combustion boat and note the weight into the rack table.

12.3.2 Add 10% HCl drop by drop until no further reaction occurs to each pre-weighted sample. Add 2 additional drops to verify the reaction is complete.

Note: The sample must be weighed prior to adding HCl!

12.3.3 Dry the samples in the oven at 75°C to remove excess moisture and HCl.

12.4 Epic Pro/LimsLink.

12.4.1 Samples are batched in Epic Pro.

12.4.2 LimsLink is used as a data reduction tool to evaluate and post data to the LIMS.

12.4.3 Sample weights and instrument raw results are recorded in the instrument software.

12.4.4 Instrument QC and replicate precision are evaluated in LimsLink.

12.4.5 Acceptable data is then posted to EPIC Pro.

12.5 Sample Analysis.

12.5.1 Turn on the furnace unit, main power switch and the Compressed Oxygen

12.5.2 Enter MultiWin software through its icon.

12.5.3 *Activating the instrument.* After software is open, initialize analyzer to start furnace.

12.5.4 *Each analysis is performed as follows:* Select "Start **Measurement"** box on main screen. Click on Plus sign on top and type in a name for the AnalysisGroup, click OK. Select Analysis Group that was created in the right hand column and select OK box at the bottom. Enter the Sample names in the "Name" box, & enter the weights in mg in the "Sequence entry" tab on the bottom. After all samples are entered, hit the checkmark icon on top to activate samples & hit OK. When prompted to save under different name, hit "Yes" and enter in a name. To load dried samples, return to Sequence > Analysis sequence > edit to be able to rotate autosampler. To rotate autosampler, use the blue arrow icons on the top right of toolbar. When the temperature is within range, the pump will start. Hit the "**Start Measurement"** button to begin. To edit sequence at any time, return to Analysis Sequence edit screen and adjust accordingly.

12.5.5 *CCV Analysis:* Weigh 100mg of CAL4 (Primary source CCV standard) in ceramic boat and load into the auto-sampler. Enter the exact weight into the software program.

12.5.6 *CCB Analysis:* Place a blank boat on the auto-sampler and enter the weight 1000mg (the maximum weight used). All CCB analyses which detect Integral Area Units (AU) less than the Integral (AU) in the CAL0 of the calibration curve will result in an Integral Area Unit (AU) of 0"B!". The B! signifies this on the Analyses Table raw data print-out.

12.5.7 *CRDL Analysis:* Run a Reporting Limit Verification Standard (CRDL) at the beginning of each batch before the MB/LCS by weighing 5mg of primary standard.

12.5.8 *IC Check:* Run after the ICV/ICB/CRDL & at the beginning of a schedule after the initial CCV/CCB. Prepare by weighing 50mg of 2^{o} standard, adding acid and drying in the oven with samples prepped to be run.

12.5.9 *Batch QC:*

12.5.9.1 When running a Method Blank (MB), load a blank boat and enter 1000mg.

12.5.9.2 A Laboratory Control Spike (LCS) is run by weighing 500mg of secondary spike standard.

12.5.9.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD) are run by adding 250mg of secondary spike standard, after sample has been acidified and dried, along with a variable weight of the parent sample for each the MS and MSD.

12.5.9.4 One sample is analyzed in quadruplicate as the precision control sample.

12.5.10 *Samples:* For each field sample in an analytical batch, weigh 1g or less into the boat. Run a CCV/CCB every 10 samples and at the end of the run.

12.5.11 While running samples, no injections can be used if they are above the high point in the calibration curve. If an injection is above the curve, weigh out a smaller amount of the sample and reanalyze the injection.

12.5.12 To determine that the sample concentration is less than the reporting limit, at least 1.0000 grams must be utilized.

12.5.13 *Continuing Analytical QC:* Run a CCV/CCB every 10 samples and at the end of the run.

12.5.14 *Printing data:* When the run is complete, the results will open. Select the samples desired to print and hit the print icon. This will print the summary of each rep. Each file selected can be printed separately giving a detailed analysis by selecting **Analysis Table > Print Analysis Report.**

12.6 Shutdown

12.6.1 System automatically goes into standby (decreased temp and oxygen switched off) at end of run.

12.6.2 Turn off the furnace unit, main power switch, and the **Compressed Oxygen.**

13. QUALITY CONTROL

13.1 Refer to the most current version of the Pace Quality Manual Appendix I *Quality Control Calculations* and SOP S-GB-Q-009 *Common Laboratory Calculations and Statistical Evaluation of Data* for equations and calculation details.

13.2 **Initial Calibration Verification (ICV)**

13.2.1 The ICV must be run immediately following the instrument calibration. The ICV must be prepared from stock standard obtained from a different source than the stock standard used to prepare the initial calibration and must be prepared at a level at or near the mid range of the calibration curve.

13.2.2 The result of the ICV must fall within the range of 90%-110%.

13.2.3 If outside the acceptance criteria, rerun once. If still outside the range, the problem must be corrected before continuing and the affected samples reanalyzed.

13.3 **Calibration Blanks – Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)**

13.3.1 The ICB must be analyzed after the ICV and before samples. The CCB must be analyzed after each CCV and before samples.

13.3.2 The absolute value must be < LOQ.

13.3.3 When the absolute value of the measurements, are greater than the LOQ, the blank may be immediately reanalyzed. If the reanalyzed blank passes, continue with analysis. If the reanalyzed blank fails, recalibrate and reanalyze all samples back to the last acceptable instrument blank.

13.3.4 No samples may be reported if bracketed by an ICB or CCB that is outside of the control limits, with the following exceptions:

13.3.4.1 If the sample concentration is greater than ten times the absolute measurement in the ICB or CCB, the samples do not need to be reanalyzed and can be reported without qualification.

13.3.4.2 For positive blank failures, with a sample that is a non-detect, the sample does not need to be reanalyzed and can be reported without qualification.

13.3.5 All analyses which detect Integral Area Units (AU) less than the Integral (AU) in the CAL0 of the calibration curve will result in an Integral Area Unit (AU) of 0"B!". The B! signifies this on the Analyses Table raw data print-out.

13.4 **Inorganic Carbon (IC) Check –** This check is used to verify the efficient removal of inorganic carbon prior to carbon analysis.

13.4.1 The IC Check is analyzed after calibration and prior to any samples.

13.4.2 The absolute value if the IC Check result must be less than the LOQ.

13.4.3 If outside the acceptance criteria, rerun once. If still outside the range, the problem must be corrected before continuing and the affected samples reanalyzed.

13.5 **Continuing Calibration Verification (CCV)**

13.5.1 Each analytical run must begin and end with a CCV and a CCV must be run every 10 samples.

13.5.2 The CCV must be prepared from the primary source as the mid-point calibration standard and the result must fall within the range of 90%-110%. If outside the range, rerun once.

13.5.3 If outside the acceptance criteria, rerun once. If still outside the range, the problem must be corrected before continuing and the affected samples reanalyzed.

13.6 **Method Blank**

13.6.1 The MB is an acidified ceramic boat analyzed exactly like a sample. The MB is used to verify that interferences caused by contaminants in the solvents, reagents, glassware, etc. are known and minimized.

13.6.2 A MB must be analyzed with each batch of samples or every 20 samples, whichever is more frequent.

13.6.3 Acceptance Criteria: The MB is evaluated for both positive and negative bias and must have an absolute value less than the LOQ. For samples reporting down to the LOD, the MB measurements are evaluated to the LOD. In these cases qualify applicable samples for MB measurements from >LOD to <LOQ.

13.6.4 If the MB is greater than the LOQ, perform the following:

13.6.4.1 Check for errors in calculations. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.6.4.2 If there is sufficient sample available and hold time remaining, re-prepare the MB and all associated. If the MB is less than the LOQ in this analysis, accept the second set of data. If the MB is still outside the RL after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant MB.

13.6.4.3 If sufficient sample volume is not available, report the sample data with a qualifier flag on each of the samples associated with the non-compliant MB. Contact the project manager regarding the occurrence.

13.6.5 MB data qualifying

13.6.5.1 In the absence of project specific requirements, samples with concentrations greater than 10 times the absolute blank measurement may be reported unqualified.

13.6.5.2 In the absence of project specific requirements, samples that are non-detect may be reported unqualified if the blank measurement demonstrates a positive bias.

13.6.5.3 In the absence of project specific requirements, samples that are non-detect must be qualified if the blank measurement demonstrates a negative bias between and including the LOD and LOQ. Non-detect samples may not be reported with a blank negative bias greater than the LOQ.

13.6.5.4 For samples that need qualification resulting from MB measurements that are positive, apply a B data qualifier to the analyte. B = “Analyte was detected in the associated method blank.”

13.6.5.5 For samples that need qualification resulting from MB measurements that are negative, apply a hand entered qualifier with the measurement and the units. "Analyte was measured in the associated method blank at a concentration of -#.# units."

13.7 **Laboratory Control Sample (LCS)**

13.7.1 A LCS prepared from an independent source must be performed with every batch or every 20 environmental samples, whichever is more frequent.

13.7.2 The LCS must be evaluated for accuracy and must meet the laboratory generated control limits before samples are analyzed. If no in-house limits are in use, then a range of 80 - 120% will be used. If the LCS recovery does not meet the acceptance criteria corrective action must be taken and the LCS recovery must be acceptable before proceeding with sample analysis. A LCSD is performed when requested by the client or when there is insufficient sample volume to perform a matrix spike / matrix spike duplicate. The LCSD must be evaluated to the same criteria as the LCS. The LCS/LCSD must be evaluated for precision and must meet the laboratory generated control criteria.

13.7.3 Should the LCS and/or the LCSD fail either accuracy or precision criteria, it can be re-analyzed once. Should they fail a second time, find and correct the problem, then reanalyze the entire batch.

13.8 **Matrix spike/Matrix spike duplicate**

13.8.1 A MS/MSD pair must be prepared and analyzed every 10 samples. The MS must be a duplicate of the aliquot used for sample analysis.

13.8.2 Calculate the percent recovery, corrected for concentration measured in the parent sample, and compare to the in-house generated limits. If no in-house limits are in use then a range of 80 - 120% will be used. Calculate the precision between the MS and MSD and compare to the in-house generated limits. If no in-house limits are in use, then an upper limit of 20% will be used.

13.8.3 If one or both spike recoveries are outside in-house accuracy acceptance criteria, the parent sample, the MS, and the MSD are given the appropriate data qualifier. If the RPD is outside in-house precision criteria, then the parent sample, the MS and the MSD are given the appropriate data.

13.9 **Reporting Limit Verification Standard (CRDL)**

13.9.1 A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration and after the initial CCV/CCB of each new batch.

13.9.2 The CRDL must recover within 60-140% of true value.

13.9.3 If outside the limits, reanalyze once. If still outside the limits, recalibrate.

13.10 **Precision Control Sample (RSD)**

13.10.1 A minimum of one sample per batch of 20 or fewer samples is analyzed in quadruplicate.

13.10.2 The Relative Standard Deviation and average are calculated for the four replicates.

13.10.3 If the RSD resulting from the four replicates is 40% or greater, the batch is re-prepared. See Attachment I for the 15 Analysis Precision Study.

13.11 When preparation of a sample exceeds 14 days past the time of collection, notify the project manager before proceeding. If a sample is run past 14 days after collection, flag the result with appropriate data qualifier.

13.12 If a sample was diluted due to matrix effects and the result is a non-detect, the result must be qualified with appropriate data qualifier.

14. DATA ANALYSIS AND CALCULATIONS

14.1 All data produced by the EA4000 must be processed through the appropriate curve.

$$c = (k1 * I + k0) / V$$

Where:

c is the final concentration (mg/kg)
k0 and k1 are constants derived from the calibration curve
I is the integral area units
V is the sample volume (mg)

14.2 Final concentration is exported to LIMS Link where it is back calculated to get the posted LIMS Link value.

$$\text{Final Concentration (mg/kg)} \times \frac{\text{Initial weight (mg)}}{1000\text{mg}} = \text{posted LIMSLink value (mg)}$$

14.3 Calculations in LIMS:

Soil:

$$\text{LIMS Link result (mg)} \times \left(\frac{1000 \text{ (mg)}}{\text{Sample weight (g)}} \right) = \text{TOC (mg/Kg)}$$

14.4 The result in mg/kg is divided by 10,000 to express the result as a percentage (%w/w).

14.5 Precision Control Sample average result calculation as mg/kg:

$$\text{Average result of 4 Injections} = ((TOC1) + (TOC2) + (TOC3) + (TOC4))/4$$

14.6 Precision Control Sample RSD Calculation:

The Relative Standard Deviation is calculated from the four replicates used to calculate the standard deviation and average.

$$\text{Relative Standard Deviation} = \left(\frac{\text{Standard Deviation}}{\text{Mean (Sec 14.5)}} \right) X\ 100$$

14.7 MS/MSD Calculation:

$$\% \text{ Recovery} = \frac{(SSR - SR)}{SA} X\ 100$$

Where:

SSR = Spike sample result
SR = Sample result
SA = Spike added

14.8 MS/MSD Precision Calculation:

The precision is calculated based on the % recovery of the matrix spike / matrix spike duplicate (MS/MSD) result.

$$\text{QC Sample \% RPD} = \left(\frac{|\text{MS - MSD}|}{(\text{MS+MSD})/2} \right) \text{X } 100$$

15. DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

Table H: Quality Control/Acceptance Criteria

Preparation Method ⇨ Quality Control Measure ⇩	**Lloyd Kahn** **Frequency**	**Acceptance Criteria**
Method Blank	One per batch of samples, up to 20m whichever is more frequent.	Project Specific or Less than the RL (Lowest curve standard.
Laboratory Control Spike and Duplicate	One per batch of samples, up to 20, whichever is more frequent. An LCSD is required if MS/MSD is not performed.	Project Specific or For solids 80 –120% with 20% RPD
Matrix Spike / Matrix Spike Duplicate	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent.	Project Specific or For solids 80 –120% with 20% RPD
Initial Calibration	Minimum of 4 standards plus blank at least once per year.	Correlation Coefficient of 0.995
CRDL	After the calibration and following the initial CCV/CCB in each batch..	60-140%
Calibration Verification (ICV/CCV)	ICV – analyzed after calibration but before samples. CCV – analyzed after every 10 samples.	Project specific or Recovery between 90 – 110%
Calibration Blank (ICB/CCB)	ICB – analyzed after ICV. CCB – analyzed after every CCV pair.	Project specific or Less than RL (Lowest curve standard)
Precision Control	One sample run in quadruplicate per batch of 20 or fewer samples.	RSD <40% or 3 times the standard deviation of the 15 analysis study, whichever is tighter.
Inorganic Carbon Check	After the ICV/ICB/CRDL and following the initial CCV/CCB in each analytical sequence.	Less than LOQ

16. CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

Table I: Data Assessment

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**TOC If these conditions are not achieved ⇩**
Method Blank	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Initial Calibration	• 4
CRDL standard	• 5
Initial / Continuing Calibration Verification	• 6
Initial / Continuing Calibration Blank	• 7
Precision Control Sample	• 8
Inorganic Carbon Check	• 5
Holding Time Compliance	• 9

1. In the absence of project specific requirements, sample detects less than 10 times the method blank contamination level is reported with the appropriate data qualifier. Sample detects greater than 10 times the method blank contamination are reported without qualification.

2. In the absence of project specific or method requirements, in-house generated limits will be used. If the MS or MSD fail because the concentration of the spike is less than 25% of the concentration of the parent, use appropriate flag for the parent sample. If the parent, MS, or MSD is greater than the top standard in the curve, dilute and reanalyze the parent, MS, and MSD following the above guidance. If the concentration of the spike is greater than 25% of the concentration of the parent, use appropriate flag for the parent sample if either the MS and/or MSD fails. If the MS and MSD fails precision control limits flag the parent with the appropriate precision data qualifier.

3. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged with the appropriate accuracy and appropriate precision qualifier to reflect the deficiencies.

4. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.

5. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

6. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. If the ICV/CCV recovers greater than the control limit and the samples bracketing the out of control ICV/CCV are non-detects, the results may be reported without a flag.

7. If ICB/CCB is outside the control limits reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. Samples that are > 10X the concentration in the CCB the samples do not have to be reanalyzed.

8. If the Precision Control Sample results in an RSD ≥40% or the result of the Precision Control Study (whichever is tighter), then the entire batch including samples and quality control will be rerun.

9. Notify Project Manager by submitting a LabTrack Ticket and flag with the appropriate data qualifier.

17. CONTINGENCIES FOR HANDLING OUT-OF CONTROL OR UNACCEPTABLE DATA

17.1 See section 16.

18. METHOD PERFORMANCE

18.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

18.2 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

18.3 An initial demonstration of capability (IDOC) must be performed per the most recent version of S-ALL-Q-020, *Orientation and Training Procedure*s (most current revision or replacement). A continuing demonstration of capability (CDOC) must be performed annually. A record of the DOCs will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

18.4 At a minimum, the 40CFR part 136 appendix b study must be performed every year, per the most recent version of S-GB-Q-020, *Determination of the LOD and LOQ* (most current revision or replacement). Additional studies may be performed to achieve a realistic LOD and LOQ. This is to be done for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

18.5 Linear Calibration Range - The linear calibration range must be determined initially and verified quarterly and whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. If any verification data exceeds the initial values by ± 10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

18.6 Periodic performance evaluation (PE) samples are analyzed per S-GB-Q-021, *PE/PT Program* (current revision or replacement), to demonstrate continuing competence. All results are stored in the QA office. At a minimum, these are performed twice a year for the aqueous and soil matrices.

19. METHOD MODIFICATIONS

19.1 The 15 analysis Lloyd Kahn RSD study has been performed and is included. When this study results in 3 times the standard deviation exceeding 40%, then 40% will be used as the acceptance criteria. This is tighter than the how the limits are created based on Lloyd Kahn.

19.2 Hydrochloric acid is used in this SOP instead of 1:1 phosphoric acid.

19.2.1 The 1:1 phosphoric acid did not dry when heated to 75°C or at more elevated temperatures of 105°C. Liquid residue was present after 24 hours of heating.

19.2.2 Hydrochloric acid is recommended by the instrument manufacture.

20. INSTRUMENT / EQUIPMENT MAINTENANCE

20.1 See EA4000 TOC Analyzer Operating Manual.

21. TROUBLESHOOTING

21.1 See EA4000 TOC Analyzer Operating Manual.

22. SAFETY

22.1 All samples, standards, and reagents should be treated as hazardous. Safety glasses, gloves, and lab coats are to be worn. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by a safe technique. Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion.

22.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of any chemical. A reference file of Safety Data Sheets (SDS) is made available to all personnel involved in this cleaning process, and is located at by the following link; https://msdsmanagement.msdsonline.com/c0ce0b0a-17d3-4f3c-afc6-25352729b299/ebinder/?nas=True.

22.3 Regulated soil samples are to be handled in accordance with Pace SOP: S-GB-S-001, Regulated Soil Handling (most current revision or replacement).

23. WASTE MANAGEMENT

23.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

23.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the most current revision or replacement of S-GB-W-002, *Waste Handling and Management*.

24. POLLUTION PREVENTION

24.1 Pollution prevention encompasses any technique or procedure that reduces or eliminates the quantity or toxicity of waste at the point of generation.

24.2 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

24.3 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

25. REFERENCES

25.1 Determination of Total Organic Carbon in Sediment by Lloyd Kahn Method, July 27, 1988

25.2 USEPA Test Methods for Evaluating Solid Wastes, SW 846, 3rd Edition, Methods 9060A

25.3 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version

25.4 PASI Quality Manual, current revision

25.5 Multi EA4000 Operation Manual

26. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ADDENDA ETC.

26.1 Attachment I: Precision Control Study

26.2 Attachment II: Flowchart

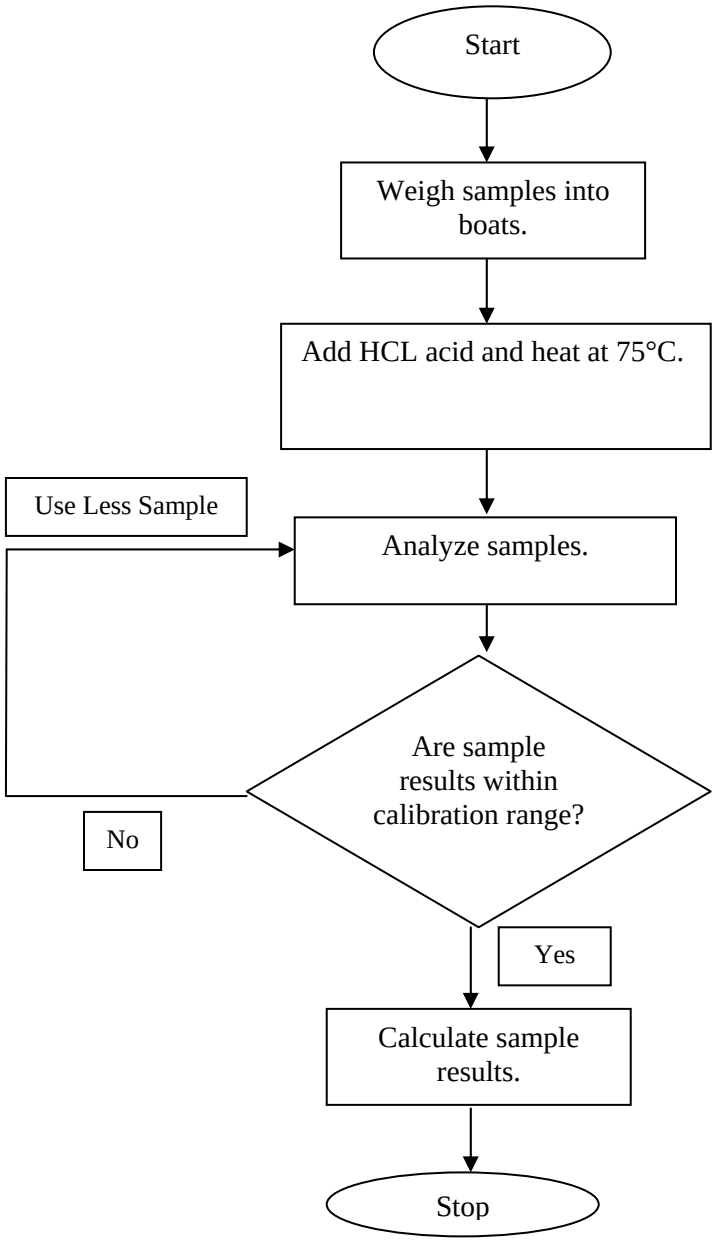
27. REVISIONS

Revision Number	Reason for Change	Date
S-GB-I-076-Rev.01	Section(s) 7 13.11: Table A updated hold time to 14 days. Section 12: Added clarification that analysis is completed with one injection per QC/Sample. Section 14: Removed quad calculations. Reformatted calculations.	10Apr2015
S-GB-I-076-Rev.02	Throughout Document: Updated Pace Analytical Services, Inc to Pace Analytical Services, LLC General: made administrative edits that do not affect the policies or procedures within the document. Throughout Document: Updated Pace Analytical Services, Inc to Pace Analytical Services, LLC, and information pertaining to the Inorganic Carbon (IC) check. Section(s) 10.1 and 10.2: Updated with current standards. Added 10% HCL and IC solutions. Added Expiration Date and Storage conditions. Section 13.3: Added ICB/CCB Criteria under one section, deleted out 13.4 and 12.1.4.	26Apr2017

ATTACHMENT I: PRECISION CONTROL STUDY

Sample ID	Result mg/Kg
REP 1	18639
REP 2	12215
REP 3	19669
REP 4	23486
REP 5	26832
REP 6	17037
REP 7	21269
REP 8	28646
REP 9	25435
REP 10	31628
REP 11	25059
REP 12	26506
REP 13	22003
REP 14	30472
REP 15	15831
Average	22982
Standard Deviation	5587
3 x STD	16761
RSD	24.3%
3 x RSD	72.9%

ATTACHMENT II: FLOWCHART



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STANDARD OPERATING PROCEDURE

Determination of Metals by Inductively Coupled Plasma (ICP) Spectroscopy

Reference Methods: SW-846 6010B, SW-846 6010C and EPA 200.7; SM 2340B-2011

SOP NUMBER:	S-GB-M-005-REV.09
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-M-005-REV.08

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 07/16/18

Kate Verbeten, Laboratory Quality Manager — Date: 6/22/18

Chad Rusch, Department Manager — Date: 7/13/2018

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

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

Table of Contents

1. Purpose/Identification of Method

1.1 This Standard Operating Procedure (SOP) documents the procedures used by PASI – Wisconsin to determine the concentration of specific metals in environmental water, wipe, paint chips, sludges, soils, and solid samples. The laboratory utilizes the ICP (Inductively Coupled Plasma – Optical Emission Spectrometer) and bases these documented procedures on those listed in EPA SW-846 Method 6010B, 6010C and EPA 200.7. Sample preparation procedures are based on SW-846 Methods 3010A, 3050B, and EPA-200.7.

2. Summary of Method

2.1 Samples are digested, excluding filtered groundwater for 6010B/6010C analysis, by heating with appropriate acids and oxidizing agents to solubilize the target elements. Portions of the digestates (or filtered, acidified groundwater samples) are pumped into a nebulizer to produce an aerosol. The aerosol is aspirated into the torch of an Inductively Coupled argon Plasma Optical Emission Spectrometer (ICP-OES) where it is evaporated and decomposed into atoms and ions. The plasma energy causes the target atoms to become excited and, during relaxation, emit characteristic light in the visible and/or ultraviolet emissions. Each element in the sample emits photons at a discrete wavelength(s), which are specific to that element. The light emissions are separated into wavelength and order by passing through a prism and onto an Echelle grating. The signal is then read and quantified by a Charge Injection Device (CID). The intensities of the wavelengths are proportional to the quantity of the target elements that is determined through a comparison to a known concentration (a calibration curve). The signals received from the CID are digitized and relayed to the instrument computer as an analytical signal.

2.2 Background correction is required to compensate for spectral interferences. Background is measured adjacent to analyte lines at a wavelength selected to be free of spectral interference and which reflects the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a correction would actually degrade the analytical result.

3. Scope and Application

3.1 This procedure may be used to determine concentrations of trace metals in water, wipe, paint chip, sludge, soil, and solid samples. A list of applicable elements, wavelengths used, and on instrument concentrations used to validate LOQs are shown in Table 3.1.

Table 3.1 – Elements, wavelengths, and on instrument CRDL RL concentrations used to validate LOQs.

Element		Wavelength (nm)	RL (µg/L)
Ag	Silver	328.0	10.0
Al	Aluminum	396.1	500
As	Arsenic	189.0	20.0
B	Boron	208.9	40
Ba	Barium	455.4	5.0
Be	Beryllium	313.0	4.0
Ca	Calcium	317.9	500
Cd	Cadmium	228.8	5.0
Ce	Cerium	404.0	NA
Co	Cobalt	228.6	5.0
Cr	Chromium	267.7	10.0
Cu	Copper	324.7	10.0
Fe	Iron	259.9	100
K	Potassium	766.4	1,000
Mg	Magnesium	279.0	1,000
Mn	Manganese	257.6	5.0
Mo	Molybdenum	202.0	10
Na	Sodium	589.5	500
Ni	Nickel	231.6	10.0
Pb	Lead	220.3	12.0
Sb	Antimony	206.8	20.0
Se	Selenium	196.0	20.0
Si	Silicon	221.7	NA
Sn	Tin	189.9	25
Sr	Strontium	407.7	5.0
Ti	Titanium	334.9	5.0
Tl	Thallium	190.8	40.0
V	Vanadium	292.4	10.0
Zn	Zinc	206.2	40.0

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

3.3 This method cannot be substituted for other similar published methods where permit or regulatory compliance is required.

3.4 Current Method Detection Limits can be found in current LIMS or can be provided by the Quality Department.

4. Applicable Matrices

4.1 This SOP is applicable to un-digested dissolved aqueous samples analyzed by 6010B or 6010C.

4.2 This SOP is applicable to digested aqueous (dissolved, total, waste) samples analyzed by 6010B, 6010C, and 200.7.

4.3 This SOP is applicable to digested solid/soil/sludge samples analyzed by 6010B, 6010C, and 200.7.

4.4 This SOP is applicable to digested paint chip samples analyzed by 6010B, 6010C, and 200.7.

4.5 This SOP is applicable to digested wipe samples analyzed by 6010B, 6010C, and 200.7.

5. Limits of Detection and Quantitation

5.1 All current MDLs and LOQs are listed in the LIMS and are available by request from the Quality Manager. The lowest concentrations that element recoveries are verified at with a standard can be found in Table 3.1.

6. Interferences

6.1 Spectral Interferences – Overlap of emission lines from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena and stray light can contribute to spectral interferences. These interferences can typically be minimized by careful selection of quantitation wavelengths, background correction, and inter-element corrections.

6.2 Physical Interferences –Changes in sample viscosity, surface tension, or other effects associated with sample transport and nebulization can produce significant inaccuracies, especially in samples containing high concentrations of dissolved solids and acids. Dissolved solids may build up on the nebulizer tip, altering the sample flow rate and causing instrument drift. These effects can be minimized by sample dilution, use of a specially designed high-solids nebulizer, or an argon humidifier. Use of internal standards helps in recognizing sample introduction issues.

6.3 Chemical Interferences – Molecular compound formation, ionization effects, and solute vaporization effects are typically not significant with ICP determinations. If observed, they can be minimized by careful selection of plasma and spectrometer operating parameters.

6.4 Memory Interferences – Sample deposition on the nebulizer tubing, spray chamber, and plasma torch can cause apparent sample carryover. Memory interferences can be minimized by flushing the system with rinse blanks between samples. If memory interference is suspected for a sample, the sample must be re-analyzed after a sufficient rinse period.

6.5 High Salt Concentrations – High salt concentrations in sample digestates can cause signal suppression and confuse interference tests. Use of internal standards helps in recognizing signal suppression.

7. Sample Collection, Preservation, Shipment and Storage

7.1 The lab provides appropriate bottle ware, including preservative, for requested testing. Where applicable, the bottle ware is demonstrated to be fee of target analytes. When bottle ware not originating from the lab is used, the data may be qualified with either one or both of the following data qualifiers:

7.1.1 Sample field preservation does not meet EPA or method recommendations for this analysis.

7.1.2 Sample container did not meet EPA or method requirements.

7.2 Collection, Preservation, Storage and Hold Times

Sample type	Collection per sample	Preservation	Storage	Hold time
Soil/ Solid/ Wipe/Paint Chip/Sludge	Pre-cleaned plastic or glass containers. Refer to Pace SOP S-GB-Q-025, *Sample Homogenization and Sub-Sampling* (current revision or replacement), for obtaining representative aliquots.	No Preservation	Refrigerated at ≤6°C	Up to 6 months
Total Metals – Aqueous	Pre-cleaned plastic containers with HNO_3	Nitric Acid (HNO_3) to pH<2, preserved at time of collection	Room Temperature	Up to 6 months
Dissolved Metals – Aqueous(1)	Pre-cleaned plastic containers – Filter sample at time of collection through a 0.45µm membrane filter.	Nitric Acid (HNO_3) to pH<2, filtered then preserved at time of collection.	Room Temperature	Up to 6 months
TCLP/SPLP/ASTM(2)	Pre-cleaned plastic containers.	Filtered then preserved at time of digestion. -Refrigerate at ≤6°C until preservation. -Nitric Acid (HNO_3) to pH<2	Refrigerate at ≤6°C	From Field Collection to Leach Extraction: 180 Days. From Leach Extraction to Determinative Analysis: 180 Days. (Total Elapsed Time: 360 Days).

(1) If filtration cannot be performed in the field, the sample must be taken in a pre-cleaned, unpreserved plastic container and transported to the lab as soon as possible. The sample must be filtered and then preserved to a pH <2. The sample must sit for **24 hours** prior to preparation, to ensure that the sample does not have a buffering effect that raises the pH to above <2. All lab filtered samples are qualified for improper field preservation.

(2) TCLP Extracts are not required to sit for 24 hours prior to digestion after the addition of nitric acid.

7.3 Preservative Check - The pH of samples must be verified to be <2 and documented in the Sample Receiving or Metals pH logbook prior to taking an aliquot for analysis. If a sample has a pH>2, additional preservative must be added to bring the sample to pH<2. Acid volume shall not to exceed 2% of the container capacity. Once adjusted, the sample must be allowed to sit for 24 hours prior to preparation. If the sample is not able to maintain a preservation of a pH of<2, then it must be qualified as such.

8. Definitions

8.1 Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions. In addition to those listed in the QAM, the following are additional terms found in this SOP.

8.2 Instrumental Detection Limit (IDL) – The concentration equivalent to a signal, due to the analyte, which is equal to the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with ten consecutive measurements per day at the same wavelength.

8.3 Instrument Check Standard – A multi-element standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. This is the same as the Continuing Calibration Verification Standard (CCV) referred to in the calibration section of this SOP.

8.4 Spectral Interference Check Solution (SIC) – A solution of selected analytes of higher concentrations used to evaluate the procedural routine for correcting known inter-element spectral interferences. This is also known as the Inter-element Correction Solution (ICSA).

8.5 Linear Detection Range – Defined as the upper limit of quantitation for an analyte. The LDR is determined as the upper range limit of an observed signal that deviates no more than 10% from the level extrapolated from the lower standards.

8.6 Interference Check Sample - (ICSAB) – A solution containing both interfering and analyte elements of known concentration that can be used to verify background and inter-element correction factors.

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

9.1 Instrumentation

Equipment	Vendor	Model / Version	Description / Comments
iCAP System	Thermo Scientific	ICAP 6500	Serial Number: 20073913
Autosampler	ESI	SC4 DX	X4DXS-HS-TSP-16-111004
Data System	iTEVA	2.0.039	
Recirculator	Neslab	ThermoFlex900	Serial Number: 107271037

9.2 General Supplies

Item	Vendor (or equivalent)	Catalog # (or equivalent)	Description
Argon – high purity grade	PraxAir	-----	Bulk
Autosampler Vials	Fisher Scientific	14-375-150	15 mL Polypropylene Test Tubes
Autosampler Pump Tubing	Analytical West	PT-2130PS-F PT-2200SAS PT-2080PS-F	black/black 0.76mm ID – Carrier 1.30mm ID – Waste orange/green 0.38mm ID – Internal Standard
Digestion Vials	SCP Science	010-500-263	Pre-cleaned polypropylene 50-mL screw cap vials.
Mechanical Pipettes and Tips	Eppendorf	Various	Or equivalent
Filter paper	Whatman	541 Filter Paper	
pH Strips	Fisherbrand	13-640-500	pH range 0 to 3
Y Connectors	Hewlett-Packard	G1820-65106	
Duo Torch / Duo Ceramic Cone	Thermo Fisher Scientific	8423-120-51241 / 84223-120-51261	
Spray Chamber/Spray Chamber adapter	Thermo Fisher Scientific	8423-120-51411 / 8423-120-51251	
SC-FAST Probe	ESI	SC-5037-3995-150	7” Teflon/Carbon Probe 1.0mmID
SC-FAST Waste Line	ESI	SC-0323-0002-215	Waste Line
SC-FAST Valve	ESI	SC-0599-1024	F7 Valve Head
	ESI	ES-2501-PPF2	
	ESI	ES-2501-PPMZ	
Peri-Pump	ESI		Fluoropolymer union, barbed
Nebulizer Line	ESI	SC-0317-0250-30	
Nuts and Ferrules	ESI	SC-0599-0116-K	For high flow 1/16” tubing
Nuts and Ferrules	ESI	SC-0599-0108-W	For high flow 1/8” tubing
Vacuum Line	ESI	SC-0321-32-215	For SC-FAST high flow valve
Sample Loop	ESI	SC-0318-15	1.5mL sample loop
Nebulizer	ESI	ES-2040	Micro Flow PFA-St nebulizer

9.3 Glassware

Glassware	Description
Volumetric Flasks	Class A
Graduated Cylinders	Class A

10. Reagents and Standards

10.1 Reagents

Reagent	Concentration/ Description	Requirements/ Vendor/ Item #	Expiration Date
Nano-pure Water	ASTM Type II, or equivalent (18mOhm or higher resistivity)	Nano-pure Water	NA
Nitric Acid (HNO_3)	Trace metals grade, Fisher Insta-analyzed, or equivalent	J.T Baker Cat #9598-34 or equivalent	Manufacturer's recommended expiration date or 2 years from receipt/made date, whichever is sooner
Hydrochloric Acid (HCl)	Trace metals grade, Fisher Insta-analyzed, or equivalent	Fisher Cat # A508 or equivalent	
Hydrogen Peroxide (H_2O_2)	30% certified reagent grade; trace metals grade if available. Stabilized solutions come with Sodium added.	Fisher Cat # H325-4 or equivalent	
Acidified Reagent Water	5mL Nitric Acid and 5mL Hydrochloric Acid per 100mL Nano-pure water	NA	

10.2 Standards

10.2.1 Standards are used in the calibration of the instrument through the calibration verification, sample analysis, and continuing calibration verification.

10.2.2 Primary standards are the calibration standards and those that are made from the same source as the calibration standards.

10.2.3 Secondary standards are made from a source that is from a different vendor/manufacturer than the calibration source.

10.2.4 Whenever possible, standards are prepared from commercially available multi-component stock solutions. Single stock standards may also be utilized.

10.3 Standards, Reagents, and Spike Solutions are logged as follows:

10.3.1 Stock standards have a copy of their certificate of analysis (COA) scanned and saved on the network. The standard is logged into the LIMS (Epic Pro) and referenced to the scanned COA. Please see the SOP G-ALL-IT-004 (most current revision or equivalent) for more detailed instructions.

10.3.2 Reagents are logged in the same manner.

10.4 Standard Definitions

Standard 6010B/6010C	Standard 200.7	Description	Comments
Initial Calibration Standard(s)	Initial Calibration Standard(s)	Standard(s) prepared from single and/or multi-element standard(s) at appropriate acid concentrations.	Calibration standards can be made and used for 6 months unless a standard used to make them expires earlier.
Initial Calibration Verification Standard (ICV)	Quality Control Sample (QCS) & 1st IPC	Standard prepared near the midpoint of the calibration range and is used to verify the accuracy of the calibration and instrument performance.	Must be prepared from a source independent of CCV and Calibration Solutions.
Continuing Calibration Verification Standard (CCV)	Instrument Performance Check Solution (IPC)	Standards prepared from single and/or multi-element standards at appropriate acid concentrations. Solutions containing all analyte elements are prepared at a concentration near the mid-point of the calibration range. This standard verifies the accuracy of the calibration curve.	May be prepared from the same source as the calibrations standards
Reporting Limit Verification Standard (RLVS)	NA	A standard prepared and analyzed at the RL (near the LOQ) to demonstrate the detection capability and verify the LOQ.	NELAC requirement, a client specific requirement for certain QAPPs
Inter-element correction solution (ICSA)	Spectral Interference Solution (SIC)	A solution prepared with high concentrations of interfering elements (Al, Ca, Fe, Mg...). This is run daily at a minimum to verify the inter-element correction factors.	Al, Ca, Fe, Mg
Inter-element correction solution (ICSAB)	NA	A solution prepared with high concentrations of interfering elements and low level concentrations of the other target elements. This is analyzed daily and immediately following the ICSA solution.	Not a 6010B, 6010C, or 200.7 requirement, but may be required on a client specific basis.
Internal Standard (IS)	Internal Standard (IS)	A solution added to all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard solution contains a non-target element (yttrium (Y)) at a concentration yielding an appropriate final concentration in the sample.	Y at 5ppm with Li. Added in-line to all samples and standards.
Single Element Standards	Single Element Standards	Stock standards purchased from venders containing one element. Used for checking IECs and may be used for checking linear ranges.	Must be 99.99% or more pure.
Spiking Standard	Spiking Standard	This solution contains all target analytes and should not be prepared from the same standards as the calibration standards.	Prepared from a source independent of CCV and Calibration Solutions.
Method Blank (MB)	Laboratory Reagent Blank (LRB)	This blank must contain all the reagents, in the same volumes as used for samples and must be carried through the complete processing of samples with the samples.	
Laboratory Control Sample (LCS)	Laboratory Fortified Blank (LFB)	Lab water spiked with the reagents of interest at a known concentration. It must contain all the reagents, in the same volumes as used for samples and must be carried through the complete processing of samples with the samples.	Spiked from a source independent of CCV and Calibration Solutions.
Matrix Spike (MS), Matrix Spike Duplicate (MSD)	Laboratory Fortified Sample Matrix (LFM)	Aliquots of environmental sample spiked with known concentrations of target analytes.	Spiked from a source independent of CCV and Calibration Solutions.

10.5 Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	Concentrated reference solution purchased directly from approved vendor	Manufacturer's recommended expiration date.	Manufacturer's recommended storage conditions.
Intermediate and Working Standard Solutions	Reference solutions prepared by dilutions of the stock solution	Should be prepared as needed or at least every 6 months. The intermediate or working standard can not exceed the expiration date recommended by the manufacturer for each component used.	Store at room temperature

10.6 Calibration Working Standard – Dilutions and Concentrations

Pace Custom Standard (Stock Standard)	Element Components	Stock Concentration	Stock Volume Used	Acid Used	Final Total Volume	Final Concentration in Standard
Metals STK1 = Spex #1 (XFSMN-26-250A)	As	100 mg/L	2 mL	10 mL HNO_3 / 10 mL HCl	200 mL	1.0 mg/L
	Ba	100 mg/L				1.0 mg/L
	Be	100 mg/L				1.0 mg/L
	Cd	100 mg/L				1.0 mg/L
	Co	100 mg/L				1.0 mg/L
	Cr	100 mg/L				1.0 mg/L
	Cu	100 mg/L				1.0 mg/L
	Mn	100 mg/L				1.0 mg/L
	Ni	100 mg/L				1.0 mg/L
	Pb	100 mg/L				1.0 mg/L
	Se	100 mg/L				1.0 mg/L
	Sr	100 mg/L				1.0 mg/L
	Tl	100 mg/L				1.0 mg/L
	V	100 mg/L				1.0 mg/L
	Zn	100 mg/L				1.0 mg/L
Metals STK2 = Spex #2 (XFSMN-27-250A)	B	100 mg/L	4 mL			2.0 mg/L
	Mo	100 mg/L				2.0 mg/L
	Sb	100 mg/L				2.0 mg/L
	Si	500 mg/L				10 mg/L
	Sn	100 mg/L				2.0 mg/L
	Ti	100 mg/L				2.0 mg/L
	Ag	50 mg/L				1.0 mg/L
Metals STK3 = Spex #3 (XFSMN-28-250A)	Al	1,000 mg/L	10 mL			50 mg/L
	Ca	1,000 mg/L				50 mg/L
	Fe	1,000 mg/L				50 mg/L
	K	1,000 mg/L				50 mg/L
	Mg	1,000 mg/L				50 mg/L
	Na	1,000 mg/L				50 mg/L
Ce-STK	Ce	1,000 mg/L	0.20 mL			1.0 mg/L

Or Equivalent

10.7 CCV Working Standard – Dilutions and Concentrations

Pace Custom Standard (Stock Standard)	Element Components	Stock Concentration	Stock Volume Used	Acid Used	Final Total Volume	Final Concentration in Standard
Metals STK1 = Spex #1 (XFSMN-26-250A)	As	100 mg/L	5.0 mL	50 mL HNO_3/ 50 mL HCl	1000 mL	0.5 mg/L
	Ba	100 mg/L				0.5 mg/L
	Be	100 mg/L				0.5 mg/L
	Cd	100 mg/L				0.5 mg/L
	Co	100 mg/L				0.5 mg/L
	Cr	100 mg/L				0.5 mg/L
	Cu	100 mg/L				0.5 mg/L
	Mn	100 mg/L				0.5 mg/L
	Ni	100 mg/L				0.5 mg/L
	Pb	100 mg/L				0.5 mg/L
	Se	100 mg/L				0.5 mg/L
	Sr	100 mg/L				0.5 mg/L
	Tl	100 mg/L				0.5 mg/L
	V	100 mg/L				0.5 mg/L
	Zn	100 mg/L				0.5 mg/L
Metals STK2 = Spex #2 (XFSMN-27-250A)	B	100 mg/L	10.0 mL			1.0 mg/L
	Mo	100 mg/L				1.0 mg/L
	Sb	100 mg/L				1.0 mg/L
	Si	500 mg/L				5.0 mg/L
	Sn	100 mg/L				1.0 mg/L
	Ti	100 mg/L				1.0 mg/L
	Ag	50 mg/L				0.5 mg/L
Metals STK3 = Spex #3 (XFSMN-28-250A)	Al	1,000 mg/L	25.0 mL			25 mg/L
	Ca	1,000 mg/L				25 mg/L
	Fe	1,000 mg/L				25 mg/L
	K	1,000 mg/L				25 mg/L
	Mg	1,000 mg/L				25 mg/L
	Na	1,000 mg/L				25 mg/L
Ce-STK	Ce	1,000 mg/L	0.50 mL			0.5 mg/L

10.8 ICV (Second Source) Working Standard – Dilutions and Concentrations

Pace Custom Standard (Stock Standard)	Element Components	Stock Concentration	Stock Volume Used	Acid Used	Final Total Volume	Final Concentration in Standard
Metals SPK1 = IV #1 (PA-STD-1B)	As	200 mg/L	0.5 mL	10 mL HNO_3/ 10 mL HCl	200 mL	0.5 mg/L
	Ba	200 mg/L				0.5 mg/L
	Be	200 mg/L				0.5 mg/L
	Cd	200 mg/L				0.5 mg/L
	Co	200 mg/L				0.5 mg/L
	Cr	200 mg/L				0.5 mg/L
	Cu	200 mg/L				0.5 mg/L
	Mn	200 mg/L				0.5 mg/L
	Ni	200 mg/L				0.5 mg/L
	Pb	200 mg/L				0.5 mg/L
	Se	200 mg/L				0.5 mg/L
	Sr	200 mg/L				0.5 mg/L
	Tl	200 mg/L				0.5 mg/L
	V	200 mg/L				0.5 mg/L
	Zn	200 mg/L				0.5 mg/L
Metals SPK2 = IV #2 (PA-STD-2B)	B	200 mg/L	1.0 mL			1.0 mg/L
	Mo	200 mg/L				1.0 mg/L
	Sb	200 mg/L				1.0 mg/L
	Si	1,000 mg/L				5.0 mg/L
	Sn	200 mg/L				1.0 mg/L
	Ti	200 mg/L				1.0 mg/L
	Ag	100 mg/L				0.5 mg/L
Metals SPK3 = IV #3 (PA-STD-3B)	Al	2,000 mg/L	2.5 mL			25 mg/L
	Ca	2,000 mg/L				25 mg/L
	Fe	2,000 mg/L				25 mg/L
	K	2,000 mg/L				25 mg/L
	Mg	2,000 mg/L				25 mg/L
	Na	2,000 mg/L				25 mg/L

10.9 Spiking Standard 6000-SPK (for LCS and MS/MSD) – Dilutions and Concentrations

Pace Custom Standard (Stock Standard)	Element Components	Stock Concentration	Stock Volume Used	Acid Used	Final Total Volume	Final Concentration in Standard	Spike Concentration
Metals SPK1 = IV #1 (PA-STD-1B)	As	200 mg/L	25 mL	12 mL HNO_3	200 mL	25 mg/L	500 µg/L
	Ba	200 mg/L				25 mg/L	500 µg/L
	Be	200 mg/L				25 mg/L	500 µg/L
	Cd	200 mg/L				25 mg/L	500 µg/L
	Co	200 mg/L				25 mg/L	500 µg/L
	Cr	200 mg/L				25 mg/L	500 µg/L
	Cu	200 mg/L				25 mg/L	500 µg/L
	Mn	200 mg/L				25 mg/L	500 µg/L
	Ni	200 mg/L				25 mg/L	500 µg/L
	Pb	200 mg/L				25 mg/L	500 µg/L
	Se	200 mg/L				25 mg/L	500 µg/L
	Sr	200 mg/L				25 mg/L	500 µg/L
	Tl	200 mg/L				25 mg/L	500 µg/L
	V	200 mg/L				25 mg/L	500 µg/L
	Zn	200 mg/L				25 mg/L	500 µg/L
Metals SPK2 = IV #2 (PA-STD-2B)	B	200 mg/L	25 mL			25 mg/L	500 µg/L
	Mo	200 mg/L				25 mg/L	500 µg/L
	Sb	200 mg/L				25 mg/L	500 µg/L
	Si	1,000 mg/L				1,25 mg/L	2,500 µg/L
	Sn	200 mg/L				25 mg/L	500 µg/L
	Ti	200 mg/L				25 mg/L	500 µg/L
	Ag	100 mg/L				12.5 mg/L	250 µg/L
Metals SPK3 = IV #3 (PA-STD-3B)	Al	2,000 mg/L	25 mL			250 mg/L	5,000 µg/L
	Ca	2,000 mg/L				250 mg/L	5,000 µg/L
	Fe	2,000 mg/L				250 mg/L	5,000 µg/L
	K	2,000 mg/L				250 mg/L	5,000 µg/L
	Mg	2,000 mg/L				250 mg/L	5,000 µg/L
	Na	2,000 mg/L				250 mg/L	5,000 µg/L

10.10 Low Level Check Standard (6010CRDL-INT) Intermediate

Pace Custom Standard (Stock Standard)	Element Components	Stock Concentration	Stock Volume Used*	Acid Used	Final Total Volume	Final Concentration in Standard
6010CRDL-STK = 4400-161007AM01	Ag	10 mg/L	10 mL	5 mL HNO_3 / 5 mL HCl	100 mL	1,000 µg/L
	Al	500 mg/L				50,000 µg/L
	As	20 mg/L				2,000 µg/L
	B	40 mg/L				4,000 µg/L
	Ba	5 mg/L				500 µg/L
	Be	4 mg/L				400 µg/L
	Ca	500 mg/L				50,000 µg/L
	Cd	5 mg/L				500 µg/L
	Co	5 mg/L				500 µg/L
	Cr	10 mg/L				1,000 µg/L
	Cu	10 mg/L				1,000 µg/L
	Fe	100 mg/L				10,000 µg/L
	K	1,000 mg/L				1000,000 µg/L
	Mg	1,000 mg/L				1000,000 µg/L
	Mn	5 mg/L				500 µg/L
	Mo	10 mg/L				1,000 µg/L
	Na	500 mg/L				50,000 µg/L
	Ni	10 mg/L				1,000 µg/L
	Pb	12 mg/L				1,200 µg/L
	Sb	20 mg/L				2,000 µg/L
	Se	20 mg/L				2,000 µg/L
	Sn	25 mg/L				2,500 µg/L
	Sr	5 mg/L				500 µg/L
	Ti	5 mg/L				500 µg/L
	Tl	40 mg/L				4,000 µg/L
	V	10 mg/L				1,00 µg/L
	Zn	40 mg/L				4,000 µg/L

10.11 Low Level Check Standard (ICP-CRDL) Working Solution – Dilutions and Conc.

Low Level Check Standard Intermediate	Element Components	Stock Concentration	Stock Volume Used*	Acid Used	Final Total Volume	Final CRDL Concentration
6010CRDL-INT = CRDL Intermediate	Ag	1,000 µg/L	2 mL	10 mL HNO_3 / 10 mL HCl	200 mL	10 µg/L
	Al	50,000 µg/L				500 µg/L
	As	2,000 µg/L				20 µg/L
	B	4,000 µg/L				40 µg/L
	Ba	500 µg/L				5 µg/L
	Be	400 µg/L				4 µg/L
	Ca	50,000 µg/L				500 µg/L
	Cd	500 µg/L				5 µg/L
	Co	500 µg/L				5 µg/L
	Cr	1,000 µg/L				10 µg/L
	Cu	1,000 µg/L				10 µg/L
	Fe	10,000 µg/L				100 µg/L
	K	100,000 µg/L				1,000 µg/L
	Mg	100,000 µg/L				1,000 µg/L
	Mn	500 µg/L				5 µg/L
	Mo	1,000 µg/L				10 µg/L
	Na	50,000 µg/L				500 µg/L
	Ni	1,000 µg/L				10 µg/L
	Pb	1,200 µg/L				12 µg/L
	Sb	2,000 µg/L				20 µg/L
	Se	2,000 µg/L				20 µg/L
	Sn	2,500 µg/L				25 µg/L
	Sr	500 µg/L				5 µg/L
	Ti	500 µg/L				5 µg/L
	Tl	4,000 µg/L				40 µg/L
	V	1,000 µg/L				10 µg/L
	Zn	4,000 µg/L				40 µg/L

10.12 Inter-element Correction Solution (ICP-ICSA) Working Solution – Dilutions and Conc.

Pace Standard #	Vendor	Stock Catalog Number	Stock Volume Used	Final Total Volume	Acid Used	Element Components	Final Concentration in Standard	Stock Concentration
Single Element Al	Ultra Scientific	ICP-113	5 mL	200 mL	10 mL HNO_3 / 10 mL HCl	Al	250 mg/L	10,000 mg/L
Single Element Ca	Ultra Scientific	ICP-120	10 mL			Ca	500 mg/L	10,000 mg/L
Single Element Mg	Ultra Scientific	ICP-112	10 mL			Mg	500 mg/L	10,000 mg/L
Single Element Fe	Ultra Scientific	ICP-126	4 mL			Fe	200 mg/L	10,000 mg/L

10.13 Inter-element Correction Solution (ICP-ICSAB) Working Solution – Dilutions and Conc.

Pace Standard #	Vendor	Stock Catalog Number	Stock Volume Used	Final Total Volume	Acid Used	Element Components	Final Concentration in Standard	Stock Concentration
Single Element Al	Ultra Scientific	ICP-113	4.5 mL	200 mL	10 mL HNO_3 / 10 mL HCl	Al	225 mg/L	10,000 mg/L
Single Element Ca	Ultra Scientific	ICP-120	9.5 mL			Ca	475 mg/L	10,000 mg/L
Single Element Mg	Ultra Scientific	ICP-112	9.5 mL			Mg	475 mg/L	10,000 mg/L
Single Element Fe	Ultra Scientific	ICP-126	3.5 mL			Fe	175 mg/L	10,000 mg/L
Metals SPK1	Inorganic Ventures	PA-STD-1B	0.5 mL			As	0.5 mg/L	200 mg/L
						Ba	0.5 mg/L	200 mg/L
						Be	0.5 mg/L	200 mg/L
						Cd	0.5 mg/L	200 mg/L
						Co	0.5 mg/L	200 mg/L
						Cr	0.5 mg/L	200 mg/L
						Cu	0.5 mg/L	200 mg/L
						Mn	0.5 mg/L	200 mg/L
						Ni	0.5 mg/L	200 mg/L
						Pb	0.5 mg/L	200 mg/L
						Se	0.5 mg/L	200 mg/L
						Sr	0.5 mg/L	200 mg/L
						Tl	0.5 mg/L	200 mg/L
						V	0.5 mg/L	200 mg/L
						Zn	0.5 mg/L	200 mg/L
Metals SPK2	Inorganic Ventures	PA-STD-2B	1.0 mL			B	1.0 mg/L	200 mg/L
						Mo	1.0 mg/L	200 mg/L
						Sb	1.0 mg/L	200 mg/L
						Si	5.0 mg/L	1,000 mg/L
						Sn	1.0 mg/L	200 mg/L
						Ti	1.0 mg/L	200 mg/L
						Ag	0.5 mg/L	100 mg/L
Metals SPK3	Inorganic Ventures	PA-STD-3B	2.5 mL			Al	25 mg/L	2,000 mg/L
						Ca	25 mg/L	2,000 mg/L
						Fe	25 mg/L	2,000 mg/L
						K	25 mg/L	2,000 mg/L
						Mg	25 mg/L	2,000 mg/L
						Na	25 mg/L	2,000 mg/L
Single Element Ni	Ultra Scientific	ICP-028	0.1 mL			Ni	0.5 mg/L	1,000 mg/L

10.14 Internal Standard Solution – Dilutions and Concentrations

Pace Standard #	Stock Catalog Number	Stock Volume Used	Final Total Volume	Acid Used	Element Components	Final Concentration in Standard	Stock Concentration
ICP-IS	ICP-139 (ULTRA SCIENTIFIC)	0.5 mL	1000 mL	50 mL HNO_3 / 50 mL HCl	Yttrium	5 mg/L	10,000 mg/L
	CGLI10 (Inorganic Ventures)	100 mL			Lithium	1,000 mg/L	10,000 mg/L

11. Calibration and Standardization

11.1 Rinse Time – Both the SW846 6010 methods and EPA 200.7 specify a minimum of a 1.0 min rinse time. The sample loads for about 14 seconds. For the remainder of the 2.0 min plus timeframe the system is being rinsed.

11.2 Nebulizer Flow Rate – This is to be done at set-up, or after an operating condition change. A 10,000µg/L Yttrium standard will yield a "bullet" emission about 10mm beyond load coil. Adjust the nebulizer flow rate to modify the "bullet" location.

11.3 Solution Uptake Rate – This is a visual check of a bubble in the loop to verify that the sample is reaching the nebulizer in sufficient time for analysis. This should be done when the timing is suspected to be off. Adjust the pump settings if adjustments are needed.

11.4 Profile - The iCAP 6500 ICP will automatically check a carbon reference line against ambient air conditions each time the plasma is ignited to maintain wavelength accuracy.

11.5 Daily Initial Calibration

11.5.1 Allow the instrument 30 minutes to warm up after igniting the torch.

11.5.2 The ICP must be calibrated each time it is set up for analysis or every 24 hours according to the manufacturer's instructions.

11.5.3 Calibration requires analysis of a Calibration Blank and at least one level of calibration solution. The ICP software will create a calibration curve using linear regression.

11.5.4 Calibration standards can be made and used for 6 months unless a standard used to make them expires earlier. It would then expire on that date. Instrument standardization date and time must be recorded in the raw data.

11.6 During the determination, the software uses the ratio of analyte and internal standard intensities to adjust the final concentration values. Ratios are based on the intensities in the sample vs. the calibration blank intensities.

11.7 Calibration Verification- Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. This is accomplished by analyzing and passing the following QC points: ICV, ICB, CRDL, and ICSA standards. Additional verification is required periodically throughout sample analysis as dictated by the method being cited. These QC points may include CCVs, CCBs, ICSAs, ICSABs, and/or CRDLs.

12. Procedure

12.1 ICP System Preparation

12.1.1 Preventative Maintenance

Inspect the sample introduction system including the nebulizer, torch, injector tube and up-take tubing for salt deposits, dirt and debris that could restrict solution flow and affect instrument performance. Document all maintenance in ICP maintenance logbook.

12.1.2 Operating Parameters

Set up and configure the ICP according to manufacturer's operating instructions using operating parameters shown in the following table.

Table 11.3.1 - Operating Parameter for ICP Systems

Operating Parameter	ICAP 6500 20073913
Argon Flow	80 L/min
Nebulizer Flow	0.70 L/min
RF Output	1175 W
Pump Speed	30 rpm
Aux Gas Flow	0.5 L/min
Coolant Gas Flow	15 l/min

12.1.3 Calibrate ICP according to Section 11.

12.1.4 Batch Sequence - If using an auto-sampler, enter an auto-sampler sequence into the ICP data system per manufacturer's instructions. Calibration blanks, standards, initial checks, and inter-element correction standards shall be run before analysis of environmental samples. All samples, including calibration, checks, and other standards, can also be run manually.

12.1.5 For dissolved batches prepare the batch QC as follows:

12.1.5.1 MB – Add 10 mL of acidified reagent water to an auto-sampler tube.

12.1.5.2 LCS/LCSD – Add 0.20 mL of 6000-SPK to 10 mL of acidified reagent water in an auto-sampler tube.

12.1.5.3 MS/MSD – Add 0.20 mL of 6000-SPK to 10 mL of parent sample in an auto-sampler tube.

12.1.6 Load auto-sampler tray according to the vial position on the sequence table.

12.1.7 Analyze all standards, quality control samples, and environmental samples.

Table 12.0 – 6010C Example analytical sequence after calibration of a blank and a standard.

Auto-sampler Position	Sample Description	Auto-sampler Position	Sample Description
1	ICV	27	Sample 15
2	ICB	28	Sample 16
3	CRDL	29	CCV
4	ICSA *	30	CCB
5	CCV	31	Sample 17
6	CCB	32	Sample 18
7	MB1	33	Sample 19
8	LCS1	34	Sample 20
9	Sample 1	35	MB2
10	Sample 1 Matrix Spike	36	LCS2
11	Sample 1 Matrix Spike Duplicate	37	Sample 21
12	Sample 2	38	Sample 22
13	Sample 3	39	Sample 22 Matrix Spike
14	Sample 4	40	Sample 22 Matrix Spike Duplicate
15	Sample 5	41	CCV
16	Sample 6	42	CCB
17	CCV	43	Sample 25
18	CCB	44	Sample 26
19	Sample 7	45	Sample 27
20	Sample 8	46	Sample 28
21	Sample 9	47	Sample 28 Matrix Spike
22	Sample 10	48	Sample 28 Matrix Spike Duplicate
23	Sample 11	49	CCV
24	Sample 12	50	CCB
25	Sample 13	51	CRDL
26	Sample 14		

* ICSAB will follow the ICSA if needed/requested by client.

12.2 Data Reduction

12.2.1 **Quantitative Analysis –** The instrument produces results in µg/L. If the initial sample aliquot and final digestate volumes are the same, the ICP data system will calculate the concentration of each element directly. If the initial and final volumes are different, the actual values are posted into the LIMS system and calculations are performed in the LIMS.

12.2.2 Analysts should be aware situations where possible carryover can occur. This can be seen when highly concentrated samples are analyzed followed by analysis of detections with decreasing concentration. Every element reacts differently and sample matrix can play a role as well. Should carryover be suspected by the analyst, the affected sample(s) should be reanalyzed.

12.2.3 Samples with element concentrations that exceed 90% of the upper linear range must be diluted and re-analyzed if reporting that element and/or if that element interferes with another element that is being reported.

12.2.4 Any sample in which any element value is below the instrument detection limit or LOQ must be reported as less than the LOQ (or ND) for that specific element. Do not report data below the element LOQ concentration unless it is qualified as an "estimated" result with a "J".

12.2.5 LimsLink is used to transfer data from the instrument to the LIMS system.

13. Quality Control

There are three levels of quality control utilized in this SOP. They consist of Method QC, Instrument QC, and Prep/Batch QC.

13.1 Refer to the most current version of the Pace Quality Manual Appendix I Quality Control Calculations and SOP S-GB-Q-009 *Common Laboratory Calculations and Statistical Evaluation of Data* for equations and calculation details.

13.2 **Instrument QC**: Prior to the analysis of samples, and in some cases during the analysis run, the following quality control must be generated and/or within limits: Internal Standards, Interference Correction Solutions A and B (ICSA and ICSAB), Initial Calibration Verification (ICV), Continuing Calibration Verification (CCV), RLVS / CRDL standards, and Initial and Continuing Calibration Blanks (ICB and CCB).

13.2.1 **Internal Standards –** Yttrium is used as an internal standard. Yttrium is not calibrated for. Precision of the Yttrium reps are evaluated using < or = 5% RSD. Accuracy of the Yttrium average count levels are evaluated using 50-150% recovery as compared to the calibration blank. If either of these criteria is not meet, the sample or quality control standard must be rerun, possibly at a dilution. Criteria may be tighter to meet certain client or project specifications.

13.2.2 **Multiple Instrument Integration RSD** – The RSD is required to be evaluated between multiple instrument integrations. The RSD must be less than or equal to 20%, if the analyte concentration is greater than the RL. If the RSD is greater than 20%, the laboratory must reanalyze the sample.

13.2.3 The ICSA and ICSAB solution are used to verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run, prior to the analysis of any samples. By client request the ICSA and ICSAB may also be analyzed at the end of the analytical sequence. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. The control limits for the elements in the ICSAB solution that are in the linear range must be within 80 to 120% of the expected recovery. Non-spiked elements must have a result less than the LOQ unless there is a known contaminant. In this case the result minus the known contaminant must result in a concentration less than the LOQ. If an element of interest does not meet these criteria, then the problem must be corrected, the instrument recalibrated, and the run reanalyzed.

13.2.4 The ICV is analyzed to check the accuracy of the curve. It must be evaluated before any samples are analyzed. The ICV should be at or near (or lower than) the midpoint of the calibration curve, derived from a source independent of the calibration standards, and must recover within 90 to 110% of the expected

value for 6010B and 6010C. For 200.7 the ICV must recover within 95 to 105% of the expected value and have an RSD of <3%. If these limits are not met for an element of interest, the problem must be corrected, the instrument recalibrated, and the run reanalyzed. If the ICV fails high and the samples are non-detects, then they may be reported. Pace WI satisfies the 200.7 QCS and first Instrument Performance Check (IPC) criteria using the ICV.

13.2.5 Reporting Limit Verification Standard (RLVS/RL/CRDL): With every Initial Calibration, a standard corresponding to the Level of Quantitation (LOQ) must also be analyzed and meet established acceptance criteria. The concentrations in the CRDL are determined to be the reporting limit (RL). The RLVS is analyzed prior to any samples being analyzed. For 6010C and by client request it will also be analyzed at the end of the analytical sequence. Additional RLVSs may be analyzed throughout the analytical sequence at the analyst's discretion. The limits for the RLVS are +/- 40% of the true concentration for 6010B and 200.7. The limits for the RLVS are +/- 30% of the true concentration for 6010C. The analysis of this standard demonstrates the instruments ability to quantify down to the LOQ with known accuracy.

13.2.6 The CCV is analyzed to check for calibration drift. The CCV is run after every 10 samples and again at the end of samples. It must quantitate within 90 to 110% of the expected value. Any sample analyzed under out-of-control calibration must be reanalyzed, following the successful re-calibration of the instrument. If the CCV fails high and the samples are non-detects, then they may be reported. Pace WI satisfies the 200.7 Instrument Performance Check (IPC) criteria using the CCV, with the exception of the first IPC.

13.2.7 The ICB is analyzed to check the accuracy of the curve. The CCBs are analyzed to check for calibration drift. In the absence of project specific reporting limits, the results of the calibration blanks must be less than the LOQ. The ICB is run after the ICV and the CCBs are run after the CCVs. If the ICB or CCB fails high for an analyte and the samples are non-detects or are greater than 10x the blank value, then they may be reported.

13.3 **Batch Quality Control** - A batch will consist of 20 or fewer samples. Batch Quality Control will include a Method Blank (MB), Laboratory Control Spike (LCS), Matrix Spike (MS), Matrix Spike Duplicate (MSD). It may also include a Laboratory Control Spike Duplicate (LCSD), Post Spike (PS), a Serial Dilution (SDL), Duplicate (DUP), additional MS/MSDs, and/or Standard Reference Material (SRM).

13.3.1 The Method Blank is used to verify that interferences caused by contaminants in the solvents, reagents, glassware, etc. are known and minimized. The method blank is processed through all digestions, etc., which were performed on the samples in the batch. For a method blank to be acceptable, in the absence of project specific criteria, the concentration shall not be higher than the highest of the following: The LOQ, or ten percent of the regulatory limit of concern for that analyte, or ten percent of the measured concentration in a particular sample of interest. Each sample in the batch is assessed against the above criteria to determine if the sample results are acceptable. Any sample associated with an unacceptable blank is either flagged, re-prepped for analysis, or if re-prepping is not an alternative, the results are reported with the appropriate data qualifying codes. For negative instrument measurements >LOD and <LOQ qualify sample results that are non-detections and <10 times the measurement with "Analyte was measured in the associated method blank at a concentration of -#.# units." Make sure to enter the concentration and applicable sample units.

13.3.2 A laboratory control sample (LCS) consists of a control matrix, which has been spiked, with the analytes(s) of interest or compounds representative of those analytes. Laboratory Control Samples are analyzed at a minimum of 1 per batch of 20 or fewer samples or preparation method. Results of the LCS are expressed in terms of percent recovery, and are used to determine batch acceptance. Acceptance limits can be generated based on laboratory generated data and are not to exceed 80 to 120% of the expected recovery for 6010B and 6010C, or 85 to 115% for 200.7. If these limits are not met and the failure is confirmed by a single re-analysis, with the instrument in control, then the entire batch will be re-digested and re-analyzed. Data for high LCS failure can be reported if the analyte is non-detection.

13.3.3 An LCS Duplicate may be analyzed to evaluate laboratory precision. The LCSD must also meet the criteria for the LCS. The Relative Percent Difference (RPD) will be calculated between the LCS and LCSD. The RPD is calculated as outlined below:

The control limit for RPD is based on laboratory generated data and is not to exceed 20%. If outside this limit, verify with another analysis. If the RPD is still outside of criteria, the batch must be re-digested and analyzed provided sufficient sample volume. If there in not enough sample volume to re-digest, then the data must be qualified. Data generated with LCS samples that fall outside the established acceptance criteria are judged to be out-of-control. These data are considered suspect and the corresponding samples are reanalyzed or reported with qualifiers.

NOTE: In the event where adequate sample is not supplied by the client to perform a Matrix Spike/ Matrix Spike Duplicate, the LCS and duplicate can lend insight on the precision of the analysis.

13.3.4 Matrix spikes (MS and MSD) are performed to evaluate the effect of the sample matrix upon analytical methodology. A separate aliquot of sample is

spiked with the analyte of interest and analyzed with the sample. For 6010B and 6010C an MS and MSD are performed at a minimum frequency of 5% per batch. One pair in 20 samples, per matrix type, per sample preparation method and are performed more frequently where regulations require. For 200.7, an MS/MSD pair, are performed at a 10% frequency per batch. Matrix spike recoveries are evaluated against in-house control limits. The recovery must not exceed 75 to 125% of the expected recovery for 6010B or 6010C. The recovery must not exceed 70 to 130% of the expected recovery for 200.7. If outside this recovery, the parent is flagged with an appropriate data qualifier. If the recovery of an analyte is outside this range but the spike level in not at least 25% the background concentration in the parent sample, the data is flagged with an appropriate data qualifier. The RPD between the MS and MSD must be less than 20 %. If outside this limit, the parent is given an appropriate data qualifier. The parent sample for the MS/MSD is chosen at random unless specified by a client. Poor performance in a matrix spike generally indicates a problem with the sample composition, and not the laboratory analysis, and results are used to assist in data assessment. A matrix effect is indicated if the LCS data are within acceptance criteria but the matrix spike data exceed the acceptance criteria. Prior to calculating recovery, the parent sample concentration (results <Reporting MDL = 0) is subtracted from the spike aliquot concentrations.

13.3.5 The Post Spike (PS) can be run to verify matrix interferences. An analyte spike added to a portion of a prepared sample, or its dilution, must be recovered to within 80 to 120% (85 to 115% for 200.7) of the known value. If the spike is not recovered within the specified limits with the instrument in control, then the sample has a confirmed matrix effect. The sample is diluted and spiked until acceptable recoveries are achieved. A PS is run for 6010C batches, by client request, and for QC 3 or 4 data deliverable work orders.

13.3.6 The Serial Dilution (SDL) can be run to check for matrix interferences. If the analyte concentration is within the linear dynamic range (LDR) of the instrument and sufficiently high (minimally, a factor of at least 10 times greater than the lower limit of quantitation for the diluted sample, or 50 times the RLVS standard for the parent sample) an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If these limits are not met then an interference effect must be suspected and the data qualified with an SD flag. If the analytes of interest are greater than the LDR in the parent sample, the sample can be diluted and an SDL done off of the dilution.

13.3.7 A Duplicate (DUP) is run to verify precision either from within the lab or from sampling. Typically the MSD or LCSD serve as the precision control for a sample batch. These will have concentrations for target elements greater than the LOQ, where as a typical sample may not. Sample DUPs are analyzed when requested by the client or QAPP. For concentrations ≥ the LOQ two separate aliquots processed in the same batch must have an RPD ≤ 20%. Each aliquot must be ≥ LOQ. If they do not have an RPD within criteria and no errors are found, qualify the DUP and Parent with an R1 data qualifier.

13.3.8 An SRM can be digested and analyzed upon client request and lab pre-approval. It is a sample of known concentration chosen to resemble the matrix

being analyzed. An SRM is digested and analyzed with each batch of coarse/fine Pb samples.

14. Data Analysis and Calculations

14.1 The iTEVA software performs all calculations necessary to convert raw counts per second data into quantitative concentration results.

14.2 Relative Percent Difference (RPD)

$$RPD = \frac{|D_1 - D2|}{(D_1, + D_2,)/2} \times 100$$

Where:
RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate)

14.3 % Recovery = [Result –True Value] / True Value * 100

14.4 Aqueous Sample Calculation:

$$\frac{\text{Raw Data result (µg/L)} * DF * VF}{V_I} = \text{Final Result (µg/L)}$$

Where:
DF = Dilution Factor
V_F = Final Volume (L)
V_I = Initial Sample Volume (L)

14.5 Soil Sample Calculation:

$$\frac{\text{Raw Data result (µg/L)} * DF * V_F}{W_S \times \%S} = \text{Final Result (mg/kg dry weight)}$$

Where:
DF = Dilution Factor
V_F = Final Volume (L)
V_I = Initial Sample Volume (L)
W_S = Sample weight (grams)

%S = Percent solids/ 100
Example: For a sample that is 97.6% solid use 0.976

14.6 Wipe Sample Calculation:

$$\frac{\text{Raw data result (µg/L)} * VF * DF}{1 \text{ wipe}} = \text{Final Result (Total µg)}$$

Where:
DF = Dilution Factor
V_F = Final Volume (L)

14.7 Determination of Hardness by SM 2340B: The measure to precipitate soap was the original definition of Hardness. The main two ion species that are responsible for hardness are Calcium and Magnesium. Current Total Hardness is defined as the sum of Calcium (Ca) and Magnesium (Mg) concentration expressed as Calcium Carbonate ($CaCO_3$)

14.7.1 Hardness as $CaCO_3$ in mg/L = 2.497 * $[Ca_{\text{in mg/L}}]$ + 4.118 * $[Mg_{\text{in mg/L}}]$

14.8 IEC calculations - To set up Initial IEC, run single element standards with only background correction points in place. The standards are run at the linear range.

$$IEC = \frac{\text{Element result (µg/L)}}{\text{Interfering element result (µg/L)}}$$

Where the Element result (µg/L) is the apparent concentration.

This ratio is entered in the IEC table in the method file. Type the ratio under the k1 header in the appropriate row. Enter a negative before the ratio if it is a negative interference.

14.9 Evaluate sample results for anomalies. Element results that are more negative than the reporting level suggest significant interferences that are uncorrected. Even if the affected element is not being reported this should trigger an evaluation of the peaks for the elements that are being reported to see if they are affected. This type of interference can be caused by rare earth elements that typically affect multiple wavelengths.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

Analytical Method Criteria⇨ Data Assessment Measure ⇩	6010B/6010C Frequency	6010B/6010C Acceptance Criteria	200.7 Frequency	200.7 Acceptance Criteria
MB	One per batch, not to exceed 20samples.	>LOD<LOQ - Qualify > LOQ – Re-digest w/ exceptions	One per batch, not to exceed 20samples.	>LOD<LOQ - Qualify > LOQ – Re-digest w/ exceptions
LCS/LCSD	One LCS per batch, not to exceed 20samples. LCSD performed by client request or if insufficient sample volume for MS/MSD.	±20% recovery of the true value. ≤20% RPD	One LCS per batch, not to exceed 20samples. LCSD performed by client request or if insufficient sample volume for MS/MSD.	±15% recovery of the true value. ≤20% RPD
MS/MSD	One pair per batch of 20 or fewer samples.	±25% recovery of the true value. ≤20% RPD	One pair per batch of 10 or fewer samples.	±30% recovery of the true value. ≤20% RPD
PS	6010B- By client request, once per batch of 20 or fewer samples. 6010C- Once per batch of 20 or fewer samples.	±20% recovery of the true value.	By client request.	±15% recovery of the true value.
SDL	6010B – By client request, once per batch of 20 or fewer samples. 6010C- Once per batch of 20 or fewer samples.	±10% RPD referenced to the parent.	By client request.	±10% RPD referenced to the parent.
DUP	By client request.	≤20% RPD	By client request.	≤20% RPD
SRM	One per batch of 20 or fewer samples. Coarse/Fine Pb analysis.	Reference only. Client specific acceptance criteria.	Possible if pre-approved from a client request.	
ICV	Once right after calibration, prior to any samples being analyzed.	±10% recovery of the true value.	Once right after calibration, prior to any samples being analyzed.	±5% recovery of the true value. RSD <3%.
ICB	Once right after ICV.	<RL	Once right after ICV.	<RL
ICSA	Prior to any samples, typically after the CRDL.	±20% recovery of the true value. <RL for analytes with no concentration.	Prior to any samples, typically after the CRDL.	±20% recovery of the true value. <RL for analytes with no concentration.
ICSAB	After the ICSA.	±20% recovery of the true value.	After the ICSA, by client request.	±20% recovery of the true value.
CRDL (RL Standard)	6010B - After the ICB. 6010C - After the ICB and bracketing samples.	6010B - ±40% recovery of the true value. 6010C - ±30% recovery of the true value.	Prior to samples being analyzed, after the ICB.	±40% recovery of the true value.
CCV	Bracket every 10 or fewer samples. After any samples.	±10% recovery of the true value.	Bracket every 10 or fewer samples. After any samples.	±10% recovery of the true value.
CCB	Right after CCVs.	<RL	Right after CCVs.	<RL

16. Corrective Actions for Out-of-Control Data

Analytical Method Criteria⇨ Data Assessment Measure ⇩	If acceptance criteria are not achieved ⇒
MB	• 1
LCS/LCSD	• 2
MS/MSD	• 3
PS	• 4
SDL	• 5
DUP	• 6
SRM	• 7
ICV	• 8
ICB	• 9
ICSA	• 10
ICSAB	• 11
CRDL	• 12
CCV	• 13
CCB	• 14

1. If not <LOQ, verify by second analysis. If second analysis confirms contamination for target analyte at or greater than the LOQ*, re-digest sample batch and batch QC provided sufficient sample volume remains. If insufficient sample volume remains, consult with project manager and client on how to proceed. For MB detections greater than or equal to the LOD but less than the LOQ qualify applicable sample results*.
   * For any positive MB failures, samples that are non-detection need not be qualified. In addition, samples that are greater than 10 times the MB detection need not be qualified and can be reported.

2. If LCS/LCSD fail criteria, verify by second analysis. If second analysis confirms LCS (LCSD) failure*, re-digest sample batch and batch QC provided sufficient sample volume remains. If insufficient sample volume remains, consult with project manager and client on how to proceed. * For any biased high LCS/LCSD failures, samples that are non-detection may be reported without qualification.

3. If the parent, MS, or MSD is greater than the reportable linear dynamic range, dilute and reanalyze the parent, MS, and MSD. If the concentration of the spike is less than 25% of the concentration of the parent the MS and MSD recoveries are not evaluated. Any failures resulting from this are qualified appropriately. If the concentration of the spike is greater than 25% of the concentration of the parent, appropriately qualify the parent sample if either the MS and/or MSD fail accuracy. If the MS and MSD fail precision control limits flag the parent with the appropriate precision data qualifier.
4. If the PDS is not recovered within the specified limits with the instrument in control, dilute the parent and re-spike the diluted sample until the PS recovers within acceptance criteria.

5. If the SDL limits are not met, then an interference effect must be suspected and the data qualified with an appropriate data qualifier. If the analytes of interest are greater than the LDR in the parent sample, the sample is diluted and an SDL done off of the dilution.

6. If the DUP fails precision control limits flag the parent with the appropriate precision data qualifier.

7. For Coarse/Fine Pb analysis only. The SRM is digested and analyzed only to demonstrate analyte recovery in a standard reference material.

8. If ICV fails, verify by second analysis. If second analysis confirms ICV failure, correct the issue and recalibrate the instrument. No data may be reported unless there is a passing ICV for that target analyte.

9. If ICB fails, verify by second analysis. If second analysis confirms ICB failure, correct the issue and recalibrate the instrument. No data may be reported unless there is a passing ICB for that target analyte, unless the failure is biased high and the sample is non-detection, or the sample concentration is greater than 10 times the detection in the ICB for that target analyte.

10. If ICSA fails, verify by second analysis. If second analysis confirms ICSA failure, the system is out of control. Correct the issue and recalibrate the instrument. No data may be reported unless there is a passing ICSA for that target analyte.

11. If ICSAB fails, verify by second analysis. If second analysis confirms ICSAB failure, the system is out of control. Correct the issue and recalibrate the instrument. No data may be reported unless there is a passing ICSAB for that target analyte.

12. If CRDL fails, verify by second analysis. If second analysis confirms CRDL failure, the system is out of control. . Correct the issue and recalibrate the instrument. No data may be reported unless there is a passing CRDL for that target analyte. * For any positive CRDL failures, samples that are non-detection may be reported without qualification. In addition, samples that have concentrations greater than the CCV may also be reported, provided the bracketing CCVs are within control.

13. If CCV fails, verify by second analysis. If second analysis confirms CCV failure, correct the issue and recalibrate the instrument. On unattended sequence, CCVs may fail and then pass later in the sequence. No data may be reported unless bracketed by passing CCVs for that target analyte, unless the CCV fails high and the sample is non-detection.

14. If CCB fails, verify by second analysis. If second analysis confirms CCB failure, correct the issue and recalibrate the instrument. On unattended sequence, CCBs may fail and then pass later in the sequence. No data may be reported unless bracketed by passing CCBs unless the failure is biased high and the sample is non-detection, or the sample concentration is greater than 10 times the detection in the CCB for that target analyte.

Note: Second analysis for verification must pass for all target elements to be completely valid. If Pb is the only target element that fails on the first analysis and passes on the second analysis, it is valid. However, if As passes on the first, but then fails on the verification, then that QC point is no longer within control for As.

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

See section 16 Corrective Actions for Out-of-Control Data

18. Method Performance

18.1 **LOD/LOQ** - At a minimum, the 40CFR part 136 appendix b study must be performed every year, per the most recent version of S-GB-Q-020, *Determination of the LOD and LOQ* (most current revision or replacement). Additional studies may be performed to achieve a realistic LOD and LOQ. This is to be done for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

18.2 **An initial demonstration of capability (IDOC)** – IDOCs must be performed per the most recent version of S-ALL-Q-020, *Orientation and Training Procedure*s (most current revision or replacement). A continuing demonstration of capability (CDOC) must be performed annually. A record of the DOCs will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

18.3 **Linear Dynamic Range Study (LDR)** - It is a Pace best practice to perform this linear dynamic range study determination once, keep the data. The study is conducted for each element by analyzing increasing concentrations (at least 3 levels) until the results generated exceed ±10% difference from the true value. The highest concentration within the 10% criteria is the maximum of the linear range for that element. Subsequent studies are performed with a single high point to verify the LDR. The linear dynamic range verification study is performed in conjunction with the IEC studies at a minimum of every 6 months.

18.4 **Instrument Detection Limits (IDLs)** in µg/L are estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with ten consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least quarterly.

18.5 **Inter-Element Corrections (IECs)** - IECs go through a full evaluation a minimum of once every six months. This is done simultaneously with the Linear Dynamic Range Studies. Adjustments may also be made if ICSA analysis demonstrates the need for an IEC to be updated sooner. IECs are calculated from observed interferences witnessed from the analysis of single element standard analyzed at the LDR. The observed element interference result is divided by the on instrument reading of the interfering element. This factor is entered into the IEC tab on the element list of the method in the instrument software.

18.6 **Lower limit of quantitation check sample (LLQC)** - The LLQC samples should be analyzed after establishing the LOQs, and on an as needed basis to demonstrate the desired the detection capability. The LLQC sample is carried through the entire preparation and analytical procedure. Acceptance criteria are ±30% of the true value.

18.7 **Periodic performance evaluation (PE)** - PE samples are analyzed per the most recent version of S-GB-Q-021 *PE/PT Program* (most current revision or replacement), to demonstrate continuing competence. All results are stored in the QA office. These are performed twice a year per matrix.

18.8 **Quality Control Sample (QCS from 200.7)** - This standard is from a source different than that of the calibration standards. It is made using the same acids and concentrations as the calibration standards. This standard is used to validate the calibration standards and the calibration. For 200.7 analysis Pace WI combines the QCS and first IPC criteria and meets them with the ICV. The acceptance criteria is +/-5% of the true value with the RSD on four replicates being <3%.

19. Method Modifications

19.1 The digestion procedures are based on, but differ somewhat from 200.7, 3010A, and 3050B. Pace Wisconsin has conducted temperature, time, and side by side studies to validate the digestions utilized. Pace Wisconsin digestions are typically more aggressive with higher acid concentrations than the methods listed.

19.2 Method modifications for EPA method 6010B, 6010C, and 200.7 are as follows:

19.3 Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.

19.4 All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.

19.5 Procedures identified as “Best Practices” by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories

19.6 When there is insufficient volume provided by the client for the method specified matrix spike/matrix spike duplicate (MS/MSD), a laboratory control spike duplicate will be analyzed to demonstrate precision criteria. Laboratory batches will be qualified with the appropriate “M5” data qualifier. When performing this analysis on paint chip samples, a MS/MSD will not be completed on the samples due to high levels of elements present in the native sample.

20. Instrument/Equipment Maintenance

20.1 See Thermo ICAP 6500 Duo operator’s manual for information.

21. Troubleshooting

21.1 See Thermo ICAP 6500 Duo operator’s manual for information.

21.2 Poor linearity in a dilution series of standards.

21.2.1 Before you remake your standards, first examine the sample introduction area, making sure you’re getting a consistent flow of sample through your pump tubing and that your connectors are not too tight.

21.2.2 Then check your nebulizer and injector for visible build up. If build up is present, clean in a dilute nitric acid (HNO_3) solution for about 10-15 minutes.

21.2.3 Also examine your torch, making sure it is also reasonably clean. Lastly, check the argon tank to determine that it is not running on empty. If everything is satisfactory, then remake standards.

21.2.4 If problems persist, try a second source of standards to determine if your initial set of standards has gone bad.

21.2.5 Bubbles are collecting in the back area of the nebulizer (glass type).

21.2.6 The reason why bubbles form in this back area is because the pump tubing is not inserted deeply enough into the cavity of the nebulizer. Cut the tip of the pump tubing to be inserted into the nebulizer at a roughly 45º angle, preferably with a razor blade to obtain a nice, clean cut. Dip the cut end into a wetting agent such as dilute Triton X solution, and start to insert into the nebulizer. Using moderate pressure, begin to work the pump tubing into the nebulizer while twisting the tubing. The twisting action causes the tubing to gradually decrease in diameter, making it easier to insert deeply into the cavity.

21.3 Hard instrument failure (software related). These are generally problems associated with the software communication with the instrument.

21.3.1 Exit out of the program. Shut down the PC that is linked to the instrument itself and restart.

21.3.2 During the PC reboot process, locate the reset button(s) on the front and/or back of the instrument and depress them.

21.3.3 Enter back into the program and continue your analysis.

21.3.4 This generally will fix this type of problem, but if you encounter additional problems of this type, then a service call may be necessary for more advanced troubleshooting advice.

21.4 Peristaltic pump occasionally stutters or stops. This problem may be hard to notice since this is a gradual wearing of the belt that attaches to the pump motor and turns the rollers themselves.

21.4.1 Replace the belt if you have an available spare. If you do not have a replacement, a service call needs to be made. A service person will generally come out and install the belt but on occasion, based on your mechanical abilities, they may ship the part to you and have you perform the installation.

22. Safety

22.1 Standards and Reagents

The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound shall be treated as a potential health hazard. Special care shall be taken when handling the high-concentration acids and oxidizing reagents used for sample digestion. All digestions must be conducted in a properly functioning fume hood. The use of personal protective equipment (gloves, lab coats and safety glasses) is required.

22.2 A reference file of Safety Data Sheets (SDS) is made available to all personnel involved in this process, and is located at by the following link https://msdsmanagement.msdsonline.com/c0ce0b0a-17d3-4f3c-afc6-25352729b299/ebinder/?nas=True.

22.3 Samples

22.3.1 Although sample check-in should be notified of any hazardous samples, samples shall always be considered as “unknowns”.

22.3.2 The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

22.4 Equipment

22.4.1 ICP Radio Frequency (RF) Generator – The RF generator used to induce the atomic plasma produces a high energy radio emission. The electrical requirements for this equipment are substantial. The RF generator must only be serviced by those trained specifically for service and repair of the instrument.

22.4.2 ICP RF Coil – The wound coil around the top of the torch produces a high energy, oscillating radio frequency field. The field is substantial and may interfere with surrounding electronics including implanted medical devices. Those individuals with such devices (i.e. pacemakers) must stay clear of this instrument while in operation.

23. Waste Management

23.1 Procedures for handling waste generated during this analysis are addressed in S-GB-W-001, *Waste Handling and Management.*

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

24. Pollution Prevention

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

25. References

25.1 Pace Analytical Services, LLC Quality Manual, most current version.

25.2 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version

25.3 USEPA, SW-846, Method 6010C Revision 3, "Inductively Coupled Plasma Atomic Emission Spectrometry", February 2007.

25.4 USEPA, SW-846, Method 3010A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectrometry", December 1996.

25.5 USEPA, SW-846, Method 3050B, "Acid Digestion of Sediments, Sludges, and Soils", December 1996.

25.6 USEPA, 200.7 Revision 4.4, "Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasm-Atomic Emission Spectrometry", 1994.

25.7 Standard Methods for the Examination of Water and Wastewater, 2340B-2011 Hardness by Calculation.

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

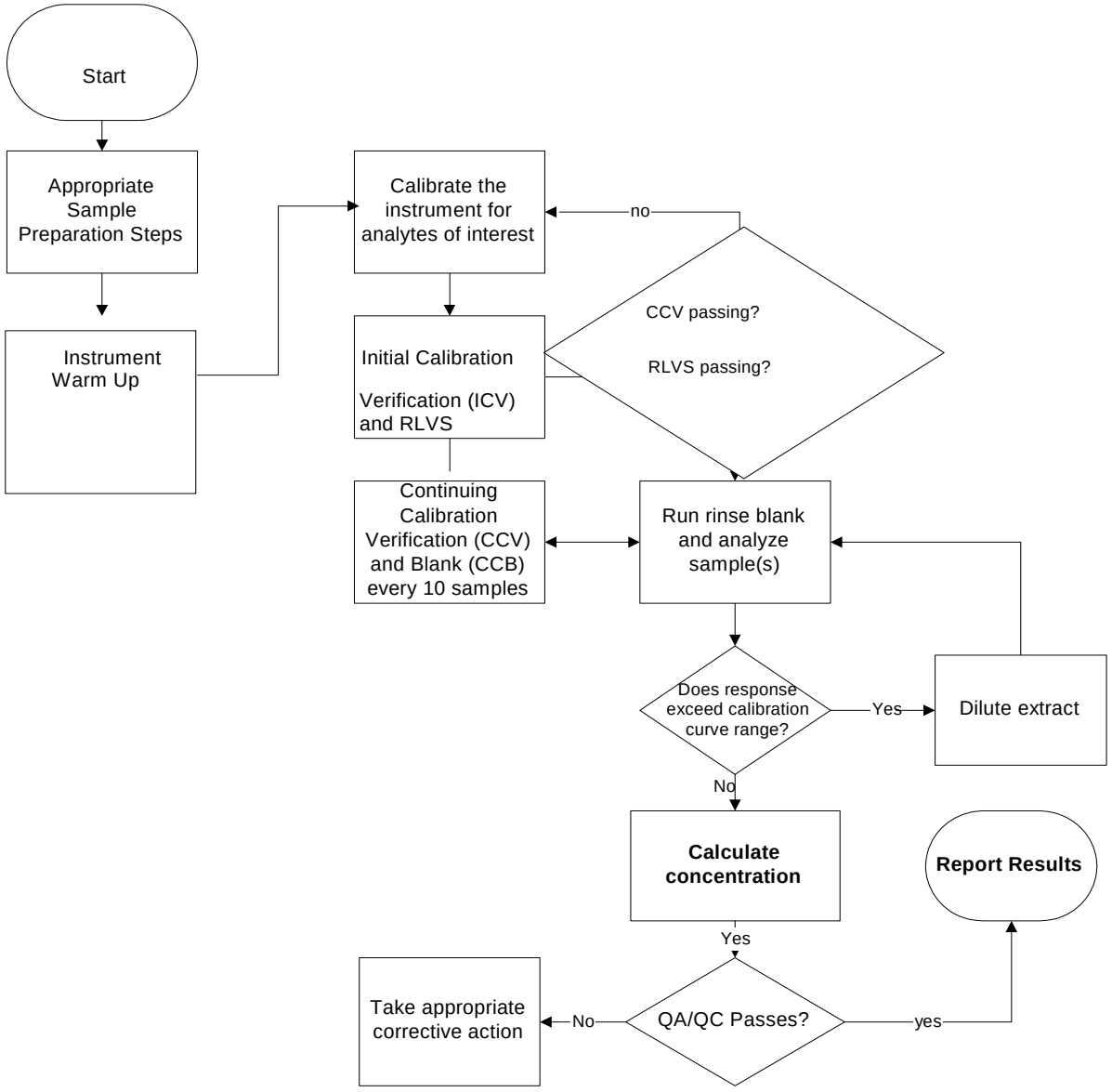
26.1 **Attachment I** – ICP Flowchart

27. Revisions

Document Number	Reason for Change	Date
S-GB-M-005-Rev.06	Throughout Document: Updated to current format of SOP: S-GB-Q-017 *Preparation of SOPs*, and updated to current SOP references. Throughout Document: Added information for 200.7 and Hardness by 2340B and 6010. Removed: Attachments with Preparation Methods Section 25: Added TNI and PASI QM references. Table 7.1: Updated Temperature to ≤6°C from 4±2°C.	11Nov2014
S-GB-M-005-Rev.07	Throughout Document: Updated from MDL to LOD, RL to LOQ; changed from ppm to mg/L. Signature Page: Updated from Inc. to LLC. And updated QM name. Section 3.1: Updated low standards. Section(s) 9.1/9.2: Deleted digestion equipment, updated vendor/catalog information. Section(s) 10.4, 13.3.3: Updated ICSAB requirement for non-spiked elements. Section 11: Added Rinse time, Nebulizer flow rate and Solution Uptake rates. Section 12.1.5: Added information for dissolved samples. Section 13: Added information on Duplicates, added Section 13.4.7. Section 27: Removed previous revision documentation which can be found in the previous SOP.	09Jan2017
S-GB-M-005-Rev.08	Section 12.2.2: Added discussion for analyst steps when possible carry-over is present. Section 18.5: IEC information updated.	21Jun2017
S-GB-M-005-Rev.09	Tables 3.1, 10.6, 10.7, 10.8 and 10.13: Si and Ce added. Section 14.9: Added	01Jun2018

Attachment I

ICP Flowchart



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STANDARD OPERATING PROCEDURE

The Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy – CETAC M-7500

Reference Methods: EPA SW-846 Methods 7470A and 7471B, EPA 245.1

SOP NUMBER:	S-GB-M-017-REV.04
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-M-017-Rev.03

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 06/13/16

Kate Verbeten, Laboratory Quality Manager — Date: 6/13/2016

Chad Rusch, Department Manager — Date: 06/13/2016

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

Any printed documents in use within a Pace Analytical Services, Inc. laboratory have been reviewed and approved by the persons listed on the cover page. They can only be deemed official if proper signatures are present.

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Table of Contents

1. Purpose/Identification of Method

1.1 The purpose of this Standard Operating Procedure (SOP) is to describe the determination of mercury in water, soil/solid samples, and biological tissue analyzed by the Cetac M-7500 instrument by EPA Methods SW846 7470A, SW846 7471B and EPA 245.1.

2. Summary of Method

2.1 Cold vapor atomic absorption utilizes the volatile property of elemental mercury at the 253.7 nm wavelength. To release mercury from organic complexes, the sample is digested with oxidizing reagents and acids in a hot block. After digestion, the oxidizing reagents are neutralized. Stannous chloride is added to reduce ionic mercury to the ground state. The Flow Injection Analysis System sweeps the volatile elemental mercury out of the sample and into the cell of an atomic absorption spectrophotometer. The absorbance signal is proportional to the amount of mercury in the sample.

3. Scope and Application

3.1 This method is applicable to water samples (including surface water and domestic and industrial wastewaters), solid samples (including soils, sediments, sludge, and solid wastes), wipes, TCLP, SPLP and ASTM leachates, and biological tissue samples.

3.2 This procedure is restricted to use by, or under the supervision of, analysts experienced in the digestion of samples for metals analysis and analysis of digestates by atomic absorption spectrometry. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1 7470A and EPA 245.1 apply to aqueous samples including surface water, dissolved water, domestic and industrial wastewaters, TCLP, SPLP, and ASTM leachates.

4.2 7471B applies to soil and solid samples.

4.3 7471M is a modified 7471B method that applies to biological tissue samples

5. Limits of Detection and Quantitation

5.1 All current LODs and LOQs are listed in the LIMS and are available by request from the Quality Manager.

6. Interferences

6.1 Samples can contain diverse matrix types, each of which may present analytical challenges. Spiked samples and Laboratory Control Samples are important for determining digestion efficiency.

6.2 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide, as NaS, do not interfere with recovery of added inorganic Mercury from D.I. water.

6.3 Copper has also been reported to interfere; however, copper concentrations as high as 10mg/L had no effect on recovery of Mercury from spiked samples.

6.4 Samples high in chlorides require up to 7.5 mL of additional potassium permanganate. During the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the Mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent. Samples may be diluted to decrease the chlorides. Alternatively, the sample may be allowed to stand for at least an hour under a hood (without active purging) to remove the chlorine.

6.5 Certain volatile organic materials that absorb at this wavelength may also interfere. A preliminary run without reagents would determine if this type of interference is present.

7. Sample Collection, Preservation, Shipment and Storage

7.1 Biota Samples

7.1.1 Biota samples can be collected in clean plastic or glass containers or plastic zip-top bags.

7.1.2 Biota samples are kept frozen at ≤-10°C until time of preparation to preserve integrity. Hold time is 28 days from removal from freezer.

7.2 Soil Samples

7.2.1 Soil and waste samples should be collected in clean wide-mouth glass containers to facilitate obtaining representative aliquots for measurement.

7.2.2 Samples should be stored at ≤6°C and analyzed as soon as possible to minimize microbiological decomposition of organic solids. Samples must be analyzed within 28 days of collection.

7.3 Wipe Samples

7.3.1 Wipe should be collected in clean wide-mouth glass containers or a digestion vessel.

7.3.2 Samples should be stored at ≤6°C and analyzed as soon as possible to minimize microbiological decomposition of organic solids. Samples must be analyzed within 28 days of collection.

7.4 Aqueous Samples

7.4.1 Water samples may be collected in plastic or glass containers and must be preserved with HNO_3 to pH <2 and stored at room temperature, acid not to exceed 2% of the estimated sample volume.

NOTE: Aqueous samples that react violently to the addition of acid may be collected without chemical preservation with proper variances approved by the regulatory authority. The responsibility of requesting this variance lies with the sample collector.

7.4.2 NOTE: Samples may be preserved in the lab. The samples may not be processed until 24 hours after preservation with a pH test of <2. Appropriate qualifier added if pH>2 after preservation Dissolved samples should be field filtered through a 0.45 micron filter prior to preservation. Samples can be filtered in the lab, but must be received unpreserved and will be qualified as not being preserved properly. A filter blank must be created when lab filtering and analyzed using method blank acceptance criterion to demonstrate the process is not affecting the data quality.

7.4.3 Samples must be analyzed within 28 days of collection.

7.5 TCLP, SPLP, and ASTM Samples

7.5.1 Leach extracts should be collected in plastic or glass containers and must be refrigerated at ≤6°C. Samples are preserved at time of digestion because leach volumes vary. The MS and MSD are not to be preserved until after they are spiked.

7.5.2 NOTE: TCLP Samples are not required to sit for 24 hours prior to digestion after the addition of nitric acid. Samples must be extracted within 28 days from field collection to leach extraction. Samples must be digested and analyzed within 28 days of the leach extraction. Total elapsed hold time is 56 days.

8. Definitions

8.1 Definitions of terms found in this SOP can also be found in the Pace Quality Manual. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP or the Pace Analytical Services' Quality Manual Glossary, Section 10.0.

8.2 Biota Control Blank (Matrix Blank) – A sample of a matrix that is used for the control spike. The biota control blank will either be catfish, tilapia, chicken, or other tissue whichever is available at the time of analysis. The biota control blank should be "farm-raised" to minimize background mercury levels. The concentration in the biota control blank will be subtracted from the concentration of the laboratory control spike when the biota control blank concentration is greater than/equal to the MDL. This is done because the biota control blank is known to have some contamination. This SOP will reference biota control blank for ease. Note: For plant material analysis, alfalfa can be used as the biota control blank matrix.

8.3 Reagent Grade – Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents, which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

8.4 Standardized Reference Material (SRM) – A certified reference material produced by the U.S. National Institute of Standards and Technology or other equivalent organization and characterized for absolute content, independent of analytical method. A SRM is analyzed with each analytical batch of biota samples.

8.5 Pace Reporting Limit (PRL) – The level at which method, permit, regulatory and client specific objectives are met. The reporting limit may never be lower than the Limit of Detection (i.e. statistically determined MDL). Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified.

9. Equipment and Supplies

9.1 Hot Block – Operated at 95 ± 3°C. Heating block should be Environmental Express "Hot Block", or equivalent.

9.2 Digestion Vials – Clean 15- mL screw cap vials, Environmental Express (SC415), or equivalent.

9.3 Digestion Vials- Clean 68-mL screw cap vials, Environmental Express (SC475), or equivalent.

9.4 Volumetric Flasks – Assorted, Class A

9.5 Graduated Cylinder – 50-mL

9.6 Mechanical Pipettes – Assorted adjustable air-displacement pipettes with disposable tips (Eppendorf or equivalent).

9.7 pH Strips

9.8 CETAC M-7500 with auto-sampler

9.9 Inert Sparging and Carrier Gas – Argon

9.10 Autosampler vials

9.11 Autosampler Pump Tubing

9.12 Specimen Cups

9.13 DORM-4 or equivalent

9.14 1570a (Trace Elements in Spinach) or equivalent

9.15 Analytical Balance – Capable of weighing to 0.001g

10. Reagents and Standards

10.1 Trace Metals Water – Nano-Pure Water

10.2 Nitric Acid (HNO_3) – 9598-34 J.T. Baker, or equivalent. The reagent is assigned a two year expiration date, not to exceed the manufacturer's expiration date.

10.3 Hydrochloric Acid (HCl) – 9530 -33 J.T. Baker, or equivalent. The reagent is assigned a two year expiration date, not to exceed the manufacturer's expiration date.

10.4 Sulfuric Acid (H_2SO_4) – 9681-33 J.T. Baker, or equivalent. The reagent is assigned a two year expiration date, not to exceed the manufacturer's expiration date.

10.5 $KmnO_4$ neat – P279-500 Fisher Scientific. The reagent is assigned a five year expiration date, not to exceed the manufacturer's expiration date.

10.6 $K_2S_2O_8$ neat – 3238-01 J.T. Baker. The reagent is assigned a five year expiration date, not to exceed the manufacturer's expiration date.

10.7 $NH_2OH{\bullet}HCl$ neat – H330-500 Fisher Scientific. The reagent is assigned a five year expiration date, not to exceed the manufacturer's expiration date.

10.8 $SnCl_2$ neat – T142-500 Fisher Scientific. The reagent is assigned a five year expiration date, not to exceed the manufacturer's expiration date.

10.9 Potassium Permanganate ($KmnO_4$) solution (5%) – Dissolve 50.0 g of $KmnO_4$ into ~800 mL of trace metals water. Dilute to 1000 mL. The reagent is assigned a one month expiration date.

10.10 Potassium Persulfate ($K_2S_2O_8$) solution (5%) – Dissolve 50.0 g of $K_2S_2O_8$ into ~800 mL of trace metals water. Dilute to 1000 mL. Warm to dissolve. The reagent is assigned a one month expiration date.

10.11 Hydroxylamine Hydrochloride ($NH_2OH{\bullet}HCl$) Solution (12%) – Dissolve 120 g NaCl and 120g $NH_2OH{\bullet}HCl$ in ~800 mL of trace metals water. Dilute to 1000 mL. The reagent is assigned a one month expiration date.

10.12 Stannous Chloride Solution (SnCl2) – Dissolve 100.0 g of SnCl in ~ 800 mL of trace metals water. Add 70 mL of HCl. Dilute to 1000 mL. The reagent is assigned a one week expiration date.Discard if oxidized or precipitate forms.

10.13 Acid Rinse Solution- Add 125 mL of HCl and 125 mL concentrated Nitric acid in ~1000 mL of trace metals water dilute to 2,500 mL. The reagent is assigned a six month expiration date.

10.14 Diluent – Each method diluent needed is digested weekly and assigned a one week expiration date. Diluent is made of digested blanks, digested according to method and SOP procedures.

10.15 Analytical Standards – Standard solutions are required for calibration, calibration checks, and sample spiking solutions. The following describes the contents of each type of solution. The commercial sources for stock solutions, recipes for preparing dilutions and working standards, and concentrations in standard solutions are presented in Table 1, Table 2, and Table 3.

Table 1: Standard Definitions

Standard 7470A/7471B	**Standard 245.1**	**Description**	**Comments**
Initial Calibration Standard(s)	Initial Calibration Standard(s)	Standards prepared from single and/or multi-element standard(s) at appropriate acid concentrations. Solutions containing all analyte elements are prepared at a concentration near the mid-point of the calibration range for single point calibration.	Working standards are made daily.
Initial Calibration Verification Standard (ICV)	Quality Control Sample (QCS) & 1st IPC	Standard prepared near the midpoint of the calibration range and is used to verify the accuracy of the calibration and instrument performance.	Must be prepared from a source independent of CCV and Calibration Solutions.
Continuing Calibration Verification Standard (CCV)	Instrument Performance Check Solution (IPC)	Standards prepared from single and/or multi-element standards at appropriate acid concentrations. Solutions containing all analyte elements are prepared at a concentration near the mid-point of the calibration range. This standard verifies the accuracy of the calibration curve.	May be prepared from the same source as the calibrations standards
Reporting Limit Verification Standard (RLVS)	NA	Must be performed after ICV/ICB and prior to samples. For 7471B it is also required at the end of the analytical sequence. For 7471B the recovery must be between 70 and 130% to report sample data. All other methods must be between 60-140%.	NELAC requirement, a client specific requirement for certain QAPPs
Single Element Standards	Single Element Standards	Stock standards purchased from venders containing one element. Used for checking IECs and may be used for checking linear ranges.	Must be 99.99% pure.
Spiking Standard	Spiking Standard	This solution contains all target analytes and should not be prepared from the same standards as the calibration standards.	Prepared from a source independent of CCV and Calibration Solutions.
Method Blank (MB)	Laboratory Reagent Blank (LRB)	This blank must contain all the reagents, in the same volumes as used for samples and must be carried through the complete processing of samples with the samples.	
Laboratory Control Sample (LCS)	Laboratory Fortified Blank (LFB)	Lab water spiked with the reagents of interest at a known concentration. It must contain all the reagents, in the same volumes as used for samples and must be carried through the complete processing of samples with the samples.	Spiked from a source independent of CCV and Calibration Solutions.
Matrix Spike (MS), Matrix Spike Duplicate (MSD)	Laboratory Fortified Sample Matrix (LFM)	Aliquots of environmental sample spiked with known concentrations of target analytes.	Spiked from a source independent of CCV and Calibration Solutions.

Note: This SOP will utilize the terms for standards listed in the 7470A/7471B column.

Table 2: Stock Standards

Standard	**Concentration**	**Vendor**	**Catalog #**
Hg Calibration Stock	1000µg/mL	High-Purity Standards	CGHG1-1
ICV Calibration Stock	1000µg/mL	Inorganic Ventures, Inc.	100033-1

Standards are used until they expire based on the manufacturer's expiration date.

Table 3: Intermediate and Calibration Standards 7471B and 7471M for Tissue

Standard	Stock Standard	Conc.	Amount Used	Amount of conc. HNO_3 used	Final Volume (with trace metals water)	Final Conc.
Hg ICV Stock	-	1000µg/mL	-	-	-	1000 µg/mL
Hg Calibration Intermediate	Hg Calibration Stock	1000µg/mL	20 µL	6.0 mL	200 mL	100 ppb
Hg ICV Intermediate (100 ug/L CVAA Hg Spk)	Hg ICV Stock	1000 µg/mL	20 µL	6.0 mL	200 mL	100 ppb
Hg Cal. 0	-	-	-	-	50 mL	0.0 ppb
Hg Cal. 1 and PRLs	Hg Cal. Intermediate	100 ppb	100 µL	-	50 mL	0.2 ppb
Hg Cal. 2	Hg Cal. Intermediate	100 ppb	500 µL	-	50 mL	1.0 ppb
Hg Cal. 3	Hg Cal. Intermediate	100 ppb	1250 µL	-	50 mL	2.5 ppb
Hg Cal. 4	Hg Cal. Intermediate	100 ppb	2500 µL	-	50 mL	5.0 ppb
Hg Cal. 5	Hg Cal. Intermediate	100 ppb	5000 µL	-	50 mL	10.0 ppb
Hg ICV	Hg ICV Intermediate	100 ppb	2000 µL	-	50 mL	4.0 ppb
Hg CCV	Hg Cal. Intermediate	100 ppb	2500 µL	-	50 mL	5.0 ppb
Hg ICB/CCB	-	-	-	-	50 mL	0.0 ppb

All intermediate dilution solutions have a 1 month expiration (This standard expiration time is based on Section 7.9 of EPA 1631 Revision E, August 2002). Working solutions must be prepared fresh daily. Solutions may be stored at room temperature.

Table 4: Intermediate and Calibration Standards 7470A and 245.1

Standard	Stock Standard	Conc.	Amount Used	Amount of conc. HNO_3 used	Final Volume (with trace metals water)	Final Conc.
Hg ICV Stock	-	1000µg/mL	-	-	-	1000 µg/mL
Hg Calibration Intermediate	Hg Calibration Stock	1000µg/mL	20 µL	6.0 mL	200 mL	100 ppb
Hg ICV Intermediate (100 ug/L CVAA Hg Spk)	Hg ICV Stock	1000 µg/mL	20 µL	6.0 mL	200 mL	100 ppb
1000 ug/L CVAA Hg Spk	Hg ICV Stock	1000 µg/mL	100 µL	3.0 mL	100 mL	1000 ppb
Hg Cal. 0	-	-	-	-	10 mL	0.0 ppb
Hg Cal. 1 and PRLS	Hg Cal. Intermediate	100 ppb	20 µL	-	10 mL	0.2 ppb
Hg Cal. 2	Hg Cal. Intermediate	100 ppb	100 µL	-	10 mL	1.0 ppb
Hg Cal. 3	Hg Cal. Intermediate	100 ppb	250 µL	-	10 mL	2.5 ppb
Hg Cal. 4	Hg Cal. Intermediate	100 ppb	500 µL	-	10 mL	5.0 ppb
Hg Cal. 5	Hg Cal. Intermediate	100 ppb	1000 µL	-	10 mL	10.0 ppb
Hg ICV	Hg ICV Intermediate	100 ppb	400 µL	-	10 mL	4.0 ppb
Hg CCV	Hg Cal. Intermediate	100 ppb	500 µL	-	10 mL	5.0 ppb
Hg ICB/CCB	-	-	-	-	10 mL	0.0 ppb

All intermediate dilution solutions have a 1 month expiration (This standard expiration time is based on Section 7.9 of EPA 1631 Revision E, August 2002). Working solutions must be prepared fresh daily. Solutions may be stored at room temperature.

11. Calibration and Standardization

11.1 A digested calibration curve is made up every time there are samples prepared. The curve is associated to the sample batch(es) it is prepped with. Calibration requires analysis of a calibration blank and at least five levels of calibration solutions. The lowest calibration concentration is the pace reporting limit.

11.2 The resultant correlation coefficient must be greater than 0.995. If this does not occur, then the instrument must be recalibrated and or the calibration curve and the associated samples must be re-prepped.

11.3 The calibration curve must pass an Initial Calibration Verification (ICV) that is analyzed after the calibration standards and before any samples. The ICV concentration is near the midpoint of the calibration curve and is made from a source other than the one used to make the calibration standards.

11.4 Pace Reporting Limit Standard (PRL or CRDL Std.) – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration (typically after the ICB) with recovery 70-130% of true value for 7471B. All other methods must recover within 60-140%. If outside the limits, reanalyze once. If still outside the limits, recalibrate. When analyzing by 7471B, CRDLs must, at a minimum, bracket all samples.

11.5 Every ten samples or less must be bracketed by Continuing Calibration Verifications (CCV). The CCV concentration is near the midpoint of the calibration curve.

11.6 For 7470A, 7471M and 7471B the ICV and CCV limits are ± 10% of their expected values. For 245.1 the ICV acceptance limits are ± 5% and the CCV limits are ± 10% of their expected values. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

11.7 An acceptable Initial Calibration Blank (ICB) must be analyzed after the ICV.

11.8 Continuing Calibration Blanks (CCBs) are analyzed after the CCVs.

11.9 The control limit for the ICB and CCB is the absolute value, less than the Pace Reporting Limit. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

12. Procedure

12.1 Sample Preparation

12.1.1 Water Samples – 7470A and 245.1

12.1.1.1 Verify preservation in the samples by checking their pH with a test strip (completed upon receipt in Sample Receiving Department).

12.1.1.2 Prior to analysis, the samples and the calibration curve must be digested.

12.1.1.3 Turn on the hot block and set the temperature to maintain a sample temperature of 95±3°C. Before placing samples in the hot block, verify that the temperature is correct and adjust as required. Record the temperature in the sample logbook. Verify that the hood is functioning.

12.1.1.4 Use the 15 mL digestion tubes.

12.1.1.5 Add 10 mL of trace metals water minus the volume of standard to be added and add the appropriate amounts (as shown in Table 4) of Hg Calibration Intermediate and Hg ICV Intermediate to digestion vials for the curve, ICV, CCV, ICB, and CCB.

12.1.1.6 Add 10 mL of trace metals water to a digestion vial for the Method Blank.

12.1.1.7 Add 10.0 mL of trace metals water and 0.05 mL of 1000 ug/L CVAA Hg Spk to two digestion vials for the Laboratory Control Spike and Laboratory Control Spike Duplicate. Only prep LCSD if requested by client or there is not enough sample to run an MS/MSD.

12.1.1.8 Add 10 mL of each well-mixed sample to digestion vials.

12.1.1.9 To prepare a Matrix Spike and Matrix Spike Duplicate, a sample with sufficient volume is chosen at random or assigned by the client, at a frequency of 5% for 7470A and 7471B methods and 10% for 245.1. An additional 10 mL of this sample, along with 0.05 mL of 1000 ug/L CVAA Hg Spk, is added to two digestion vials.

NOTE: TCLP, SPLP, and ASTM extracts must be spiked prior to nitric acid preservation. One MS must be prepared per sample matrix (ie: soil and wood chips would each require a separate matrix spike).

12.1.1.10 To each digestion vial add 0.25 mL of concentrated nitric acid. Swirl the digestion vials gently.

12.1.1.11 To each digestion vial add 0.5 mL of concentrated sulfuric acid. Swirl the digestion vials gently.

12.1.1.12 Add 1.5 mL of 5% $KmnO_4$, swirl the digestion vials gently, and let stand for 15 minutes. If a sample does not maintain a purple or brown color, use a smaller amount of a fresh aliquot of sample.

12.1.1.13 Add 0.8 mL of 5% Persulfate solution. Place lid or cap on tube so as to allow pressure to vent but minimizing evaporation. Swirl the digestion vials gently.

12.1.1.14 Digest samples for 2 hours at 95±3°C.

12.1.1.15 Remove samples and let cool to room temperature.

12.1.1.16 Add 0.5 mL of 12% hydroxylamine hydrochloride solution. Shake the digestion vials gently to clear the $KmnO_4$.

12.1.1.17 Sample volumes are consistent and said to be 10 mL. Samples are now ready for analysis.

12.1.2 Soil/Solid/Wipe Samples – 7471B

12.1.2.1 Prior to analysis the samples and calibration curve must be digested.

12.1.2.2 Turn on the hot block and set the temperature to maintain a sample temperature of 95±3°C. Before placing samples in the hot block to digest, verify that the temperature is correct and adjust as required. Record the temperature in the electronic prep log. Verify that the hood is functioning.

12.1.2.3 Use the 50 mL digestion tubes for soils, solid, and wipe samples.

12.1.2.4 Add 2.5 mL of Nano-Pure water and add the appropriate amounts (as shown in Table 3) of Hg Calibration Intermediate and Hg ICV Intermediate to digestion vials for the curve, ICV, CCV, ICB, and CCB.

12.1.2.5 Prepare one Method Blank by adding glass beads (or equivalent) to a digestion vial.

12.1.2.6 Prepare the Laboratory Control Spike (LCS) for soils, wipes, and wastes by adding glass beads (or equivalent) to a digestion vial. Then, add 2.5 mL of Hg ICV Intermediate (100 ug/L CVAA Hg Spk) to the digestion vial. Only prep a Laboratory Control Spike Duplicate (LCSD) if requested by client or there is not enough sample to run an MS/MSD. Prepare the LCSD in the same fashion as the LCS.

12.1.2.7 Weigh 0.3 to 0.34 g of homogenized sample into a labeled digestion vial. Record the weight to the nearest 0.01 g in the digestion prep log. For samples with high liquid content, a larger sample size may be used, as long as the digestion is complete. For wipes, put the WHOLE wipe in the digestion vial.

12.1.2.8 To prepare a Matrix Spike and Matrix Spike Duplicate, a sample with sufficient volume is chosen at random. Weigh 2 additional 0.3g aliquots into digestion vials. Add 2.5 mL of Hg ICV Intermediate (100 ug/L CVAA Hg Spk) to each vial.

12.1.2.9 Add 2.5 mL of Nano-pure water to all QC and samples. Swirl digestion vials to gently mix.

12.1.2.10 To each digestion vial add 0.7 mL of concentrated nitric acid. Swirl digestion vials to gently mix.

12.1.2.11 To each digestion vial add 2.1 mL of concentrated hydrochloric acid. Swirl digestion vials to gently mix.

12.1.2.12 Heat for 2 minutes on a block set to reach 95±3°C and then allow the samples to cool.

12.1.2.13 Add about 25 mL of Nano-pure water to all QC and samples. Swirl digestion vials to gently mix.

12.1.2.14 Slowly add 7.5 mL of 5% KmnO4 to all samples and batch QC. Samples may react violently if added too quickly.

12.1.2.15 Place cap on tube so as to allow pressure to vent but minimizing evaporation, swirl the digestion vials gently, and let stand for 15 minutes. If a sample does not maintain a purple or brown color, use a smaller amount of a fresh aliquot of sample.

12.1.2.16 Digest samples for 30 minutes at 95±3°C.

12.1.2.17 Remove samples and let cool to room temperature.

12.1.2.18 Bring to a final volume of 50mL with nanopure.

12.1.2.19 Add 3.0 mL of 12% hydroxylamine hydrochloride solution. Cap the digestion vials and gently shake to clear $KmnO_4$.Samples are consistent and said to have a final volume of 50 mL. Samples are now ready for analysis.

12.1.3 Biota Samples – 7471M

12.1.3.1 50 mL digestion vials are used for Biota samples.

12.1.3.2 Prior to analysis the samples and calibration curve must be digested.

12.1.3.3 Turn on the hot block and set the temperature to maintain a sample temperature of 95±3°C. Before placing samples in the hot block to digest, verify that the water temperature is correct and adjust as required. Record the temperature in the electronic prep log. Verify that the hood is functioning.

12.1.3.4 Add 2.5 mL of Nano-Pure water and add the appropriate amounts (as shown in Table 3) of Hg Calibration Intermediate and Hg ICV Intermediate to digestion vials for the curve, ICV, CCV, ICB, and CCB.

12.1.3.5 Prepare one Method Blank. For biota analysis, leave the Method Blank empty. A Biota Control Blank is also prepared by weighing 0.6 g of homogenized biota control blank tissue into a digestion vial.

12.1.3.6 Prepare the LCS for biota samples by weighing 0.6 g of homogenized biota control blank into the digestion vial. Add 2.5 mL of Hg ICV Intermediate (100 ug/L CVAA Hg Spk) the vial. Only prep a Laboratory Control Spike Duplicate (LCSD) if requested by client or there is not enough sample to run a MS/MSD. Prepare the LCSD in the same fashion as the LCS.

12.1.3.7 For biota samples, weigh approximately 0.05 g of Standard Reference Material into a labeled digestion vial. If biota samples are plants, use approximately 0.6 g of SRM 1570a. The analytical balance must read to at least 4 places past the decimal.

12.1.3.8 Weigh 0.6 g of homogenized sample into a labeled digestion vial. Record the weight to the nearest 0.01 g in the digestion prep log.

12.1.3.9 To prepare a Matrix Spike and Matrix Spike Duplicate, a sample with sufficient volume is chosen at random. Weigh 2 additional 0.6g aliquots into digestion vials. Add 2.5 mL of Hg ICV Intermediate (100 ug/L CVAA Hg Spk) to each vial.

12.1.3.10 To each digestion vial add 0.7 mL of concentrated nitric acid. Swirl digestion vials to gently mix.

12.1.3.11 To each digestion vial add 2.1 mL of concentrated hydrochloric acid. Swirl digestion vials to gently mix.

12.1.3.12 Heat for 2 minutes on a block set to reach 95±3°C and then allow the samples to cool.

12.1.3.13 Add about 25 mL of Nano-pure water to all QC and samples. Swirl digestion vials to gently mix.

12.1.3.14 Slowly add 7.5 mL of 5% KmnO4 to all samples and batch QC. Samples may react violently if added too quickly.

12.1.3.15 Place cap on tube so as to allow pressure to vent but minimizing evaporation, swirl the digestion vials gently, and let stand for 15 minutes. If a sample does not maintain a purple or brown color, use a smaller amount of a fresh aliquot of sample

12.1.3.16 Digest samples for 30 minutes at 95±3°C.

12.1.3.17 Remove samples and let cool to room temperature.

12.1.3.18 Bring to a final volume of 50 mL with nanopure.

12.1.3.19 Add 3.0 mL of 12% hydroxylamine hydrochloride solution. Cap digestion vials and gently shake to clear $KmnO_4$. Samples are consistent and said to have a final volume of 50 mL. Samples are now ready for analysis.

12.2 Basic System Operation – Analytical: This portion of the SOP is designed to allow the user to set up and run a method, print a sample report, then shut down using the more basic software functions. For a more detailed explanation of the many other options, the user should refer to the Reference Manual.

12.2.1 Verify the carrier argon gas supply is on.

12.2.2 Switch on the CETAC M-7500.

12.2.3 Verify the computer is on. If not, switch on the computer and enter network password and click on Start.

12.2.4 Go to programs, CETAC QuickTrace, and click on QuickTrace.

12.2.5 To create a new worksheet from a Template, Click on File, New From. Click on the browse button to select a Template worksheet, then enter the new File name (ex. Naming file 0713111AJT denotes the month, date, year, and analyst. The number at the end of the each run within a day's output.). Click Save. Click ok.

12.2.6 To open an existing worksheet, select Open, and select the desired worksheet. The worksheet will open to the sequence page.

12.2.7 To enter sample information, go to the sequence page. Follow the Template to fill in Ids for the Calibration QC and samples, under the sample label column

12.2.8 A typical sequence will consist of the following in order: a calibration curve (5 standards plus a blank), an ICV immediately followed by an ICB, a CRDL, a CCV immediately followed by a CCB. At this point a batch consisting of samples and batch QC can be analyzed. At a maximum of every 10 batch injections a CCV immediately followed by a CCB must be analyzed. The batch must also end with CCV immediately followed by a CCB. For 7471B, a CRDL must bracket the samples.

12.2.9 Go to File, Save to ensure changes to the worksheet are saved.

In the Method Editor Page the Conditions are set at:

Gas Flow (mL/min)	100
Pump Speed (%)	50
Sipper Depth (mm)	145
Sample Uptake (s)	35
Rinse Time (s)	95
Read Delay Time (s)	Varies with peak profile.
Replicate Read Time (s)	1.5
Replicates	4

12.2.10 Under Method editor, click QC Tests to Set the QC concentration and the control limits.

12.2.11 On the Sequence Parameters page hit the control button to set up when the QC will be analyzed, i.e. after calibration, after 10 samples, and at the end. IF re-calibration occurs the QC must be analyzed at the same frequency. This page also allows you to put the system into standby mode. The options allow you turn the pump on "slow" or "off. It also allows you to turn the Lamp off and Gas off.

12.2.12 The Sequence Parameters under the reports button allows you to customize the report printout by selecting solution information, report contents, and default number format.

12.2.13 Under the Sequence Editor page click on Manual QC, specify what to do if calibration QC fails, for example stop analysis, flag and continue, repeat-flag and continue, recalibrate and repeat, recalibrate and repeat with samples, or reslope and repeat.

12.2.14 On the Auto QC page of the Sequence Editor, specify what QC to run at the end of a run and corrective action if QC fails

12.2.15 Under the Sequence Editor click Sequence... This is where you determine the number of samples in the analysis and how often calibrations will be performed.

12.2.16 The analysis screen is accessed by clicking on the analysis button, from the main toolbar. This screen is where analysis controls and displays are located.

12.3 Starting the Analysis

12.3.1 Prepare the required reagents: Acid Rinse solution and reducing agent.

12.3.2 Turn on the lamp and carrier gas. A minimum 15 minute warm-up time is required.

12.3.3 Put peristaltic tubing in place, and clamp in place.

12.3.4 Place the auto-sampler rinse tubing into the Acid Rinse bottle. If rinse pump is not on make sure it's on by clicking on the instrument page and clicking "pump on". Make sure to have probe down at this time as well.

12.3.5 Place the SnCl2 line in a bottle of reagent water and start the peristaltic pump. Inspect flow to make sure lines are flowing correctly and not pulsing.

12.3.6 Wet the GLS (Gas Liquid Separator) center post. In the software click on the instrument icon, click analyzer, set gas flow to 350-mL/min and change pump speed to 100%. Pinch the drain line until 2 or 3 bubbles go to the top of the GLS center post. Then release the drain line and allow liquid to restore itself.

12.3.7 Attach GLS exhaust tube to GLS center post and close the optical cabinet door. Place reagent capillaries in appropriate reagent bottles.

12.3.8 Open the appropriate worksheet and verify that the gas flow and pump speed in the worksheet matches what is listed in instrument/analyzer, if the flow and the speed is not the same make the necessary change or click the auto set icon on the menu bar. This will stabilize the instrument before auto-zeroing and running a peak profile.

12.3.9 Record the Lamps mA's in a daily instrument logbook by clicking on the instrument icon, clicking on analyzer, "status of lamp".

12.3.10 Peak profile the high standard of the calibration. To do this click on Method Editor, read a sample icon, and then choose the location of high standard. Record the concentration of the peak profile standard in a daily instrument logbook. The read delay time is adjusted here as well.

12.3.11 Hit the GO icon to start the calibration. Once the calibration is complete a dialog window will generate stating, "Continue with Analysis" Click YES if satisfied with Calibration or click NO to re-analyze Calibration.

12.3.12 Hit the STOP icon to immediately end an analysis that is currently running. The auto-sampler probe will immediately return to the rinse station. Stopping an analysis in progress will prevent data from being saved for that sample.

12.3.13 To stop the analysis after the current sample select the Stop/After solution item from the analyze menu.

Note: If you stop during sample uptake, or before the rinse has been completed, make sure you allow sufficient time in the rinse station before re-starting the analysis.

12.3.14 If you stopped the analysis, you can simply restart by clicking the GO button. The analysis will begin at the next un-analyzed solution within the sequence.

12.3.15 To restart the analysis from the beginning you will need to generate the sequence again. Open the Sequence Editor, make any desired changes, click on Generate Sequence. Then click GO to start analysis over.

12.3.16 To read a single sample, click on the icon, analyze single sample. A dialog window will be brought up where you will enter the tube position, sample label, sample type, and other information if desired.

Note: Using the read sample feature may invalidate your QC setup. If you have stopped during a batch analysis to read a single sample, it will be inserted into the sequence after the last analyzed sample.

12.3.17 When the run is complete the instrument will automatically go into standby mode. Depending what options you have selected from sequence parameters, this may turn off or slow the pump, turn off the lamp, and/or the carrier gas flow.

12.3.18 To export the data, go to File then Export. Go to K:\Metals\CVAA\40HG2\, enter file name, and click Save. .

12.4 System Shutdown

12.4.1 Place the inlet of the SnCl2 line in a container of 10% nitric acid rinse (use a 500mL container; use 50mL of Nitric acid and dilute to 500 with nanopure water)) for 10 minutes.

12.4.2 Once the SnCl2 is rinsed with 10% nitric acid rinse, place the SnCl2 line into DI water for 1 minute to rinse system.

12.4.3 Remove the SnCl2 line from the DI water and raise lines out of rinse solution. Run the pump until the lines are dry.

12.4.4 Raise the probe from the rinse station by clicking on the instrument icon and by clicking the Move Sipper Up button. Turn off peristaltic pump by clicking the Pump Off button.

12.4.5 Release all four peristaltic pump channel clamps and remove the tubing from the channel.

12.4.6 Remove the GLS exhaust tube from the GLS center post.

12.4.7 Turn off the gas and lamp by clicking on the instrument icon, then click analyzer. Turn the Lamp Off and set the gas to 0.

12.4.8 Close out of the software

13. Quality Control

13.1 Calibration Blanks – Calibration blanks (ICB and CCB) may not contain concentrations in excess of the LOQ. If blank results are not acceptable, analysis of the sequence should be halted. Corrective actions could include preparation of fresh calibration standards and blanks.

13.2 Calibration Checks (ICV and CCV)

13.2.1 For 7470A, 7471M and 7471B the ICV and CCV limits are ± 10% of their expected values. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

13.2.2 For 245.1 the ICV acceptance limits are ± 5% and the CCV limits are ± 10% of their expected values. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

13.3 Pace Reporting Limit Standard (PRL or CRDL Std.)

13.3.1 A standard prepared at the concentration of the lowest calibration point. It is analyzed after the ICV/ICB. When analyzing by 7471B the CRDL must also bracket all samples.

13.3.2 The CRDL must recover from 70-130% of true value for 7471B. The rest of the methods must be 60-140% recovery. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

13.4 Batch – A preparation (digestion) batch will consist of up to 20 samples.

13.5 Laboratory Control Spike (LCS)

13.5.1 A Laboratory Control Spike (LCS) must be prepared and analyzed with every sample batch or every 20 samples, whichever is more frequent.

13.5.2 A Laboratory Control Spike Duplicate (LCSD) is performed if there is insufficient sample available for a MS/MSD or if requested by the client.

13.5.3 For methods 7470A and 7471B the acceptance criterion is 85-115%. For method 245.1 the acceptance criterion is 70-130% recovery. For method 7471BM the acceptance criterion is based on historical.

13.5.4 If the LCS and or LCSD are outside of acceptance criterion, then all the samples prepared in the batch must be re-prepped and re-analyzed.

13.5.5 When a LCSD is included, the acceptance criterion for precision is 20% RPD. If insufficient sample remains to re-prep and re-analyze, the data qualifiers is given to all associated samples.

13.6 Method Blank (MB)

13.6.1 A MB must be prepared and analyzed with every sample batch or every 20 samples, whichever is more frequent.

13.6.2 The MB must not contain mercury at a concentration at or above the LOQ.

13.6.3 Any samples digested with an unacceptable method blank must be re-prepped and analyzed unless the sample concentrations are less than the level being reported at or more than 10 times the value found in the method blank.

13.6.4 In those cases that LOD reporting is required, the MB must be evaluated to the LOD. For LOD reporting, an appropriate data qualifier is given to samples associated with ± MB hits between the ± LOD and ± LOQ where the sample results are less than 10 times the value found in the method blank.

13.6.5 For negative instrument measurements >LOD and <LOQ qualify sample results that are non-detections and <10 times the measurement with “Analyte was measured in the associated method blank at a concentration of -#.# units.” Make sure to enter the concentration and applicable sample units.

13.7 Matrix Spike/ Matrix Spike Duplicate (MS/MSD)

13.7.1 A MS/MSD pair must be prepared and analyzed for each batch or every 20 samples that are similar in matrix at a frequency of 5% for 7470A and 7471B methods and 10% for 245.1.

13.7.2 For TCLP, SPLP, and ASTM samples one Matrix Spike (MS) must be prepared per sample matrix (ie: soil and wood chips would each require a separate matrix spike).

13.7.3 The sample used for MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows. No field, filter, trip, or equipment blanks can be used for MS/MSD.

13.7.4 For methods 7470A and 7471B the acceptance criterion is 85-115%. For method 245.1 the acceptance criterion is 70-130%. For method 7471BM the acceptance criterion is generated from historical.

13.7.5 If one or both spike recoveries are outside recovery acceptance criterion , the parent sample and failing QC point are given an appropriate data qualifier.

13.7.6 If the precision is outside the 20% RPD criterion, the parent sample and QC point are given an appropriate data qualifier.

13.8 Duplicate Sample (DUP)

13.8.1 Typically the method requirements for duplicate sample analysis are met with the MSD or LCSD, but based on client request a DUP may also be prepared and analyzed.

13.8.2 The DUP is evaluated for precision with the parent sample. If the RPD is outside 20% RPD criterion the parent sample and DUP are given an appropriate data qualifier. Parent sample is chosen at random or assigned by the client.

13.9 For dissolved samples filtered in house a filter blank is created. The filter blank is evaluated and qualified the same as a method blank.

13.10 All reported results must be within the range of the calibration curve. Dilute when results are greater than the high standard in the curve.

14. Data Analysis and Calculations

14.1 **Water/TCLP/SPLP/ASTM Samples** – Since initial sample aliquot and final digestate volumes are the same, the mercury analyzer data system will calculate the concentration directly. No further calculations are necessary unless the sample was diluted.

14.2 Soil/Solid/Biota Samples –

$$\text{Final Result (mg/kg dry weight corrected)} = \frac{\text{Raw data result (µg/L)} * \text{Final Volume (L)} * \text{Dilution Factor}}{\text{Sample weight (g)} * \text{Dry weight for soil/solid (decimal form)}}$$

-Biota results can be reported on an as is/wet weight basis. The dry weight correction in the formula is then not applicable.

14.3 Wipes

$$\text{Final Result (Total µg)} = \frac{\text{Raw data result (µg/L)} * \text{Final Volume (L)} * \text{Dilution Factor}}{\text{1 wipe}}$$

14.4 Accuracy-

$$\text{Spike Percent Recovery} = \frac{\text{Spike Sample Result} - \text{Sample Result}}{\text{Spike Added}} \times 100$$

14.5 Precision-

$$\text{Relative Percent Difference} = \frac{\text{Spike Sample Result} - \text{Spike Sample Duplicate Result}}{(\text{Spike Sample Result} + \text{Spike Sample Duplicate Result})/2} \times 100$$

15. Data Assessment and Acceptance Criterion for Quality Control Measures

Table 5
QC SUMMARY

Analytical Method ⇨ Calibration Measure ⇩	**EPA SW846 7470A, 7471B, 7471BM for Tissue, 245.1** **Frequency**	**Acceptance Criterion**
Laboratory Control Spike and Laboratory Control Spike Duplicate (LCS/LCSD)	• One LCS per batch of samples, up to 20 environmental samples, whichever is more frequent. • A LCSD is required if MS/MSD is not performed or if requested by the client.	• Project Specific or • For 245.1, 7470A, and 7471B 85 – 115% with 20% RPD • For Biota by 7471BM Historical with 20% RPD
Matrix Spike / Matrix Spike Duplicate (MS/MSD)	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	• Project Specific or • For 7470A, and 747B1 85 –115% with 20% RPD • For 245.1 70-130% with 20% RPD • For Biota by 7471M Historical with 20% RPD
Method Blank (MB)	• One per batch of samples, up to 20 environmental samples, whichever is more frequent.	• Project Specific or • Less than the LOQ
Initial Calibration	• Analyzed daily before samples • Minimum 5 standards plus a blank	• Correlation coefficient must be 0.995 or greater
Initial Calibration Verification (ICV)	• Analyzed after calibration.	• 245.1 recovery must be between 95 – 105% • 7470A and 7471B recovery must be between 90 – 110%
Initial Calibration Blank (ICB)	• Analyzed after ICV.	• Project specific or • Less than LOQ
CRDL	• 7470A, 7471M Analyzed after Initial calibration blank. • 7471B – At a minimum, CRDLs must bracket all samples reported by this method.	• At the lowest calibration point • 7471B 70-130% • 7470A, 245.1, 7471M 60-140%
Continuing Calibration Verification (CCV)	• Analyzed after every 10 samples.	• Project specific or • Recovery between 90 – 110%
Continuing Calibration Blank (CCB)	• After each CCV.	• Project specific or • Less than LOQ

16. Corrective Actions for Out-Of-Control Data

Table 6

DATA ASSESSMENT/CORRECTIVE ACTION

Analytical Method Acceptance Criterion ⇨ Data Assessment Measure ⇩	**Method Citation: EPA SW846 7470, 7471, 245.1, 7471M for Tissue** **If these conditions are not achieved ⇒**
Method Blank	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Initial Calibration	• 4
Initial / Continuing Calibration Verification	• 5
Initial / Continuing Calibration Blank	• 6
Holding Time Compliance	• 7
CRDL	• 8

1. In the absence of project specific requirements, sample detects less than 10 times the method blank contamination level is reported with the appropriate data qualifier. Sample detects greater than 10 times the method blank contamination are reported without qualification.
2. In the absence of project specific or method requirements, in-house generated limits will be used. If the MS or MSD fail because the concentration of the spike is less than 25% of the concentration of the parent, use appropriate flag for the parent sample. If the parent, MS, or MSD is greater than the top standard in the curve, dilute and reanalyze the parent, MS, and MSD following the above guidance. If the concentration of the spike is greater than 25% of the concentration of the parent, use appropriate flag for the parent sample if either the MS and/or MSD fail. If the MS and MSD fail precision control limits flag the parent with the appropriate precision data qualifier.
3. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged with the appropriate accuracy and/or appropriate precision qualifier to reflect the deficiencies. Generate a Non-Conformance Memo.
4. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.
5. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.
6. If ICB/CCB is outside the control limits, reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. Samples that are > 10X the concentration in the CCB do not have to be reanalyzed or qualified.
7. Flag results with the appropriate data qualifier.
8. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

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

17.1 See Section 16, Table 6: Corrective Action.

18. Method Performance

18.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

18.2 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

18.3 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedure*s (current revision or replacement). A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager. A continuing demonstration of capability (CDOC) must be performed annually.

18.4 A linear dynamic range (LDR) study must be performed yearly. The range tested will be several factors greater than the calibration curve, but will not be extended until failure so as to not harm the instrument with high concentrations of mercury. A passing level must have a recovery within 10% of the standard being analyzed.

18.5 An annual method detection limit (MDL) study will be completed per S-GB-Q-020, *Determination of the LOD and LOQ* (current revision or replacement), for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

18.6 Periodic performance evaluation (PE) samples are analyzed per S-GB-Q-021, *PE/PT Program* (current revision or replacement), to demonstrate continuing competence. All results are stored in the QA office. At a minimum, these are performed twice a year for the aqueous and soil matrices.

19. Method Modifications

19.1 For EPA 245.1, the lab will digest the calibration curve consistent with SW846 7470A requirements. The volumes and concentrations used to make the calibration curve deviate from 7470A and 7471B. The methods are based on using 300 mL BOD bottles that are no longer currently used. The resulting calibration curve encompasses the same working range for reporting data.

19.2 EPA 245.1 and EPA 245.6 both have the stannous chloride solution being made up with 25 g of $SnCl_2 \bullet 2H_2O$ to a final volume of 250 mL with 0.5 $\underline{N}$ – H_2SO_4. EPA SW846 7470A and 7471B both have stannous sulfate being made up the same way with the option of using stannous chloride in place of the stannous sulfate. EPA SW846 7471B mentions makingthe stannous sulfate in water. The lab uses stannous chloride made from 100 g of $SnCl_2$ and 70 mL of concentrated HCl diluted to a final volume of 1,000 mL.

19.3 For SW846 7470A and EPA 245.1, the lab has chosen to use a 10mL sample volume instead of the method specified 100mL. All standards and reagents have been reduced to ensure that the ratios are still consistent with the method.

19.4 For SW846 7471A/B, the lab has chosen to use a 0.3g sample volume instead of the method specified 0.5-0.6g. All standards and reagents have been reduced to ensure that the ratios are still consistent with the method.

19.5 SW846 7471A/B has been modified to use in the digestion and analysis of biological tissue samples. Sample volume, reagents and standards have not been altered.

20. Instrument/Equipment Maintenance

20.1 Any daily or periodic maintenance must be recorded in the instrument maintenance logbook.

21. Troubleshooting

21.1 Please see the instrument manual for information on instrument troubleshooting.

22. Safety

22.1 Standards and Reagents – The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses.

22.2 Safety Data Sheets (SDSs) – A reference file of SDS are on file in the laboratory and available to all personnel. A formal safety plan has been prepared and distributed to all personnel with documented training.

22.3 Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion. All digestions must be conducted in a properly functioning fume hood.

22.4 Samples – Take precautions when handling samples. Samples should always be treated as potentially hazardous “unknowns”. The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

Note: Extreme caution must be used when preparing rodents for digestion. The samples must undergo a special procedure to destroy any Hantavirus, which may be present. Refer to the most recent version of SOP S-GB-L-002 *Small Rodent Handling and Homogenization* for details.

22.5 Analysts should take necessary safety precautions when handling chemicals and samples. Proper personal protective equipment may include safety gloves, lab coats, and safety glasses or goggles. Analysts should be familiar with the SDS sheets for all chemicals and reagents they use for this procedure and the location of the SDS sheets within the laboratory. Any questions or concerns should be taken to the laboratory Chemical Hygiene/Safety Officer.

23. Waste Management

23.1 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of S-GB-W-001, *Waste Handling and Management.*

24. Pollution Prevention

24.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

25. References

25.1 EPA Method 245.1 Revision 3.0

25.2 SW-846 7470A, Revision 1, September 1994

25.3 SW-846 7471A, Revision 1, September 1994

25.4 SW-846 7471B, Revision 2, February 2007

25.5 PASI Quality Manual, current revision

25.6 National Environmental Laboratory Accreditation Conference (NELAC), July 2003 Standards.

25.7 The NELAC Institute (TNI); Volume 1, Module 2, “Quality Systems”- most current version

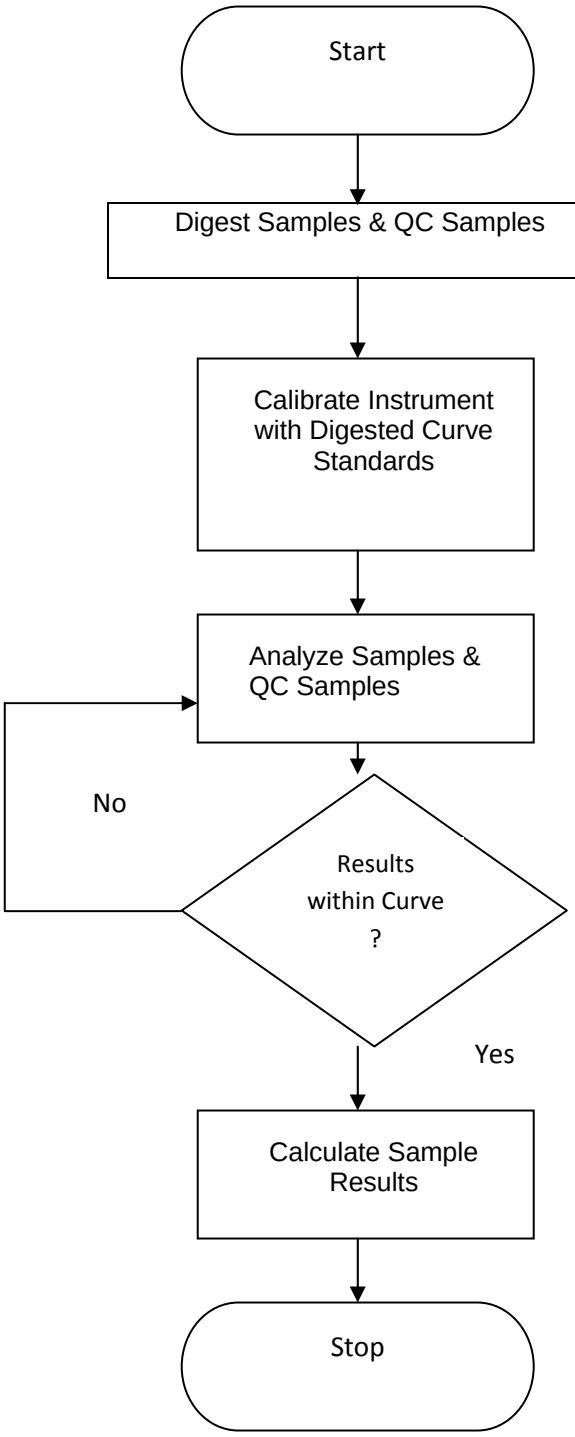
26. Tables, Diagrams, Flowcharts, and Validation data

26.1 Mercury Process Flow Chart

27. Revisions

Document Number	Reason for Change	Date
S-GB-M-017-Rev.03	Section 12.2: Solid digestion has been updated to include the heating step and increase the acid ratios. Throughout document: Included uncontrolled document disclaimer..	26Jun2015
S-GB-M-017-Rev.04	Cover page: Updated QM name. Section 7.4.2: Added field filter information. Section 7.5: Updated leach sample information. Section 9.4: Deleted balance since also listed in Section 9.15. Section 10: Updated to include expiration dates. Section 10.14: Diluent added. Table 3: Changed to Table for 7471B Solids and Tissue. Table 4: Changed to Table for 7470 and 245.1 standards. Table 5: Deleted. Section 11.1.1.7: Changed spike to 1000ug/L at 0.05mL. Section 12: Changed spike solution volumes as needed.. Section 12.1.3.12, 12.1.3.13 and 12.1.3.15: Added. Section 12.2: Entire Section re-wrote to match current practice. Section 13 and Table 5: Added QC requirements and updated table. Section 18.4: Added LDR requirement. Section 19: Updated method modifications. Throughout Document: Changed digestion temperature range from 95±5°C to 95±3°C.	13Jun2016

Mercury Process Flow Chart



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STANDARD OPERATING PROCEDURE

Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography by SW846-8082 and EPA Method 608

Reference Methods: SW-846 Method 8082 / EPA 608

SOP NUMBER:	S-GB-O-026-REV.09
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-O-026-REV.08

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 07/16/18

Kate Verbeten, Laboratory Quality Manager — Date: 7/16/18

Chris Haase, Department Manager — Date: 07/16/18

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

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

Table of Contents

1. PURPOSE / IDENTITICATION OF METHOD

1.1 The purpose of this Standard Operating Procedure (SOP) is to determine the concentration of PCBs in water, soil, sediment, waste, and biological samples in accordance with SW846 Method 8082 and EPA 608. Samples for analysis are prepared by SW846 Method 3510C, 3540C, 3541, and 3580A. See Section 25 for list of reference SOPs.

2. SUMMARY OF METHOD

2.1 Sample extracts are prepared for analysis by the appropriate sample preparation method. The procedures for extract preparation are described in separate SOPs. A volume of sample extract is injected into a GC and compounds in the effluent are detected by an ECD based on an operating program set up to achieve optimum separation and quantitation of target analytes.

2.2 Retention time windows, in combination with characteristic elution patterns from a dual-column analysis, are used in the identification of PCBs as Aroclors.

2.3 PCBs are quantified as Aroclor mixtures by comparison of their ECD response on a primary column with a calibration curve(s) constructed from the response(s) of authentic standards.

2.4 Results are reported in parts per billion (µg/kg or µg/L). Soil and sediment sample results are corrected for moisture and reported on a dry weight basis. Biological results are reported based on wet weight, or “as is” basis.

3. SCOPE AND APPLICATION

3.1 **Personnel:** This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/electron capture detection (GC/ECD) systems and interpretation of complex chromatograms. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.2 **Parameters:** A list of the Aroclors routinely analyzed, their CAS numbers and Pace Reporting Levels (PRLs) are shown in Section 5, Table 1. PRLs are subject to change based on current analytical system performance and actual sample matrices.

4. APPLICABLE MATRICES

4.1 This method is used to determine the concentration of PCBs in extracts prepared from water, soil, sediment, waste, and biological samples.

5. LIMITS OF DETECTION AND QUANTITATION

5.1 The reporting limit (PQL) of this method for Polychlorinated Biphenyls is listed in Table 1 below. All current MDLs are listed in the LIMs and are available by request from the Quality Department.

Table 1: Analyte List and Reporting Limits

Aroclor	CAS #	Aqueous PQL (µg/L)	Solid PQL (µg/Kg)	Biota PQL (µg/Kg)
AR1016	12674-11-2	0.5	50	25
AR1221	11104-28-2	0.5	50	25
AR1232	11141-16-5	0.5	50	25
AR1242	53469-21-9	0.5	50	25
AR1248	12672-29-6	0.5	50	25
AR1254	11097-69-1	0.5	50	25
AR1260	11096-82-5	0.5	50	25
AR1262*	37324-23-5	0.5	50	25
AR1268*	11100-14-4	0.5	50	25
Total PCB	NA	0.5	50	25

***Note: Aroclor 1262 and 1268 only analyzed per client request**

6. INTERFERENCES

6.1 Method interferences may be caused by contaminants (primarily phthalate esters) in solvents, reagents, glassware and other sample processing hardware that leads to discrete artifacts and/or elevated baselines. Phthalate esters are common contaminants that result from contact with flexible plastics. Contact with common plastics or rubber products must be avoided. Lab ware should be constructed of glass, stainless steel, or PTFE, must be thoroughly cleaned and dried prior to use, and should be rinsed with the appropriate solvent immediately before use.

6.2 Elemental sulfur is a common environmental contaminant in many soil, sediment and leachate samples, producing a broad peak that will confound analysis of early eluting analytes. Sulfur may be removed from extracts by treatment with copper granules or similar procedure described in a separate SOP.

6.3 Waxes, lipids, and other similar high molecular weight materials may be co-extracted from samples typically resulting in baseline elevation during GC analysis. These interferences may be removed by sulfuric acid clean up and/or column chromatography cleanup using Florisil or gel permeation chromatography (GPC), all of which are described in separate SOPs. Other halogenated pesticides and similar industrial chemicals, which can interfere with analytes of interest, may be removed by these procedures as well.

6.4 All solvents, reagents, glassware, and sample processing hardware must be routinely demonstrated to be free from interferences under the conditions of the analysis by monitoring method blanks and taking corrective action as required.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 **General Procedures** – Procedures for sample collection, preservation, and handling are described in the separate sample preparation SOPs.

Table 2: Sample Collection, Preservation, Storage and Hold time

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	One 1L amber glass	None	≤6°C	365 days
Soil/Solid (non-aqueous)	One 8oz wide glass jar	None	≤6°C	365 days
Biological Tissue	--	None	≤ -10°C	365 days or longer per client request prior to extraction, typical extraction hold time do not apply.
Extracts	ONE 10mL glass vial or 5mL copper clean vial.	None	≤6°C	365 days

8. DEFINITIONS

8.1 Refer to the Definitions Section of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

8.2 **Extract** – A solution of contaminants extracted and concentrated from a sample.

9. EQUIPMENT AND SUPPLIES

Table 9.1 - Instrumentation

Analytical Instrument/Peripherals	EPIC Pro Name
HP 6890 GC	40GCS7
Dual Electron Capture Detector	40GCS7
HP 7683 AutoSampler Tray	40GCS7
HP 7683 Injector	40GCS7
TurboChrom IV	40GCS7
HP 6890 GC	40GCS9
Dual Electron Capture Detector	40GCS9
HP 7683 AutoSampler Tray	40GCS9
HP 7683 Injector	40GCS9
TurboChrom IV	40GCS9
HP 6890 GC	40GCSB
Dual Electron Capture Detector	40GCSB
HP 7683 AutoSampler Tray	40GCSB
HP 7683 Injector	40GCSB
TurboChrom IV	40GCSB
HP 6890 GC	40GCSC
Dual Electron Capture Detector	40GCSC
HP 7683 AutoSampler Tray	40GCSC
HP 7683 Injector	40GCSC
TurboChrom IV	40GCSC

Table 9.2 - Chromatography Supplies

Item	Vendor*	Model / ID*	Catalog #	Description
Primary Analytical Column	Restek	Rtx-PesticideCLPesticides	11139	30 m, 0.32 mm ID
Confirmation Column	Restek	Rtx-CLPesticide2	11324	30m, 0.25 mm ID
Guard Column	Restek	I.P. Deactivated Guard Column	10045	5 meter, 0.53 mm ID
Fluorocarbon O-rings	Supelco	Thermo o-ring seal	21004-U	¼”
Vespel/Graphite Ferrules	Restek	0.4mm 0.8mm	20229 20230	1/16” x 0.4 mm ID 1/16” x 0.8 mm ID
CyclouniLiner	Restek	NA	22271	4 mm x 6.3 x 78.5 for Aligent GCs
Y Splitter	Restek	Universal angled Y	20404	Press-tight connector
Inlet Seals	Restek	Dual Vespel Ring	212389	Stainless steel

*Or Equivalent

Table 9.3 – General Supplies

Supply	Vendor*	Model / ID*	Catalog#	Description
Gastight Syringes	Fisher	10- µL 25- µL 50- µL 100-µL 250-µL 500-µL 1,000-µL	14-815-1 14-815-29 14-824-30 14-684-100 14-684-102 13-684-106 14-824-25	Hamilton Gastight Syringes
Glass Storage Vials	Fisher	B7921-Vo	03-377-38	20mL EPA Amber glass
Caps	Fisher	B7185-24	03-391-12F	PTFE Lined 24-400
Glass Autosampler Vials	MG Scientific	2.0mL	V300-51	Clear Glass
Autosampler vial crimp cap	Fisher	11mm crimp seal	06-406-19B	PTFE lined
Volumetric Flask	Fisher	10mL 50mL 100mL 200mL	20-812D 20-210B 20-210C 20-210D	Class A
Disposable Pasteur pipettes	MG Scientific	5 ¾” 9”	P200-1 P200-2	Glass

*Or Equivalent

9.1.1 Helium Gas – Airgas Ultra high purity or equivalent

9.1.2 Nitrogen Gas – Airgas Ultra high purity or equivalent

10. REAGENTS AND STANDARDS

10.1 **Solvents** – Hexane and acetone, pesticide grade (Table 3). All solvents are stored at room temperature and environmental conditions.

Table 3: Solvents

Reagent	Purity	Manufacturer	Vendor	Catalog #	Expiration Date
Hexane	NS Grade	Burdick & Jackson	MG Scientific	B&J-217-4	Manufacturer Exp date or 2 year from receipt
Acetone	Pesticide Grade	Burdick & Jackson	MG Scientific	B&J-010-4	Manufacturer Exp date or 2 year from receipt

10.2 **Analytical Standards** – Prepared from stock standard solutions and are required for initial calibration and continuing calibration checks (Table 4). The following describes the contents of each type of solution:

10.2.1 **Calibration and Calibration Check Standards** – Five concentration levels of calibration solutions are prepared containing equal amounts of Aroclors 1016 and 1260 (combined in the same solution named AR1660 throughout this document), as well as the surrogates decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TCMX). A single point calibration standard is required for the other Aroclor mixtures preferably at the mid-point level of the AR1016/1260 curve. A calibration check solution (ICV) is also prepared at the mid-level concentration of AR1016/1260 from second source materials.

10.2.2 **Surrogate Standard Spiking Solution** – contains decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TCMX) and is spiked into all samples prior to extraction.

10.2.3 **Matrix Spiking Solutions** – contain an Aroclor mixture that is spiked into all appropriate QC samples (LCS, MS, and MSD) prior to extraction. The Aroclor(s) spiked and/or spike amounts may be adjusted when prior knowledge of the type or concentration of Aroclor(s) present in the sample matrix is known, or to comply with project requirements.

Table 4: Standard Stock Solutions.

Standard	Concentration	Manufacturer	Catalog #	Expiration Date
Pesticide Surrogate Mix	200µg/mL each in Acetone	Restek Corporation or equivalent	32000	Manufacturer's recommended expiration date for unopened ampulated standards. 1 year after ampule is opened or on expiration date, whichever is sooner.
Aroclor 1016 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32006	
Aroclor 1221 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32007	
Aroclor 1232 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32008	
Aroclor 1242 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32009	
Aroclor 1248 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32010	
Aroclor 1254 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32011	
Aroclor 1260 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32012	
Aroclor 1262 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32409	
Aroclor 1268 Mix	1000µg/mL in Hexane	Restek Corporation or equivalent	32410	
Aroclor 1016	1000µg/mL in Isooctane	Supelco or equivalent	4-8097	
Aroclor 1260	1000µg/mL in Isooctane	Supelco or equivalent	4-4809	

***Note: Aroclor 1262 and 1268 only analyzed upon client request**

10.3 **Preparation of Analytical Standard Solutions** – Standards are prepared from commercially available stock solutions. The sources of the stock solutions, recipes for preparing dilutions and working standards, and concentrations in all solutions are shown in Table 5. All standards are prepared in hexane and stored in amber vials with PTFE-lined screw caps at ≤6 ºC.

10.4 **Stability of Analytical Standards** – Stock solutions of Aroclor mixtures must be replaced within 1 year of preparation. All dilutions and working standard solutions must be replaced within 6 months of preparation or sooner if the standards show signs of degradation. As each standard from the vendor is opened, record all pertinent information in the stock standard logbook. Record all standard preparations in the working standard logbook.

Table 5: Preparation of Analytical Standard Solutions.

Analytical Standard	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Expiration Date
TCMX/DCB Stock Solution	Pesticide Surrogate Mix	1000µL	20mL of Hexane	10µg/mL	1 year from date of preparation or the expiration date listed for the stock source, whichever is sooner.
AR1221 Stock Solution	Aroclor 1221 Mix	1000µL	10mL of Hexane	100µg/mL	
AR1232 Stock Solution	Aroclor 1232 Mix	1000µL	10mL of Hexane	100µg/mL	
AR1242 Stock Solution	Aroclor 1242 Mix	1000µL	10mL of Hexane	100µg/mL	
AR1248 Stock Solution	Aroclor 1248 Mix	1000µL	10mL of Hexane	100µg/mL	
AR1254 Stock Solution	Aroclor 1254 Mix	1000µL	10mL of Hexane	100µg/mL	
AR1262 Stock Solution	Aroclor 1262 Mix	1000µL	10mL of Hexane	100µg/mL	
AR1268 Stock Solution	Aroclor 1268 Mix	1000µL	10mL of Hexane	100µg/mL	
AR1660 Stock Solution	Aroclor 1016 Mix Aroclor 1260 Mix	1000µL each	10mL of Hexane	100µg/mL each	
AR1660 ICV Stock Solution	Aroclor 1016 Aroclor 1260	1000µL each	10mL of Hexane	100µg/mL each	
AR1221-3 Calibration Standard	AR1221 Stock Solution TCMX/DCB Stock Solution	AR1221 500µL TCMX/DCB 500µL	100mL of Hexane	AR1221 0.5µg/mL TCMX/DCB 0.05µg/mL	6 mo. From date of preparation or the expiration date listed for the stock source, whichever is sooner.
AR1232-3 Calibration Standard	AR1232 Stock Solution TCMX/DCB Stock Solution	AR1232 500µL TCMX/DCB 500µL	100mL of Hexane	AR1232 0.5µg/mL TCMX/DCB 0.05µg/mL	
AR1242-3 Calibration Standard	AR1242 Stock Solution TCMX/DCB Stock Solution	AR1242 500µL TCMX/DCB 500µL	100mL of Hexane	AR1242 0.5µg/mL TCMX/DCB 0.05µg/mL	
AR1248-3 Calibration Standard	AR1248 Stock Solution TCMX/DCB Stock Solution	AR1248 500µL TCMX/DCB 500µL	100mL of Hexane	AR1248 0.5µg/mL TCMX/DCB 0.05µg/mL	
AR1254-3 Calibration Standard	AR1254 Stock Solution TCMX/DCB Stock Solution	AR1254 500µL TCMX/DCB 500µL	100mL of Hexane	AR1254 0.5µg/mL TCMX/DCB 0.05µg/mL	
AR1262-3 Calibration Standard	AR1262 Stock Solution TCMX/DCB Stock Solution	AR1262 500µL TCMX/DCB 500µL	100mL of Hexane	AR1262 0.5µg/mL TCMX/DCB 0.05µg/mL	
AR1268-3 Calibration Standard	AR1268 Stock Solution TCMX/DCB Stock Solution	AR1268 500µL TCMX/DCB 500µL	100mL of Hexane	AR1268 0.5µg/mL TCMX/DCB 0.05µg/mL	
AR1660-1 Calibration Standard	AR1660 Stock Solution	AR1660 50µL	100mL of Hexane	AR1660 0.05µg/mL	6 mo. From date of preparation or the expiration

Analytical Standard	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Expiration Date
and PRLS	TCMX/DCB Stock Solution	TCMX/DCB 100µL		TCMX/DCB 0.01µg/mL	date listed for the stock source, whichever is sooner.
AR1660-2 Calibration Standard	AR1660 Stock Solution TCMX/DCB Stock Solution	AR1660 200µL TCMX/DCB 200µL	100mL of Hexane	AR1660 0.2µg/mL TCMX/DCB 0.02µg/mL	
AR1660-3 Calibration Standard	AR1660 Stock Solution TCMX/DCB Stock Solution	AR1660 1000µL TCMX/DCB 1000µL	200mL of Hexane	AR1660 0.5µg/mL TCMX/DCB 0.05µg/mL	
AR1660-4 Calibration Standard	AR1660 Stock Solution TCMX/DCB Stock Solution	AR1660 800µL TCMX/DCB 1000µL	100mL of Hexane	AR1660 0.8µg/mL TCMX/DCB 0.10µg/mL	
AR1660-5 Calibration Standard	AR1660 Stock Solution TCMX/DCB Stock Solution	AR1660 1000µL TCMX/DCB 1500µL	100mL of Hexane	AR1660 1.0µg/mL TCMX/DCB 0.15µg/mL	
AR1660-3 ICV Calibration Standard	AR1660 ICV Stock Solution TCMX/DCB Stock Solution	AR1660 500µL TCMX/DCB 500µL	100mL of Hexane	AR1660 0.5µg/mL TCMX/DCB 0.05µg/mL	

***Note: Aroclor 1262 and 1268 only analyzed upon client request**

11. CALIBRATION

11.1 Initial Calibration (ICAL)

11.1.1 Analysis of Standards

11.1.1.1 The initial calibration includes analysis of a five-point calibration curve of AR1660 at concentrations of 0.05, 0.2, 0.5, 0.8, and 1.0µg/mL, which includes TCMX and DCB at concentrations of 0.01, 0.02, 0.05, 0.1, and 0.15µg/mL respectively. Inject a single point standard of Aroclors 1221, 1232, 1242, 1248, 1254, 1262, and 1268 at 0.5µg/mL.

11.1.1.2 Other calibration ranges may be substituted to meet expected concentrations of samples to be analyzed. If historical data indicates a specific Aroclor is present (or by client request) a five point initial calibration may be performed for the Aroclor of concern instead of using the AR1660 mixture. Please see Table 5 on instructions of the preparation of Aroclor standards referencing the 5 point calibration for AR 1660.

11.1.1.3 Three to ten (preferably seven) peaks must be selected for each Aroclor, except for Aroclor 1221 which only requires a minimum of three peaks. . The peaks chosen for quantitation should be at least 25% of the height of the largest peak in each Aroclor and should have minimal co-elution with the peaks of other Aroclors.

11.1.2 **Retention Time (RT)** – Retention time windows are used for compound identifications in samples. The RT for all components in all standards must be within the windows specified for both columns.

11.1.2.1 Make at least three injections of all analytes of interest over a 72-hour period.

11.1.2.2 Record the retention time for each selected peak for each Aroclor mixture, to three decimal places. Calculate the mean and standard deviation for each peak.

11.1.2.3 The width of the retention time window is defined as ± 3 standard deviations of the mean established. The minimum retention window will be ± 0.03 minutes.

11.1.2.4 Establish the center of the RT window for each Aroclor mixture and surrogate using the absolute RT from the calibration verification standard at the beginning of the analytical shift. Optionally, the Initial Calibration RT windows may continue to be used as long as method criteria are met. For samples run during the same shift as an initial calibration, use the RT of the mid-point standard in the Initial calibration as the center of the RT window.

11.1.2.5 When conducting Aroclor analysis, it is important to determine that common single-component pesticides such as DDT, DDD, and DDE do not elute at the same retention times as the target Aroclors. In conjunction with determining the retention time windows, the analyst should analyze a standard containing the DDT analogs. The standard only needs to be analyzed when the retention time windows are being determined. It is not part of the routine initial calibration or calibration verification steps in the method, nor are there any performance criteria with the analysis of the standard. If it is determined that any of the DDT analogs elute at the same retention time as an Aroclor peak that was chosen for quantitation, then the analyst must either adjust the GC conditions to achieve better resolution, or choose another peak that is characteristic of that Aroclor and does not correspond to a peak from a DDT analog.

11.1.3 **Response Factors (RF)** – Individually tabulate the area responses for each of the five or more peaks selected for each Aroclor versus concentration of the five-point calibration standards for each GC column. Calculate RF for each peak using the following equation:

$$RF = \frac{A_x}{C_x}$$

Where:
A_x = Total area of analyte response.
C_x = Concentration of the analyte in the solution (µg/mL).

11.1.4 **Acceptance Criteria** –

11.1.4.1 SW-846 8082: The percent relative standard deviation (%RSD) of the five calibration factors for each peak of each Aroclor, (1016 and 1260) along with the surrogates must be ≤ 20%. If this is the case, linearity can be assumed, and the average RF can be used for quantitation. If the %RSD is >20%, a linear calibration curve may be used if the correlation coefficient is ≥ 0.99. **The results for both columns must meet calibration acceptance criteria.**

11.1.4.2 EPA Method 608: The percent relative standard deviation (%RSD) of the five calibration factors for each peak of each Aroclor, (1016 and 1260) along with the surrogates must be ≤ 10%. If this is the case, linearity can be assumed, and the average RF can be used for quantitation. If the %RSD is >10%, a linear calibration curve may be used if the correlation coefficient is ≥ 0.99. **The results for both columns must meet calibration acceptance criteria.**

11.1.5 **Initial Calibration Verification (ICV)** – In order to consider **t**he initial calibration acceptable, an ICV standard must be analyzed. For every five point Initial Calibration, a standard corresponding ICV must also be analyzed.The ICV standard must be from a second source stock and meet the same criteria as the continuing calibration verification standard before the initial calibration may be considered valid.

11.1.6 **Continuing Calibration Verification (CCV)** – A midpoint calibration check standard must be injected at the beginning and end of each 12-hour analysis period, and at intervals of not less than once every 20 samples, for calibration verification. If the response factor (area/concentration) of the check standard deviates by more than 15% from the initial average response factor, the calibration is considered out of control and analysis must be stopped.

11.1.7 **Acceptance Criteria** –

11.1.7.1 SW-846 8082: The percent difference (%D) is determined for every analyte and must be within ±15% of the calibration curve. Calculate %D for each peak using the following equation:

$$\%D = \left(\frac{R_1 - R_2}{R_1} \right) x100$$

Where:
R_1 = Mean Response factor from the ICAL
R_2 = RF calculated from the CCV

11.1.7.1.1 First determine whether the average %D for all of the peaks for each specific Aroclor with a five-point calibration is ≤ 15%. Each individual Aroclor must be evaluated separately. The average %D for all of the peaks used for quantitation must be ≤ 15% to meet the acceptance criteria.

11.1.7.1.2 If the ending calibration verification standard exceeds 15%D criteria on the high side (i.e., an increase in sensitivity) samples that had no Aroclors detected do not need to be reanalyzed. If the continuing calibration standard criterion is exceeded on the low side (i.e. a drop in sensitivity) all samples analyzed since the last acceptable CCV must be re-analyzed.

11.1.7.2 EPA Method 608: The percent recovery is determined for every analyte and must be within ±15% of the predicted response. Calculate percent recovery for each peak using the following equation:

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

11.1.7.2.1 If the response factor (area/concentration) of the check standard deviates by more than 15% from the initial average response factor, the calibration is considered out of control and analysis must be stopped. . If the Aroclors themselves are acceptable, evaluate each surrogate to determine if their recovery is within 15% of the predicted response.

11.1.7.2.2 If the ending calibration verification standard exceeds the 15% recovery criteria on the high side (i.e., an increase in sensitivity) samples that had no Aroclors detected do not need to be reanalyzed. If the continuing calibration standard criterion is exceeded on the low side (i.e. a drop in sensitivity) all samples analyzed since the last acceptable CCV must be re-analyzed

11.1.8 **All samples must be bracketed by acceptable calibration verifications on both columns.** Perform corrective action such as injection port or column maintenance. Prior to the analysis of any subsequent samples acceptable calibration verification must be established. In the event that this cannot be achieved, a new initial calibration must be performed.

11.1.9 **Reporting Limit Verification Standard (RLVS)** – For every five point Initial Calibration, a standard corresponding to the Pace reporting limit (PRL) must also be analyzed. The RLVS is analyzed prior to any samples being analyzed, and monthly thereafter. The limits are ± 40% of the true concentration. The analysis of this standard demonstrates the instruments ability to report down to the reporting limit with known accuracy. If outside the limits, reevaluate the low level standards. If still outside the limits, recalibrate.

12 PROCEDURE

12.1 Sample Preparation – All sample extracts and standard solutions must be allowed to warm to room temperature before analysis.

12.2 GC/ECD System Preparation – Verify instrument parameters as set up for current operating conditions.

12.2.1 GC Column Conditions

Carrier Gas	UHP Helium
Flow Rate	3.4 mL/min.
Make-up Gas	UHP Nitrogen
Flow Rate	35.0 mL/min.
Detector Temp.	300°C
Injector Temp.	205°C
Injection	Splitless

12.2.2 GC Temperature Program

Initial Temp.	110°C
Initial Time	0.5 min.
Rate 1	30.00°C/min.
Final Temp. 1	200°C
Final Time 1	1.00 min.
Rate 2	12.00°C/min.
Final Temp. 2	220°C
Final Time 2	0.00 min.
Rate 3	30.00°C/min.
Final Temp. 3	305°C
Final Time 3	6.00 min.

12.3 **Batch Sequence** – Generate a sequence to run a batch of samples and the associated quality control samples.

12.3.1 **Initial Calibration** – For example, the batch for initial calibration should include the following:

Series of 2-3 Primes
Solvent Blank (Hexane)
AR1660-1 (0.05µg/mL)
AR1660-2 (0.2µg/mL)
AR1660-3 (0.5µg/mL)
AR1660-4 (0.8µg/mL)
AR1660-5 (1.0µg/mL)
Solvent Blank (Hexane)
AR1660-3 ICV
AR1660-1 (0.1µg/mL) (PRLS)

12.3.2 **Sample Analysis** – For example, the typical batch for analysis of PCBs should include the following:

AR1660-301 CCV (0.5µg/mL)
(20 samples or 12-hour period)
Method Blank
Laboratory Control Spike
Samples
Matrix Spike/Matrix Spike Duplicate
Duplicate Sample(s)
AR1660-302 CCV (0.5µg/mL)

12.4 **Load Autosampler** – Load the autosampler with the appropriate primes, solvent blanks, standards and samples for the batch as it was created.

12.5 **Analyze Samples** – Analyze all standards, quality control samples, and environmental samples.

12.5.1 The method blank and LCS extracted along with the samples should be analyzed on the same instrument as the samples.

12.5.2 If the analyst determines that interferences could be removed by sulfuric acid cleanup and/or sulfur removal, then the analyst will perform the necessary cleanups and re-analyze the samples. The blank and LCS will also undergo the same cleanups and be re-analyzed.

12.6 Qualitative Analysis of Results

12.6.1 **Quantitative Identification (Primary Column)**

12.6.2 **PCB aroclor results will be quantitated and reported from the primary column Rtx-CLPesticide column. The peaks used for Aroclor identification are labeled as the specific Aroclor Chromatograms. Please see Attachment III: PCB Aroclor Pattern and Peak Selection Chromatograms.**

12.6.2.1 To be identified as an Aroclor, peaks present in a sample extract must fall within the established retention time window for a specific Aroclor. Once the Aroclor pattern has been tentatively identified, compare the responses of 3 to 10 major peaks in either the single-point, or one of the five-point calibration standards for the corresponding Aroclor with the peaks observed in the sample extract (Please see Attachment III for example chromatograms of peaks chosen). An overlay of the standard chromatogram onto the sample chromatogram may be required to clearly identify patterns and determine peak overlap between Aroclors.

12.6.2.2 Additionally, environmental "weathering" of PCBs may complicate reliable identification and quantitation. Alternate peaks may be chosen due to weathering or other known interferences. In severely degraded patterns in unknown samples, the analyst would choose the Aroclor standard pattern which most closely resembles the unknown sample.

12.6.2.3 Once the sample is processed in the Target processing software, the analyst will review the chromatograms to first determine Aroclor pattern matches. Then they will manually integrate the chromatogram using baseline adjustments, peak splitting and peak assignment to mimic the standard Aroclor pattern used for calibration.

12.6.2.4 Since the chromatograms for many Aroclor mixtures overlap, the presence of multiple mixtures may complicate their quantitation. Peaks that exhibit high bias due to Aroclor overlap or matrix interferences may be removed from quantitated result by the analyst. It will be left to analyst's discretion to use their experience in data analysis to determine when peak removal is acceptable. A minimum of 3 peaks must be used to quantitate unknown samples and standards.

12.6.2.5 Aroclors 1232, 1016, 1242 and 1248 will not be identified in the same unknown sample due to the PCB congener sharing which occurs within these Aroclor patterns. Therefore, the laboratory does not bias the PCB Total data high due to PCB Aroclor overlap that would occur if these were to be reported on the same unknown sample.

12.6.3 **Qualitative Confirmation**

12.6.4 **Reported PCB Aroclor results will be confirmed by Aroclor pattern presence on the Rtx-CLPesticide2 column as follows.**

12.6.4.1 Qualitative confirmation is completed using a second GC column of dissimilar stationary phase. Dual-column analysis is performed for qualitative confirmation only, however the same initial and continuing calibration criteria apply to both columns as outlined in Section 11.1.4.

12.6.4.2 Since Aroclors provide distinct multiple peak patterns which may be identified by an experienced analyst, confirmation on the second column may be based on pattern recognition. No manual integrations such as peak splitting, baseline drawing and peak assigning will be performed on the samples for confirmation. These chromatograms will not be evaluated for Aroclor overlap, matrix interferences or RPD between the two columns. The sample concentration and surrogates will not be evaluated and sample dilutions will not be determined from the raw results. Only laboratory quality control standards are subject to manual manipulation.

13 QUALITY CONTROL

13.1 Calibration Checks

13.1.1 **ICAL** – If initial calibration criteria are not met, check standards preparation procedure for errors. Prepare new standards as required and re-run the calibration.

13.1.2 **Continuing Calibration Verification** – If the CCV criteria are not met, check system parameters, identify and correct likely causes, and re-run the check. An acceptable check is required to report sample results for the applicable batch.

13.1.3 **Reporting Limit Verification Standard (RLVS)** – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration and monthly thereafter, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate. The AR1660 0.05µg/mL initial calibration standard is used as the PRLS

13.2 **Surrogate Recoveries** – Surrogate compound(s) must be added to all samples, spikes, control samples and method blanks, prior to analysis as indicators of method accuracy. Laboratory-based accuracy limits should be used for acceptance criteria. If these criteria are not met, check system parameters, identify and correct likely causes, and re-run the samples.

13.2.1 If **both** surrogate recoveries fail this criterion, re-extraction of the sample may be necessary. If surrogate recoveries are higher than the acceptance criteria and target compounds are less than the reporting limit, the results may be reported with an appropriate footnote. If recoveries appear out of control due to sample matrix, report the results with an appropriate footnote.

13.2.2 One surrogate is allowed to be outside of the control limits. For instance, if an interfering peak obscures one surrogate, then that one surrogate may be excluded. The surrogate is considered diluted out and not evaluated when the dilution performed brings the theoretical on-column concentration below the concentration of the low standard in the initial calibration curve.

13.3 **Method Blank** –The method blank must not contain analyte responses at or above the reporting limit. If the results are not acceptable, re-analyze the method blank. If the problem persists, conduct maintenance to clean the analytical system. An acceptable method blank is required to report sample results for the applicable batch.

13.3.1 One surrogate is allowed to be outside of the control limits. For instance, if an interfering peak obscures one surrogate, then that one surrogate may be excluded. The surrogate is considered diluted out and not evaluated when the dilution performed brings the theoretical on-column concentration below the concentration of the low standard in the initial calibration curve.

13.3.2 If the blank contains any analyte of interest above the reporting limit, all of the associated samples, matrix spikes, and laboratory control spikes **must** be re-extracted unless the sample concentration is greater than 10X the amount found in the blank or the analyte is not detected in an associated sample. For Wisconsin projects this criteria will be "Above the LOD".

13.4 **LCS Recoveries** – One LCS must be analyzed with each batch of 20 samples. Laboratory-based accuracy limits should be used to for acceptance criteria. For EPA Method 608 see Attachment II for acceptance criteria. For Biota samples, if laboratory limits chart too narrow, limits will be set to 60-130%. An acceptable LCS is required to report sample results for the applicable batch.

13.4.1 If the laboratory control spike does not meet the recovery criteria, the results of all QC performed with the batch will be evaluated by the analyst. Corrective actions include re-extraction of the samples or reanalysis of the extracts.

13.4.2 One LCSD must be analyzed with each batch of 20 samples if inadequate sample is available to perform a MS/MSD. Laboratory-based accuracy limits should be used to for acceptance criteria. An acceptable LCSD is required to report sample results for the applicable batch.

13.5 **MS/MSD Recoveries** –

13.5.1 SW-846 8082: One MS/MSD pair should be analyzed with each batch of 20 samples. Laboratory-based accuracy limits should be used to for acceptance criteria. The sample use for the MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows.

13.5.2 EPA Method 608: One MS/MSD pair should be analyzed at a rate of 10% of the samples being analyzed. See Attachment II from Method 608 for acceptance criteria. The sample used for the MS/MSD pair is either determined by the client or selected at random from the client sample as sample volume allows.

13.5.3 If a matrix spike recovery fails this criterion, the recovery of the other spiked sample in the MS/MSD pair should be evaluated. If recovery failures are duplicated then the sample matrix is suspected as the problem and the data should be flagged and the failures discussed in the sample narrative.

13.6 **Duplicate and MS/MSD RPDs** – Five percent of all environmental samples should be analyzed in duplicate. A MS/MSD pair is also an acceptable duplicate analysis. If results are not acceptable, check for possible sample preparation problems and re-analyze if needed. Report the results with an appropriate data qualifier.

14 DATA ANALYSIS AND CALCULATIONS

14.1 Calculate Results

14.1.1 The amount of Aroclor is calculated using the individual response factor (single point) for each of the 3 - 10 characteristic peaks chosen for quantitation of that specific Aroclor. If Aroclor 1016 and/or 1260 is being quantified use the average response factor from the AR1660 curve. Use the single point response factor from the initial calibration for all other Aroclors. Surrogates are quantified based on the average response factors for TCMX and DCB analyzed with the AR1660 curve. A concentration is determined using each of the characteristic peaks and then those concentrations are averaged to determine the on-column concentration of that Aroclor based on the primary column.

14.1.2 If the initial on-column result of a sample extract exceeds the calibration range, the extract must be diluted and re-analyzed. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve. The GC data system will calculate concentration of each parameter as µg/mL on-column in the extract. Concentrations in samples are then calculated based on sample size, total volume of the final extract, any dilution factor, and any correction factor.

14.1.2.1 Water and Water-Miscible Waste Samples

$$\text{Final Concentration } (\mu\text{g/L}) = \frac{(C_x)(DF)(U_f)(V_t)}{(V_i)(V_o)}$$

Where:
C_x = On-column concentration in extract (µg/mL).
DF = Dilution factor.
U_f = Correction factor.
V_t = Volume of final extract (µL).
V_i = Volume injected (µL).
V_o = Volume of water sample extracted (mL).

14.1.2.2 Soil/Solid, Waste and Biological Samples

$$\text{Final Concentration } (\mu\text{g/Kg}) = \frac{(C_x)(DF)(U_f)(V_t)}{(V_i)(W_s)(S)}$$

Where:
C_x = On-column concentration in extract (µg/mL).
DF = Dilution factor.
U_f = Correction factor.
V_t = Volume of final extract (µL).
V_i = Volume injected (µL).
W_s = Weight of sample extracted (g).
S = Percent Solids (biological samples not corrected for percent solids).

14.1.3 Air monitoring sample result calculations use a time/volume relationship to calculate PCB concentration. (See Section 26, Table 8 for example.)

$$\text{Final Concentration } (\mu\text{g/L}) \text{ or } (\text{mg/m3}) = \frac{(C_x)(DF)(U_f)(V_t)}{(V_i)(V_s)}$$

Where:
C_x = On-column concentration in extract (µg/mL).
DF = Dilution factor.
U_f = Correction factor.
V_t = Volume of final extract (µL).
V_i = Volume injected (µL).
V_s = Volume of air sampled (L).
S = Percent Solids (biological samples not corrected for percent solids).

Volume of air sampled L = LPM * T

Where:
LPM = Liters per Minute of air sampled.
T = Sampling time in minutes.

14.2 **Quality Control Results** – Calculate recoveries for the surrogates in all samples; spiked analytes in LCS and MS/MSD samples; and Relative Percent Differences (RPD) for duplicate and MS/MSD samples.

15 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

Table 6: Quality Control

Analytical Method ⇨ Quality Control Measure ⇩	**SW846 8082 and EPA 608**
Initial Calibration	Minimum of five levels; lowest level at or below PQL.
Initial Calibration Verification Standard (ICV)	After every initial calibration.
Calibration Verification Standard (CCV)	One at the beginning of a 12 hour time clock, every 20 injections or more frequent.
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent.
Laboratory Control Spike	One per batch of samples, up to 20 environmental samples, whichever is more frequent.
Matrix Spike and Duplicate	Sw-846 8082: One pair per batch of samples, up to 20 environmental samples, whichever is more frequent. EPA 608: One pair per 10 samples analyzed.
Method Validation	Annually
MDL	Annually
Surrogate Standards	Added to every sample.
Reporting Limit Verification Standard (RLVS)	After every calibration and monthly thereafter.

16 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

Table 7: Corrective Actions

Analytical Method Acceptance Criteria⇨ Calibration Measure ⇩	**SW846 8082** **Frequency**	 **Acceptance Criteria**
Initial Calibration	• Installation of new column • Creation of new analytical method • CCV fails criteria	• Use Average Calibration and relative standard deviation (%RSD) is ≤ 20%.
Initial Calibration Verification (ICV)	• Immediately after the ICAL.	• Percent Difference (%D) is ≤ 15%
Continuing Calibration Verification (CCV)	• At the beginning of every 12 hour shift, every 20 injections, or more frequent	• Percent Difference (%D) is ≤ 15%
Method Blank	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	• Less than the Reporting Limit
Laboratory Control Spike and Duplicate	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	• In house limits determined.
Matrix Spike and Duplicate	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	• In house limits determined.
MDL's	• Annually	• 1-10 times the MDL should be equal to the spike concentration that was used to determine the MDL's
Method Validation	• Annually	• In house limits determined.
Surrogate Standards	• Added to every sample.	• In house limits determined.
Reporting Limit Verification Standard (RLVS)	• After every initial calibration and monthly thereafter	• 60-140%

17 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

17.1 See Section 13, 15 and 16.

18 METHOD PERFORMANCE

18.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

18.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

18.1.2 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

18.1.3 An annual method detection limit (MDL) study will be completed per S-GB-Q-020, *Determination of the LOD and LOQ* (most current revision or replacement), for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

18.1.4 Periodic performance evaluation (PE) samples are analyzed per S-GB-Q-021, *PE/PT Program* (most current revision or replacement), to demonstrate continuing competence. All results are stored in the QA office.

19 METHOD MODIFICATIONS

19.1 Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.

19.2 All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.

19.3 Procedures identified as “Best Practices” by PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories.

19.4 If a client fails to provide sufficient volume for the method required Matrix Spike/Matrix Spike Duplicate (MS/MSD), the laboratory will analyze a Laboratory Control Spike Duplicate to demonstrate precision. The analytical batch will be qualified with the “M5” data qualifier.

19.5 Calibration standards are to be made in Hexane, not in isooctane as stated in EPA method 608.

20 INSTRUMENT AND EQUIPMENT MAINTENANCE

20.1 Any daily or periodic maintenance must be recorded in the instrument daily logbook. Additional information may be found in the most current revision of SOP: S-GB-Q-008, *Preventative, Routine, and Non-routine Maintenance.*

21 TROUBLESHOOTING

21.1 Please see the instrument operating manual for information on instrument troubleshooting.

22 SAFETY

22.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Reduce exposure by use of hood, gloves, lab coats and safety glasses. Cautions are included for known extremely hazardous materials.

22.2 A reference file of Safety Data Sheets (SDS) is made available to all personnel involved in the chemical analysis,, and is located at the following link: https://msdsmanagement.msdsonline.com/c0ce0b0a-17d3-4f3c-afc6-25352729b299/ebinder/?nas=True. A formal safety plan has been prepared and is distributed to all personnel with documented training.

23 WASTE MANAGEMENT

23.1 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of S-GB-W-001, *Waste Handling and Management*.

24 POLLUTION PREVENTION

24.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

24.2 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

25 REFERENCES

25.1 Pace Analytical Quality Manual- most current version.

25.2 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems" – most current version.

25.3 USEPA, SW-846, Method 8082, "Polychlorinated Biphenyls (PCBs) by Gas Chromatography", December 1996.

25.4 USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

25.5 Appendix A to part 136, Methods for organic chemical analysis of municipal and industrial wastewater, "Method 608 – Organochlorine Pesticides and PCBs"

25.6 Pace Analytical Services, LLC – Green Bay, SOP S-GB-O-053, "*Separatory Funnel Extraction*, most current revision or replacement.

25.7 Pace Analytical Services, LLC – Green Bay, SOP S-GB-O-031, "*Extraction of Biological Samples for Organochlorine Pesticides/PCBs*", most current revision or replacement.

25.8 Pace Analytical Services, LLC – Green Bay, SOP S-GB-O-040, "*Extraction of Wipes and Oil for PCB Analysis"*, most current revision or replacement.

25.9 Pace Analytical Services, LLC – Green Bay, SOP S-GB-O-041, "*Extraction of PCBs Using the Automated Soxhlet*", most current revision or replacement.

25.10 Pace Analytical Services, LLC – Green Bay, SOP S-GB-O-032, "*Gel Permeation Chromatography*", most current revision or replacement.

25.11 Pace Analytical Services, LLC – Green Bay, SOP S-GB-O-034 *Sulfuric Acid Cleanup"*, most current revision or replacement.

25.12 Pace Analytical Services, LLC – Green Bay, SOP S-GB-O-036, "*Florisil Cleanup for PCBs*", most current revision or replacement.

25.13 Pace Analytical Services, LLC – Green Bay, SOP S-GB-O-038, "*Silica Gel Cleanup of Organochlorine Pesticides and PCBs*", most current revision or replacement.

25.14 Pace Analytical Services, LLC – Green Bay, SOP S-GB-O-039, "*Copper Cleanup for the Removal of Sulfur from PCB Samples*", most current revision or replacement.

26 TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ADDENDA ETC.

Attachment I: Air monitoring calculation sheet. Example

Pace Analytical	Document Name: NIOSH Method 5503 (mod) PCBs in Air	Document Revised: 30-Nov-2017
	Document No.: F-GB-O-133-Rev.02	Issuing Authority: Pace Green Bay Quality Office

PCBs in Air

Client: Tetra Tech
Date/Time Collected:
Project number:
Project name: FOX RIVER
Pace Project #:

Method: NIOSH 5503 (modified)
Date/Time Extracted:
LPM:
Time (minutes):
Volume of Air sampled (L): 0.00

		Pace Sample ID:	(Front)	Pace Sample ID:	(Back)	
Client Sample ID	**Test Parameter**	**Result in ug**	**results in ug/L or mg/m3**	**Result in ug**	**results in ug/L or mg/m3**	**<10% breakthrough front to back sections**
		Date Analyzed: Analyst:		Date Analyzed: Analyst:		
	PCB-1016 (Aroclor 1016)	< 0.05	< #DIV/0!	< 0.05	< #DIV/0!	#DIV/0!
	PCB-1221 (Aroclor 1221)	< 0.05	< #DIV/0!	< 0.05	< #DIV/0!	#DIV/0!
	PCB-1232 (Aroclor 1232)	< 0.05	< #DIV/0!	< 0.05	< #DIV/0!	#DIV/0!
	PCB-1242 (Aroclor 1242)	< 0.05	< #DIV/0!	< 0.05	< #DIV/0!	#DIV/0!
	PCB-1248 (Aroclor 1248)	< 0.05	< #DIV/0!	< 0.05	< #DIV/0!	#DIV/0!
	PCB-1254 (Aroclor 1254)	< 0.05	< #DIV/0!	< 0.05	< #DIV/0!	#DIV/0!
	PCB-1260 (Aroclor 1260)	< 0.05	< #DIV/0!	< 0.05	< #DIV/0!	#DIV/0!
	PCB-1268 (Aroclor 1268)	< 0.05	< #DIV/0!	< 0.05	< #DIV/0!	#DIV/0!
	PCB, Total	< 0.05	< #DIV/0!	< 0.05	< #DIV/0!	#DIV/0!
	Tetrachloro-m-xylene (S)		58-120%*		58-120%*	
	Decachlorobiphenyl (S)		59-109%*		59-109%*	

* acceptable range for surrogate recovery

Secondary Data Review: _____ Date: _____

Wipe MDL = 0.02212 µg/mL.

Volume of air sample = 0.1423LPM * 481M = 68.45L

Final volume of extract = 2mL

Result in µg = On column or MDL * final volume of extract (0.02212 * 2) = 0.04424 µg

Attachment II: EPA Method 608, Table 3

Table 3—QC Acceptance Criteria—Method 608

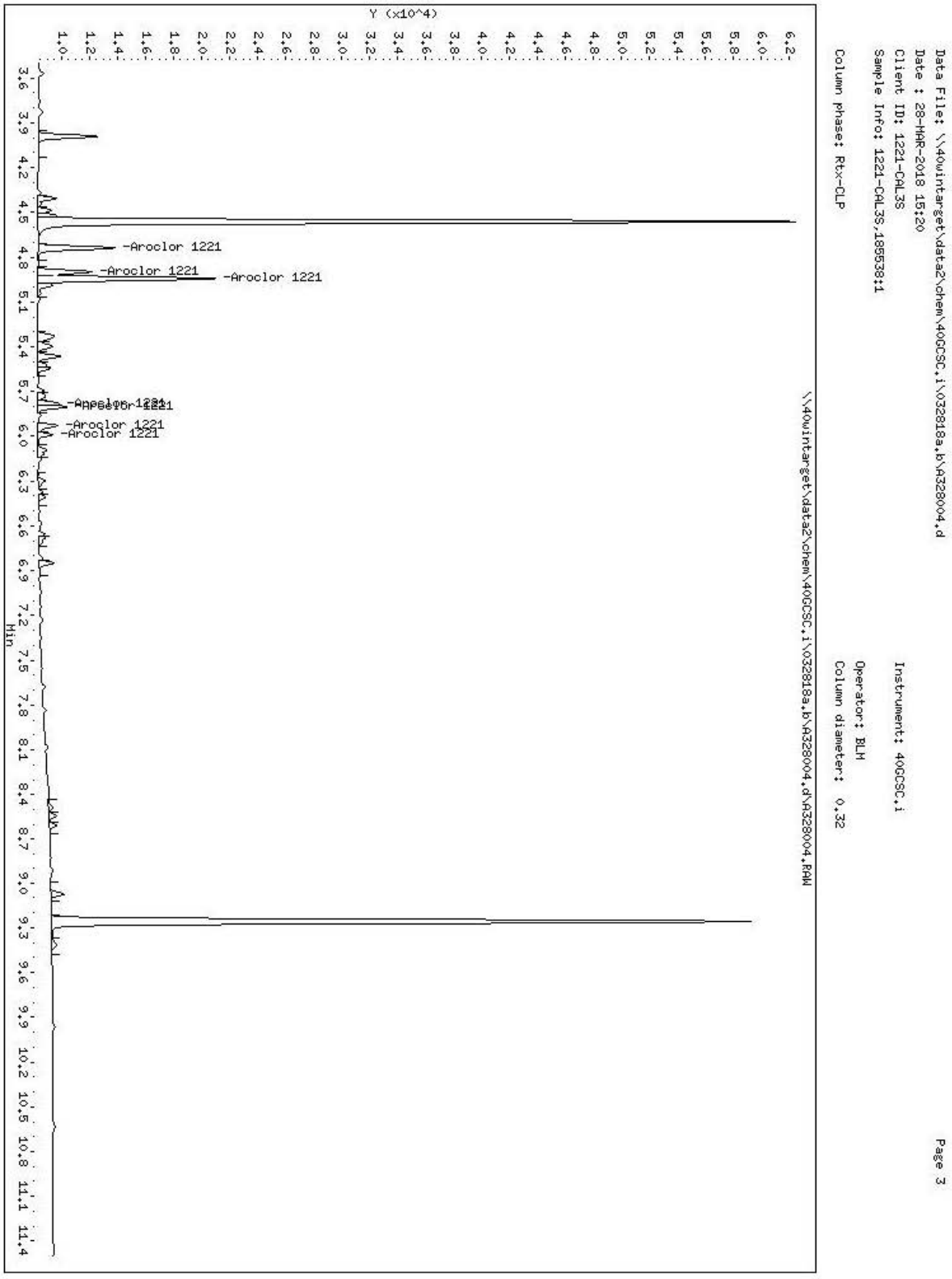
Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for P, P_s %)
Aldrin	2.0	0.42	1.08 - 2.24	42 - 122
α-BHC	2.0	0.48	0.98 - 2.44	37 - 134
β-BHC	2.0	0.64	0.78 - 2.60	17- 147
δ-BHC	2.0	0.72	1.01 - 2.37	19 - 140
γ-BHC	2.0	0.46	0.86 - 2.32	32 - 127
Chlordane	50	10.0	27.6 - 54.3	45 - 119
4,4'-DDD	10	2.8	4.8 - 12.6	31 - 141
4,4'-DDE	2.0	0.55	1.08 - 2.60	30 - 145
4,4'-DDT	10	3.6	4.6 - 13.7	25 - 160
Dieldrin	2.0	0.76	1.15 - 2.49	36 - 146
Endosulfan I	2.0	0.49	1.14 - 2.82	45 - 153
Endosulfan II	10	6.1	2.2 - 17.1	D - 202
Endosulfan Sulfate	10	2.7	3.8 - 13.2	26 - 144
Endrin	10	3.7	5.1 - 12.6	30 - 147
Heptachlor	2.0	0.40	0.86 - 2.00	34 - 111
Heptachlor epoxide	2.0	0.41	1.13 - 2.63	37 - 142
Toxaphene	50.0	12.7	27.8 - 55.6	41 - 126
PCB-1016	50	10.0	30.5 - 51.5	50 - 114
PCB-1221	50	24.4	22.1 - 75.2	15 - 178
PCB-1232	50	17.9	14.0 - 98.5	10 - 215
PCB-1242	50	12.2	24.8 - 69.6	39 - 150
PCB-1248	50	15.9	29.0 - 70.2	38 - 158
PCB-1254	50	13.8	22.2 - 57.9	29 - 131
PCB-1260	50	10.4	18.7 - 54.9	8 - 127

s = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).
P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).
D = Detected; result must be greater than zero.

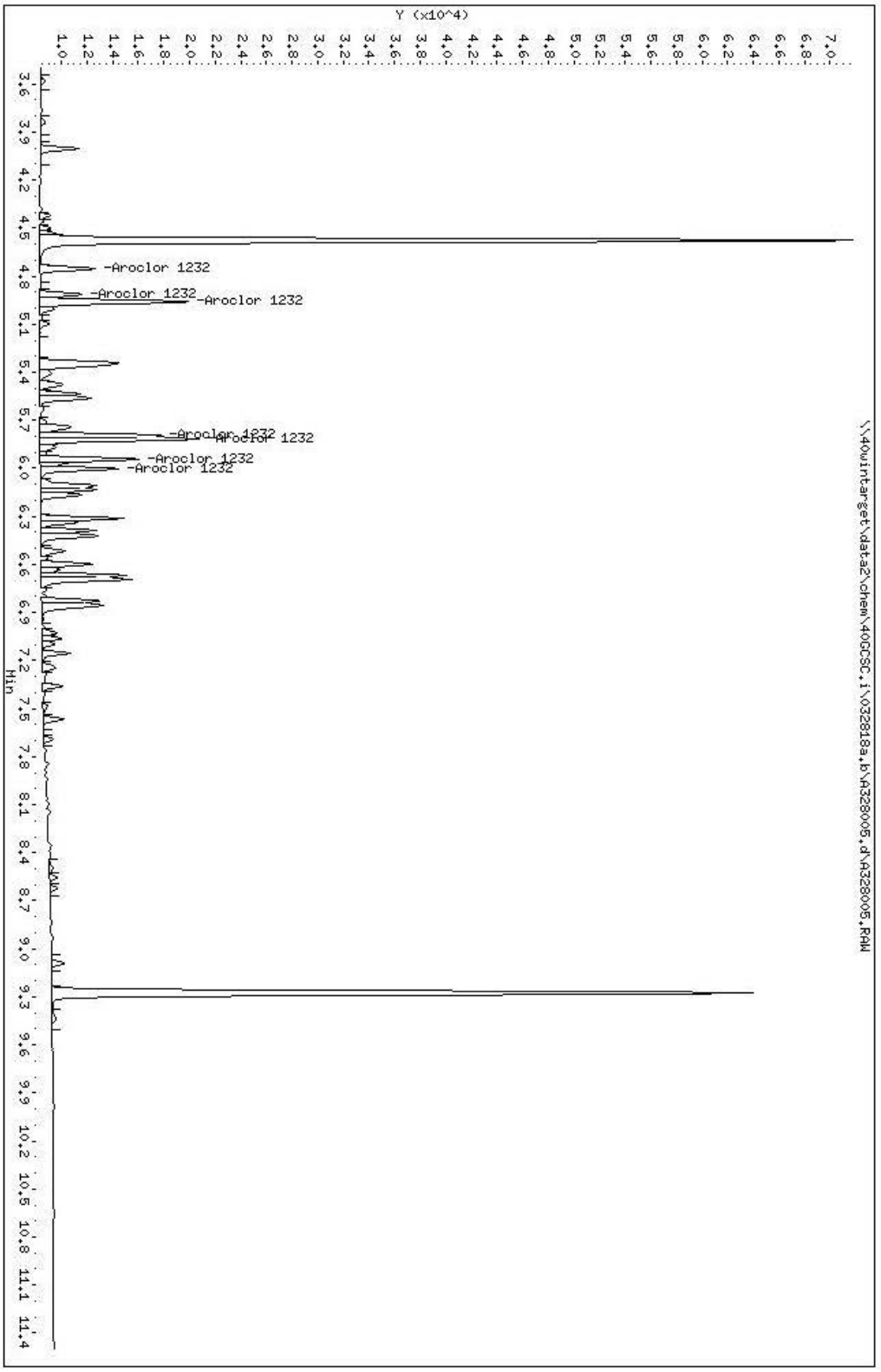
NOTE: These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

Attachment III: PCB Aroclor Patterns and Peak Selection

Aroclor 1221



Aroclor 1232



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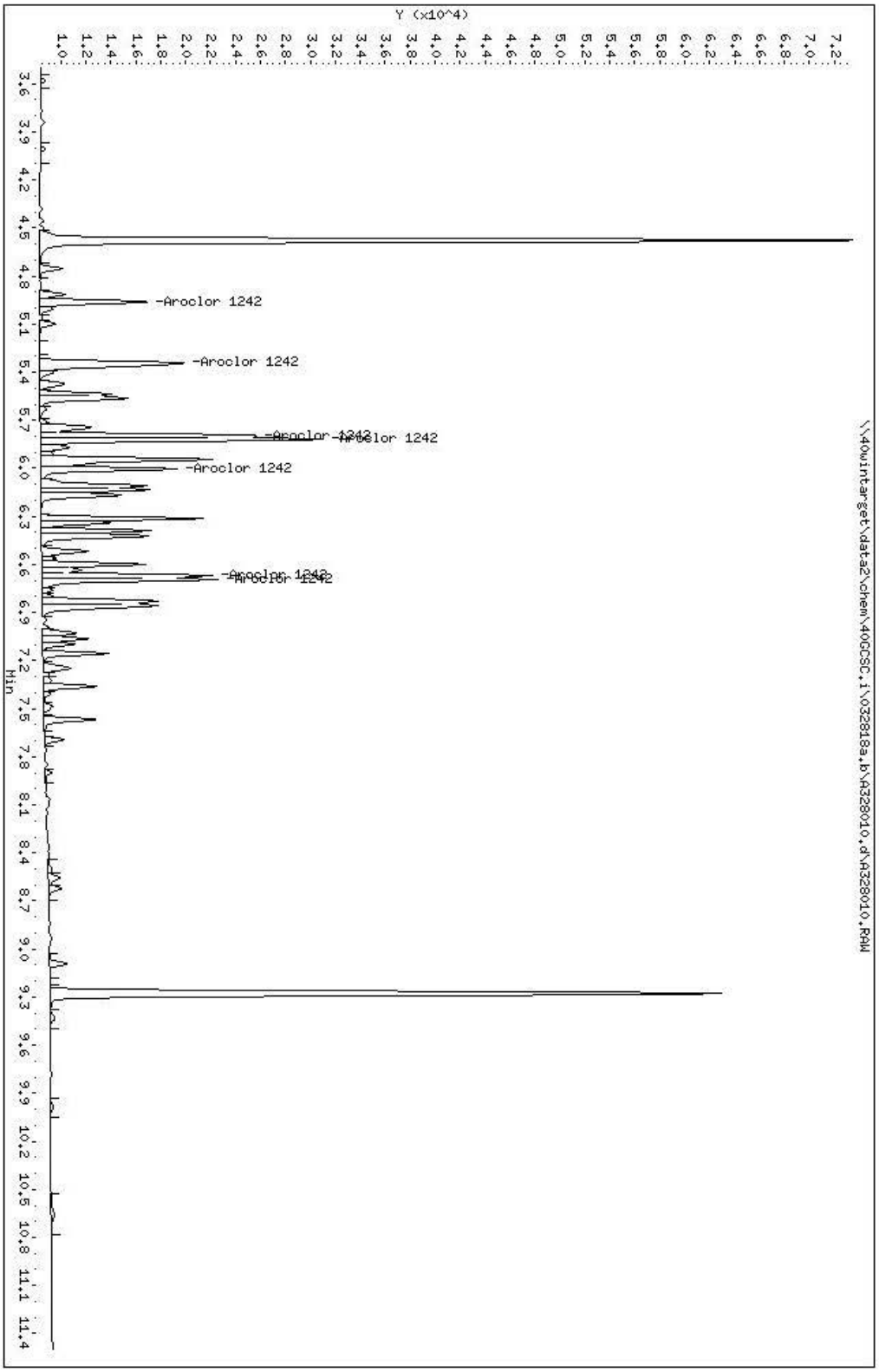
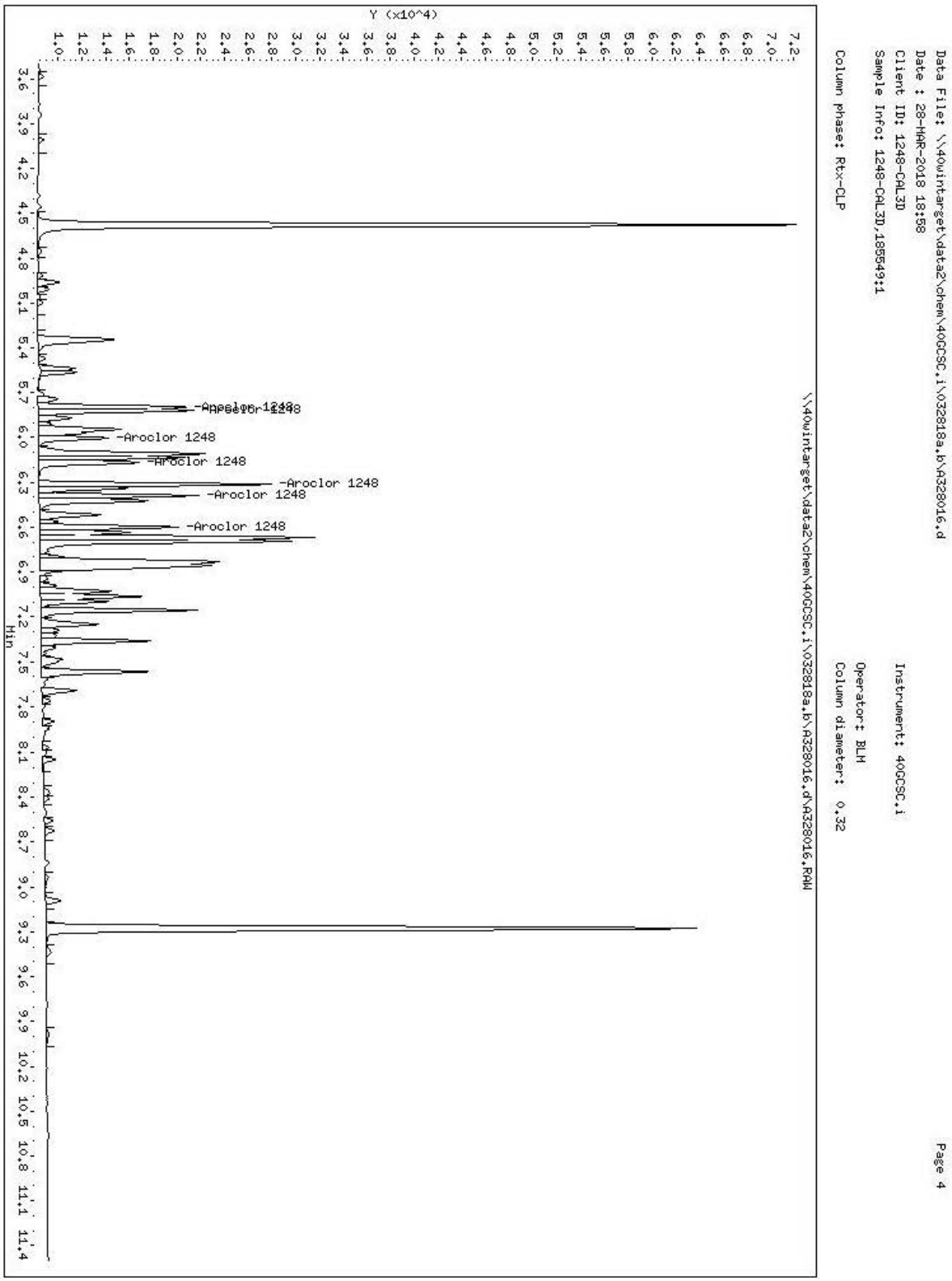
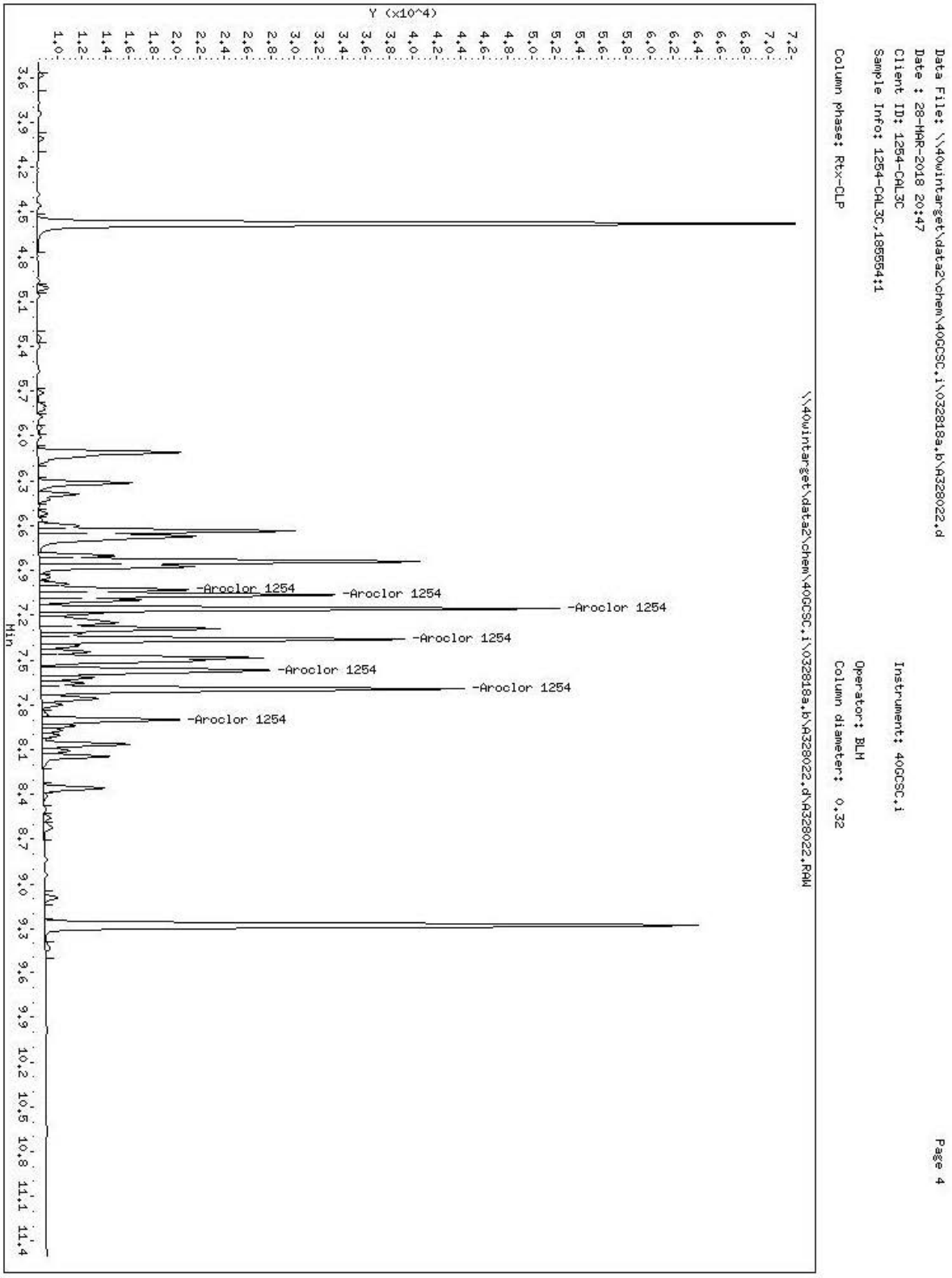


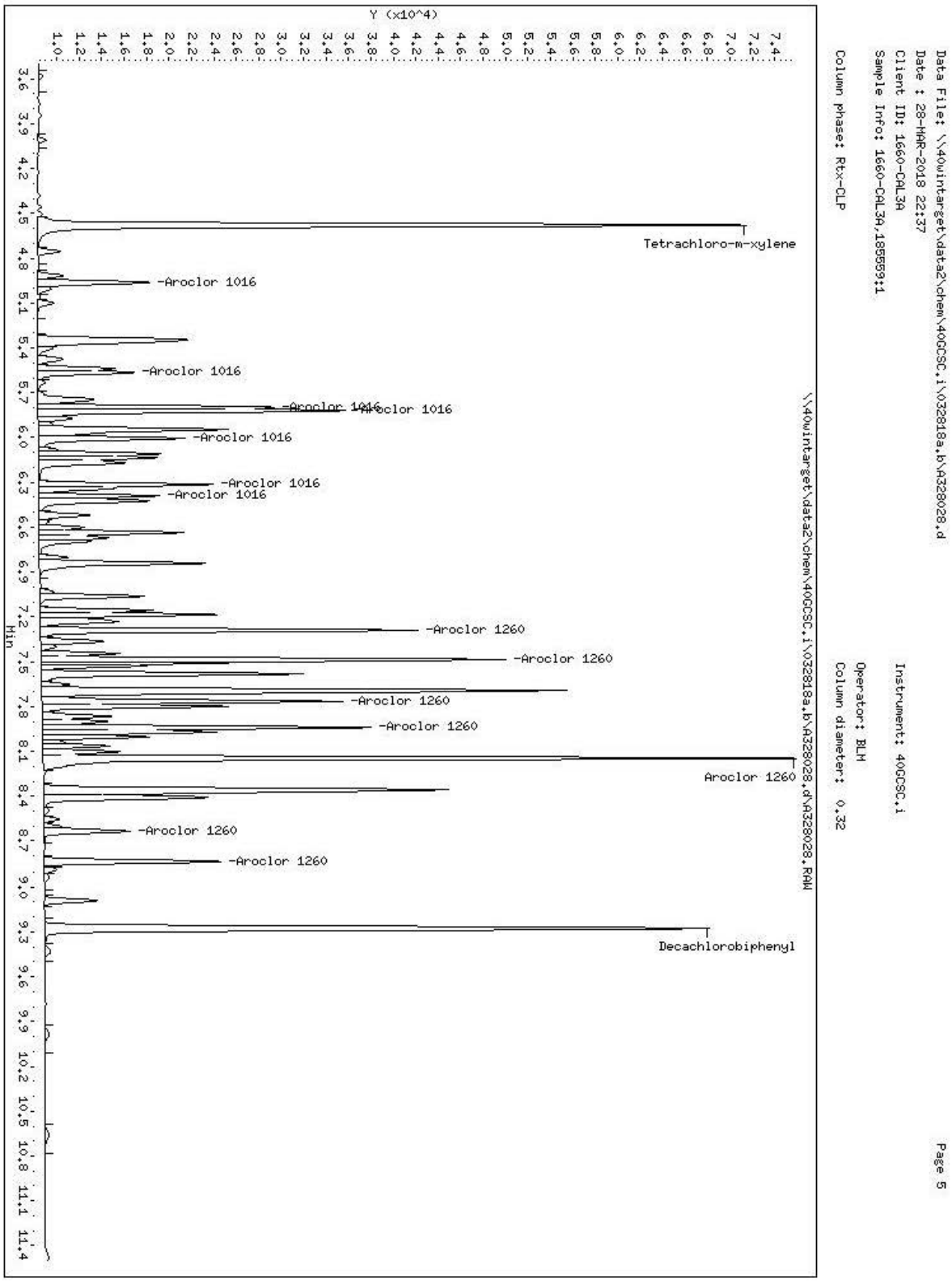
Aroclor 1248



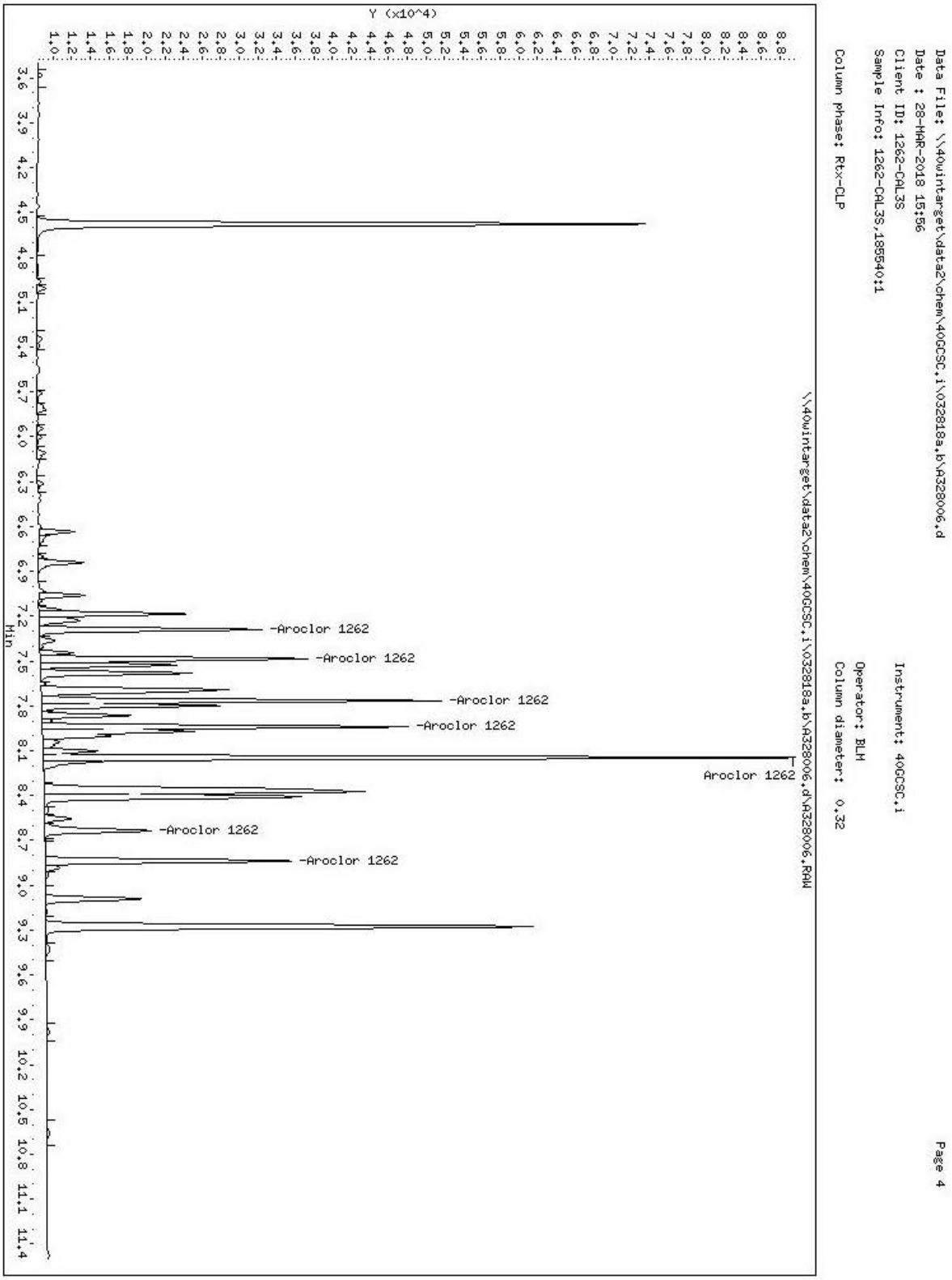
Aroclor 1254



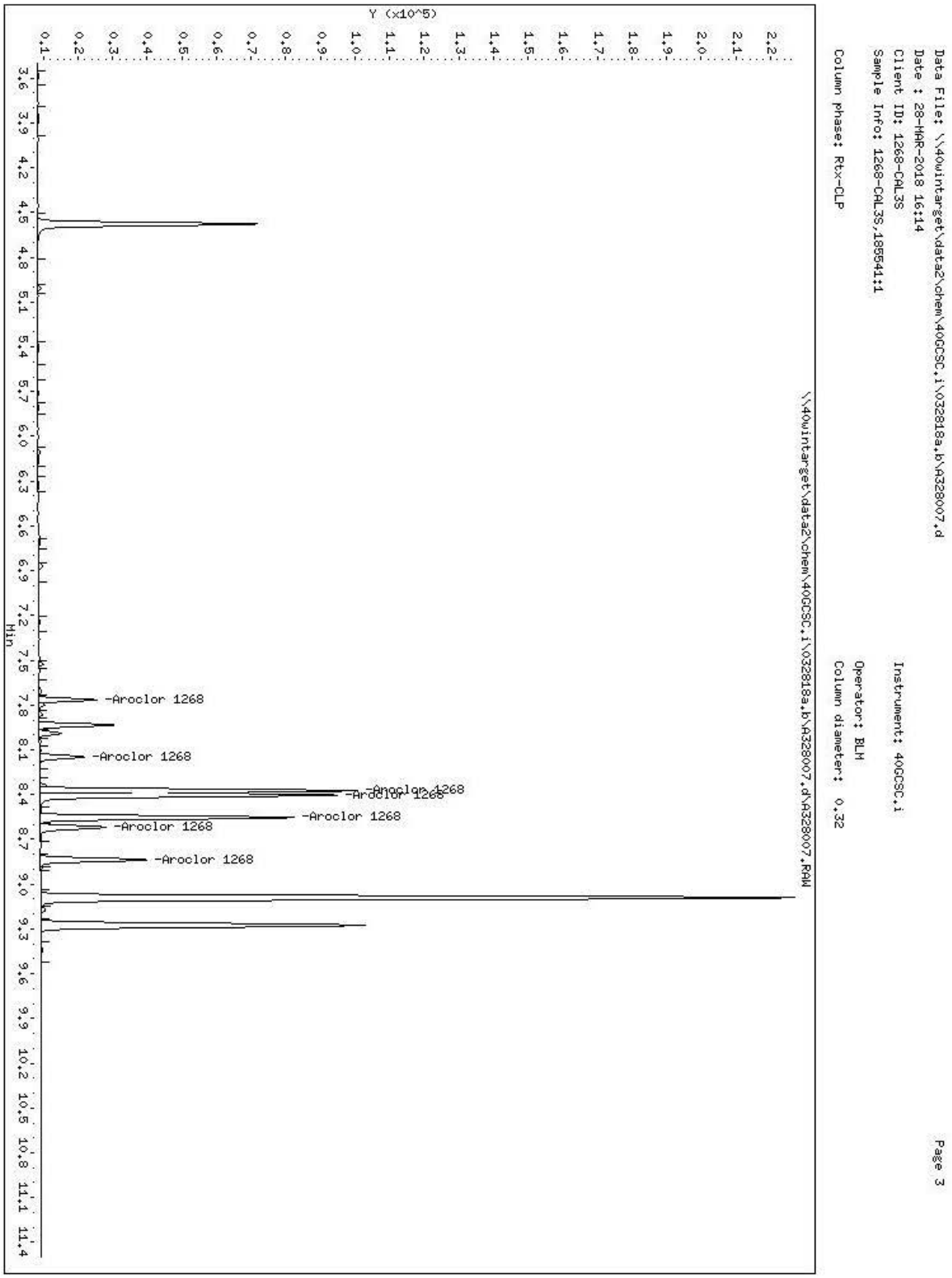
Aroclor 1660



Aroclor 1262



Aroclor 1268



27 REVISIONS

Revision Number	Reason for Change	Date
S-GB-O-026-Rev.07	Updated SOP format. Throughout document: Updated SOP references. Table 5 and Section 11: Updated calibration curve and reporting limit.	13Jan2014
S-GB-O-026-Rev.08	Section(s) 11.1.4, 11.1.7.2, 13.4, 13.6.2, 14.1, 25 and Table(s) 6 and Attachment II: Added EPA 608 Method Criteria. Section(s) 11.1.1.3 and 14.1.1: Allow use of 3 peaks for quantitation. Section 12.6.2.1: Removed confirmation by GC/MS. Section 19.5: Added Method Modification for solvent as hexane. Section 26: Added EPA Method 608 Table 3. Throughout Document: Added Uncontrolled Footer Statement.	18Jun2015
S-GB-O-026-Rev.09	Signature Page: Updated from Inc to LLC, updated QM name. General: made administrative edits that do not affect the policies or procedures within the document. Section 8: Removed definitions found in current Pace QAM. Section(s) 9 and 10: Updated to Table format, corrected Cat# for Confirmation Column. Section 12.2.2: Updated GC Temperature Program Section 12.6 and references throughout document: Clarified used of dual column confirmation is qualitative only. Added language to clarify the Aroclor Quantitative and Qualitative selection. Section 13.3.2: Changed MB qualification is needed when results are 10X the detection in the MB. Section 22.2: added SDS link and information. Section 25: Added Pace and TNI references. Section 26: Added updated NIOSH Worksheet Section 27: removed previous revisions which can be found in prior version of SOP Attachment III: Added PCB Aroclor Chromatograms..	16Jul2018

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STANDARD OPERATING PROCEDURE

Analysis of Organochlorine Pesticides by Gas Chromatography

Reference Methods: SW-846 8081A/B/ EPA 608

SOP NUMBER	S-GB-O-027-Rev.08
EFFECTIVE DATE	Date of Final Signature
SUPERSEDES	S-GB-O-027-Rev.07

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 07/02/15

Kate Grams, Laboratory Quality Manager — Date: 7/2/15

Chris Haase, Department Manager — Date: 7/2/15

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

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

S-GB-O-027-REV.08

TABLE OF CONTENTS

1. PURPOSE/IDENTIFICATION OF METHOD

1.1 The purpose of this Standard Operating Procedure (SOP) is to describe the analysis of various organochlorine pesticides in water, soils, sediments, biological tissue, and solid waste compliant with SW-846 Method 8081A/B and EPA 608. Samples for analysis are prepared by SW846 Method 3510C, 3540C, 3541, and 3550B. See Section 25 for list of reference SOPs.

2. SUMMARY OF METHOD

2.1 A volume of sample extract in hexane is injected into a gas chromatograph (GC) and the compounds in the GC effluent are detected by an electron capture detector (ECD) and then analyzed.

3. SCOPE AND APPLICATION

3.1 Personnel: This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/electron capture detection (GC/ECD) systems and interpretation of complex chromatograms. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.2 Parameters: This method is used to determine the concentration of the various organochlorine pesticides listed in Section 5, Table 1: Analyte List and Reporting Limits, utilizing a gas chromatograph equipped with dual electron capture detectors. Reporting limits are subject to change based on current analytical system performance and actual sample matrices.

4. APPLICABLE MATRICES

4.1 This SOP is applicable to the analysis of organochlorine pesticides in aqueous, soils, solids, domestic and industrial wastes and biological samples.

5. LIMITS OF DETECTION AND QUANTITATION

5.1 The reporting limits (PQL) of this method for Organochlorine Pesticides are listed in Table 1 below. All current MDLs are listed in the LIMS and are available by request from the Quality Department.

Table 1: Analyte List and Reporting Limits

Compound	CAS #	Aqueous PQL (µg/L)	Solid PQL (µg/Kg)	Biota PQL (µg/Kg)
2,4'-DDD (o,p'-DDD)	53.19-0	0.05	1.7	2.5
2,4'-DDE (o,p'-DDE)	3424-82-6	0.05	1.7	2.5
2,4'-DDT (o,p'-DDT)	789-02-6	0.05	1.7	2.5
4,4'-DDD (p,p'-DDD)	72-54-8	0.10	3.3	5.0
4,4'-DDE (p,p'-DDE)	72-55-9	0.10	3.3	5.0
4,4'-DDT (p,p'-DDT)	50-29-3	0.10	3.3	5.0
Aldrin	309-00-2	0.050	1.7	2.5
alpha-BHC	319-84-6	0.050	1.7	2.5
alpha-Chlordane	5103-71-9	0.050	1.7	2.5
beta-BHC	319-85-7	0.050	1.7	2.5
cis-Nonachlor	5103.73-1	0.05	1.7	2.5
Delta-BHC	319-86-8	0.050	1.7	2.5
Dieldrin	60-57-1	0.10	3.3	5.0
Endosulfan I	959-98-98	0.050	1.7	2.5
Endosulfan II	33213-65-9	0.10	3.3	5.0
Endosulfan Sulfate	1031-07-8	0.10	3.3	5.0
Endrin	72-20-8	0.10	3.3	5.0
Endrin Aldehyde	7421-93-4	0.10	3.3	5.0
Endrin Ketone	53494-70-5	0.10	3.3	5.0
gamma-BHC (Lindane)	58-89-9	0.050	1.7	2.5
gamma-Chlordane	5103-74-2	0.050	1.7	2.5
Heptachlor	76-44-8	0.050	1.7	2.5
Heptachlor Epoxide	1024-57-3	0.050	1.7	2.5
Hexachlorobenzene	118-74-1	0.050	1.7	2.5
Methoxychlor	72-43-5	0.50	17	25
Mirex	2385-85-5	0.05	1.7	2.5
Oxychlordane	27304-13-8	0.05	1.7	2.5
Pentachloroanisole	1825-21-4	0.050	1.7	2.5
trans-Nonachlor	39765-80-5	0.05	1.7	2.5
Toxaphene	8001-35-2	3.0	100	150
Technical chlordane	57-74-9	1.0	33	50

6. INTERFERENCES

6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware. These interferences lead to discrete artifacts or elevated baselines in gas chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences by running reagent blanks and method blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates, which are easily extracted during laboratory operations. Avoiding the use of such plastics in the laboratory can best minimize interferences from phthalates.

6.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. Cleanup procedures such as Gel Permeation Chromatography (GPC), Florisil cartridge cleanup, Silica Gel Separation, and sulfur removal are available for the most common interference's encountered. These cleanup procedures are described separately in the most current revision or replacement of the laboratory SOPs: S-GB-O-032 *Gel Permeation Chromatography Clean-up by SW846 3640A*, S-GB-O-037, *Florisil Cartridge Clean-up for Organochlorine Pesticide Samples,* S-GB-O-038, *Silica Gel Clean-up for Organic Analysis* and S-GB-O-039 *Copper Clean-up for the Removal of Sulfur from PCB and Toxaphene Samples.*

7. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Table 2: Sample Collection, Preservation, Storage and Hold Time

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	One 1L amber glass	None	≤6°C	7 days
Soil/Solid (non-aqueous)	One 8oz wide glass amber jar	None	≤6°C	14 days
Biological Tissue	--	None	≤ -10°C	365 days or longer per client request prior to extraction, typical extraction hold time do not apply.
TCLP/SPLP	One 1L amber glass	None	≤6°C	14 days to leach, 7 days to for solvent extraction after the tumbling process has occurred.
Extracts	ONE 5 or 10mL glass amber vial.	None	≤6°C	40 days

8. DEFINITIONS

8.1 Refer to Section 10.0 of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

9. EQUIPMENT AND SUPPLIES (INCLUDING COMPUTER HARDWARE AND SOFTWARE)

9.1 Instrumentation

9.1.1 Gas Chromatograph: HP5890, HP6890 or HP7890 GC with dual electron capture detectors (or equivalent). The following are the gas chromatographic analytical conditions:

Table 3: Recommended Gas Chromatograph Operating Conditions

Operating Condition	40GCS6; HP5890	40GCSG; HP7890
Carrier Gas:	Helium 2.0 mL/min flow rate	Helium 2.0 mL/min flow rate
Make-up Gas:	Nitrogen 65 mL/min flow rate	Nitrogen 65 mL/min flow rate
Detector Temperature:	300°C	300°C
Injector Temperature:	200°C	200°C
Injection:	Splitless	Splitless
Injection Volume:	2 µL	2 µL
Initial Temperature:	180°C	130°C
Initial Hold Time:	1.0 min	0.5 min
Temperature Ramp:	20°C/min to 220°C, hold 1.0 min., 3°C/min to 226°C , hold 1.0 min, 20°C/min to 300°C, hold 2.8 min	20°C/min to 200°C, hold 0.0 min., 10°C/min to 230°C , hold 0.0 min, 20°C/min to 310°C, hold 3.0 min
Total Run Time:	13.5 min.	14.0 min.

9.1.2 GC Autosampler: HP7673A or HP 7693

9.1.3 Detector: ECD

9.1.4 Gas Chromatograph Columns: RTX-CLP, 30 m x 0.32 mm ID, .25µm film thickness (Restek or equivalent) and a RTX-CLP2, 30 m x 0.32 mm ID, .25 µm film thickness, (Restek, or equivalent). Other analytical columns may be used based on projects specific requirements. Columns are mounted in a dual GC/ECD with a single injection port/guard column connected to a glass Y-splitter.

9.1.5 Data Processor: ChemStation/HP Target

9.2 Glassware and Materials

9.2.1 Gastight Syringes – any size ranging from 10µL to 1000µL (Hamilton series 1000 or equivalent)

9.2.2 Autosampler Vials: 2 mL glass vials with crimp top caps.

9.2.3 Helium gas – Airgas Ultra high purity or equivalent

9.2.4 Nitrogen gas – Airgas Ultra high purity or equivalent

10. REAGENTS AND STANDARDS

10.1 Solvents – Hexane and acetone, pesticide grade.

Table 4: Solvents

Reagent	Purity	Manufacturer	Vendor	Catalog #	Expiration Date
Hexane	NS Grade	Burdick & Jackson	MG Scientific	B&J-217-4	Manufacturer Exp date or 2 year from receipt
Acetone	Pesticide Grade	Burdick & Jackson	MG Scientific	B&J-010-4	Manufacturer Exp date or 2 year from receipt

10.2 Stock Standard Solutions: Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or an independent source. Shelf life of standard solutions is 1 year from the date of preparation or the expiration date on the vendor label; whichever is earliest (see Table 5 for stock standards).

10.3 Calibration Standards: Single component standards are prepared from stock standard solutions at 5 concentration levels. One of the concentration levels should be at a concentration near, but above the method detection limit. Separate calibration standards are required for each multi-component target analyte (e.g. Toxaphene and Technical Chlordane). Shelf life of the calibration standards is 6 months from the date of preparation or the expiration date of the stock standard solution; whichever is earliest (see Table 6 for standard preparation.).

10.4 Surrogate Standards: Surrogate standards are used to monitor the performance of the method. They are added to all calibration standards. Shelf life of the surrogate standards is 6 months from the date of preparation or the expiration date of the stock standard solution; whichever is earliest (see Tables 5 and 6).

10.5 Performance Evaluation Mixture (PEM): A standard comprised of DDT and Endrin, which is analyzed at the beginning of every 12 hours to determine compound breakdown (see Tables 5 and 6).

Table 5: Stock Standards

Standard	Stock Standard	Conc.	Amount Used	Final Volume	Solvent Used	Final Conc.	Expiration Date
TCMX/DCB Stock	Restek Pesticide Surrogate Mix	200 µg/mL	1.0 mL	20 mL	Hexane	10 µg/mL	Manufacturer's recommended expiration date for unopened ampulated standards. 1 year after ampule is opened or on expiration date, whichever is sooner.
Pesticide A/B Stock	Restek Organochlorine A/B Mix	8-80 µg/mL	1.0	10 mL	-	0.8-8.0µg/mL	
Pesticide C-Mix Stock	O2Si	100µg/mL	1.0	50 mL	-	2.0µg/mL	
Tech. Chlordane Stock Solution	Restek Chlordane Mix	1000µg/mL	1.0	10 mL	-	100 µg/mL	
Toxaphene Stock	Restek Toxaphene Mix	1000µg/mL	1.0 mL	10 mL	Hexane	100 µg/mL	
Pesticide A/B ICV Stock	O2Si	0.4-4.0µg/mL	10.0 mL	200 mL	Hexane	0.4-4.0 µg/mL	
Pesticide C-Mix ICV Stock	Absolute Stds	100 µg/mL	1.0 mL	50 mL	Hexane	2.0 µg/mL	
Different Lot # than Calibration Std	Restek Toxaphene Mix	1000µg/mL	1.0 mL	10 mL	Hexane	100 µg/mL	
PEM Stock Solution	O2Si	200µg/mL	1.0 mL	20 mL	Hexane	10 µg/mL	

o2si and Restek Pesticide A/B contains alpha-BHC, beta-BHC, delta-BHC, gamma-BHC, Aldrin, Heptachlor, Heptachlor epoxide, Endosulfan I, Endosulfan II, Dieldrin, Endrin, Endrin aldehyde, Endosulfan sulfate, and Endrin ketone, 4,4'DDE, 4,4'-DDD, 4,4'-DDT alpha-chlordane, gamma-chlordane, and Methoxychlor.

Pesticide C-Mix contains 2,4'-DDT, 2,4'-DDD, 2,4'-DDE, Hexachlorobenzene, Pentachloroanisole, Oxychlordane, trans-Nonachlor, cis-Nonachlor, Mirex and Isodrin. Isodrin is not a reported compound.

Table 6: Preparation of Analytical Standard Solutions

Standard	Pesticide Stock Standard	Amount Used (µL)	Final Conc. (µg/mL)	Surrogate Stock Standard	Amount Used (µL)	Final Conc. (µg/mL)	Solvent Used	Final Volume (mL)	Expiration Date
PEST-1 & RLVS	Pesticide A/B Stock	250	0.0050-0.050	TCMX/DCB Stock	40	0.010	Hexane	40	6 months from preparation or the expiration date listed for the stock source, whichever is sooner.
PEST-2	Pesticide A/B Stock	250	0.010-0.10	TCMX/DCB Stock	40	0.020	Hexane	20	
PEST-3	Pesticide A/B Stock	500	0.020-0.20	TCMX/DCB Stock	100	0.050	Hexane	20	
PEST-4	Pesticide A/B Stock	1000	0.040-0.40	TCMX/DCB Stock	200	0.10	Hexane	20	
PEST-5	Pesticide A/B Stock	1000	0.080-0.80	TCMX/DCB Stock	120	0.12	Hexane	10	
PEST-4 ICV	Pesticide A/B ICV Stock	1000	0.040-0.40	TCMX/DCB Stock	100	0.1	Hexane	10	
INDC-1 & RLVS	Pesticide C-Mix Stock	50	0.005	TCMX/DCB Stock	20	0.010	Hexane	20	

Standard	Pesticide Stock Standard	Amount Used (µL)	Final Conc. (µg/mL)	Surrogate Stock Standard	Amount Used (µL)	Final Conc. (µg/mL)	Solvent Used	Final Volume (mL)	Expiration Date
INDC-2	Pesticide C-Mix Stock	100	0.010	TCMX/DCB Stock	40	0.020	Hexane	20	6 months from preparation or the expiration date listed for the stock source, whichever is sooner.
INDC-3	Pesticide C-Mix Stock	200	0.020	TCMX/DCB Stock	100	0.050	Hexane	20	
INDC-4	Pesticide C-Mix Stock	400	0.004	TCMX/DCB Stock	200	0.10	Hexane	20	
INDC-5	Pesticide C-Mix Stock	800	0.080	TCMX/DCB Stock	240	0.12	Hexane	20	
INDC-4 ICV	Pesticide C-Mix ICV Stock	400	0.040	TCMX/DCB Stock	200	0.1	Hexane	20	
TOX-1 & RLVS	Toxaphene Stock	75	0.3	TCMX/DCB Stock	12.5	0.005	Hexane	25	
TOX-2	Toxaphene Stock	125	0.5	TCMX/DCB Stock	25	0.01	Hexane	25	
TOX-3	Toxaphene Stock	375	1.5	TCMX/DCB Stock	50	0.02	Hexane	25	
*TOX-4	Toxaphene Stock	1200	3.0	TCMX/DCB Stock	200	0.05	Hexane	40	
TOX-5	Toxaphene Stock	1000	4.0	TCMX/DCB Stock	250	0.10	Hexane	25	
TOX-6	Toxaphene Stock	1250	5.0	TCMX/DCB Stock	375	0.15	Hexane	25	
TOX-4 ICV	Toxaphene ICV Stock	1200	3.0	TCMX/DCB Stock	200	0.050	Hexane	40	
TCHLOR-1 & RLVS	Technical Chlordane Stock	10	0.10	TCMX/DCB Stock	10	0.010	Hexane	10	
TCHLOR-2	Technical Chlordane Stock	20	0.20	TCMX/DCB Stock	20	0.020	Hexane	10	
TCHLOR-3	Technical Chlordane Stock	40	0.40	TCMX/DCB Stock	50	0.050	Hexane	10	
*TCHLOR-4	Technical Chlordane Stock	80	0.80	TCMX/DCB Stock	100	0.10	Hexane	10	
TCHLOR-5	Technical Chlordane Stock	100	1.0	TCMX/DCB Stock	120	0.12	Hexane	10	
PEM Working Standard	PEM Stock Solution	0.6 mL	0.15	NA	NA	NA	Hexane	40	

* Level used in 1 point calibration of multicomponent.

11. CALIBRATION AND STANDARDIZATION

11.1 Prime (or deactivate) the column by injecting a pesticide standard mixture at the high point in the calibration curve. Inject this standard mixture prior to beginning the initial calibration or calibration verification at the beginning of the analytical sequence.

11.2 A solvent blank may be run following the prime to verify there is no carryover or contamination introduced from the injection process. Solvent blanks may be placed into the analytical sequence at any position by the analyst to demonstrate that the analytical system is not contaminated. Solvent blanks, however, may not be routinely placed immediately prior to continuing calibration verification standards, PEM's, etc.

11.3 A Performance Evaluation Mixture (PEM), a standard comprised of DDT and Endrin, will be analyzed before samples are analyzed and at the beginning of every 12 hours for all methods except EPA 608. If the breakdown for either compound exceeds 15%, corrective action must be taken prior to calibration. Breakdown is calculated by the following equations:

$$\% \text{ Breakdown DDT} = \frac{\text{Response (DDD + DDE)}}{\text{Response (DDD + DDE + DDT)}} * 100$$

$$\% \text{ Breakdown Endrin} = \frac{\text{Response (Endrin aldehyde + Endrin Ketone)}}{\text{Response (Endrin + Endrin aldehyde + Endrin Ketone)}} * 100$$

11.3.1 The PEM standard is not analyzed when Toxaphene is the only analyte being quantified and reported from the analysis.

11.4 Initial Calibration: The initial calibration includes the analysis of five concentrations of each single component pesticide and surrogate compound and a single point calibration for each multi-component analyte (unless otherwise necessary for a specific project). See SW-846 Method 8000B for additional guidelines on proper initial calibration and calibration verification.

11.4.1 The initial calibration sequence contains the following injections that must be analyzed before any samples. (Sequence subject to change):

1. PEM
2. Toxaphene – LVL 4
3. T-Chlordane – LVL 4
4. Pesticide A/B Mix #5
5. Pesticide A/B Mix #4
6. Pesticide A/B Mix #3
7. Pesticide A/B Mix #2
8. Pesticide A/B Mix #1
9. Pesticide C Mix #1
10. Pesticide C Mix #2
11. Pesticide C Mix #3
12. Pesticide C Mix #4
13. Pesticide C Mix #5
14. Hexane
15. PEM
16. CRDL AB (RVLS)
17. CRDL C (RVLS)
18. Initial Calibration Verification –A/B Mix
19. Initial Calibration Verification – C Mix

11.5 Initial Calibration Acceptance Criteria

11.5.1 Linear Calibration using Average Response Factors: Calculate the response factor (RF) for each analyte at each concentration, the mean response factor, and the relative standard deviation (RSD) of the response factors using the formulas below.

$$\text{Response Factor (RF)} = \frac{\text{Peak Area}}{\text{Standard concentration (µg/mL)}}$$

$$\%\text{RSD} = \frac{\text{Standard Deviation}}{\text{Average Response Factor}}$$

11.5.2 For SW846 8081A/B: Any target analyte which has calibration factors with a relative standard deviation (RSD) of less than 20% is considered valid and the average response factor may be used for quantitation purposes. If the %RSD exceeds 20%, the analyst must use linear regression for determining analyte concentrations.

11.5.3 For EPA 608: Any target analyte which has calibration factors with a relative standard deviation (RSD) of less than 10% is considered valid and the average response factor may be used for quantitation purposes. If the %RSD exceeds 10%, the analyst must use linear regression for determining analyte concentrations.

11.5.4 If linear regression is used, the intercept should not be forced through the origin. The regression calculation will generate a correlation coefficient "r". In order to be used for quantitative purposes the r-value must be greater than 0.99.

11.5.5 All initial calibration and calibration verification criteria apply to both analytical columns.

11.5.6 The initial calibration may continue to be used as long as the analytical system meets acceptance criteria. If the technical acceptance criteria for the initial calibration are not met, inspect the system for problems. Perform instrument maintenance as necessary and recalibrate the instrument.

11.6 Initial Calibration Verification

11.6.1 To ensure the calibration standards are at the correct concentration, an initial calibration verification (ICV) will be analyzed against the initial calibration curve prior to the analysis of samples. The ICV is a midpoint of the Pesticide A/B Mix, (and Pesticide C Mix if included in the initial calibration) and must be from a different source or from a different lot number from the same vendor.

11.6.1.1 For SW846 8081A: The difference between each individual compound response of the ICV and initial calibration standard must be within 15% of one another on the basis of each compound or the average across all compounds.

11.6.1.2 For SW846 8081B: The difference between each individual compound response of the ICV and initial calibration standard must be within 20% of one another.

11.6.1.3 For EPA 608: The difference between each individual compound response of the ICV and initial calibration standard must be within 15% of one another.

11.6.2 The injection of the first ICV begins the 12-hour clock in which samples may be analyzed.

11.7 Continuing Calibration Verification

11.7.1 Continuing Calibration Verification (CCV) will include the injection of the PEM standard, midpoint calibration checks of the Pesticide A/B Mix, and Pesticide C Mix if included in the sample analyte list.

11.7.2 A PEM and CCV must be analyzed every 12 hours or 20 samples, whichever is more frequent. It is recommended that calibration verification be performed after every 10 samples to minimize reruns due to calibration verification failure.

11.7.2.1 For SW846 8081A: The difference between each individual compound response of the CCV and initial calibration standard must be within 15% of one another on the basis of each compound or the average across all compounds.

11.7.2.2 For SW846 8081B: The difference between each individual compound response of the CCV and initial calibration standard must be within 20% of one another.

11.7.2.3 For EPA 608: The difference between each individual compound response of the CCV and initial calibration standard must be within 15% of one another.

11.7.3 Sample data is not acceptable unless bracketed by acceptable analyses of a CCV. Any samples not bracketed by an acceptable CCV must be reanalyzed. The ending PEM of a sequence may fail breakdown and samples can be reported.

11.8 Initial Calibration Verification and Continuing Calibration Verification Acceptance Criteria

11.8.1 The percent difference (%D) is determined for all analytes in the ICV/CCV. The individual compound %D must be within the above listed method criteria of the calibration curve for each analyte.

$$\%D = \frac{R_2 - R_1}{R_2} * 100$$

Where: R_1 = Theoretical Value
R_2 = Calculated Amount

The analyst should verify that the software is using appropriate values for calculations.

11.8.2 If the acceptance criteria for the ICV is not met, inspect the gas chromatographic system for problems. Re-inject the standard; if acceptance criteria is not met, then a new initial calibration must be performed.

11.8.3 Results may be reported for CCV failures, biased high, if failed compounds are not detected in samples.

11.8.4 Any analyte, for any reason, not meeting the CCV acceptance criteria must be qualified, if reported to the client.

11.9 Retention Time Windows

11.9.1 Retention time windows are determined for all single and multi-components analytes.

11.9.1.1 Make at least four injections of all analytes of interest over a 72-hour period.

11.9.1.2 Record the retention time (RT) for each analyte, and selected peaks for multi-component analytes, to three decimal places. Calculate the mean and standard deviation for each peak.

11.9.1.3 The width of the retention time window is defined as $\pm$ 3 standard deviations of the mean established. The minimum retention window will be $\pm$ 0.030 minutes.

11.9.1.4 Establish the center of the RT window for each analyte and surrogate using the absolute RT from the calibration verification standard at the beginning of the analytical shift. Optionally, the initial calibration retention time windows may continue to be used as long as the method criteria are met. For samples run during the same shift as an initial calibration, use the RT of the mid-point standard in the initial calibration.

11.9.1.5 RT windows must be calculated on each column and instrument when a new GC column is installed. Additional guidance is provided in SW846 8000B.

11.9.2 The retention time of each analyte must fall within its respective retention time window for all standards. If not, the gas chromatographic system must be evaluated. Re-inject the standard; if not acceptable then a new calibration must be performed.

11.10 Reporting Limit Verification Standard (RVLS) – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration and monthly thereafter. Recovery must be 60-140% of true value to be accepted. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

12. PROCEDURE

12.1 Sample Analysis

12.1.1 For SW846 8081A/B a matrix spike/matrix spike duplicate must be prepared and analyzed at least once for each matrix type per every twenty samples. For EPA 608 a matrix spike/matrix spike duplicate must be prepared and analyzed at least once for each matrix type per every ten samples. The sample use for the MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows. If insufficient sample volume is available to perform a MS/MSD, a laboratory control spike and laboratory control spike duplicate will be used instead.

12.1.2 Analysis of a sample on both GC columns is required for all samples, blanks, matrix spikes, matrix spike duplicates and laboratory control samples.

12.1.3 The laboratory will identify and quantify peaks based on RT and the average calibration factor established during the initial calibration sequence.

12.1.4 The PEM and Continuing calibration verification are analyzed every 20 samples (not to exceed 12 hours) or less during an analytical sequence in order to monitor retention times, calibration factors, and column performance. (It is recommended that calibration verification be performed after every 10 samples to minimize reruns due to calibration verification failure.) Sample data can be collected only as long as the results for this standard fall within the defined limits. If two consecutive unacceptable standards are run, all extracts run since the previous acceptable standards must be reanalyzed. The ending PEM of the sequence is allowed to fail.

12.1.5 Failure to meet any of the criteria established in this method must be thoroughly documented, and technical justification for the validity of the data must be presented to the section supervisor.

12.2 Quantitation of Analytes

12.2.1 Analytes must be quantified with a laboratory data system. Peak area is the basis for quantitation.

12.2.2 Quantitation of *single response pesticides* and surrogate standards is performed using the column designated as the primary column. This column will generally be the RTX-CLP, however, the analyst may specify either column as the primary column. The primary column must be used unless there is a documented reason (i.e. interference) for using the confirmation column for quantitation.

12.2.2.1 The identification and quantification of peaks is based on RT and the average calibration factor established during the initial calibration sequence.

12.2.2.2 A tentative identification of an analyte occurs when a peak from a sample extract falls within the retention time window. Each tentative identification must be confirmed by a second GC column of dissimilar stationary phase.

12.2.2.3 Quantitation of *multi-response analytes* can be done this way. The analyst may choose 4 to 6 of the largest peaks for quantitation. The peaks chosen for quantitation should have minimal co-elution with other peaks in the chromatogram. Use each peak chosen in the standard to calculate a calibration factor for that peak. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the 4 to 6 resulting concentrations are averaged to provide the final result for the multi-response analyte in the sample.

13. QUALITY CONTROL

13.1 Method Blanks

13.1.1 Method blanks are an analyte-free matrix spiked with surrogate solution, extracted, and analyzed by the same procedure that is used with the associated samples.

13.1.1.1 In order to be acceptable, a method blank analysis cannot contain any of the analytes listed in this method above the reporting limit. All samples associated with a contaminated method blank must be re-extracted and reanalyzed unless the analyte concentration in the sample is greater than 20 times the amount found in the method blank, the analyte is not detected in the associated sample, or other approval is given directly by the supervisor.

13.1.2 The surrogate retention times must be within the retention time windows for both tetrachloro-m-xylene and decachlorbiphenyl. The surrogate recovery limits are established annually and distributed in the analytical laboratory. When surrogate recoveries in the method blank do not meet the recovery limits, the method blank is reanalyzed and/or the samples re-extracted.

13.2 Matrix Spike/Matrix Spike Duplicate

13.2.1 The analyte and surrogate retention times must be within the windows specified during the initial calibration or current continuing calibration.

13.2.2 The percent recovery and the relative percent difference between the recoveries of each of the compounds in the matrix spike samples will be calculated and reported by using the following equations:

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:
SSR = Spike sample result
SR = Sample result
SA = Spike added

$$RPD = \frac{|MSR - MSDR|}{1/2\,(MSR + MSDR)} \times 100$$

Where:
RPD = Relative percent difference
MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

13.2.3 The limits for matrix spike/matrix spike duplicate compound recoveries and RPD limits are established and distributed in the analytical area. Failure to meet these limits requires corrective action by the laboratory in accordance with S-GB-Q-027 *Corrective Action / Preventative Action Process*, most current revision or replacement.

13.3 Laboratory Control Spike

13.3.1 The percent recoveries and the relative percent difference between the recoveries of each of the compounds in the LCS/LCSD will be calculated and reported using the following equation:

$$\text{LCS/LCSD Recovery} = \frac{\text{LCSR}}{\text{SA}} \times 100$$

Where: LCSR = Lab control spike/duplicate recovery
SA = Spike added

$$\text{RPD} = \frac{|\text{LCSR} - \text{LCSDR}|}{1/2\,(\text{LCSR} + \text{LCSDR})} \times 100$$

Where: RPD = Relative percent difference
LCSR = Laboratory control spike recovery
LCSDR = Laboratory control spike duplicate recovery

13.3.2 The limits for LCS/LCSD compound recoveries and RPD limits are established and distributed in the analytical area. Due to number of analytes fortified into the LCS, a small percentage of sporadic marginal failures may be tolerated (i.e. will not trigger re-extraction and analysis of the entire batch.) If more than 10% of the analytes are outside of the control limits, the samples are re-extracted or re-analyzed. For EPA 608 the limits must be met in EPA Method 608, Table 3.

13.4 Surrogate recoveries

13.4.1 Surrogate recoveries must be evaluated using laboratory established control limits. If both surrogate recoveries fail these criteria, re-extract the sample. One surrogate is allowed to be outside of the control limits.

13.4.2 Surrogates are not evaluated in samples where the surrogates are diluted below the low level standard concentration of the surrogates.

13.4.3 Surrogate recoveries will be calculated and reported using the following calculation:

$$\textbf{S}\text{urrogate Percent Recovery} = \frac{Q_d}{Q_a} \times 100$$

Where: Q_d = Quantity determined by analysis
Q_a = Quantity added

14. DATA ANALYSIS AND CALCULATIONS

14.1 Calculations

Aqueous samples:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(V_t)(D)}{(Cf)\,(V_i)}$$

Soil, Solid, Biota samples:

$$\text{Concentration } (\mu g/Kg) \text{ (Dry weight basis)} = \frac{(A_x)(V_t)(D)}{(Cf)(W)(S)}$$

Where:
- A_x = Area or peak height for an analyte
- V_t = Final volume of extract in mL
- D = Dilution factor
- Cf = Average calibration factor
- W = Initial sample weight (Kg)
- Vi = Initial sample volume (L)
- S = %Solids/100

Biota samples are typically reported on an "as is" or wet weight basis. The dry weight correction portion of the formula is typically not utilized.

14.2 Data Evaluation

14.2.1 For samples where a second analysis is performed at a dilution, the results that are reported from the second analysis are qualified with a "D".

14.2.2 The analyst should compare the analyte concentrations between the two columns used for analysis. The RPD between the two columns should be < 40. If the RPD between the two results is greater than 40 but less than or equal to 100 the analyst should evaluate the chromatogram for interfering peaks that are co-eluting with the analyte. If an interference is determined to be present, report the lower of the two values and qualify the result with a "P" data qualifier. If no interference is determined to be present, report the higher of the two values and qualify the result with a "P" data qualifier.

14.2.3 Additional data qualifiers may be used dependent upon project specific requirement.

15. DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

15.1 See Section 13 and Table 7 Below:

Table 7: Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples, per matrix.	Target analytes must be less than reporting limits	Re-extract and re-analyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analytes	One per preparation batch of up to 20 samples, per matrix.	SW846 8081A/B: Lab Generated Limits EPA 608: Attachment I, Method 608 Table 3, Range for Ps. Refer to the LIMS for acceptance limits.	Re-extract and re-analyze associated samples if original LCS is outside acceptance limits. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analytes	SW846 8081A/B: One MS/MSD set per preparation batch of up to 20 samples or one spiked sample per month. (EPA 608 one set for every 10 samples).	SW846 8081A/B: Lab Generated Limits EPA 608: Attachment I, Method 608 Table 3, Range for P. Refer to the LIMS for acceptance limits.	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Surrogate	Applicable surrogate compound	Added to each sample, standard and method blank	Lab-generated limits Refer to the LIMS for acceptance limits.	Samples with surrogate failures must be re-extracted and reanalyzed. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported surrogate data must be qualified. 2) If surrogate result is >QC limits, and sample results are non-detect, the sample results may be reported without qualifiers. The surrogate must be qualified. 3) MS/MSD surrogate recovery failures do not constitute the re-extraction or reanalysis of samples but the surrogate data must be qualified.

16. CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

16.1 See Section 13 and Table 7.

17. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

17.1 See Section 13 and Table 7.

18. METHOD PERFORMANCE

18.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

18.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

18.1.2 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedures,* most current revision or replacement. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

18.1.3 An annual method detection limit (MDL) study will be completed per S-GB-Q-020, *Determination of the LOD and LOQ,* most current revision or replacement, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

18.1.4 Periodic performance evaluation (PE) samples are analyzed per S-GB-Q-021, *PE/PT Program*, most current revision or replacement to demonstrate continuing competence. All results are stored in the QA office.

19. METHOD MODIFICATIONS

19.1 Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.

19.2 All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.

19.3 Procedures identified as “Best Practices” by PACE 3P Programs will be incorporated into this document as minimum requirements for Pace Laboratories.

19.4 SW846 8081A and 8081B is a method written for aqueous and solid matrices, the laboratory has modified the method to accommodate biological tissues.

19.5 If a client fails to provide sufficient volume for the method required Matrix Spike/Matrix Spike Duplicate (MS/MSD), the laboratory will analyze a Laboratory Control Spike Duplicate to demonstrate precision. The analytical batch will be qualified with the “M5” data qualifier.

20. INSTRUMENT/EQUIPMENT MAINTENANCE

20.1 Any daily or periodic maintenance must be recorded in the instrument daily logbook. Additional information may be found in the most current revision of SOP: S-GB-Q-008, *Preventative, Routine, and Non-routine Maintenance.*

21. TROUBLESHOOTING

21.1 Please see the instrument operating manual for information on instrument troubleshooting.

22. SAFETY

22.1 **Standards and Reagents** - The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Standard solutions should be prepared in a hood.

22.2 **Samples** - Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

22.3 A reference file of Safety Data Sheets (SDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training.

23. WASTE MANAGEMENT

23.1 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of S-GB-W-001, *Waste Management and Handling*, most current revision or replacement.

24. POLLUTION PREVENTION

24.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

24.2 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

25. REFERENCES

25.1 Pace Quality Assurance Manual- most current version.

25.2 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.3 USEPA, SW-846, Method 8000C, Revision 3, March 2003.

25.4 USEPA, SW-846, Method 8081A, Revision 1, December 1996.

25.5 USEPA, SW-846, Method 8081B, Revision 2, February 2007

25.6 40CFR, Part 136, Appendix A, EPA Method 608.

25.7 S-GB-O-053 (most current revision or replacement), *Separatory Funnel Extraction by SW846 3510C.*

25.8 S-GB-O-054 (most current revision or replacement), *Ultrasonic Extraction by SW846 3550B.*

25.9 S-GB-O-031 (most current revision or replacement), *Extraction of Biological Samples for Organochlorine Pesticides/PCBs.*

25.10 S-GB-O-043 (most current revision or replacement), *Extraction of Toxaphene Using Automated Soxhlet.*

26. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ADDENDA, ETC.

26.1 Attachment I: EPA Method 608, Table 3.

27. REVISIONS

SOP Number	Revision	Date
S-GB-O-027-Rev.03	Updated Signature Page. Section 9.3 & 9.4 – Update expiration dates. Section 9 – Table 1 – Updated with current information. Section 9 – Table 2 – Updated with current information. Section 9 – Table 3 – Updated with current information. Updated Section 10. Section 11.1.4 – Added PEM information. Section 11.4.3 – Deleted. Section 16 – Appendix A updated.	April 30, 2009
S-GB-O-027-Rev.05	Throughout Document: Updated Waste Handling and Management SOP to S-GB-S-006 Throughout Document: Removed all references to State of South Carolina criteria. Section 10.6.1 and 10.8.1: Added language of the acceptance criteria being the average of all compounds reported must be <15%. Section 11.2.3.2: Deleted Section 11.3 Calculations: Removed GPC From Calculation, it is a 1:1 dilution.	13Jul2011
S-GB-O-027-Rev.06	General: Updated SOP format Updated SOP references throughout document. Throughout Document: Added language to address update to MUR and SW846 8081B..	13Jan2014
S-GB-O-027-Rev.07	Table 2: Included TCLP/SPLP Leach hold-times. Table 3: Updated to include 40GCSG. Table(s) 4 and 5: Updated to current standard amounts and concentrations. Section 11.6.1: Clarified second source requirement. Section 11.8.3: Added additional CCV requirement. Section 25: Included Pace and TNI references.	10Dec2014
S-GB-O-027-Rev.08	Title Page, Section 1.1 and 25: Added EPA 608 References. Section(s) 11.3, 11.5, 11.6, 11.7: Added EPA 608 Method requirements. Section 12.1.1: Added MS/MSD per every 10 samples. Table 7: Added. Section 13.2.3: Updated SOP reference. Attachment I: EPA 608, Table 3 added..	17Jun2015

Attachment I: Method 608 Table 3

Table 3—QC Acceptance Criteria—Method 608

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for P, P_s %)
Aldrin	2.0	0.42	1.08 - 2.24	42 - 122
α-BHC	2.0	0.48	0.98 - 2.44	37 - 134
β-BHC	2.0	0.64	0.78 - 2.60	17- 147
δ-BHC	2.0	0.72	1.01 - 2.37	19 - 140
γ-BHC	2.0	0.46	0.86 - 2.32	32 - 127
Chlordane	50	10.0	27.6 - 54.3	45 - 119
4,4'-DDD	10	2.8	4.8 - 12.6	31 - 141
4,4'-DDE	2.0	0.55	1.08 - 2.60	30 - 145
4,4'-DDT	10	3.6	4.6 - 13.7	25 - 160
Dieldrin	2.0	0.76	1.15 - 2.49	36 - 146
Endosulfan I	2.0	0.49	1.14 - 2.82	45 - 153
Endosulfan II	10	6.1	2.2 - 17.1	D - 202
Endosulfan Sulfate	10	2.7	3.8 - 13.2	26 - 144
Endrin	10	3.7	5.1 - 12.6	30 - 147
Heptachlor	2.0	0.40	0.86 - 2.00	34 - 111
Heptachlor epoxide	2.0	0.41	1.13 - 2.63	37 - 142
Toxaphene	50.0	12.7	27.8 - 55.6	41 - 126
PCB-1016	50	10.0	30.5 - 51.5	50 - 114
PCB-1221	50	24.4	22.1 - 75.2	15 - 178
PCB-1232	50	17.9	14.0 - 98.5	10 - 215
PCB-1242	50	12.2	24.8 - 69.6	39 - 150
PCB-1248	50	15.9	29.0 - 70.2	38 - 158
PCB-1254	50	13.8	22.2 - 57.9	29 - 131
PCB-1260	50	10.4	18.7 - 54.9	8 - 127

$\bar{s}$ = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).
P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).
D = Detected; result must be greater than zero.

NOTE: These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

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STANDARD OPERATING PROCEDURE

Extraction of PCBs Using the Automated Soxhlet

Reference Methods: SW-846 Method 3541

SOP NUMBER:	S-GB-O-041-REV.07
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-O-041-REV.06

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 04/20/17

Kate Verbeten, Laboratory Quality Manager — Date: 4/20/17

Chris Haase, Department Manager — Date: 4/20/17

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

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

Table of Contents

1. PURPOSE / IDENTIFICATION OF METHOD

1.1 The purpose of this Standard Operating Procedure (SOP) is to describe the extraction of soil and sediment samples compliant with SW-846 Method 3541 prior to PCB analysis.

2. SUMMARY OF METHOD

2.1 A measured mass of sample, typically 10 grams, is mixed with sodium sulfate until it is free flowing. The sample mixture is transferred into a cellulose extraction thimble. The thimbles are placed in extraction beakers and solvent is added. The beakers are loaded into the automated soxhlet unit. The samples are subjected to a pre-programmed heat and pressure extraction cycle, which isolates the organic components from the sample mixture by contact with the solvent. The extract is concentrated to a final volume and subjected to necessary cleanups prior to analysis, as needed.

3. SCOPE AND APPLICATION

3.1 This procedure is applicable to extraction and concentration of PCBs from soil or sediment samples. Extracts may be prepared by this method for analysis by SW-846 Method 8082/8082A as per the latest revision of Pace Analytical Services, LLC's SOP S-GB-O-026, *Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography,* S-GB-O-047, *Analysis of Polychlorinated Biphenyls (PCB's) by Gas Chromatography by 8082A* and S-GB-048, *Analysis of Fox River Polychlorinated Biphenyls (PCBs) by Gas Chromatography*.

3.2 The policies and procedures contained in this SOP are applicable to all personnel involved in the preparation of extracts for chromatographic analysis.

4. APPLICABLE MATRICES

4.1 This procedure is applicable to extraction and concentration of PCBs from soil or sediment samples.

5. LIMITS OF DETECTION AND QUANTITATION

5.1 Not Applicable to this SOP.

6. INTERFERENCES

6.1 Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

6.2 Interferences co-extracted from samples will vary considerably depending on the source of the material. Contaminants that may interfere with the analysis may be removed from the extracts using any combination of cleanups including, but not limited to, Florisil slurry, Copper cleanup, and Sulfuric Acid cleanup. These cleanup procedures are described in separate SOPs.

7. SAMPLE COLLECTION, PRESERVATION, AND SHIPMENT AND STORAGE

TABLE 7.1: Sample Collection, Preservation, Shipment, Storage and Hold time

Sample type	Container	Preservation	Shipment	Storage	Hold time
Solid/Sludge	Amber Glass with Teflon lined lids	≤6°C	≤6°C, State of WI: Received on Ice	≤6°C	Must be extracted within 365 days of collection.
Extracts	Glass with Teflon lined lids	NA	NA	≤6°C	Must be analyzed within 365 days of extraction.

8. DEFINITIONS

8.1 Refer to the Glossary Section of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

9. EQUIPMENT AND SUPPLIES

Table 9.1: Equipment

Equipment	Manufacturer	Model(s)	Serial #	Description / Comments
Computer	-Lenovo	E530C	00371-OEM-8992671-00437	Balance to Computer Interface Connection
Analytical Balance	OHAUS Corp.	AR5120	D3191218320-780	Capable of weighing 300g ± 0.01g
Soxtherm Extractor with Controllers	Gerhardt	SE-30 SE-416	Various	With Controller
Turbo Vap II Concentration Station	Zymark	NA	Various	
NIST Verified Thermometer	Fisher Scientific	15-077-61	NA	Stem Range -50 +300˚C

Table 9.2: General Supplies

Supply	Vendor*	Model / ID	Catalog #	Description
Beaker	VWR	150mL Plastic	414004-147	
Spatulas	Fisher	Stainless Steel	14-375-20	NA
Copper BBs	Walmart	Crossman Copperhead	NA	Copper plated, pre-cleaned prior to use.
Glass Extraction beakers	VWR	54x130	14236-107	For Soxtherm Unit
Wire Thimble holders	Sinkler	NA	NA	Made in-house
Cellulose Extraction Thimbles	Whatman	Item 84	2800338	ID33mm, OD37mm, L80mm
Gastight syringes	Fisher	250-µL 500-µL 1,000-µL	14-684-102 13-684-106 14-824-25	Hamilton Gastight syringes
Funnels	HGF Scientific Fisher	Pyrex	NA	Glass funnel Powder funnel
Disposable Pasteur pipettes	MG Scientific	5 3/4” 9”	P200-1 P200-2	Glass
Turbo Vap tubes	Biotage	Turbovap	C103187	200mL with 1mL endpoint stem
Turbo Vap Rack	Biotage	Inert Stainless Steel	C42567	Auxiliary rack 200mL for Evap tubes
Boiling Chips	Fisher	09-191-20	See Model	450 g
Glass Culture Tubes	MG Scientific	9mL CG 15mL CG	T102-1CS T102-3CS	PTFE screw cap lined lids
Wash bottles, PTFE	Fisher	NA	NA	One for each solvent

10. REAGENTS AND STANDARDS

Table 10.1: Reagents

Reagent	Concentration/ Description	Requirements/ Vendor/ Item #*	Expiration Date
Sodium Sulfate	Certified A.C.S. Anhydrous (10-60 mesh), granular, baked at 400°C for 4 hours before use following Pace Analytical Services, Inc SOP: S-GB-O-028, *Preparation of Anhydrous Sodium Sulfate, Sand, and Glass Wool for Extraction Purposes*.	MG Scientific / catalog # 3375-09	Manufacturer's recommended expiration date or 5 years from receipt, whichever is sooner.
Ottawa Sand	Analyte-free, mesh size 20-30, baked at 400°C for 4 hours before use following Pace Analytical Services, Inc SOP: S-GB-O-028, *Preparation of Anhydrous Sodium Sulfate, Sand, and Glass Wool for Extraction Purposes*.	Fisher Brand S23-3	
Methylene Chloride	Extraction solvent / Burdick & Jackson, pesticide grade or equivalent	Fisher Scientific / 010-4	
Hexane	Extraction solvent / JT Baker, pesticide grade or equivalent	Avantor / Material # 9262-03	
Acetone	Standard solvent / Burdick & Jackson, pesticide grade or equivalent	Fisher Scientific / 010-4	
Deionized Water	Type I ASTM	---	NA

10.2: PCB Stock Standards

Standard	Components	Conc. (µg/mL)	Vendor	Catalog #	Storage	Expiration Date
PCB Standard	AR1016/1260 AR1242 AR1248 AR1254 AR1260	1000	O2Si	130011-03 03027S-07 030276-15 030277-06-5PAK 030278-05	Ambient	Manufacturer's recommended expiration date for unopened ampulated standards. 6 month after ampule is opened or on expiration date, whichever is sooner.
Surrogate	Tetrachloro-m-xylene (TMX) Decachlorobiphenyl (DCB)	2000	O2Si	130023-15	Refrigerate ≤6°C	

Table 10.3: Spiking Solutions

Standard	Stock Standard	Conc. (µg/mL)	Amount Used (mL)	Final Volume	Solvent Used	Final Conc.	Expiration Date

				(mL)		(µg/mL)	
Surrogate spiking solution	TMX DCB	2000	1.0	1000	Acetone	2.0	6 months after made date or on expiration date, whichever is sooner
PCB Matrix Spike	One of either Aroclor 1016, 1242, 1248, 1254, or 1260 or any combination*	1000	1.0	200	Acetone	5.0	

Historical data or requirements of specific projects may determine the analytes and concentrations added to the sample spikes.

11. CALIBRATION

11.1 Refer to the most current version of S-GB-Q-030, *Support Equipment*, for the proper procedure to calibrate the analytical balance.

12. PROCEDURE

12.1 As Received Sample Extraction

12.1.1 Rinse the soxhlet extraction beakers with 4:1 Hexane/Acetone. Label with sample identification. Add boiling chips or copper BBs to the bottom and set aside.

12.1.2 Weigh approximately 10g of sample into a 150 mL plastic beaker. Record the mass of the sample in the electronic prep log to the nearest tenth of a gram. Repeat the process for all samples and quality control samples. Ottowa sand is used as the matrix for the quality control samples. In cases where samples received are powdery or dry, samples may be weighed directly into the cellulose thimble and automated soxhlet extraction beaker

12.1.3 Add enough anhydrous sodium sulfate to each beaker while mixing to create a dry, free-flowing mixture. The sample should appear granular.

12.1.4 Transfer the mixture from the 150 mL plastic beaker to a cellulose extraction thimble. Place the thimble in an automated soxhlet extraction beaker equipped with a wire thimble holder. Transfer all samples and quality control samples using the same process. Label each extraction beaker with the LIMs number or quality control measure identifier.

12.1.5 Spike each thimble with 500 µL of 2.0 µg/mL surrogate spiking solution. Apply directly to dried sample in thimble.

12.1.6 Spike each laboratory control spike (LCS) and matrix spike (MS/MSD) with 1 mL of 5.0 µg/mL PCB Matrix Spike solution. The volume and concentration of the matrix spiking solution may vary depending on the project requirements**.**

12.1.7 Push the wire thimble basket down into the extraction beaker.

12.1.8 Dispense approximately 140 mL of 4:1 hexane/acetone into the side of the automated extraction solvent beaker, allowing the solvent to overflow the top of the soil but below the top of the thimble.

12.1.9 Load the extraction beakers onto the automated soxhlet unit

12.2 Air-Dry Sample Extraction

12.2.1 Rinse the soxhlet extraction beakers with 4:1 Hexane/Acetone. Label with sample identification. Add boiling chips or copper BBs to the bottom and set aside.

12.2.2 Label each extraction beaker with the LIMs number or quality control measure identifier.

12.2.3 Weigh approximately 10g of sample directly into cellulose extraction thimble in an automated soxhlet extraction beaker equipped with a wire thimble holder. Record the mass of the sample in the extraction log to the nearest tenth of a gram. Repeat the process for all samples and quality control samples. Ottowa sand is used as the matrix for the quality control samples.

12.2.4 Add enough anhydrous sodium sulfate to cover the top of the soil.

12.2.5 Spike each thimble with 500 µL of 2.0 µg/mL surrogate spiking solution. Apply directly to dried sample in thimble.

12.2.6 Spike each laboratory control spike (LCS) and matrix spike (MS/MSD) with 1 mL of 5.0 µg/mL PCB Matrix Spike solution. Alternatively, a sample duplicate may be required in place of the matrix spike duplicate. The volume and concentration of the matrix spiking solution may vary depending on the project requirements**.**

12.2.7 Push the wire thimble basket down into the extraction beaker

12.2.8 Slowly dispense approximately 140 mL of 4:1 hexane/acetone into the cellulose extraction thimble contained in the automated soxhlet extraction beaker.

12.2.9 Load the extraction beakers onto the automated soxhlet unit.

12.2.10 Verify the automated soxhlet extraction settings (program 02) as summarized here.

Extraction temperature	180°C
Boil Time	45 min
Solvent Reduction	2 x 15 mL
Extraction Time	45 min
Cycle Time	1 hour 38 minutes
Solvent	4:1 Hexane/Acetone

12.2.11 Start the extraction process. Rotate the extraction beakers slightly to insure seal of top o-ring. The process will produce approximately 90 mL of extract.

12.2.12 Turn on the power to the TurboVap. Turn on the nitrogen flow to 16 psi. Allow the TurboVap to warm to 55°C.

12.2.13 Record the temperature in the electronic prep log.

12.2.14 Transfer the extracts from the extraction beakers to labeled TurboVap tubes. Rinse the extraction beaker with hexane and add the rinse to the TurboVap tubes. Concentrate the extracts to less than 10 mL. Remove from the TurboVap.

12.2.15 Quantitatively transfer the extracts to labeled vials. Adjust the final volume to 10 mL using hexane.

12.3 Extract Cleanups

12.3.1 Copper BBs that are added to the extraction vessel must be cleaned before use. The BBs will be placed in a metal bowl that has been rinsed with Methylene Chloride. Methylene Chloride is then added to the bowl until all of the BB's are covered in solvent. The mixture is then stirred to ensure that all of the BBs surface area has made contact with the solvent. Let the mixture stand for 1 minute. Decant the solvent using a Buchner funnel and 1000 mL side arm flask. Repeat this procedure one more time. A third rinse will be performed but this time Hexane will be substituted for the Methylene Chloride. Allow the BBs to air dry before storing them in a glass jar that has been labeled with the standard log number and cleaning date.

12.3.2 Extracts are Sulfuric Acid.

12.3.3 Additional cleanups may be performed, refer to the Florisil Cleanup SOP.

13. QUALITY CONTROL

13.1 One method blank is extracted with each extraction batch of 20 or fewer samples of the same matrix. .

13.2 A laboratory control spike is extracted with each extraction batch of 20 or fewer samples of the same matrix.

13.3 A matrix spike and a matrix spike duplicate must be performed with each extraction batch when appropriate sample volume is present, otherwise a laboratory control spike duplicate will be performed. Matrix spikes are used to indicate matrix effects on the analysis of the analytes of interest. The sample used for the MS/D pair is either determined by the client or selected at random from client samples as sample volume allows.

13.4 Surrogate standards must be added to all samples, laboratory control spikes, matrix spikes, and method blanks prior to extraction. Surrogates are used to monitor the efficiency of the method on each sample and possible matrix related effects.

13.5 All quality control samples (MB, LCS, MS, MSD, and duplicate samples) must undergo the same preparation and cleanup methods as the samples in the batch. The acceptance criteria and corrective actions are described in the determinative method SOPs.

14. DATA ANALYSIS AND CALCULATIONS

14.1 Not Applicable to this SOP.

15. DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

15.1 Not Applicable to this SOP.

16. CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

16.1 Not Applicable to this SOP.

17. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

17.1 Not Applicable to this SOP.

18. METHOD PERFORMANCE

18.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Quality Manual.

18.2 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

18.3 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedure*s. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

18.4 An annual method detection limit (MDL) study will be completed per S-GB-Q-020, *Determination of the LOD and LOQ*, most current revision or replacement, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

18.5 Periodic performance evaluation (PE) samples are analyzed per S-GB-Q-021, *Proficiency Testing Program*, most current revision or replacement, to demonstrate continuing competence. All results are stored in the quality assurance office.

19. METHOD MODIFICATIONS

19.1 Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure

19.2 All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.

19.3 Procedures identified as “Best Practices” by PACE 3P Programs will be incorporated into this document as minimum requirements for Pace Laboratories.

19.4 If a client fails to provide sufficient volume for the method required Matrix Spike/Matrix Spike Duplicate (MS/MSD), the laboratory will analyze a Laboratory Control Spike Duplicate to demonstrate precision. The analytical batch will be qualified with the “M5” data qualifier.

20. INSTRUMENT/EQUIPMENT MAINTENANCE

20.1 Refer to most current revision or replacement of S-GB-Q-030, *Support Equipment.* Additional information can be obtained in the automated soxhlet operating manual.

21. TROUBLESHOOTING

21.1 Refer to the automated soxhlet operating manual.

22. SAFETY

1.1 **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel, they are located at the following link: https://msdsmanagement.msdsonline.com/c0ce0b0a-17d3-4f3c-afc6-25352729b299/ebinder/?nas=True. Standard solutions should be prepared in a hood whenever possible.

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

23. WASTE MANAGEMENT

23.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

23.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of S-GB-S-006, *Waste Handling and Management*

24. POLLUTION PREVENTION

24.1 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

25. REFERENCES

25.1 USEPA, SW-846, Method 3541, "Automated Soxhlet Extraction", September 1994.

25.2 Pace Quality Assurance Manual- most current version.

25.3 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4 Pace analytical SOP S-GB-O-026, *Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography*, most current review or revision.

25.5 Pace Analytical SOP S-GB-O-047, *Analysis o f Polychlorinated Biphenyls (PCB's) by Gas Chromatography by 8082A*, most current review or revision.

25.6 Pace Analytical SOP S-GB-O-048, *Analysis of Fox River Polychlorinated Biphenyls (PCBs) by Gas Chromatography*, most current review or revision.

26. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ETC.

26.1 Not Applicable

27. REVISIONS

Document Number	Reason for Change	Date
SGBO-041-Rev.06	Section 7.1: Updated to ≤6°C from 4±2°C. Section 10.7: PCB Spike amount change to 1.0mL. Section 25: Added appropriate references.	17Dec2014
S-GB-O-041-Rev.07	Signature Page: Updated Inc to LLC, updated QM name. General: made administrative edits that do not affect the policies or procedures within the document. Sections 9 and 10: Updated to Table Format. Section 22: Added SDS location	04Apr2017

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STANDARD OPERATING PROCEDURE

DETERMINATION OF SEMI-VOLATILE ORGANICS BY GC/MS

Reference Methods: EPA SW-846 Method 8270C / EPA 625

Local SOP Number:	S-GB-O-049-Rev.07
Effective Date:	Date of Final Signature
Supersedes:	S-GB-O-049-Rev.06
SOP Template Number:	SOT-ALL-O-001-rev.01

APPROVALS

Nils Melberg, Laboratory General Manager — Date: 06/21/17

Kate Verbeten, Laboratory Quality Manager — Date: 6/21/17

Chris Haase, Laboratory Department Manager — Date: 6/21/17

PERIODIC REVIEW

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

Signature	Title	Date

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1. Purpose/Identification of Method

This Standard Operating Procedure (SOP) documents the procedures used by PASI – Green Bay to determine the concentration of Semi-volatile Organic Compounds (SVOCs) in environmental samples. The laboratory utilizes GC/MS and bases these documented procedures on those listed in EPA SW-846 Method 8270C/ EPA 625. The Green Bay laboratory currently processes water samples by automated separatory funnel using Method SW846 3510C, soil samples by Microwave Extraction using Method SW846 3546 and biota samples by soxhlet extractor using Method SW846 3540C. The latest revision of Pace's SOPs S-GB-O-053 *Separatory Funnel Extraction of Water Samples for Semivolatile Analysis* (most current revision or replacement), S-GB-O-045 *Microwave Extraction for the Determination of Polynuclear Aromatic hydrocarbon, Base/Neutral/Acids, and Total Petroleum Hydrocarbons on Solid Matrices* (most current revision or replacement), and S-GB-O-033 *Extraction of Biological Samples for Base Neutral/Acid and PAH-SIM Analysis* (most current revision or replacement) for these extraction techniques are available from the quality office.

2. Summary of Method

2.1. Sample extracts are prepared for analysis by an appropriate sample preparation method. The semivolatile organic compounds are introduced into the gas chromatograph (GC) by injecting an aliquot of the sample extract. The GC conditions are programmed to separate the analytes. The GC effluent is directly introduced to a mass spectrometer (MS) for both identification and quantification of analytes. Analytes are identified by comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using a multi-point calibration curve.

3. Scope and Application

3.1. This procedure may be used to determine concentrations of neutral, acidic, and basic semivolatile organic compounds in extracts prepared from many types of water samples, soil samples and wastes. Analytes must be soluble in dichloromethane and amenable to capillary gas chromatography. Specific compound classes include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols. A list of applicable compounds is shown in Table 11.1 Calibration Standard Compound Concentrations. Pace Reporting Levels (PRLs) are also shown for water and soil samples. PRLs are subject to change based on current analytical system performance and actual sample matrices.

3.2. This method is applicable to most water and solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, and other solid samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix related modifications must be documented within the analytical data.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of semi-volatile configured GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.4. This method cannot be substituted for other similar published methods where permit or regulatory compliance is required.

4. Applicable Matrices

4.1. This SOP is applicable to soils/sediments, solid wastes, tissue, wipes and aqueous matrices.

5. Limits of Detection and Quantitation

5.1. The reporting limit (LOQ) for all analytes is listed in Table 11.1 for the listed methods. All current MDLs are listed in the LIMS and are available by request from the Quality Manager.

6. Interferences

6.1. Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

6.2. Matrix interferences may result from materials co-extracted from some samples.

6.3. Significant phthalate contamination may result at any time if consistent quality control is not practiced. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

6.4. Contamination by carryover can occur when high concentration extracts are analyzed prior to low concentration extracts. The contamination may also cause degradation of labile analytes. Whenever carryover is suspected, the affected extracts should be re-analyzed. If significant degradation of the GC/MS systems is suspected, system performances samples should be analyzed and corrective action taken as needed.

7. Sample Collection, Preservation, Shipment and Storage

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

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	One 1L amber glass Samples to be analyzed for EPA 625 must be checked for residual chlorine. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well.	None	0-<6°C	7 days
Soil/Solid (non-aqueous)	One 8oz wide glass jar	None	0-<6°C	14 days
Biota	-	None	≤ -10°C until extraction	1 year when frozen
TCLP	One 1L Amber Glass	None	0-<6°C	TCLP Leachates must be solvent extracted within 7 days of the completion of the process.
Extracts	2 mL amber glass vials	None	≤ -10°C	40 days

8. Definitions

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

8.1. **Toxicity Characteristic Leaching Procedure (TCLP) –** An extraction procedure used to determine if a sample is acceptable for upland disposal. The extraction procedure is meant to simulate the leaching of contaminants under the environmental conditions typically found in a landfill.

8.2. **Run Sequence Log** – A logbook that lists all injections and analyses performed on a particular piece of equipment regardless of the use of the data collected from each analysis.

8.3. **Tune Period** – The period after the DFTPP instrument tune check within which analyses may be performed.

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

9.1. **Table 9.1 - Instrumentation**

Analytical Instrument/Peripherals	EPIC Pro Name	Serial Number
HP 5890 Series II GC	40MSS1	3336A57925
HP 5972 Mass Selective Detector	40MSS1	3501A02320
HP 7673 AutoSampler Tray	40MSS1	3526A39072
HP 7673 Injector	40MSS1	3009A20936
HP Controller	40MSS1	3526A02233
Alcatel 2005 Rough Pump	40MSS1	265402
HP 5890E GC	40MSS6	3310A49571
HP 5972A Mass Selective Detector	40MSS6	3524A03107
HP 18596A AutoSampler Tray	40MSS6	2920A10670
HP 6890 Injector	40MSS6	US0000692
HP 7673 Controller	40MSS6	3113A25880
Edwards E2M2 Rough Pump	40MSS6	53747
Agilent 7890A GC	40MSS8	CN10705029
Agilent 5975C Mass Selective Detector	40MSS8	US71226404
HP Autosampler tray G2614A	40MSS8	US93806114
HP injector G2613A	40MSS8	US93909562
Edwards E2MS Rough Pump	40MSS8	69070
Agilent 7890B	40MSSA	CN15483197
Agilent 5977A Mass Selective Detector	40MSSA	US1422L235
Agilent Autosampler tray G4514A	40MSSA	CN13330090
Agilent injector G4513A	40MSSA	CN14510236
Edwards E2M2 Rough Pump	40MSSA	DUO25

9.2. **Table 9.2 - Chromatography Supplies**

Item	Vendor	Model / ID	Catalog #	Description
Analytical Column	Restek	XTI-5 w/ Integraguard	12223-124	30 m, 0.25 mm ID, 0.25 df
Analytical Column	Phenomenex	ZB Semivolatiles Guardian	7HG-G027-11-GGC	20m, 0.18 mm ID, 0.18 df
Fluorocarbon O-rings	Restek		20377	
Vespel/Graphite Ferrules	Restek		20229	1/16" x 0.4 mm ID
Gooseneck Splitless Liner	Restek		20800	4 mm x 6.5 x 78.5 for Aligent GCs
Uniliner	Restek	Drilled Uniler	20771	w/hole in bottom
Inlet Seals	Restek	Dual Vespel Ring Inlet Seals	212389	Stainless steel

9.3. **Table 9.3 - Glassware**

Glassware	Description	Vendor / Item # / Description
Volumetric Flasks	10mL, 25mL, 50mL	Class A
Glass Storage Vials	5mL, 10mL, 12mL, with Teflon-lined screw caps	MG Scientific / T102-3-INV, T102-1-INV V138-19, B510-1
Glass Autosampler Vials	2.0mL with Teflon-lined crimp or screw caps	MG Scientific / V300-3 / V300-20N

9.4. **Table 9.4 - General Supplies**

Supply	Description	Vendor/Item #
Gas tight syringes	10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL, as needed, Hamilton or equivalent.	Fisher Scientific/Various
Pipettes	Borosilicate Glass 9" Pipette	MG Scientific / D200-9

10. Reagents and Standards

10.1. **Table 10.1 – Reagents**

Reagent/Standard	Concentration/ Description	Manufacturer/Vendor/Item #
Methylene Chloride (Dichloromethane)	Pesticide Grade or equivalent / $MeCl_2$	MG Scientific / # 9266-8P
Methanol	Purge and Trap Grade or equivalent / MeOH	Burdick & Jackson / VWR Scientific / 232-1
Acetone	Pesticide Grade or equivalent/ Acetone	Burdick and Jackson / 010-4

10.2. **Table 10.2 - Standard Definitions**

Standard	Description	Comments
Tune Standard	Decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine solution in dichloromethane used to verify ion response ratios and system inertness prior to analysis	Must inject no more than 50ng on column
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	Method requires a minimum of 5 levels
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	
Second Source Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the accuracy of the calibration curve.	
Internal Standard	A solution added to all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard is used to adjust response ratios to account for instrument drift.	1,4 Dichlorobenzene-d4 Naphthalene-d_8 Acenaphthene-d_{10} Phenanthrene-d_{10} Chrysene-d_{12} Perylene-d_{12}
Surrogate Standard	A solution added to all samples, spikes, control samples, and method blanks prior to analysis.	Nitrobenzene-d_5 2-Fluorobiphenyl Terphenyl-d_{14} Phenol-d_6 2-Fluorophenol 2,4,6-Tribromophenol
Spiking Standard	This solution contains 70 target analytes and should not be prepared from the same standards as the calibration standards.	

10.3. **Table 10.3 - Standard Storage Conditions**

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date for unopened ampulated standards. ▪ Stock standards must be replaced 1 year after ampule is opened or on expiration date, whichever is sooner.	▪ Manufacturer's recommended storage conditions ▪ When standard is opened, record all information in the standard logbook.
Intermediate and Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ 1 year from preparation or the expiration date listed for the stock source, whichever is sooner. ▪ Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	▪ Store in amber vials with Teflon lined screw caps ▪ <-10 like sample extracts ▪ If stock source conditions conflict, store according to method requirements.

10.4. **Standard Sources**: Standards are prepared from commercially available multi-compound stock solutions and neat materials by multiple dilutions. The sources of the stock solutions and neat

materials, recipes for preparing dilutions and working standards, and concentrations for all compounds are presented in table 9.4. All intermediate standards are prepared using dichloromethane and stored in glass vials with Teflon lined caps or as recommended by the standard manufacturer.

10.5. **Preparation Procedures:**

10.5.1. **Internal Standard Stock solution:** Restek brand Internal Standard Mix, 4000µg/mL, catalog #31006 (contains six internal standards: acenaphthene-d10; chrysene-d12; 1,4-dichlorobenzene-d4; naphthalene-d8; perylene-d12; and phenanthrene-d10), or equivalent. Add 10µL of internal standard solution to 1000µL of every standard, sample, and QC sample injected.

10.5.2. **Surrogate Standard stock solutions:** Restek brand Base Neutral surrogate mix, 5000µg/mL, catalog #31082 (contains four surrogate standards: 2-fluorobiphenyl; nitrobenzene-d5; p-terphenyl-d14; 1,2-Dichlorobenzene-d4 (advisory)). Restek brand Acid surrogate mix, 7500µg/mL, catalog #31083 (contains four surrogate standards: 2-fluorophenol; phenol-d6; 2,4,6-tribromophenol; 2-chlorophenol-d4 (advisory)), or equivalent.

10.5.3. **Surrogate Standard working solution (for extractions)**: dilute 5.0mL of both the Restek Base Neutral stock surrogate solution (#31082) and the Restek Acid stock surrogate solution (#31083) to 50mL with Acetone, or equivalent. This gives a final concentration of 500µg/mL per Base Neutral surrogate compound and 750µg/mL per Acid surrogate compound. The extraction analyst spikes each water and soil sample with 100µL of this working solution.

10.5.4. **DFTPP tuning solution:** dilute 1250µL of Supelco DFTPP stock standard (catalog #47548-U; 1000µg/mL) to a total volume of 25mL with methylene chloride for a final concentration of 50µg/mL, or equivalent. The stock standard also contains 4,4'-DDT, benzidine, and pentachlorophenol for assessing column degradation. Information for the standards preparation and expiration dates are affixed to the outside of the vial, and is easily accessible through Epic Pro LIMS. The standard material will be kept in a freezer at -10°C.

10.5.5. **Initial Calibration curve standards**: the following four stock standards, or equivalent, are used to prepare the initial calibration curve:

10.5.5.1 8270 Custom Mix 1, Restek Custom Mix at 200ug/mL cat.#52939

10.5.5.2 1,4-Dioxane, Restek, 2000µg/mL, catalog #30287

10.5.5.3 2,3,4,6-Tetrachlorophenol, AccuStandard, 2000µg/mL, catalog #A-029S-D-10X

10.5.5.4 1,2,4,5-Tetrachlorobenzene, Absolute Standards, 1000µg/mL, catalog #70274

10.5.5.5 **Initial Calibration Intermediate Standard:** Dilute 3mL of 200µg/mL Restek 8270 Custom Mix 1, 300µL of the 2000µg/mL 1,4-Dioxane solution, 300 µL of the 2000 µg/mL 2,3,4,6-Tetrachlorophenol solution, and 600 µL of 1000µg/mL 1,2,4,5-Tetrachlorobenzene to 5.0mL with dichloromethane, or equivalent. The resulting intermediate standard has a concentration of 120mg/L for each compound.

10.5.6. **Working Standard Preparation**: Working calibration standards are prepared in dichloromethane or a water soluble solvent. Standards made for direct analysis on the GC/MS are made in dichloromethane. Standards made for addition into samples as part of the preparation are made into Acetone. Depending on the volume of each solution needed, the standards are brought to volume in volumetric flasks or prepared in smaller, glass vials and brought to volume by additions of solvent with micro syringes.

10.5.6.1 **Initial Calibration Verification stock standards (second-source)**

10.5.6.1.1 O2si, 200ug/mL, Catalog #113881-05.

10.5.6.1.2 n-Nitrosodiphenylamine, Supelco, 5000ug/mL, Catalog #46702-U.

10.5.6.1.3 Supelco, 1,4-Dioxane, catalog #48367, 2000µg/mL.

10.5.6.1.4 Absolute Standards, 2,3,4,6-tetrachlorophenol, catalog #92389, 5000µg/mL, or equivalent.

10.5.6.1.5 Supelco, 1,2,4,5-Tetrachlorobenzene, catalog #40177, 1000µg/mL.

10.5.6.2 **Initial Calibration Verification working standard (second source):** Dilute 250µL of the custom 8270 second source standard #113881-05, 10µL of 2,3,4,6-Tetrachlorophenol #560028, 25µL of 1,4-Dioxane #48367, 50µL of 1,2,4,5-Tetrachlorobenzene #40177, 10uL of 5000ug/mL n-Nitrosodiphenylamine, 10uL of 5000ug/mL B/N surrogate mix, 6.7uL of 7500ug/mL Acid surrogate mix and 10µL of the stock internal standard solution (9.5.1) to 1mL with dichloromethane, or equivalent. This gives a final concentration of 50ppm.

10.5.6.3 **LCS/MS Standard working solution:** Supelco 70 Component Custom MCS Mix catalog #861389-U, 200µg/mL. Supelco n-Nitrosodiphenylamine, catalog #46702-U, 5000µg/mL, or equivalent. The extraction analyst spikes each LCS/LCSD and matrix spike sample with 250µL of the LCS mix and 10µL of the n-NDPA solution. This produces a concentration of 50µg/mL.

10.5.6.4 **Other calibrations**: Other compounds are analyzed per client requests. Curves are prepared at levels similar to those of the standards above. The calibration standards and the second source standards are as follows: Calibration Standards, Benzidine, Calibration Standard, Supelco Catalog #40005, 5000µg/mL. Second Source, Restek, catalog #31441, 1000µg/mL; EPA CLP SOW OLM4 mix, Calibration Standard, Supelco Catalog#47514-U, 2000µg/mL. Second Source, Absolute Standards, catalog #19253, 2000µg/mL, or equivalent. Minnesota Phenols Samples required Calibration Standard Supelco 500ug/mL, cat.#LC12745, o2si, catalog #114055-05, 500 µg/mL. Phenol and 345-trichlorophenol, first source, Absolute Standards, second source; o2Si

10.5.6.5

10.5.7. Store at -10°C or less in amber Teflon-sealed containers. The solutions should be checked frequently for stability.

10.6. **Calibration Standard Preparation**: Calibration standards are made into dichloromethane for the purpose of direct analysis by the analytical instrumentation. The standards must be made in a volumetric fashion. Several alternatives exist but the method employed by Pace – Green Bay utilizes glass autosampler vials according to the following procedure. The individual standards can be made according to the details provided in table 10.3.

Table 10.4 – Working Standard Dilutions and Concentrations

Standard	Standard(s) Amount	Solvent	Solvent Volume	Final Total Volume	Final Concentration
Calibration Std 1	41.5µL	Dichloromethane	958.5µL	1010µL	5ppm
Calibration Std 2	83µL	Dichloromethane	917µL	1010µL	10ppm
Calibration Std 3	209µL	Dichloromethane	791µL	1010µL	25ppm
Calibration Std 4	417µL	Dichloromethane	583µL	1010µL	50ppm
Calibration Std 5	667µL	Dichloromethane	333µL	1010µL	80ppm
Calibration Std 6	833µL	Dichloromethane	167µL	1010µL	100ppm
Calibration Std 7	1000µL	Dichloromethane	0µL	1010µL	120ppm
Continuing Calibration Verification Standard	417µL	Dichloromethane	583µL	1010µL	50ppm

10.7. Traceability of Calibration Standards—The calibration standards purchased from vendors have been manufactured according to the following guidelines

10.7.1. Identity of neat material verified by GC/MS

10.7.2. Purity of neat material determined by GC/FID or GC/ECD. Correction for impurities is made when purity is less than 97%. Standards are prepared gravimetrically to a precision of 0.5%. All weights are traceable to NIST.

10.7.3. Analyte concentration verified by capillary gas chromatography. Standards tested for stability and homogeneity.

10.7.4. Standards are expiration dated.

10.8. Standard Labeling—All working calibration standards will have a label attached to the bottle identifying the following (Epic pro standard labels do not contain all the following)

10.8.1. Name of Solution

10.8.2. PASI, LLC. Standard ID Number

10.8.3. PASI, LLC. Lab Lot ID (for Stock standards and reagents)

10.8.4. Preparation Date

10.8.5. Preparer's initials

10.8.6. Concentration

10.8.7. Expiration Date

11. Calibration and Standardization

11.1. **Tune Verification –** The mass spectrometer tune status must be verified prior to initial calibration and at the beginning of each analytical sequence. If the current tune status does not meet the ion ratio criteria in the method (see section 12.2), follow the equipment manufacturers' instructions for re-tuning the mass spectrometer. The tune status must be verified after the tuning procedures. Refer to section 12.2 for details on the analysis and evaluation of this standard.

11.2. **Initial Calibration:**

11.2.1. **Analysis of Standards**: An initial calibration curve using a minimum of five points is analyzed prior to analyzing client samples. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values. Refer to table 11.1 for compound concentrations.

Table 11.1: Laboratory PQL and Calibration Standard Compound Concentrations

Analyte	PQL water (µg/L)	PQL soil (µg/kg)	PQL Biota (µg/kg)	Std 1 µg/L	Std 2 µg/L	Std 3 µg/L	Std 4 µg/L	Std 5 µg/L	Std 6 µg/L	Std 7 µg/L
Acenaphthene	5.0	167	330	5.0	10	25	50	80	100	120
Acenaphthylene	5.0	167	330	5.0	10	25	50	80	100	120
Aniline	5.0	167	N/A	5.0	10	25	50	80	100	120
Anthracene	5.0	167	330	5.0	10	25	50	80	100	120
Benz(a)anthracene	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(a)pyrene	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(b)fluoranthene	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(g,h,i)perylene	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(k)fluoranthene	5.0	167	330	5.0	10	25	50	80	100	120
Benzoic acid	10	330	N/A	5.0	10	25	50	80	100	120
Benzyl alcohol	10	330	N/A	5.0	10	25	50	80	100	120
4-Bromophenylphenyl ether	5.0	167	330	5.0	10	25	50	80	100	120
Butylbenzylphthalate	5.0	167	330	5.0	10	25	50	80	100	120
Carbazole	5.0	167	330	5.0	10	25	50	80	100	120
4-Chloro-3-methylphenol	5.0	167	330	5.0	10	25	50	80	100	120
4-Chloroaniline	10	333	330	5.0	10	25	50	80	100	120
bis(2-Chloroethoxy)methane	5.0	167	330	5.0	10	25	50	80	100	120
bis(2-Chloroethyl) ether	5.0	167	330	5.0	10	25	50	80	100	120
bis(2-Chloroisopropyl) ether	5.0	167	330	5.0	10	25	50	80	100	120
2-Chloronaphthalene	5.0	167	330	5.0	10	25	50	80	100	120
2-Chlorophenol	5.0	167	330	5.0	10	25	50	80	100	120
4-Chlorophenylphenyl ether	5.0	167	330	5.0	10	25	50	80	100	120
1,2-Diphenylhydrazine	5.0	167	N/A	5.0	10	25	50	80	100	120
Chrysene	5.0	167	330	5.0	10	25	50	80	100	120
Dibenz(a,h)anthracene	5.0	167	330	5.0	10	25	50	80	100	120
Dibenzofuran	5.0	167	330	5.0	10	25	50	80	100	120
1,2-Dichlorobenzene	5.0	167	330	5.0	10	25	50	80	100	120
1,3-Dichlorobenzene	5.0	167	330	5.0	10	25	50	80	100	120
1,4-Dichlorobenzene	5.0	167	330	5.0	10	25	50	80	100	120
3,3'-Dichlorobenzidine	10	330	330	5.0	10	25	50	80	100	120
2,4-Dichlorophenol	5.0	167	330	5.0	10	25	50	80	100	120
Diethylphthalate	5.0	167	330	5.0	10	25	50	80	100	120
2,4-Dimethylphenol	5.0	167	330	5.0	10	25	50	80	100	120
Dimethylphthalate	5.0	167	330	5.0	10	25	50	80	100	120
Di-n-butylphthalate	5.0	167	330	5.0	10	25	50	80	100	120
4,6-Dinitro-2-methylphenol	5.0	333	670	5.0	10	25	50	80	100	120
2,4-Dinitrophenol	10	333	670	5.0	10	25	50	80	100	120
2,4-Dinitrotoluene	5.0	167	330	5.0	10	25	50	80	100	120
2,6-Dinitrotoluene	5.0	167	330	5.0	10	25	50	80	100	120
Di-n-octylphthalate	5.0	167	330	5.0	10	25	50	80	100	120
bis(2-Ethylhexyl)phthalate	5.0	167	330	5.0	10	25	50	80	100	120
Fluoranthene	5.0	167	330	5.0	10	25	50	80	100	120
Fluorene	5.0	167	330	5.0	10	25	50	80	100	120
Hexachloro-1,3-butadiene	10	333	330	5.0	10	25	50	80	100	120
Hexachlorobenzene	5.0	167	330	5.0	10	25	50	80	100	120
Hexachlorocyclopentadiene	5.0	167	330	5.0	10	25	50	80	100	120
Hexachloroethane	5.0	167	330	5.0	10	25	50	80	100	120
Indeno(1,2,3-cd)pyrene	5.0	167	330	5.0	10	25	50	80	100	120
Isophorone	5.0	167	330	5.0	10	25	50	80	100	120

Analyte	PQL water (µg/L)	PQL soil (µg/kg)	PQL Biota (µg/kg)	Std 1 µg/L	Std 2 µg/L	Std 3 µg/L	Std 4 µg/L	Std 5 µg/L	Std 6 µg/L	Std 7 µg/L
2-Methylnaphthalene	5.0	167	330	5.0	10	25	50	80	100	120
2-Methylphenol	10	333	330	5.0	10	25	50	80	100	120
3&4-Methylphenol	5.0	167	330	5.0	10	25	50	80	100	120
Naphthalene	5.0	167	330	5.0	10	25	50	80	100	120
2-Nitroaniline	5.0	167	330	5.0	10	25	50	80	100	120
3-Nitroaniline	5.0	167	670	5.0	10	25	50	80	100	120
4-Nitroaniline	10	333	670	5.0	10	25	50	80	100	120
Nitrobenzene	5.0	167	330	5.0	10	25	50	80	100	120
2-Nitrophenol	5.0	167	330	5.0	10	25	50	80	100	120
4-Nitrophenol	10	333	670	5.0	10	25	50	80	100	120
N-Nitrosodimethylamine	5.0	167	330	5.0	10	25	50	80	100	120
N-Nitroso-di-n-propylamine	5.0	167	330	5.0	10	25	50	80	100	120
N-Nitrosodiphenylamine	5.0	333	330	5.0	10	25	50	80	100	120
Pentachlorophenol	10	330	670	5.0	10	25	50	80	100	120
Phenanthrene	5.0	167	330	5.0	10	25	50	80	100	120
Phenol	5.0	167	330	5.0	10	25	50	80	100	120
Pyrene	5.0	167	330	5.0	10	25	50	80	100	120
Pyridine	5.0	167	330	5.0	10	25	50	80	100	120
1,2,4-Trichlorobenzene	5.0	167	330	5.0	10	25	50	80	100	120
2,4,5-Trichlorophenol	5.0	167	670	5.0	10	25	50	80	100	120
2,4,6-Trichlorophenol	5.0	167	330	5.0	10	25	50	80	100	120
1,4-Dioxane	10	330	N/A	5.0	10	25	50	80	100	120
1,2,4,5-Tetrachlorobenzene	5.0	167	N/A	5.0	10	25	50	80	100	120
2,3,4,6-Tetrachlorophenol	10	167	N/A	5.0	10	25	50	80	100	120
Acetophenone	10	333	N/A	5.0	10	25	50	80	100	N/A
Atrazine	10	333	N/A	5.0	10	25	50	80	100	N/A
Benzaldehyde	10	333	N/A	5.0	10	25	50	80	100	N/A
Benzidine	50	1670	N/A	5.0	10	25	50	80	100	N/A
Caprolactam	10	333	N/A	5.0	10	25	50	80	100	N/A
Biphenyl	10	333	N/A	5.0	10	25	50	80	100	N/A

11.2.2. An analyte must be present and calibration curve in control in order to be reported on the target analyte list. Analytes identified by mass spectral match but not present and in control in the calibration table may be reported as Tentatively Identified Compounds (TICs). Guidelines for identification are listed in Section 12.15. Results for these TICs should be reported only on a present/absent basis. However, quantitative results may be reported provided they are qualified as estimated values.

11.2.3. Calibration Response Factors: Response factors (RF) establish the relationship of the instruments response in comparison with the concentration of any given analyte. The RF includes the concentration and response of the internal standard as well. By relating the IS concentration and response in an inverse manner, the target analyte concentration is adjusted to account for drift in the instrument on a per injection basis. As instrument response increases as indicated by the response of the internal standard, the concentration of the target is mathematically decreased, and vice versa.

11.2.4. To calculate the RF for any given calibration standard (or calibration verification standard), tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound

relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation:

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L).

11.2.5. Most, if not all modern chromatography data systems are capable of calculating this factor and using it to quantify analyte concentrations. The 8270C method has minimum requirements that these response factors must meet in order to be considered valid. The method uses a subset of the target analyte list to evaluate the performance of the system. These compounds are referred to as the System Performance Check Compounds or the SPCCs. The SPCCs serve as an indicator of instrument sensitivity and, by meeting a minimum value, ensure that the laboratory has adequate sensitivity to analyze and reliably report data for environmental samples.

11.2.6. **Calibration Curve Fit**: The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. The curve is produced in several ways depending on the nature of the "goodness of fit".

11.2.7. **Average Response Factor (ARF)**: The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. It is in the most basic sense, a linear regression that is forced through zero at the origin. Because of its simplicity and the interception of the y axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of the ARF (see Table 11.2):

$$\%RSD = \left(\frac{SD \times 100}{ARF}\right)$$

Where:

SD = Standard deviation of the averaged RFs for a given compound

11.2.8. The average response factor is also used to diagnose the integrity of the chromatography system as it relates to calibration linearity. The ***Calibration Check Compounds (CCCs)*** are a subset of the target analyte list that must meet specific criteria (see Table 11.2) for the calibration to be acceptable. For the CCCs, the %RSD for each is compared to the method criteria. If that of any CCC exceeds the criteria, the system needs to be inspected for potential sources of errors and recalibrated.

11.2.9. **Linear Regression**: The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y=ax+b where "a" is the slope of the line and "b" is the y intercept. In order to use this curve fit technique, a minimum of 5 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument is linear in nature but does not necessarily intercept the y axis at

the origin. However, because the linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve (see Table 11.2).

11.2.10. **Non-linear Regression**: The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument gradually decreases with increasing concentrations. Using this technique, an analyst may be able to generate calibration curves with correlation coefficients very close or equivalent to 1.000. However, because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. Likewise, high levels of contamination may not be able to be calculated due to regression equations with multiple intercepts of either axis on the calibration plot.

11.2.11. A calculation of the coefficient of determination (COD) is used to determine the acceptability of a non-linear regressed curve (see Table 11.2). Either the low or high calibration points may be dropped to meet linearity criteria provided the laboratory meets the minimum 5 calibration point requirements. Points within the center of the curve may not be dropped unless an obvious problem is discovered and documented and permission of the supervisor or the quality manager is obtained. The point must be dropped in its entirety. Re-analysis if performed should be within the same 12 hour time window and must occur within 8 hours of the original analysis.

11.3. **Calibration Verification**:

11.3.1. Low Level Calibration Check(CRDL): The lowest range of the calibration will be checked by either refitting the lowest calibration point against the calibration curve or re-analyzing the lowest calibration point. The CRDL must be checked before running any sample from MN and must meet a recovery of 60-140% of the expected value. Any compounds failing must be flagged in MN samples as failing to meet CRDL limits.

11.3.2. **Second Source Verification**: In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

11.3.3. Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification (ICV)***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the ICV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

$$\%\ Difference = \frac{(RFccv - AveRFcal)}{AveRFcal} * 100$$

$$\%\ Drift = \frac{(Result\ CCV - True\ Value\ CCV)}{True\ Value\ CCV} * 100$$

11.3.4. **Continuing Calibration Verification (CCV)**: As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***. The validity of the initial calibration is checked at the beginning of every analytical sequence and every 12 hours thereafter for as long as the instrument is analyzing samples and is accomplished by analyzing a midpoint calibration standard (CCV).

11.3.5. The values obtained from the analysis of the CCV are compared to the true values and a percent change calculated. The percent change must meet the method specified criteria for the analysis to proceed for an additional 12 hours.

11.3.6. The actual determination of change in instrument response is based on the type of curve fit used for each analyte. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the CCV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

$$\%\ Difference = \frac{(RFccv - AveRFcal)}{AveRFcal} * 100$$

$$\%\ Drift = \frac{(Result\ CCV - True\ Value\ CCV)}{True\ Value\ CCV} * 100$$

Table 11.2: Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Response Factor	%RSD ≤ 15%	If not met, try linear regression fit
	Linear Regression	r ≥ 0.99	If not met, try non-linear regression fit
	Non-linear Regression	COD ≥ 0.99	If not met, remake standards and recalibrate
System Performance Check Compounds (SPCCs)	N-Nitroso-di-n-propylamine Hexachlorocyclopentadiene 2,4-Dinitrophenol 4-Nitrophenol	Avg RF ≥ 0.05 Avg RF ≥ 0.05 Avg RF ≥ 0.05 Avg RF ≥ 0.05	Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, poor purging efficiency, and active sites in the column or chromatographic system.
Calibration Check Compounds (CCCs)	Acenaphthene 1,4-Dichlorobenzene Hexachlorobutadiene N-Nitrosodiphenylamine Di-n-octylphthalate Fluoranthene Benzo[a]pyrene 4-Chloro-3-methylphenol 2,4-Dichlorophenol 2-Nitrophenol Phenol Pentachlorophenol 2,4,6-Trichlorphenol	%RSD < 30%	%RSD for the calibration check compounds (CCC's) must be ≤30% regardless of curve fit used. If the CCCs are not included on a list of analytes for a project, and therefore not included in the calibration standards, then all compounds of interest must meet a ≤15% RSD criterion.
Second Source Verification Standard	Immediately after each initial calibration	% Drift ±30%	Acceptance criteria are ±30% for all analytes, with allowances for 5% of compounds at ±40%. See current revision of S-GB-Q-026. Additional client specific requirements for the analysis of contract samples requires that all compounds must be within ±20%.
Continuing Calibration Verification	Prior to the analysis of any samples and every 12 hours thereafter		If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back.
	SPCCs	Must meet response criteria listed above	
	Internal Standard RT	RT ± 30 sec	Use midpoint calibration standard as reference
	Internal Standard Response	50 – 200%	Use midpoint calibration standard as reference
	CCCs	RF ± 20% Diff.	Use for Avg RF calibration curves
		Result ± 20% Drift	Use for linear and non-linear calibration curves
	Non-CCC Targets	EPA 8270 Criteria: RF ± 50% Diff. Result ± 50% Drift EPA 625 Criteria: RF ± 20% Diff. Result ± 20% Drift	Some programs may require control over non-CCC target analytes. In the absence of specified criteria, use those listed

11.4. **Calibration Corrective Actions:**

11.4.1. Calibration Linearity Problems:

11.4.1.1 Check instrumentation/equipment condition. Document instrument maintenance in the logbook.

11.4.1.2 Perform another initial calibration.

11.4.1.3 No data can be reported.

11.4.1.4 Generate Non-Conformance Memo.

11.4.2. Second Source Verification Problems:

11.4.2.1 Check instrumentation/equipment condition. Document instrument maintenance in the logbook.

11.4.2.2 Perform another initial calibration.

11.4.2.3 No data can be reported.

11.4.2.4 Generate Non-Conformance Memo.

11.4.3. Continuing Calibration Verification Problems:

10.4.3.1. Reanalyze the original CCV standard to determine instrument consistency.

10.4.3.2. Prepare and analyze a new CCV standard to determine preparation consistency/standard integrity.

10.4.3.3. Document instrument maintenance.

10.4.3.4. Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

10.4.3.5. Complete recalibration of instrument.

10.4.3.6. If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

10.4.3.7. *Exceptions:* If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis.

12. Procedure

12.1. **Operating Parameters:** Configure the GC/MS system to match the following operating parameters based on instrument configuration. The parameters themselves are saved as a method on the chromatography data system. By loading the last method used, the instrument will auto-configure to match the parameters from the last time the system was operated under that method. Verify that the settings in the software match the appropriate configuration.

Table 12.1: Instruments and Operating Parameters

GC/MS Instrument 40MSS1	
GC: Hewlett Packard model 5890	MS: Hewlett Packard model 5972A
Operating Parameters:	Operating Parameters:
Initial Temp: 40°C	Acquisition mode: SCAN
Temp Program: hold 1.0 min at 40°C, ramp at 18°C/min to 100°C, then ramp at 15°C/min to 290°C, hold 5.95min, then ramp at 40°C/min to 320°C and hold for 1 min	Mass Range: 35-500
Final Temp: 320°C	
Transfer Line Temp: 300°C	
Column: Restek XTI-5 (30m; 0.25mm ID and 0.25µm film thickness)w/Integraguard	
Purge Flow: 40mL/min	
GC/MS Instrument 40MSSA	
GC: Agilent 7890B	MS: Hewlett Packard model 5977A
Operating Parameters:	Operating Parameters:
Initial Temp: 45°C	Acquisition mode: SCAN
Temp Program 45°C hold 1.00min, ramp at 30°C/min to 260°C hold for 0min, then ramp at 6°C/min to 295°C and hold for 0 min, then ramp at 25C/min to 325C and hold for 2min	Mass Range: 35-550
Final Temp: 325°C	
Transfer Line Temp: 300°C	
Column: Phenomenex ZB-Semivolatile Guardian 30 m, 0.25 ID(mm), 0.25 film thickness(mm)	
Split Ratio: L/minb 10:1	
GC/MS Instrument 40MSS8	
GC: Agilent 7890A	MS: Hewlett Packard model 5975
Operating Parameters:	Operating Parameters:
Initial Temp: 45°C	Acquisition mode: SCAN
Temp Program 45°C hold 1.00min, ramp at 30°C/min to 260°C hold for 0min, then ramp at 6°C/min to 295 °C and hold for 0 min,then ramp 25C/min to 325C and hold for 2 min.	Mass Range: 35-550
Final Temp: 325°C	
Transfer Line Temp: 300°C	
Column: Phenomenex ZB-Semivolatile Guardian 30 m, 0.25 ID(mm), 0.25 film thickness(mm)	
Split Ratio: 10:1	
GC/MS Instrument 40MSS6 used for Minnesota Phenols Samples	
GC: Hewlett Packard model 5890	MS: Hewlett Packard model 5972A
Operating Parameters:	Operating Parameters:
Initial Temp: 50°C	Acquisition mode: SCAN
Temp Program 50°C, ramp at 18°C/min to 150°C, then ramp at 3°C/min to 167°C , then ramp at 40°C/min to 320°C and hold for 2.5 min	Mass Range: 35-500
Final Temp: 320°C	
Transfer Line Temp: 300°C	
Column: Phenomenex ZB-Semivolatiles (30m; 0.25µm ID, 0.25 df)	
Split Flow: 100mL/min	

12.2. **Tune Verification**: At the beginning of each analytical sequence, prior to the analysis of any standards or samples, the mass spectrometer tune conditions must be verified. This is done by analyzing a standard containing DFTPP. The tune verification standard can be combined with the CCV standard provided that the amount of DFTPP introduced into the system meets the method criteria. For semi-volatile analysis, the system must also be verified for inertness. This is done simultaneously by the inclusion of DDT, benzidine and pentachlorophenol. DDT is used to verify breakdown conditions; benzidine and pentachlorophenol are used to check for tailing due to system activity.

12.2.1. After the analysis of this standard, the mass spectrum of DFTPP must be evaluated against the following criteria:

Mass (m/z)	Ion Abundance criteria
51	10.0-80.0% of m/z 198
68	<2.0% of m/z 69
69	Present
70	<2.0% of m/z 69
127	10.0-80.0% of m/z 198
197	<2.0% of m/z 198
198	Base peak, >50% of Mass 442
199	5.0-9.0% of m/z 198
275	10.0-60.0% of m/z 198
365	>1% of m/z 198
441	Present, but less than m/z 443
442	>50.0% of m/z 198
443	15.0-24.0% of m/z 442

12.2.2. To evaluate the tune spectra, following the operating instructions for the chromatography data system to access the data file and obtain mass spectra for DFTPP. If the software has a program or macro for automatically selecting the spectra and evaluating the response ratios, use this option. Otherwise, the spectra must be obtained in one of the following manners, in the listed order:

1. **Using an average of three scans, centered on the apex of the peak; or,**
2. **Using an average of all scans across the width of the peak, taken at half height; or,**
3. **Using an average of all scans taken across the width of the peak from baseline to baseline.**

A background scan taken immediately before but not including the peak must be subtracted.

12.2.3. Once obtained, evaluate the ion ratios against the criteria listed above. If the ratios meet the criteria, then analysis may proceed for 12 hours. The window for analysis is 12 hours from the injection date / time for the DFTPP tune verification. After that, the tune must be verified again to establish a new analytical window. The same Ion Abundance Criteria used for the DFTPP tune coupled with the initial calibration must be used for all subsequent analyses associated with that initial calibration.?

12.2.4. If the ratios do not meet the criteria, refer to the following corrective actions to address the problem: Any changes made to the system must be followed with the reanalysis of a tune verification standard. Any maintenance performed on the physical mass spec components requires recalibration. “Autotunes” may be performed as long as the following CCV meets all criteria for response, retention time and sensitivity.

12.3. **Tailing Factor Verification-** Benzidine and Pentachlorophenol should be present at their normal responses, and peak tailing should not be to an excess.

12.3.1. **Column performance test for base / neutrals –** At the beginning of each day that the base / neutral fraction is to be analyzed for benzidine, the benzidine tailing factor must be calculated. The benzidine tailing factor must be less than 3.0.

12.3.2. **Column performance test for acids –** At the beginning of each day that the acid fraction is to be determined, the pentachlorophenol tailing factor must be calculated. The pentachlorophenol tailing factor must be less than 5.0.

12.3.3. **Tailing factor calculation –** Refer to Attachment II: Tailing Factor Calculation.

12.3.4. The tailing factor of 3.0 for Benzidine and 5.0 for Pentachlorophenol must not be exceeded. If the tailing factor for either exceeds this amount, corrective action must be taken prior to the analysis of samples(unless all compounds required by samples analyzed after this tune and check meet Calibration Check Compound(CCC) limits). The tailing factor must be verified by the analysis of another tailing factor standard after corrective action is taken. Follow the following steps to return the system to an acceptable operating condition.

12.3.4.1 Perform front-end maintenance on the GCMS System.

12.3.4.2 Begin the run again by re-analyzing the DFTPP tune solution.

12.4. **Breakdown Verification-** The GC/MS system must be sufficiently inert such that DDT will not breakdown excessively while in the injection port. The inertness is assessed by calculating the percent breakdown of DDT into the products DDD and DDE. The calculation is performed as follows:

$$\%DDT\ Breakdown = \left(\frac{(DDD + DDE)}{(DDT + DDD + DDE)}\right) * 100$$

12.4.1. The % breakdown **must not exceed 20%.** If the breakdown of DDT exceeds this amount, corrective action must be taken prior to analysis of samples(unless all compounds required by samples analyzed after this tune and check meet Calibration Check Compound(CCC) limits. The breakdown must be verified by the analysis of another breakdown standard after corrective action is taken. Follow the following steps to return the system to an acceptable operating condition.

12.4.1.1 Perform front-end maintenance on the GCMS System

12.4.1.2 Begin the run again by re-analyzing the DFTPP tune solution.

12.5. **Calibration Verification**: After the instrument tune conditions are verified and the system meets tune criteria, the instrument must undergo calibration verification. If it has already been determined that the instrument needs to be recalibrated, follow the procedures listed in section 11.2 (Analysis of Standards). Otherwise, analyze a Continuing Calibration Verification Standard to determine the current calibration status.

12.6. If the CCV meets control criteria, the system is deemed to be in control and analysis of samples may commence. If the CCV does not meet control criteria, follow the corrective action procedures listed section 11.4.3 (Continuing Verification Problems). If the tune verification has been combined with the CCV, the 12 hour analysis window begins from the analysis date / time of the CCV.

12.7. *Note:* In situations where the instrument will run unattended (i.e., overnight), the analyst may load sequential CCVs in anticipation of that the first in the series may fail due to carry over from a previous sample. If so, the CCV must be evaluated according to the protocol set forth in the Quality Assurance Manual within the Equipment and Measurement Traceability section.

12.8. **Sample Preparation**-

12.8.1. **Water Samples**: Aqueous samples are prepared according to EPA 3510C. These procedures are contained in a separate standard operating procedure. Refer to SOP number S-GB-O-053 *Separatory Funnel Extraction of Water Samples for Semivolatile* (most current revision or replacement) for details on the preparation of aqueous samples.

12.8.1.1 Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10µL of the internal standard solution.

12.8.2. **Soil Samples**: Solid samples are prepared according to EPA 3546. These procedures are contained in a separate standard operating procedure. Refer to SOP number S-GB-O-045 *Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons, Base/Neutral/Acids, and Total Petroleum Hydrocarbons in Solid Matrices* (most current revision or replacement) for details on the preparation of soil or solid samples.

12.8.2.1 Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10µL of the internal standard solution.

12.8.3. **Biota Samples:** Biota samples are prepared according to EPA Method 3540C. These procedures are contained in a separate standard operating procedure. Refer to S-GB-O-033 *Extraction of Biological Samples for Base Neutral/Acid and PAH-SIM Analysis* (most current revision or replacement) for details on the preparation of biota samples.

12.8.3.1 Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 5µL of the internal standard solution.

12.9. **Dilutions**

12.9.1. Dilutions on sample extracts must be prepared in a volumetric fashion. Sample aliquots should be taken in volumetric syringes and brought to volume by the addition of solvent via an appropriate syringe. In the event a dilution is made to bring a target analyte into calibration range, the analyst should make a dilution such that the target analyte is roughly the equivalent of the mid calibration point whenever possible. If dilutions are made on extracts that already contain internal standards, a proportional aliquot of internal standard solution must be added to the diluted extract based on the volume of diluent used.

12.10. **Sample Analysis-**

12.10.1. GC/MS System Preparation

12.10.1.1 Operating Parameters – Set up the instrument parameters shown in Table 12.1

12.10.1.2 System Tuning and GC Performance Checks – Analyze the Tuning Solution and tune the mass spectrometer to meet the criteria shown in Section 12.2. Verify acceptable GC system performance as described in Section 12.2. Print out a tune report.

12.10.1.3 Batch Sequence – Generate a sequence to run a batch of samples.

Initial Calibration – The typical batch for initial calibration should include:

Tune Standard
Calibration Level 1
Calibration Level 2
Calibration Level 3
Calibration Level 4
Calibration Level 5
Calibration and System Performance Solution

Sample Analysis – The typical batch for sample analysis should include the following. Preparation of LCS, MS, MSD, and Duplicate sample extracts is described in the appropriate sample preparation SOP.

Tune Standard
Calibration and System Performance Solution
Instrument Blank
Method Blank
Laboratory Control Sample
Laboratory Control Sample Duplicate
20 samples
Matrix Spike
Matrix Spike Duplicate

Autosampler – Load the Autosampler with standards and samples for the batch created above.

12.10.1.4 Analyze Samples – Analyze all standards, quality control samples, and environmental samples.

12.10.1.5 Process all runs with Target software

12.10.1.6 View sample chromatograms and verify analyte identifications (Section 12.11).

12.10.1.7 Post data to EPIC Pro.

12.11. **Data Reduction**

12.11.1. Qualitative Analysis: This must be done on every sample and quality control standard.

12.11.1.1 **Retention Time Comparison:** The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of RT in the presence of co eluting components.

12.11.1.2 **Mass Spectrum Comparison:** The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met:

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.
- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.
- Additional client specific requirements for the analysis of contract samples requires all ions present in the reference mass spectrum at a relative intensity > 10% must be present in the sample spectrum.
- Due to limitations of the “Target” software, analyst discretion is advised.

Table 12.2 Primary and Secondary quantitation ions for target compounds[2]

Analyte	Primary Ion	Secondary Ions
Phenol	94	65, 66
Bis (2-Chloroethyl) ether	63	93, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
Benzyl Alcohol	108	79, 107
1,2-Dichlorobenzene	146	148, 111
2-Methylphenol	108	107, 79
Bis (2-Chloroisopropyl)ether	45	77, 121
3&4-Methylphenol	108	107, 79
N-Nitroso-di-n-propylamine	70	43, 101
Hexachloroethane	117	201, 199
1,4-Dioxane	88	58, 43
Benzaldehyde	105	106, 77
N-Nitrosodimethylamine	42	74
Aniline	93	66, 39
Acetophenone	105	77, 120
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	109, 65
2,4-Dimethylphenol	107	122, 121
Benzoic acid	122	105, 77
Bis(2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Caprolactam	55	56, 113
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	127, 164
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
Acenaphthylene	152	153
2,6-Dinitrotoluene	165	63, 89
3-Nitroaniline	138	108, 92
Acenaphthene	154	153, 152
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65,39
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 89
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	108, 92
1,2,4,5-Tetrachlorobenzene	216	214, 179
2,3,4,6-Tetrachlorophenol	232	131, 166
4,6-Dinitro-2-methylphenol	198	51, 105

Analyte	Primary Ion	Secondary Ions
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	283.7	142, 249
Atrazine	200	173, 58
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	176, 179
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 203
Benzidine	184	185, 92
Pyrene	202	200, 203
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
Chrysene	228	226, 229
Bis(2-ethylhexyl)phthalate	149	167, 279
Di-n-octylphthalate	149	167, 43
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253,125
Indeno(1,2,3-cd)pyrene	276	138, 277
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
Carbazole	167	168,169

[2]The information in this table was taken from Method 8270C. Please refer to the method for additional compounds and their applicable ions.

Analyte	Primary Ion	Secondary Ions
Internal Standards		
1,4-Dichlorobenzene-d_4	152	150, 115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265
Surrogates		
2-Fluorophenol (acid)	112	64
Phenol-d_6 (acid)	99	71
Nitrobenzene-d_5 (BN)	82	128, 54
2-Fluorobiphenyl (BN)	172	171
2,4,6-Tribromophenol (acid)	329.8	331.8, 141
Terphenyl-d_{14} (BN)	244	122, 212

[2]The information in this table was taken from Method 8270C. Please refer to the method for additional compounds and their applicable ions.

12.11.2. Internal Standard Assignment List (from Method SW-846 8270C-Table 5): this section lists the internal standard compounds and all target compounds that are assigned to each internal for quantitation:

1,4-Dichlorobenzene – d4
Aniline
Benzyl alcohol
Bis (2-chloroethyl)ether
Bis(2-chloroisopropyl)ether
2-Chlorophenol
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
2-Fluorophenol (surrogate)
Hexachloroethane
2-Methylphenol
4-Methylphenol
N-Nitroso-dimethylamine
N-Nitroso-di-n-propylamine
Phenol
Phenol-d6 (surrogate)
1,4-Dioxane
Pyridine
2-Chlorophenol-d4 (advisory surrogate)
Benzaldehyde
1,2-Dichlorobenzene-d4 (advisory surrogate)

Naphthalene-d8
Acetophenone
Benzoic acid
Bis(2-chlorethoxy)methane
4-Chloroaniline
4-Chloro-3-methylphenol
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dimethylphenol
Hexachlorobutadiene
Isophorone
2-Methylnaphthalene
Naphthalene
Nitrobenzene
Nitrobenzene-d8 (surrogate)
2-Nitrophenol
1-Methylnaphthalene
1,2,4-Trichlorobenzene

Acenaphthene-d10
Acenaphthene
Acenaphthylene
1,2-Diphenylhydrazine
2-Chloronaphthalene
4-Chlorophenyl phenyl ether
Dibenzofuran
Diethyl phthalate
Dimethyl phthalate
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Fluorene
2-Fluorobiphenyl (surrogate)
Hexachlorocyclopentadiene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
4-Nitrophenol
Biphenyl
2,4,6-Tribromophenol (surrogate)
2,4,6-Trichlorophenol
2,4,5-Trichlorophenol
1,2,4,5-Tetrachlorobenzene

Phenanthrene-d10
Atrazine
Anthracene
4-Bromophenyl phenyl ether
Di-n-butyl phthalate
4,6-Dinitro-2-methylphenol
Carbazole
Fluoranthene
Hexachorobenzene
N-Nitroso-diphenylamine
Pentachlorophenol
Phenanthrene

Chrysene-d12
Benzidine
Benzo(a)anthracene
Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Chrysene
3,3'-Dichlorobenzidine
Pyrene
Terphenyl-d6 (surrogate)
Di-n-octylphthalate

Perylene-d12
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(a)pyrene
Dibenz(a,h)anthracene
Indeno(123,cd)pyrene

12.12. Quantitative Analysis- Quantitation is based on the integrated abundance of the target analyte's quantitation ion using the internal standard technique.

12.12.1. **Raw Data Results:** The GC/MS data system will calculate the concentration of each analyte as µg/L (or ng/mL). For water samples, no further calculations are necessary unless a dilution of the sample has been performed. If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

12.13. **Tentatively Identified Compounds (TICs)** – For some samples, identification may be desired for non-target compounds. A mass spectral library search may be conducted to attempt assignment of tentative identifications. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications.

12.13.1. Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum;

12.13.2. The relative intensities of the major ions should agree within ± 20%;

12.13.3. Molecular ions present in the reference spectrum should be present in the sample spectrum;

12.13.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds;

12.13.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

12.13.6. For additional information on the determination of TICs, please see SOP: S-ALL-O-038, *Processing of TICs for GCMS* (most current revision or replacement).

13. Quality Control

13.1. Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per 20 samples	Target analytes must be less than reporting limit.	Qualify results and/or re-extract associated samples. ***Exceptions:*** If sample ND, report sample without qualification; If sample result >10x MB detects, report sample with appropriate qualifier indicating blank contamination; If sample result <10x MB detects, and sample cannot be re-extracted, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	Method specified compounds: **Base Neutrals**: 1,2,4-Trichlorobenzene; Acenaphthene; 2,4-Dinitrotoluene; Pyrene; N-nitroso-di-n-propylamine; 1.4-Dichlorobenzene **Acids**: Pentachlorophenol; Phenol; 2-Chlorophenol; 4-Chloro-3-methylphenol; 4-Nitrophenol *OR (alternative)* 70 compound LCS Mix	One per batch of up to 20 samples	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to the TNI standard.	At analyst discretion, Re-analyze the LCS to verify failure; If LCS passes, review samples for potential injection problems; If problem persists, check spike solution; Re-extract samples where possible. ***Exceptions:*** If LCS recovery is > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. Also, if the MS/MSD meet QC requirements, they may be used as acceptable criteria for the LCS.
Matrix Spike (MS)	Method specified compounds: **Base Neutrals**: 1,2,4-Trichlorobenzene; Acenaphthene; 2,4-Dinitrotoluene; Pyrene; N-nitroso-di-n-propylamine; 1.4-Dichlorobenzene **Acids**: Pentachlorophenol; Phenol; 2-Chlorophenol; 4-Chloro-3-methylphenol; 4-Nitrophenol *OR (alternative)* 70 Compounds LCS Mix	One per batch of up to 20 samples EPA 625: One per batch of up to 10 samples	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to the TNI standard.	If LCS and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One for every 5% of all environmental samples EPA 625: One for every 10% of all environmental samples	Laboratory Derived Limits	Report results with an appropriate footnote.

13.2. **Table 13.2 – Sample Quality Control Criteria**

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	1,4-Dichlorobenzene-d4 Naphthalene-d8 Acenaphthene-d10 Phenanthrene-d10 Chrysene-d12 Perylene-d12	Added to all standards, samples, spikes, control samples, and method blanks prior to analysis	**Retention Time:** RT must be ± 30 seconds from last calibration check on all samples	**Retention Time Failure:** If matrix interference is NOT probable, the analytical system must be checked for source of retention time shifting; Affected samples should be reanalyzed in the absence of an obvious instrument or matrix related interference.
Surrogate Standards	Nitrobenzene-d5 2-Fluorobiphenyl Terphenyl-d14 Phenol-d6 2-Fluorophenol 2,4,6-Tribromophenol	Added to all samples, spikes, control samples and method blanks prior to analysis	Laboratory derived limits	1 Base neutral and 1 Acid surrogate are allowed to be outside of recovery limits before action is taken. Assess impact of sample matrix. In the absence of obvious matrix interference (high background, extremely dark extract), re-extract sample. ***Exceptions:*** Surrogate recovery above criteria and target compounds < RL, result may be reported with appropriate footnote. Surrogate recovery out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote.

14. Data Analysis and Calculations

14.1. **Results Calculation- Aqueous Samples:**

$$\text{Concentration } (\mu\text{g/L}) = \frac{(C_x)(V_x)(DF)}{(V_s)}$$

Where:

C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
V_s = Volume of water sample extracted (mL).

14.2. **Results Calculation- Soil/Solid Samples:**

$$\text{Concentration } (\mu\text{g/kg}) = \frac{(C_x)(V_x)(1000)(DF)}{(W_s)}$$

Where:

C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
W_s = Weight of soil sample extracted (g).

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Tables 11.2, 13.1, and 13.2.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Tables 11.2, 13.1, and 13.2

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

17.1. Refer to Tables 11.2, 13.1, and 13.2.

18. Method Performance

18.1. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually per S-GB-Q-020, *Determination of LOD and LOQ* (most current revision or replacement) for each matrix per instrument.

18.2. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, Orientation and *Training Procedures*, (most current revision or replacement).

18.2.1. Analysis of four (4) replicates of reagent water spiked with 250µL of the 8270 LCS Spiking Solution and 10µL of nNPDA plus all other compounds that are currently reported at a concentration of 50µg/L or equivalent to the LCS. The recovery is to be within the current water LCS QC limits for the known concentrations and 30% RSD for all replicates.

18.2.2. Analysis of four (4) replicates of Ottawa sand spiked with 250µL of 8270C LCS Spiking Solution and 10µL of nNPDA plus all other compounds that are currently reported at a concentration of 1670µg/kg or equivalent to the LCS. The recovery is to be within the current LCS QC acceptance limits for the known concentration and 30% RSD for all replicates.

19. Method Modifications

19.1. Method modifications for EPA method 8270C are as follows:

- Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.
- All major modification to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.
- Procedures identified as “Best Practices” by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories.
- The laboratory follows the DFTPP Tune criteria outlined in EPA 525.2.
- The laboratory practice is to have thermal preservation at ≤6˚C. This is based on 40CFR Part 136, page 29808, footnote 18.
- If a client fails to provide the method required Matrix Spike/Matrix Spike Duplicate (MS/MSD), the laboratory will analyze a Laboratory Control Spike Duplicate to demonstrate precision. The analytical batch will be qualified with the “M5” data qualifier.

20. Instrument/Equipment Maintenance

20.1. Please refer to the instrument operations manual or the SOP S-GB-Q-008, *Preventative, Routine, and Non-routine Maintenance* (current revision or replacement).

21. Troubleshooting

21.1. Please refer to the instrument manufacturer operations manual.

22. Safety

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

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

22.3. **Equipment:** Portions of the analytical instrumentation operate at high temperatures and under positive pressure. Care must be taken to minimize accidents and injuries when working on or with this equipment. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones. The GC pneumatic system uses gas under high pressure. This high pressure introduces the risk of injury due to flying glass and other objects should a vessel or line rupture. Safety glasses are highly recommended at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-GB-W-001, *Waste Handling and Management* (most current revision or replacement).

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

24. Pollution Prevention

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

25. References

25.1. USEPA, SW-846, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), December 1996.

25.2. USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

25.3. USEPA, Method 625, Appendix A to Part 136, (1984), "Base/Neutrals and Acids".

25.4. USEPA, Method 525.2, Revision 2.0 (1995), "Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry".

25.5. Pace Quality Assurance Manual- most current version.

25.6. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.7. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: Client Specific Requirements.

26.2. Attachment II: Tailing Factor Calculation

27. Revisions

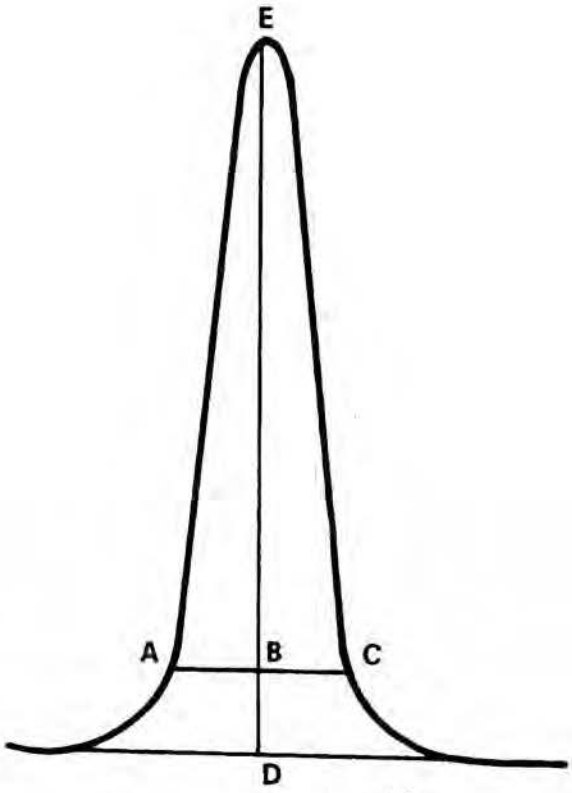
Document Number	Reason for Change	Date
S-GB-O-049-Rev.05	Throughout Document: Updated SOP format to be consistent with SOP: S-GB-Q-017 *Preparation of SOPs* Throughout Document: Renamed Tables to be consistent with current Section. Section 11.3: Changed ICV calculation criteria to match CCV calculation criteria. Table 11.Section 12.2.1: Updated DFTPP Tune Criteria to be consistent with EPA 525.2. Section 12.3: Added tailing factor criteria. Section 19: Added Modification in relation to tune criteria. Attachment II: Tailing Factor Calculation added.	30May2013
S-GB-O-049-Rev.06	Throughout Document: Updated laboratory name to Pace Analytical Services LLC – Green Bay WI Table 7.1: Updated temperature to ≤6˚C from 4±2˚C. Table 9.1 and 12.1: Updated information for 40MSS6/40MSS8, added 40MSSA. Table 9.2: Updated with current vendor information. Section 10.1: Added Acetone. Table 10.4: Changed standard and solvent amounts in calibration curve. Table 11.1: Added pyridine. Table 11.2: Updated SOP reference to most current revision. Table 11.3.1: Added CRDL language. Table 12.2: Updated 1˚ and 2˚ ions. Table 13: Updated MB criteria from 20X to 10X rule for qualification requirements. Section 22.1: Updated MSDS to SDS Section 23.1: Updated SOP reference	24Oct2016
S-GB-O-049-Rev.07	Section 12.11.1: Added to section that data reduction must be done on every sample and quality control standard.:	21Jun2017

Attachment I:

Throughout document, reference to Client Specific requirements refers to samples analyzed following: BP Technical Requirements LaMP Revision 10.1, Canadian National Railway Services and Technical Specifications Manual, GE Minimum Standards Revision 2.

Attachment II: DFTPP Tailing Factor Calculation

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)}$$



TAILING FACTOR= $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

Figure 13. Tailing factor calculation.

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STANDARD OPERATING PROCEDURE

Determination of Volatile Organics by GC/MS

Reference Methods: EPA Method SW-846 8260B with 5030B and 5035; and EPA Method 624

LOCAL SOP NUMBER:	S-GB-O-056-Rev.11
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-O-056-Rev.10
SOP TEMPLATE NUMBER:	TMP-ALL-O-002-Rev.01

LOCAL APPROVAL

Nils Melberg, Laboratory General Manager — Date: 06/21/17

Kate Verbeten, Laboratory Quality Manager — Date: 6/21/17

Scott Turner, Department Manager — Date: 6/21/2017

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

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

Table of Contents

1. Purpose/Identification of Method

This Standard Operating Procedure (SOP) documents the procedures used by PASI – Green Bay to determine the concentration of Volatile Organic Compounds (VOCs) in environmental samples. The laboratory utilizes purge-and-trap GC/MS and bases these documented procedures on those listed SW-846 Methods 5030B, 5035 and 8260B; and EPA 624.

2. Summary of Method

Volatile organic compounds are introduced into the gas chromatograph by a purge-and trap method. The analytes are purged from a sample aliquot or extract by purging with helium or nitrogen. The purged analytes are collected in a trap. At the completion of the purge time, the trap is rapidly heated and back flushed with helium to drive out the trapped analytes. The analytes are transferred into the inlet of a capillary gas chromatography column. The carrier gas flow through the column is controlled and the temperature is increased according to a set program to achieve optimum separation of purged analytes. The mass spectrometer is operated in a repetitive scan mode. Analytes are identified by the GC/MS retention times and by a comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected primary ion relative to an internal standard against a calibration curve.

3. Scope and Application

3.1. **Personnel:** This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.2. **Parameters:** This SOP applies to compounds listed in Section 11, Table 11.1 Calibration standard compound concentrations, analyzed by SW-846 Methods 5030B, 5035 and 8260B and EPA 624.This method is applicable to most organic compounds that have boiling points below 200ºC and are insoluble or slightly soluble in water. Volatile water-soluble compounds may also be determined although quantitation limits are typically higher due to their hydrophilic properties (e.g. ketones, oxygenates). This method cannot be substituted for other similar published methods where permit or regulatory compliance is required.

4. Applicable Matrices

4.1. This SOP is applicable to most water and solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, and other solid samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix related modifications must be documented within the analytical data.

5. Limits of Detection and Quantitation

5.1. The reporting limit (PQL) for all analytes can be found Section 11, Table 11.1. All current MDLs are listed in the LIMs and are available by request from the Quality Manager.

6. Interferences

6.1. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the absorbent trap. The use of polytetrafluoroethylene (PTFE, Teflon) as thread sealants, tubing, or in flow controllers is highly recommended since other materials can be sources of contamination which may concentrate in the trap during the purging.

6.2. A common source of interfering contamination is carryover. This may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive action to this condition is rinsing the purging apparatus and sample syringes with two or more portions of organic free water between samples. Analyze one or more blanks to check for cross contamination prior to sample analysis.

6.3. Since methylene chloride and acetone are common laboratory solvents, special precautions must be taken. The volatiles analysis and sample storage area should be located as far as possible from areas where these solvents are used or stored. Where possible, the volatiles analysis and sample storage area should be served by a separate HVAC system and maintained under positive pressure to prevent intrusion of contaminants. Laboratory clothing previously exposed to methylene chloride fumes during extraction procedures can contribute to sample contamination.

7. Sample Collection, Preservation, Shipment and Storage

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

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Three (3) VOA vials	Acidified w/ 1:1 HCl (1-2 drops) to pH<2, no headspace *Note:* 2-CLEVE, Styrene, and Vinyl Chloride requires an unpreserved sample.	≤6°C	Unpreserved: 7 days pH Preserved: 14 days
Low Level Aliquot Soil/Solid (non-aqueous)	One (1) 2-4 oz. wide mouth jar for % moisture **AND** Two (2) 5-g aliquots in vials with magnetic stir bar, 5.0 mL reagent water and 1.0 g sodium bisulfate as needed. *OR (alternative):* Two (2) EnCore, TerraCore or similar sampling tubes.	No preservation *OR* sodium bisulfate **Note:** If sample effervesces on contact with the preservative, the sodium bisulfate should be eliminated for that sample.	With sodium bisulfate: ≤6°C Without preservation (including EnCore, TerraCore or similar): 4 ± 2°C for up to 48 hours before storing between -7°C and -20°C, inclusive, until analysis.	Unpreserved or not stored frozen: 48 hours Preserved with sodium bisulfate or stored frozen: 14 days
High Level Aliquot Soil/Solid (non-aqueous)	One (1) 10-g aliquot in vial with 10.0 mL purge and trap grade MeOH. *OR (alternative)* One (1) 10-g aliquot in empty vial	Methanol - if sample was collected in empty vial it must be transferred into 10 mL of purge & trap grade MeOH within 48 hours of collection	With methanol: ≤6°C.	Unpreserved: 48 hours Preserved with methanol: 14 days WI Only: 21 days
TCLP Leachates	Tedlar bag or THREE (3) VOA vials.	Filled and capped to eliminate any headspace. Vials with bubbles larger than 5 mm should be discarded.	≤6°C	14 days from end of leaching procedure

Table 7.2: Trip Blank Requirements

Aqueous	Low Level Aliquot Soil/Solid	High Level Aliquot Soil/Solid
One (1) 40mL VOA vial w/ reagent DI water	One (1) 40mL VOA vial w/ 5mL sodium bisulfate (or reagent DI water) and magnetic stir bar	One (1) 40mL VOA vial w/ 5mL purge and trap grade MeOH

8. Definitions

Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions. In addition to those listed in the QAM, the following are additional terms found in this SOP.

8.1. **Run Sequence Log** – A logbook that lists all injections and analyses performed on a particular piece of equipment regardless of the use of the data collected from each analysis.

8.2. **Toxicity Characteristic Leaching Procedure (TCLP)** – An extraction procedure used to determine if a sample is acceptable for upland disposal. The extraction procedure is meant to simulate the leaching of contaminants under the environmental conditions typically found in a landfill.

8.3. **Tune Period** – The period after the BFB instrument tune check within which analyses may be performed.

9. Equipment and Supplies

Table 9.1: Equipment

Analytical Instrument/Peripherals	EPIC Pro Name
HP 5890 Series II GC	40MSV1
HP 5972 MSD	40MSV1
Archon Autosampler	40MSV1
Tekmar 3000 Purge and Trap Concentrator	40MSV1
HP 6890 GC	40MSV2
HP 5973 MSD	40MSV2
Archon Autosampler	40MSV2
Tekmar 3000 Purge and Trap Concentrator	40MSV2
Agilent 6850 GC	40MSV3
Agilent 5975 MSD	40MSV3
Tekmar Aquatek 70	40MSV3
Tekmar Stratum Purge and Trap Concentrator	40MSV3
HP 6890 GC	40MSV5
HP 5973 MSD	40MSV5
Archon Autosampler	40MSV5
Tekmar 3000 Purge and Trap Concentrator	40MSV5
HP 6890 GC	40MSV7
HP 5973 MSD	40MSV7
Archon Autosampler	40MSV7
Tekmar 3000 Purge and Trap Concentrator	40MSV7
Agilent Technologies 6850 Network GC System	40MSV8
Agilent Technologies 5975B MSD	40MSV8
EST 8100 Autosampler	40MSV8
Teledyne Tekmar 14-9800-100 Stratum Purge and Trap System	40MSV8
Agilent 5975C GCMS	40MSVA
Agilent 7890A GC	40MSVA
EST 8100 Autosampler	40MSVA
Tekmar Stratum Purge and Trap Concentrator	40MSVA
Agilent 5975C GCMS	40MSVB
Agilent 7890A GC	40MSVB
Tekmar Atomx Autosampler/Purge and Trap Conc.	40MSVB
Agilent 7890B GC	40MSVC
Agilent 5977A MSV	40MSVC
Tekmar Stratum Purge and Trap Concentrator	40MSVC
EST Centurion Autosampler	40MSVC

Table 9.2: Supplies

Supplies	Manufacturer	Vendor	Catalog #
10µL Gastight 1701	Hamilton	Fisher Scientific	14-815-1
25µL Gastight 1702	Hamilton	Fisher Scientific	14-815-29
50µL Gastight 1705	Hamilton	Fisher Scientific	14-824-30
100µL Gastight 1710	Hamilton	Fisher Scientific	13-684-100
250µL Gastight 1725	Hamilton	Fisher Scientific	13-684-102
500µL Gastight 1750	Hamilton	Fisher Scientific	13-684-106
1mL Gastight 1001	Hamilton	Fisher Scientific	14-824-25
5mL Gastight 1005	Hamilton	Fisher Scientific	13-684-96
50mL Gastight 1050	Hamilton	Fisher Scientific	14-815-195
DB-624 Capillary column, 20mX0.18 mm i.d.X1.0 µm	J&W Scientific	VWR Scientific	121-1324
K-Trap, Vocarb3000, Tekmar3000	Supelco	Supelco	24920-U
Fritless 5 mL Sparge Tube	Supelco	Supelco	22780
IceBlue Septa, 11mm	Restek	Restek	22392
Single Gooseneck Injection port liners (4mm)	Restek	Restek	20799
Gold-plated inlet seals	Restek	Restek	21306
Viton O-rings	Restek	Restek	20377
0.4mm Vespel/Graphite ferrules	Restek	Restek	20211
GCMS Filaments	Agilent Technologies	Agilent Technologies	05972-60053
Stir Bar	Fisher Brand	Fisher Brand	14-511-60A
40 mL VOA vials	QEC	QEC	3112-40mL
10 mL volumetric	Kimax Brand	Fisher Scientific	10-212AA
25 mL volumetric	Kimax Brand	Fisher Scientific	10-212BB
50 mL volumetric	Kimax Brand	Fisher Scientific	10-212A
100 mL volumetric	Kimax Brand	Fisher Scientific	10-212B
200 mL volumetric	Kimax Brand	Fisher Scientific	10-212C
500 mL volumetric	Kimax Brand	Fisher Scientific	10-218D
Pasteur Pipettes	Fisher Scientific	Fisher Scientific	13-678-20A
Pipette bulb	Fisher Scientific	Fisher Scientific	14-065B
0.1-2.5 mL Repipettor	Brinkmann	Fisher Scientific	13-688-130
1-5 mL Repipettor	Brinkmann	Fisher Scientific	13-688-131
2-10 mL Repipettor	Brinkmann	Fisher Scientific	13-688-133
5-25 mL Repipettor	Brinkmann	Fisher Scientific	13-688-134
1.8 mL amber vials & caps	Restek	Restek	24637
10 mL graduate cylinder	Kimax Brand	Fisher Scientific	08-554B “to deliver”
40 mL VOA vials HCl preserved	QEC	QEC	3112-40HCl
2 oz. jars with Teflon lids	QEC	QEC	2114-0002
Spatulas	Fisher Scientific	Fisher Scientific	14-511-60A

10. Reagents and Standards

10.1. Reagents

Table 10.1: Reagents

Reagent	Conc.	Purity	Manufacturer	Vendor	Catalog #
Methanol	100%	Purge and Trap grade	Burdick & Jackson	VWR Scientific	232-1
Sodium Bisulfate	Granular	Certified grade	Fisher Scientific	Fisher Scientific	S-240-3
Nitrogen gas		99.999%	Michigan Airgas	Michigan Airgas	
Helium gas		99.999%	Michigan Airgas	Michigan Airgas	
Reverse Osmosis (ROW) Water		Organic Free	Flowmatic	Culligan	
Ottawa Sand, 20-30 mesh		ASTM C190	Fisher Scientific	Fisher Scientific	S23-3

10.2. Analytical Standards

10.2.1. Definitions: Standards are required for mass spectrometer tuning, initial calibration, calibration verification standards, second source verification, internal standards, surrogates, and for preparing LCS, MS, and MSD samples. Table 10.2 describes the standards used. Table 10.3 lists the stock standards used. Table 10.4 lists the compounds in each stock standard.

Table 10.2: Standard Definitions

Standard	Description	Comments
Tune Standard	4-Bromofluorobenzene (BFB) solution used to verify ion response ratios prior to analysis	Must purge between 5 and 50ng
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	Method requires a minimum of 5 levels
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	
Second Source Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the accuracy of the calibration curve.	For volatiles analysis, this may be used as the LCS if analyzed once every 20 samples.
Internal Standard	A solution added all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard is used to adjust response ratios to account for instrument drift.	Pentafluorobenzene 1,4-Difluorobenzene Chlorobenzene-d5 1,4-Dichlorobenzene-d4
Surrogate Standard	A solution added to all samples, spikes, control samples, and method blanks prior to analysis.	Dibromofluoromethane Toluene-d8 4-Bromofluorobenzene
Spiking Standard	This solution contains all target analytes and should not be prepared from the same standards as the calibration standards.	For volatiles analysis, this can be used as the second source verification standard.

10.2.2. Stock Standards

Table 10.3: Stock Standards

Standard	Conc.	Purity	Manufacturer	Vendor	Catalog #
4-BFB Tuning Standard	5000 µg/mL	99%	Restek	Restek	30003-520
502.2 Cal Gases Mix	2000 µg/mL	99%	Restek	Restek	30042
502.2 ICV Gases Mix	2000 µg/mL	99%	Accustandard	Accustandard	M-502B-10X
502.2 Cal 2000 Megamix	2000 µg/mL	99%	Restek	Restek	30431
Megamix – ICV	2000 µg/mL	99%	o2si	o2si	122708-05
Vinyl Acetate	Neat	99+%	Chem Service	Chem Service	F718
Calibration Ketone Mix	5000 µg/mL	99%	Restek	Restek	30006
Ketones – ICV	2000 µg/mL	99%	o2si	o2si	121020-10
Pace GB Custom Mix #3	various µg/mL	99+%	o2si	o2si	120407-11-SS
Custom – ICV	100,000 – 200,000 µg/µL	99%	o2si	o2si	122707-05
Acrolein – CAL	Neat	99+%	Chem Service	Chem Service	N-11030-1G
2-Chloroethylvinyl Ether	2000 µg/mL	99+%	Restek	Restek	30265
Reactive Mix – ICV	100-1000 µg/mL	99%	o2si	o2si	120407-13
8260 Internal Standard	2500 µg/mL	99%	Restek	Restek	30173
8260 Surrogate Standard	2500 µg/mL	99%	Restek	Restek	30174
CLP 4.1Mega Mix	2000 µg/mL	99%	Restek	Restek	30456
502.2 Gases Mix #1	2000 µg/mL	99%	Restek	Restek	30006

10.2.3. Standard Mixes

Table 10.4: Standard Mixes

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
Restek	**4-BFB Tuning Standard**	**30003-520**	4-bromofluorobenzene	2500
Restek	**502.2 Cal Gases Mix**	**30042**	Bromomethane	2000
			Chloroethane	2000
			Chloromethane	2000
			Dichlorodifluoromethane	2000
			Trichlorofluoromethane	2000
			Vinyl Chloride	2000
Accustandard	**502.2 ICV Gases Mix =**	**M-502B-10X**	Bromomethane	2000
			Chloroethane	2000
			Chloromethane	2000
			Dichlorodifluoromethane	2000
			Trichlorofluoromethane	2000
			Vinyl Chloride	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
Restek	**502.2 Cal 2000 MegaMix**	**30431**	1,1,1,2-Tetrachloroethane	2000
			1,1,1-Trichloroethane	2000
			1,1,2,2-Tetrachloroethane	2000
			1,1,2-Trichloroethane	2000
			1,1-Dichloroethane	2000
			1,1-Dichloropropene	2000
			1,1-Dichlroethene	2000
			1,2,3-Trichlorobenzne	2000
			1,2,3-Trichloropropane	2000
			1,2,3-Trimethylbenzene	2000
			1,2,4-Trimethylbenzene	2000
			1,2-Dibromo-3-chloropropane	2000
			1,2-Dibromoethane	2000
			1,2-Dichlorethane	2000
			1,2-Dichlorobenzene	2000
			1,2-Dichloropropane	2000
			1,3,5-Trimethylbenzene	2000
			1,3-Dichlorobenzene	2000
			1,3-Dichloropropane	2000
			1,4-Dichlorobenzene	2000
			2,2-Dichloropropane	2000
			2-Chlorotoluene	2000
			4-Chlorotoluene	2000
			4-Isopropyltoluene	2000
			Benzene	2000
			Bromobenzene	2000
			Bromochloromethane	2000
			Bromodichloromethane	2000
			Bromoform	2000
			Carbon Tetrachloride	2000
			Chlorobenzene	2000
			Chloroform	2000
			cis-1,2-Dichloroethene	2000
			cis-1,3-Dichloropropene	2000
			Dibromochloromethane	2000
			Dibromomethane	2000
			Ethylbenzene	2000
			Hexachloro-1,3-butadiene	2000
			Isopropylbenzene	2000
			Methylene Chloride	2000
			m-Xylene	2000
			Naphthalene	2000
			n-Butylbenzene	2000
			n-Propylbenzene	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
			o-Xylene	2000
			p-Xylene	2000
			sec-Butylbenzene	2000
			Styrene	2000
			tert-Butylbenzene	2000
			Tetrachloroethene	2000
			Toluene	2000
			trans-1,2-Dichloroethene	2000
			trans-1,3-Dichloropropene	2000
			Trichloroethene	2000
o2si	**MegaMix – ICV**	**122708-05**	Isopropyl alcohol	20,000
			Isobutyl alcohol	20,000
			tert-butyl alcohol	10,000
			Acetonitrile	5000
			Ethyl ether	2000
			Isopropyl ether	2000
			Benzene	2000
			n-propylbenzene	2000
			sec-butylbenzene	2000
			tert-butylbenzene	2000
			1,2,4 trimethylbenzene	2000
			n-butylbenzene	2000
			naphthalene	2000
			p-cymene	2000
			1,2-dichlorobenzene	2000
			1,3-dichlorobenzene	2000
			Chlorobenzene	2000
			1,2,3-trichlorobenzene	2000
			1,2,4-trichlorobenzene	2000
			Bromobenzene	2000
			Bromochloromethane	2000
			Carbon tetrachloride	2000
			Dibromomethane	2000
			Bromodichloromethane	2000
			Bromoform	2000
			Dibromochloromethane	2000
			trans-1,2-dichloroethylene	2000
			1,1-dichloroethylene	2000
			1,1-dichloroethane	2000
			1,1,1-trichloroethane	2000
			2,2-dichloropropane	2000
			tetrachloroethylene	2000
			1,1,1,2-tetrachloroethane	2000
			1,1,2-trichloroethane	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
			1,2-dichloroethane	2000
			1,2-dibromo-3chloropropane	2000
			1,2-dibromomethane	2000
			1,1 dichloropropylene	2000
			1,2,3-trichloropropane	2000
			1,2 dichloropropane	2000
			trans-1,3-dichloropropylene	2000
			cis-1,3-dichloropropylene	2000
			1,3-dichloropropane	2000
			Iodomethane	2000
			Carbon disulfide	2000
			Methyl acetate	2000
			Cyclohexane	2000
			Methyl t-butyl ether	2000
			Ethyl t-butyl ether	2000
			tert-amyl methyl ether	2000
			1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113)	2000
			Heptane (C7)	2000
			1,2,3-trimethylbenzene	2000
			n-hexane (C6)	2000
			Isopropyl acetate	2000
			1-methylnaphthalene	2000
			2-methylnaphthalene	2000
			Acrylonitrile	2000
			Allyl chloride	2000
			Chloroform	2000
			2-chlorotoluene	2000
			4-chlorotoluene	2000
			Cis-1,2-dichloroethylene	2000
			1,4-dichlorobenzene	2000
			Cis-1,4-dichloro-2-butene	2000
			2,3-dichloro-1-propene	2000
			Ethylbenzene	2000
			Hexachlorobutadiene	2000
			Hexachloroethane	2000
			Isopropylbenzene	2000
			Methyl cyclohexane	2000
			Methylene chloride	2000
			Styrene	2000
			1,1,2,2-tetrachloroethane	2000
			Tetrahydrofuran	2000
			Toluene	2000
			Trichloroethylene	2000
			1,3,5-Trimethylbenzene	2000
			m-xylene	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
			o-xylene	2000
			p-xylene	2000
Chem Service	**Vinyl Acetate**	**F718**	Vinyl Acetate	Neat
Restek	**Calibration Ketone Mix**	**30006**	2-Butanone	5000
			2-Hexanone	5000
			4-Methyl-2-pentanone	5000
			Acetone	5000
o2si	**Ketones – ICV**	**121020-10**	2-Butanone	2000
			2-Hexanone	2000
			4-Methyl-2-pentanone	2000
			Acetone	2000
o2si	**Pace-GB Custom**	**121082-01-SS**	Dichlorofluoromethane	2000
	Mix #3		1,1,2-trichlorotrifluoroethane	2000
			Acetonitrile	5000
			Iodomethane (methyl iodide)	2000
			Allyl chloride (3-chloropropene)	2000
			Carbon disulfide	2000
			Acrylonitrile	2000
			2,3-dichloropropylene	2000
			cis-1,4-dichloro-2-butene	2000
			trans-1,4-dichloro-2-butene	2000
			1,2,3-trimethylbenzene	2000
			Hexachloroethane	2000
			2-methylnaphthalene	2000
			1-methylnaphthalene	2000
			Ethanol	100,000
			Diethyl ether (ethyl ether	2000
			2-propanol (isopropanol)	20,000
			tert-butanol (TBA)	10,000
			Methyl acetate	2000
			n-Hexane	2000
			Methyl-tert-butyl-ether (MTBE)	2000
			1-Propanol	100,000
			1,4-dioxane	100,000
			1-butanol	100,000
			Tetrahydrofuran	2000
			Cyclohexane	2000
			Heptane (C7)	2000
			tert-amyl methyl ether	2000
			Ethyl t-butyl ether	2000
			Isopropyl ether	2000
			Isobutyl alcohol	20,000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
			Methyl cyclohexane	2000
			Isopropyl acetate	2000
Chem Service	**Acrolein - Cal**	**N-11030-1G**	Acrolein	Neat
Restek	**2-chloroethylvinyl ether**	**30265**	2-chloroethylvinyl ether	2000
o2si	**Reactive Mix – ICV**	**120407-13**	2-chloroethylvinyl ether	100
			Acrolein	1000
			Vinyl Acetate	100
Restek	**8260 Internal Standard**	**30173**	Pentafluorobenzene	2500
			1,4-Difluorobenzene	2500
			Chlorobenzene-d5	2500
			1,4-Dichlorobenzene-d4	2500
Restek	**8260 Surrogate Standard**	**30174**	Dibromofluoromethane	2500
			Toluene-d8	2500
			1-Bromo-4-fluorobenzene	2500
Restek	**CLP 4.1Mega Mix**	**30456**	1,1,2-trichlorotrifluoroethane	2000
			1,1-dichloroethene	2000
			Benzene	2000
			Bromodichloromethane	2000
			Bromoform	2000
			Carbon Tetrachloride	2000
			Chlorobenzene	2000
			Chloroform	2000
			Dibromochloromethane	2000
			1,2-dichloroethane	2000
			Cis-1,2-dichloroethene	2000
			1,2-Dichloropropane	2000
			trans-1,3-dichloropropylene	2000
			cis-1,3-dichloropropylene	2000
			Ethylbenzene	2000
			Styrene	2000
			1,1,2,2-tetrachloroethane	2000
			Tetrachloroethene	2000
			Toluene	2000
			1,1,1-trichloroethane	2000
			1,1,2-trichloroethane	2000
			Trichloroethane	2000
			m&p-Xylene	4000
			o-Xylene	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
			Cyclohexane	2000
			Methylcyclohexane	2000
			1,2-dibromo-3chloropropane	2000
			1,2-Dibromoethane	2000
			Isopropylbenzene	2000
			1,2,4-Trichlorobenzene	2000
			1,3-Dichlorobenzene	2000
			1,4-Dichlorobenzene	2000
			1,2-Dichlorobenzene	2000
			Methyl acetate	2000
			Carbon disulfide	2000
			Methylene chloride (dichloromethane)	2000
			Methyl-tert-butyl ether (MTBE)	2000
			Trans-1,2-dichloroethene	2000
			1,1-dichloroethane	2000

10.2.4. Standard Storage Conditions

Table 10.5: Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	Concentrated reference solution purchased directly from approved vendor	1. Manufacturer's recommended expiration date for unopened ampulated standards. 2. Gas standards must be replaced 6 months after ampule is opened. 3. All other stock standards must be replaced 6 months after ampule is opened or on expiration date, whichever is sooner.	1. Manufacturer's recommended storage conditions 2. When standard is opened, record all information in the standard logbook.
Intermediate and Working Standard Solutions	Reference solutions prepared by dilutions of the stock solution	1. 6 months from preparation or the expiration date listed for the stock source, whichever is sooner. 2. 6 months for gas working standards. 3. Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	1. Store in amber vials with Teflon lined screw caps 2. Manufacturer's recommended storage conditions for stock source solution. 3. If stock source conditions conflict, store standard at coldest condition of any source.

10.2.5. Standard Sources

Standards are prepared from commercially available multi-compound stock solutions and neat materials by multiple dilutions. The sources of the stock solutions and neat materials are listed in Table 10.3. The recipes for preparing dilutions and all working and intermediate standards, and concentrations for all compounds are presented in Tables 10.6 and 10.7. All intermediate standards are prepared using purge and trap grade methanol and stored frozen in glass vials with Teflon lined screw caps or Mininert valves or as recommended by the standard manufacturer.

10.2.6. Preparation Procedures

Table 10.6: Intermediate Standard Preparation

Standard	Acronym	Concentration	Direction found in Section:
Level 1 Calibration Standard (MeOH Curve Only)	CAL1 (MeOH Curve Only)	0.40µg/L all compounds except as follows: 1.0 µg/L acetonitrile; 2.0 µg/L tert butyl alcohol; 4.0 µg/L acrolein, isopropanol, isobutanol; 20 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Table 10.7
Water Level 1 Calibration Standard MeOH Level 2 Calibration Standard	CAL1 (Water) CAL2 (MeOH)	1.0µg/L all compounds except as follows: 2.5 µg/L acetonitrile; 5.0 µg/L tert butyl alcohol; 10 µg/L acrolein, isopropanol, isobutanol; 50 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Table 10.7
Water Level 2 Calibration Standard MeOH Level 3 Calibration Standard	CAL2 (Water) CAL3 (MeOH)	5.0 µg/L all compounds except as follows: 12.5 µg/L acetonitrile; 25 µg/L tert butyl alcohol; 50 µg/L acrolein, isopropanol, isobutanol; 250 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Water Level 3 Calibration Standard MeOH Level 4 Calibration Standard	CAL3 (Water) CAL4 (MeOH)	20 µg/L all compounds except as follows: 50 µg/L acetonitrile,; 100 µg/L tert butyl alcohol; 200 µg/L acrolein, isopropanol, isobutanol; 1000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Water Level 4 Calibration Standard MeOH Level 5 Calibration Standard	CAL4 (Water) CAL5 (MeOH)	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Table 10.7
Water Level 5 Calibration Standard MeOH Level 6 Calibration Standard	CAL5 (Water) CAL6 (MeOH)	100 µg/L all compounds except as follows: 250 µg/L acetonitrile; 500 µg/L tert butyl alcohol; 1000 µg/L acrolein, isopropanol, isobutanol; 5000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Water Level 6 Calibration Standard MeOH Level 7 Calibration Standard	CAL6 (Water) CAL7 (MeOH)	200 µg/L all compounds except as follows: 500 µg/L acetonitrile; 1000 µg/L tert butyl alcohol; 2000 µg/L acrolein, isopropanol, isobutanol; 10000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Level 7 Calibration Standard (Water Curve only)	CAL7 (Water Curve only)	300 µg/L all compounds except as follows: 750 µg/L acetonitrile; 1500 µg/L tert butyl alcohol; 3000 µg/L acrolein, isopropanol, isobutanol; 15000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
*Optional Water Level 3 Calibration	CAL3 (Water	10 µg/L all compounds except as follows:	Table 10.7

Standard	Acronym	Concentration	Direction found in Section:
Standard * If this standard is made for a water Curve, all subsequent Water Level # will increment by 1 (i.e. 300µg/L will now be CAL8)	Curve only) *Optional	25 µg/L acetonitrile; 50 µg/L tert butyl alcohol; 100 µg/L acrolein, isopropanol, isobutanol; 500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	
Independent Calibration Verification Standard	ICV050	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Calibration Verification Standard	CCV050	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Acrolein – Cal Intermediate	Acrolein - Cal	20,000 µg/mL	Table 10.7
Vinyl Acetate – Cal Intermediate	Vinyl Acetate - Cal	10,500 µg/mL	Table 10.7
Surrogate Standard	SS	50 µg/L	Table 10.7
Internal Standard	IS	50 µg/L	Table 10.7
Method Blank	MB	< Reporting Limit	Table 10.7
BFB	TUNExxx	50 ng injection	Table 10.7
Matrix Spike/ Lab Control Spike Stock Solution - CLP 4.1List for Water and Low Level Soil Samples	MS/LCS CLP 4.1 List Stock Solution for Water and Low Level Soil Samples	100 µg/mL for all compounds	Table 10.7
Matrix Spike/Lab Control Spike Stock Solution - CLP 4.1 List for Methanol Preserved Soil Samples	MS/LCS CLP 4.1 List Stock Solution for Methanol Preserved Soil Samples	500 µg/mL for all compounds	Table 10.7
Matrix Spike/Lab Control Spike Stock Solution - Full List for Water and Low Level Soil Samples	MS/LCS Stock Solution – Full List for Water and Low Level Soil Samples	100 µg/mL all compounds except as follows: 1000 µg/mL Acrolein	Table 10.7
Matrix Spike/ Lab Control Spike Stock Solution - Full List for Methanol Preserved Soil Samples	MS/LCS Stock Solution – Full List for Methanol Preserved Soil Samples	500 µg/mL all compounds except as follows: 5000 µg/mL Acrolein	Table 10.7
MS/MSD – LCS/LCSD Spike for Water	MS/MSD	50 µg/L for most compounds, Various for	Table 10.7

Standard	Acronym	Concentration	Direction found in Section:
Samples	LCS/LCSD	others.	
MS/MSD – LCS/LCSD Spike for 624 Water Samples	MS/MSD LCS/LCSD	20 µg/L for most compounds, Various for others.	Table 10.7
MS/MSD – LCS/LCSD Spike for Low Level Soil Samples	MS/MSD LCS/LCSD	50 µg/kg for most compounds, Various for others.	Table 10.7
MS/MSD – LCS/LCSD Spike for Methanol Preserved Soil Samples	MS/MSD LCS/LCSD	2500 µg/kg for most compounds, Various for others.	Table 10.7
Extraction Blank	EBLK	< Reporting Limit	

Table 10.7: Preparation of Standards

Standard	Acronym	Concentration of Intermediate	Reagents Used	Final Volume
4-Bromofluorobenzene	BFB	50 µg/mL	100µL of 5000 µg/mL BFB into methanol	10 mL
Internal Standard	IS	250 µg/mL	5000 µL of 2500 µg/mL IS into methanol	50 mL
Surrogate Standard	SS	250 µg/mL	5000 µL of 2500 µg/mL SS into methanol	50 mL
Internal/Surrogate Std.	IS/SS	250 µg/mL	5000 µL of 2500 µg/mL IS/SS into MeOH	50 mL
Vinyl Acetate – Cal Intermediate	Vinyl Acetate - Cal	10,500 µg/mL	0.105g of neat Vinyl Acetate Diluted into methanol	10 mL
Acrolein – Cal Intermediate	Acrolein - Cal	20,000 µg/mL	0.21g of neat Acrolein 1 mL Reverse Osmosis Water Diluted into methanol	10 mL
100 µg/mL Calibration Std. 250 µg/mL acetonitrile; 500 µg/mL tert butyl alcohol; 1000 µg/mL acrolein, isopropanol, isobutanol; 5000 µg/mL 1,4-dioxane, 1-propanol, n-butanol, ethanol	CAL Stock Standard	100 µg/mL all compounds except as follows: 250 µg/mL acetonitrile,; 500 µg/mL tert butyl alcohol; 1000 µg/mL acrolein, isopropanol, isobutanol; 5000 µg/mL 1,4-dioxane, 1-propanol, n-butanol, ethanol	1250 µL of 2000 µg/mL 502.2 Calibration Gases Mix 1250 µL of 2000 µg/mL 502.2 Cal 2000 Megamix 238 µL of 10,500 µg/mL Vinyl Acetate -Cal 500 µL of 5000 µg/mL Calibration KetoneMix 1250 µL of 2000 µg/mL Pace GB Custom Mix #3 1250 µL of 20000 µg/mL Acrolein -Cal 1250 µL of 2000 µg/mL 2-Chloroethylvinyl ether Diluted into methanol Surrogates are added by the instrument during aqueous and low level soil calibration events.	25 mL
100 µg/mL Calibration Std. 250 µg/mL acetonitrile; 500 µg/mL tert butyl alcohol; 1000 µg/mL acrolein, isopropanol, isobutanol; 5000 µg/mL 1,4-dioxane, 1-propanol, n-butanol, ethanol	ICV Stock Standard	100 µg/mL all compounds except as follows: 250 µg/mL acetonitrile,; 500 µg/mL tert butyl alcohol; 1000 µg/mL, isopropanol, isobutanol; 5000 µg/mL 1,4-dioxane, 1-propanol, n-butanol, ethanol	1250 µL of 2000 µg/mL 502.2 ICV Gases Mix 1250 µL of 2000 µg/mL Megamix – ICV 1250 µL of 2000 µg/mL Ketones ICV 1250 µL of 2000 µg/mL Custom – ICV Diluted into methanol	25 mL
MeOH Level 1 Calibration Standard (MeOH Curve Only)	CAL1 (MeOH Curve Only)	0.40µg/L all compounds except as follows: 1.0 µg/L acetonitrile; 2.0 µg/L tert butyl alcohol; 4.0 µg/L acrolein, isopropanol, isobutanol; 20 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Methanol curve only dilute: 2.0 µL 100 µg/mL CAL Stock Standard and 1 µL 250 µg/mL Surrogate Standard into 490 mL reverse osmosis water and 10 mL methanol	500 mL
Water Level 1 Calibration Standard MeOH Level 2 Calibration Standard	CAL1 (Water) CAL2 (MeOH)	1.0µg/L all compounds except as follows: 2.5 µg/L acetonitrile; 5.0 µg/L tert butyl alcohol; 10 µg/L acrolein, isopropanol, isobutanol; 50 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Water Curve: Dilute 5 µL of 100 µg/mL CAL Stock Standard into 500 mL reverse osmosis water. If for a methanol curve dilute: 5 µL 100 µg/mL CAL Stock Standard and 2 µL 250 µg/mL Surrogate Standard into 490 mL reverse osmosis water and 10 mL methanol.	500 mL
Water Level 2	CAL2	5.0 µg/L all compounds	Water Curve:	50 mL

Standard	Acronym	Concentration of Intermediate	Reagents Used	Final Volume
Calibration Standard MeOH Level 3 Calibration Standard	(Water) CAL3 (MeOH)	except as follows: 12.5 µg/L acetonitrile; 25 µg/L tert butyl alcohol; 50 µg/L acrolein, isopropanol, isobutanol; 250 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Dilute 2.5 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 2.5 µL 100 µg/mL CAL Stock Standard and 1 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 1 mL methanol.	
Water Level 3 Calibration Standard MeOH Level 4 Calibration Standard	CAL3 (Water) CAL4 (MeOH)	20 µg/L all compounds except as follows: 50 µg/L acetonitrile,; 100 µg/L tert butyl alcohol; 200 µg/L acrolein, isopropanol, isobutanol; 1000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Water Curve: Dilute 10 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 10 µL 100 µg/mL CAL Stock Standard and 4 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 990 µL methanol.	50 mL
Water Level 4 Calibration Standard MeOH Level 5 Calibration Standard	CAL4 (Water) CAL5 (MeOH)	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Water Curve: Dilute 25 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 25 µL 100 µg/mL CAL Stock Standard and 10 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 960 µL methanol.	50 mL
Water Level 5 Calibration Standard MeOH Level 6 Calibration Standard	CAL5 (Water) CAL6 (MeOH)	100 µg/L all compounds except as follows: 250 µg/L acetonitrile; 500 µg/L tert butyl alcohol; 1000 µg/L acrolein, isopropanol, isobutanol; 5000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Water Curve: Dilute 50 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 50 µL 100 µg/mL CAL Stock Standard and 20 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 930 µL methanol.	50 mL
Water Level 6 Calibration Standard MeOH Level 7 Calibration Standard	CAL6 (Water) CAL7 (MeOH)	200 µg/L all compounds except as follows: 500 µg/L acetonitrile; 1000 µg/L tert butyl alcohol; 2000 µg/L acrolein, isopropanol, isobutanol; 10000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Water Curve: Dilute 100 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 100 µL 100 µg/mL CAL Stock Standard and 40 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 860 µL methanol.	50 mL
Water Level 7 Calibration Standard (Water Curve only)	CAL7 (Water Curve only)	300 µg/L all compounds except as follows: 750 µg/L acetonitrile; 1500 µg/L tert butyl alcohol; 3000 µg/L acrolein, isopropanol, isobutanol; 15000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Water Curve Only: Dilute 150 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water.	50 mL

Standard	Acronym	Concentration of Intermediate	Reagents Used	Final Volume
*Optional Water Level3 Calibration Standard * If this standard is made for a water Curve, all subsequent Water Level # will increment by 1 (i.e. 300µg/L will now be CAL8)	CAL3 (Water Curve only) *Optional	10 µg/L all compounds except as follows: 25 µg/L acetonitrile; 50 µg/L tert butyl alcohol; 100 µg/L acrolein, isopropanol, isobutanol; 500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Water Curve: Dilute 5 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water.	50 mL
Independent Calibration Verification Standard	ICV050	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Water Curve: Dilute 25 µL of 100 µg/mL ICV Stock Standard and 25 µL Reactive Mix – ICV into 50 mL reverse osmosis water. If for a methanol curve dilute: 25 µL 100 µg/mL ICV Stock Standard, 25 µL Reactive Mix – ICV and 10 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 940 µL methanol.	50 mL
Calibration Verification Standard	CCV050	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Water Curve: Dilute 25 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 25 µL 100 µg/mL CAL Stock Standard and 10 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 960 µL methanol.	50 mL
Matrix Spike/Lab Control Spike Stock Solution - TCL 4.1 List for Water and Low Level Soil Samples	MS/LCS TCL 4.1 List Stock Solution for Water and Low Level Soil Samples	100 µg/mL for all compounds	1250 µL of 2000 µg/mL CLP 4.1Mega Mix 1250 µL of 2000 µg/mL 502.2 Gases Mix #1 Dilute into methanol.	25 mL
Matrix Spike/Lab Control Spike Stock Solution - TCL 4.1 List for Methanol Preserved Soil Samples	MS/LCS TCL 4.1 List Stock Solution for Methanol Preserved Soil Samples	500 µg/mL for all compounds	2500 µL of 2000 µg/mL CLP 4.1Mega Mix 2500 µL of 2000 µg/mL 502.2 Gases Mix #1 Dilute into methanol.	10 mL
Matrix Spike/Lab Control Spike Stock Solution - Full List *	MS/LCS Stock Solution – Full List	100 µg/mL all compounds except as follows: 250 µg/mL acetonitrile; 500 µg/mL tert butyl alcohol; 1000 µg/mL	1250 µL of 2000 µg/mL 502.2 ICV Gases Mix 1250 µL of 2000 µg/mL Megamix – ICV 1250 µL of 2000 µg/mL Ketones ICV 1250 µL of 2000 µg/mL Custom – ICV Diluted into methanol	25 mL

Standard	Acronym	Concentration of Intermediate	Reagents Used	Final Volume
		isopropanol, isobutanol; 5000 µg/mL 1,4-dioxane, 1-propanol, n-butanol, ethanol		
MS/MSD – LCS/LCSD Spike for Water Samples	MS/MSD LCS/LCSD	50 µg/L for most compounds, Various for others.	Add 21 µL of the appropriate Matrix Spike/ Lab Control Spike Solution to 42 mL of sample for MS/MSD, or 42 mL of reagent water for LCS/LCSD	42 mL
MS/MSD – LCS/LCSD Spike for 624 Water Samples	MS/MSD LCS/LCSD	20 µg/L for most compounds, Various for others	Add 8.4 µL of the appropriate Matrix Spike / Lab Control Spike Solution to 42 mL of sample for MS/MSD or 42 mL of reagent water for LCS/LCSD.	42 mL
MS/MSD – LCS/LCSD Spike for Low Level Soil Samples	MS/MSD LCS/LCSD	50 µg/kg for most compounds, Various for others.	Add 2.5 µL of the appropriate Matrix Spike/ Lab Control Spike Solution to 5.0 g of sample containing 5 mL of reagent water for MS/MSD, or 5.0 g of Ottawa sand containing 5 mL of reagent water for LCS/LCSD	5 mL
MS/MSD – LCS/LCSD Spike for Methanol Preserved Soil Samples Standard List	MS/MSD LCS/LCSD	2500 µg/kg for most compounds, Various for others.	Add 50 µL of the Standard List Matrix Spike/ Lab Control Spike Solution to 10 g of sample containing 10 mL of methanol for MS/MSD, amount of Spike Solution is adjusted according to the initial methanol volume; or 10 g of Ottawa sand containing 10 mL of methanol for LCS/LCSD	10 mL
MS/MSD – LCS/LCSD Spike for Methanol Preserved Soil Samples Full List	MS/MSD LCS/LCSD	2500 µg/kg for most compounds, Various for others.	Add 250 µL of the Full List Matrix Spike/ Lab Control Spike Solution to 10 g of sample containing 10 mL of methanol for MS/MSD, amount of Spike Solution is adjusted according to the initial methanol volume; or 10 g of Ottawa sand containing 10 mL of methanol for LCS/LCSD	10 mL

*Samples to be analyzed by EPA 624 originating in the State of South Carolina must contain all analytes of interest in the LCS, MS, and MSD.

11. Calibration and Standardization

11.1. Tune Verification

The mass spectrometer tune status must be verified prior to initial calibration and at the beginning of each analytical sequence. If the current tune status does not meet the ion ratio criteria in the method (see section 11.2), follow the equipment manufacturers' instructions for re-tuning the mass spectrometer. The tune status must be verified after the tuning procedures.

11.2. Initial Calibration (ICAL)

11.2.1. Analysis of Standards

An initial calibration curve using a minimum of five points is analyzed prior to analyzing client samples. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values. Refer to table 11.1 for compound concentrations.

An analyte must be present and calibration curve in control in order to be reported on the target analyte list. Analytes identified by mass spectral match but not present and in control

in the calibration table may be reported as Tentatively Identified Compounds (TICs). Guidelines for identification are listed in Section 12.6.3. Results for these TICs should be reported only on a present/absent basis. However, quantitative results may be reported provided they are qualified as estimated values.

Table 11.1: Calibration standard compound concentrations

Analyte	PQL water µg/L	PQL soil µg/kg	PQL 5035 soil µg/Kg	Cal1 MeOH curve only µg/L	Cal2 MeOH Cal1 water µg/L	Cal3 MeOH Cal2 water µg/L	Cal4 MeOH Cal3 water µg/L	Cal5 MeOH Cal4 water µg/L	Cal6 MeOH Cal5water µg/L	Cal7 MeOH Cal6 water µg/L	Cal7 water Curve only µg/L	* Optional Cal3 water Curve only µg/L
1,1-Dichloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,1-Dichloroethene	1	50	5	-	1	5	20	50	100	200	300	10
1,1-Dichloropropene	1	50	5	-	1	5	20	50	100	200	300	10
1,1,1-Trichloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,1,2-Trichloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,1,2-Trichloro-1,1,2trifluoethane	5	50	5	-	1	5	20	50	100	200	300	10
1,1,1,2-Tetrachloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,1,2,2-Tetrachloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,2,4-Trichlorobenzene	5	250	5	-	1	5	20	50	100	200	300	10
1,2-Dichlorobenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,2-Dibromo-3-chloropropane	5	250	5	-	1	5	20	50	100	200	300	10
1,2-Dichloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,2-Dibromoethane	1	50	5	-	1	5	20	50	100	200	300	10
1,2-Dichloropropane	1	50	5	-	1	5	20	50	100	200	300	10
1,2-Dichloroethene (Total)	2	100	10	-	2	10	40	100	200	400	600	20
1,2,3-Trimethylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,2,4-Trimethylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,2,3-Trichlorobenzene	5	50	5	-	1	5	20	50	100	200	300	10
1,2,3-Trichloropropane	1	50	5	-	1	5	20	50	100	200	300	10
1,3-Dichlorobenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,3-Dichloropropane	1	50	5	-	1	5	20	50	100	200	300	10
1,3,5-Trimethylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,4-Dichlorobenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,4-Dioxane (p-Dioxane)	250	12500	250	-	50	250	1000	2500	5000	10000	15000	500
1-Methylnaphthalene	5	250	5	-	1	5	20	50	100	200	300	10
2,2-Dichloropropane	1	50	5	-	1	5	20	50	100	200	300	10
2,3-Dichloropropene	1	50	5	-	1	5	20	50	100	200	300	10
2-Butanone (MEK)	20	250	20	-	1	5	20	50	100	200	300	10
2-Chlorotoluene	1	50	5	-	1	5	20	50	100	200	300	10
2-Chloroethylvinyl ether	5	250	10	-	1	5	20	50	100	200	300	10
2-Hexanone	5	250	5	-	1	5	20	50	100	200	300	10
2-Methylnaphthalene	5	250	5	-	1	5	20	50	100	200	300	10
2-Propanol	250	12500	50	-	10	50	200	500	1000	2000	3000	100
Allyl chloride	5	250	5	-	1	5	20	50	100	200	300	10
4-Chlorotoluene	1	50	5	-	1	5	20	50	100	200	300	10
TOTAL BTEX	1	300	30	-	1	5	20	50	100	200	300	10
Carbon disulfide	5	50	5	-	1	5	20	50	100	200	300	10
Ethanol	500	NA	500	-	50	250	1000	2500	5000	10000	15000	500
Acetone	20	250	20	-	1	5	20	50	100	200	300	10
Acrolein	20	2500	50	-	10	50	200	500	1000	2000	3000	100
Acetonitrile	20	250	12.5	-	2.5	12.5	50	125	250	500	750	25
Acrylonitrile	5	250	5	-	1	5	20	50	100	200	300	10

Analyte	PQL water µg/L	PQL soil µg/kg	PQL 5035 soil µg/Kg	Cal1 MeOH curve only µg/L	Cal2 MeOH Cal1 water µg/L	Cal3 MeOH Cal2 water µg/L	Cal4 MeOH Cal3 water µg/L	Cal5 MeOH Cal4 water µg/L	Cal6 MeOH Cal5water µg/L	Cal7 MeOH Cal6 water µg/L	Cal7 water Curve only µg/L	* Optional Cal3 water Curve only µg/L
Bromochloromethane	1	50	5	-	1	5	20	50	100	200	300	10
Benzene	1	20	5	0.4	1	5	20	50	100	200	300	10
Bromobenzene	1	50	5	-	1	5	20	50	100	200	300	10
Bromodichloromethane	1	50	5	-	1	5	20	50	100	200	300	10
Bromomethane	5	250	10	-	1	5	20	50	100	200	300	10
Bromoform	1	50	5	-	1	5	20	50	100	200	300	10
cis-1,2-Dichloroethene	1	50	5	-	1	5	20	50	100	200	300	10
cis-1,3-Dichloropropene	1	50	5	-	1	5	20	50	100	200	300	10
cis-1,4-Dichloro-2-butene	5	250	10	-	1	5	20	50	100	200	300	10
Carbon tetrachloride	1	50	5	-	1	5	20	50	100	200	300	10
Cyclohexane	5	250	5	-	1	5	20	50	100	200	300	10
Chlorobenzene	1	50	5	-	1	5	20	50	100	200	300	10
Chloroethane	1	250	5	-	1	5	20	50	100	200	300	10
Chloroform	5	250	5	-	1	5	20	50	100	200	300	10
Chloromethane	1	50	5	-	1	5	20	50	100	200	300	10
Dibromochloromethane	1	50	5	-	1	5	20	50	100	200	300	10
Dichlorofluoromethane	1	50	5	-	1	5	20	50	100	200	300	10
Diethyl ether (Ethyl ether)	5	50	5	-	1	5	20	50	100	200	300	10
Dichlorodifluoromethane	1	50	5	-	1	5	20	50	100	200	300	10
Diisopropyl ether	1	50	5	-	1	5	20	50	100	200	300	10
Dibromomethane	1	50	5	-	1	5	20	50	100	200	300	10
Ethylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
Ethyl-tert-butyl ether	5	250	5	-	1	5	20	50	100	200	300	10
Hexachloro-1,3-butadiene	5	50	5	-	1	5	20	50	100	200	300	10
Hexachloroethane	5	250	5	-	1	5	20	50	100	200	300	10
Iodomethane	5	250	5	-	1	5	20	50	100	200	300	10
Isopropylbenzene (Cumene)	1	50	5	-	1	5	20	50	100	200	300	10
Isopropyl acetate	5	250	5	-	1	5	20	50	100	200	300	10
Isobutanol	50	2500	50	-	10	50	200	500	1000	2000	3000	100
Methyl acetate	10	250	20	-	1	5	20	50	100	200	300	10
Methylene Chloride	1	50	5	-	1	5	20	50	100	200	300	10
Methylcyclohexane	5	250	5	-	1	5	20	50	100	200	300	10
Methyl-tert-butyl ether	1	50	5	-	1	5	20	50	100	200	300	10
4-Methyl-2-pentanone	5	250	5	-	1	5	20	50	100	200	300	10
m&p-Xylene	2	100	10	-	2	10	40	100	200	400	600	20
Naphthalene	5	250	5	-	1	5	20	50	100	200	300	10
n-Butanol	250	12500	250	-	50	250	1000	2500	5000	10000	15000	500
n-Butylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
n-Heptane	5	250	5	-	1	5	20	50	100	200	300	10
n-Hexane	5	250	5	-	1	5	20	50	100	200	300	10
n-Propylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
n-Propanol	250	12500	250	-	50	250	1000	2500	5000	10000	15000	500
o-Xylene	1	50	5	-	1	5	20	50	100	200	300	10
p-Isopropyltoluene	1	50	5	-	1	5	20	50	100	200	300	10
sec-Butlybenzene	5	50	5	-	1	5	20	50	100	200	300	10
Styrene	1	50	5	-	1	5	20	50	100	200	300	10
trans-1,2-Dichloroethene	1	50	5	-	1	5	20	50	100	200	300	10
trans-1,3-Dichloropropene	1	50	5	-	1	5	20	50	100	200	300	10

Analyte	PQL water µg/L	PQL soil µg/kg	PQL 5035 soil µg/Kg	Cal1 MeOH curve only µg/L	Cal2 MeOH Cal1 water µg/L	Cal3 MeOH Cal2 water µg/L	Cal4 MeOH Cal3 water µg/L	Cal5 MeOH Cal4 water µg/L	Cal6 MeOH Cal5water µg/L	Cal7 MeOH Cal6 water µg/L	Cal7 water Curve only µg/L	* Optional Cal3 water Curve only µg/L
trans-1,4-Dichloro-2-butene	5	250	5	-	1	5	20	50	100	200	300	10
tert-Amyl-methyl ether	1	250	5	-	1	5	20	50	100	200	300	10
tert-Butyl Alcohol	25	1250	50	-	5	25	100	250	500	1000	1500	50
Tetrachloroethene	1	50	5	-	1	5	20	50	100	200	300	10
Tetrahydrofuran	5	250	10	-	1	5	20	50	100	200	300	10
Toluene	1	50	5	-	1	5	20	50	100	200	300	10
Trichloroethene	1	50	5	-	1	5	20	50	100	200	300	10
Trichlorofluoromethane	1	50	5	-	1	5	20	50	100	200	300	10
tert-Butylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
Xylene (Total)	3	150	15	-	3	15	60	150	300	600	900	30
Vinyl acetate	5	250	5	-	1	5	20	50	100	200	300	10
Vinyl chloride	1	50	5	-	1	5	20	50	100	200	300	10

*** If the Optional Cal 3 point is made for the Water Curve all subsequent Cal levels will increase by 1 (i.e. 300µg/L is now CAL8)**

11.2.2. Calibration Response Factors

Response factors (RF) establish the relationship of the instruments response in comparison with the concentration of any given analyte. The RF includes the concentration and response of the internal standard as well. By relating the IS concentration and response in an inverse manner, the target analyte concentration is adjusted to account for drift in the instrument on a per injection basis. As instrument response increases as indicated by the response of the internal standard, the concentration of the target is mathematically decreased, and vice versa.

To calculate the RF for any given calibration standard (or calibration verification standard), tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L).

Most, if not all modern chromatography data systems are capable of calculating this factor and using it to quantify analyte concentrations. The 8260B method has minimum requirements that these response factors must meet in order to be considered valid. The method uses a subset of the target analyte list to evaluate the performance of the system.

These compounds are referred to as the System Performance Check Compounds or the SPCCs. The SPCCs serve as an indicator of instrument sensitivity and, by meeting a minimum value, ensure that the laboratory has adequate sensitivity to analyze and reliably report data for environmental samples.

11.2.3. Calibration Curve Fit

The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. The curve is produced in several ways depending on the nature of the "goodness of fit".

Average Response Factor (ARF): The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. It is in the most basic sense, a linear regression that is forced through zero at the origin. Because of its simplicity and the interception of the y axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of the ARF (see Table 11.2).

The % RSD is calculated as follows: %RSD = SD*100 / ARF

Where: SD = Standard deviation of the averaged RFs for a given compound

The average response factor is also used to diagnose the integrity of the chromatography system as it relates to calibration linearity. The ***Calibration Check Compounds (CCCs)*** are a subset of the target analyte list that must meet specific criteria (see Table 11.2) for the calibration to be acceptable. For the CCCs, the %RSD for each is compared to the method criteria. If that of any CCC exceeds the criteria, the system needs to be inspected for potential sources of errors and recalibrated.

Linear Regression: The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y=ax+b where "a" is the slope of the line and "b" is the y intercept. In order to use this curve fit technique, a minimum of 5 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument is linear in nature but does not necessarily intercept the y-axis at the origin. However, because the linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve (see Table 11.2)

Non-linear Regression: The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument gradually decreases with increasing concentrations. Using this technique, an

analyst may be able to generate calibration curves with correlation coefficients very close or equivalent to 1.000. However, because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. Likewise, high levels of contamination may not be able to be calculated due to regression equations with multiple intercepts of either axis on the calibration plot.

Note: The State of South Carolina does not allow the use of Non-linear regression for compliance samples.

Analytes that have poor purging efficiency or are problematic compounds may require the use of Non-linear regression curves. These may include: Bromomethane, 1-Propanol, Acrolein (2-propenal), n-Butanol, 2-Butanone, Carbon Disulfide, Hexachloroethane, and 1,2-Dibromo-3-chloropropane (DBCP)

Refer to section 11.2.3 for curve fit criteria. Either the low or high calibration points may be dropped to meet linearity criteria provided the laboratory meets the minimum 5 calibration point requirements. Points within the center of the curve may not be dropped unless an obvious problem is discovered and documented. The point must be dropped in its entirety and reanalyzed. Re-analysis should be within the same 12-hour time window and must occur within 8 hours of the original analysis.

11.3. Calibration Verification

11.3.1. Second Source Verification (SCV)

In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\% \text{ Difference} = [\text{Result}_{SCV} - \text{TrueValue}_{SCV}] / \text{TrueValue}_{SCV} * 100$$

See Tables 10.6 and 10.7 for details on the preparation of this standard. See Table 11.2 for control criteria.

11.3.2. Continuing Calibration Verification (CCV)

As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***. The validity of the initial calibration is checked at the beginning of every analytical

sequence and every 12 hours thereafter for as long as the instrument is analyzing samples and is accomplished by analyzing a midpoint calibration standard (CCV).

The values obtained from the analysis of the CCV are compared to the true values and a percent change calculated. The percent change must meet the method specified criteria for the analysis to proceed for an additional 12 hours.

The actual determination of change in instrument response is based on the type of curve fit used for each analyte. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the CCV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

% Difference: $[RF_{CCV} - AvgRF_{CAL}] / AvgRF_{CALl} \times 100$

% Drift: $[Result_{CCV} - TrueValue_{CCV}] / TrueValue_{CCV} \times 100$

Table 11.2 – Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Response Factor Linear Regression Non-linear Regression	%RSD ≤ 15% r ≥ 0.99 COD ≥ 0.99	If not met, try linear regression fit If not met, try non-linear regression fit If not met, remake standards and recalibrate
System Performance Check Compounds (SPCCs)	Chloromethane 1,1-Dichloroethane Bromoform Chlorobenzene 1,1,2,2-Tetrachloroethane	Avg RF ≥ 0.10 Avg RF ≥ 0.10 Avg RF ≥ 0.10 Avg RF ≥ 0.30 Avg RF ≥ 0.30	Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, poor purging efficiency, and active sites in the column or chromatographic system.
Calibration Check Compounds (CCCs)	1,1-Dichloroethene Toluene Chloroform Ethylbenzene 1,2-Dichloropropane Vinyl Chloride	%RSD < 30%	%RSD for the calibration check compounds (CCC's) must be ≤30% regardless of curve fit used. If the CCCs are not included on a list of analytes for a project, and therefore not included in the calibration standards, then all compounds of interest must meet a ≤15% RSD criterion.
Second Source Verification Standard	Immediately after each initial calibration	% Diff ±30%	Acceptance criteria are ±30% for all analytes, with allowances for 5% of compounds @ ±40%. See ALL_Q_025_Rev.1
Continuing Calibration Verification	Prior to the analysis of any samples and every 12 hours thereafter		If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back.
	SPCCs	Must meet response criteria listed above	
	Internal Standard RT Internal Standard Response	RT ± 30 sec 50 – 200%	Use midpoint calibration standard as reference Use midpoint calibration standard as reference
	CCCs	RF ± 20% Diff. Result ± 20% Drift	Use for Avg RF calibration curves Use for linear and non-linear calibration curves Additional client specific requirements for the analysis of contract samples requires that BTEX, PAH, Oxygenates, and surrogate compounds also be considered CCCs and must meet the 20% CCV criterion.
	Non-CCC Targets	RF ± 50% Diff.* Result ±50% Drift	Some programs may require control over non-CCC target analytes. In the absence of specified criteria, use those listed *State of South Carolina requires non-CCC Compounds to meet ±30% Drift. Please Note: Analytes that have poor purging efficiency or are problematic compounds may require the use ±50% Drift. These may include: Bromomethane, 1-Propanol, Acrolein (2-propenal), n-Butanol, 2-Butanone, Carbon Disulfide, Hexachloroethane, and 1,2-Dibromo-3-chloropropane (DBCP)

11.4. Calibration Corrective Actions

11.4.1. Calibration Linearity Problems

11.4.1.1. Check instrumentation/equipment condition.

11.4.1.2. Enter maintenance in instrument maintenance logbook.

11.4.1.3. Perform another initial calibration.

11.4.1.4. No data can be reported.

11.4.1.5. Generate on Non-Conformance Memo.

11.4.2. Secondary Verification Problems

11.4.2.1. Check instrumentation/equipment condition.

11.4.2.2. Enter maintenance in instrument maintenance logbook.

11.4.2.3. Perform another initial calibration.

11.4.2.4. No data can be reported.

11.4.2.5. Generate on Non-Conformance Memo

11.4.3. Continuing Verification Problems

11.4.3.1. Reanalyze the original CCV standard to determine instrument consistency.

11.4.3.2. Prepare and analyze a new CCV standard to determine preparation consistency / standard integrity.

11.4.3.3. Document instrument maintenance

11.4.3.4. Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

11.4.3.5. Complete recalibration of instrument.

11.4.3.6. If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

Exceptions: If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis.

12. Procedure

12.1. Purge-Trap GC/MS System Preparation

12.1.1. Operating Parameters

Configure the GC/MS system to match the following operating parameters based on instrument configuration. The parameters themselves are saved as a method on the chromatography data system. By loading the last method used, the instrument will auto-configure to match the parameters from the last time the system was operated under that method. Verify that the settings in the software match the appropriate configuration.

Table 12.1 –Instruments and Operating Parameters

Component	**Settings and Consumables**	
Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 µm **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite ferrules	Pressure / Flow: 0.5-1.0 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold 20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C
Mass Spectrometer	Tune File: Named to date of tune	
Purge & Trap Concentrator	Prepurge: NO Preheat: 40°C Sample: 20°C Purge: 10 min Dry Purge: NO Desorb Preheat: 245°C Desorb: 250°C	Standby: - Bake: 270°C for 5-7 min BGB: OFF Valve: 150°C Line: 150°C Mount: N/A Transfer Line Temp: 150°C
Autosampler	Syringe Flushes: 2 Sparge Tube Flushes: 2	

12.2. Tune Verification

At the beginning of each analytical sequence, prior to the analysis of any standards or samples, the mass spectrometer tune conditions must be verified. This is done by analyzing a standard containing bromofluorobenzene (refer to table 10.2). The tune verification standard can be combined with the CCV standard provided that the amount of BFB introduced into the system meets the criteria in Section 12.2.

After the analysis of this standard, the mass spectrum of BFB must be evaluated against the following criteria.

Mass (m/z)	Ion Abundance criteria
50	15.00-40.00% of m/z 95
75	30.00-60.00% of m/z 95
95	Base peak, 100% relative abundance
96	5.00-9.00% of m/z 95
173	<2.00% of m/z 174
174	50.00-100.00% of m/z 95
175	5.00-9.00% of m/z 174
176	95.00-101.00% of m/z 174
177	5.00-9.00% of m/z 176

To evaluate the tune spectra, following the operating instructions for the chromatography data system to access the data file and obtain mass spectra for bromofluorobenzene. If the software has a program or macro for automatically selecting the spectra and evaluating the response ratios, use this option. Additionally, see Attachment III and Attachment IV on the proper techniques for evaluation of the tune file. Otherwise, the spectra must be obtained in one the following manners, in the listed order.

1. Using an average of three scans, centered on the apex of the peak; or,

2. Using an average of all scans across the width of the peak, taken at half height; or,

3. Using an average of all scans taken across the width of the peak from baseline to baseline.

A background scan taken immediately before but not including the peak must be subtracted.

Once obtained, evaluate the ion ratios against the criteria listed above. If the ratios meet the criteria, then analysis may proceed for 12 hours. The window for analysis is 12 hours from the injection date / time for the BFB tune verification. After that, the tune must be verified again to establish a new analytical window. The same Ion Abundance Criteria used for the BFB tune coupled with the initial calibration must be used for all subsequent analyses associated with that initial calibration.

If the ratios do not meet the criteria, refer to the following corrective actions to address the problem:

1. Retune the mass spectrometer following the equipment manufacturers' instructions. The tune status must be verified after the tuning procedures.
2. If this fails, change filament and retune.
3. If this fails, take down the mass spectrometer and clean the instrument.

12.3. Calibration Verification

After the instrument tune conditions are verified and the system meets tune criteria, the instrument must undergo calibration verification. If it has already been determined that the instrument needs to be recalibrated, follow the procedures listed in section 11.2 (Analysis of Standards). Otherwise, analyze a Continuing Calibration Verification Standard to determine the current calibration status.

If the CCV meets control criteria, the system is deemed to be in control and analysis of samples may commence. If the CCV does not meet control criteria, follow the corrective action procedures listed section 11.4.3 (Continuing Verification Problems). If the tune verification has been combined with the CCV, the 12 hour analysis window begins from the analysis date / time of the CCV.

Note: In situations where the instrument will run unattended (i.e. overnight), the analyst may load sequential CCVs in anticipation of that the first in the series may fail due to carry over from a previous sample. If so, the CCV must be evaluated according to the protocol set forth in the Quality Assurance Manual within Section 6 – Equipment and Measurement Traceability.

12.4. Operation of the Software Systems

12.4.1. Epic Pro

12.4.1.1. **Make Q-Batch**

12.4.1.1.1. Batching -> New Batch -> Queue = MSV
12.4.1.1.2. Click Empty Batch icon on taskbar
12.4.1.1.3. Highlight QC Rule -> F9 -> type MSV
12.4.1.1.4. Select appropriate QC Rule (i.e. MSV water) – Select OK – F10 to save
12.4.1.1.5. Record Q Batch #

12.4.1.2. **Create Standards**

12.4.1.2.1. System -> Utility -> Clone Standard by Event
12.4.1.2.2. Select Event (111 = MeOH soil curve, 115 = Water/LLsoil curve) Select OK
12.4.1.2.3. Double Click on standard event
12.4.1.2.4. Review Standard composed of – Find/Replace if necessary
12.4.1.2.5. Update expiration date to 7 days from creation – F10 to Save
12.4.1.2.6. Operations -> Standard Log -> Enter – Record Standard #'s

12.4.2. Chemstation

12.4.2.1. **Create Chemstation methods**

12.4.2.1.1. Tune MS, Save Tune file as date (i.e. 072513.u)
12.4.2.1.2. Update both DBFB and Curve method to use new tune file
12.4.2.1.3. Save Curve method as date (i.e. W072513.m)

12.4.2.2. **Set up Sequence**

12.4.2.2.1. Load pre-existing curve sequence if available
12.4.2.2.2. Change old method to the new method & copy through all files

(DBFB remains the same)

12.4.2.2.3. Change Q-Batch # in BFB, Curve and ICV files

12.4.2.3. **Start Analysis**

12.4.2.3.1. Run minimum of 2 BFB injections to ensure the tune is optimized

12.4.2.3.2. Retune or adjust as needed, repeat 2 more BFB

12.4.2.3.3. Analyze a 2 blanks to verify the system is clean and IS areas within range

12.4.2.3.4. First IS, pentafluorobenzene should be between 300,000 – 550,000 area counts

12.4.2.3.5. Raise or lower EM as necessary – You ***Must*** reanalyze BFB if voltage was adjusted

12.4.2.3.6. Reanalyze blanks to ensure correct voltage and proceed w/ analysis of curve

12.4.3. Target

12.4.3.1. **Create Method**

12.4.3.1.1. Rename existing method to new name matching Chemstation method (i.e. W072513.m)

Note: if other data in Directory was processed w/ old method a copy of that method must remain in directory as well.

12.4.3.1.2. To avoid excessive file size, Audit trail in method should be reset at a minimum of annually

The ***ONLY*** time an audit trail may be rest is prior to calibrating the instrument.

Note: The Audit trail will remain intact in previous day's folder.

Double click into method folder, highlight the .audit file and delete

12.4.3.2. **Edit Method**

12.4.3.2.1. Security -> Method unlocked

12.4.3.2.2. Global -> Calibration – Click "update Curve Parameters" to averaged

12.4.3.2.3. File -> Zero Calibration

12.4.3.2.4. Compound -> Edit Compound -> Calibration

12.4.3.2.4.1. Review all analytes to ensure all necessary points are enabled

12.4.3.2.4.2. Are any 300 points dropped? If so, mark them enabled and make note of these to change the "Max Compound Amount Limit" after the curve has been run.

12.4.3.2.5. Reports -> Tabular -> "Print Custom Report" – click "Select Format"

12.4.3.2.5.1. On toolbar a "Select" icon will appear

12.4.3.2.5.2. Click on ManIntprepostRev.mac – click "Open"

Note: It is necessary to do this ***Every*** time a calibration is zeroed, even if the macro shows up in this field as the link to the macro that was lost when the calibration was zeroed.

12.4.3.2.6. Sample -> Default Sample

12.4.3.2.6.1. Change "Lab Prep Batch" field to the new Q-Batch #

12.4.3.2.6.2. Change "Client SDG" to be the instrument and date (i.e. 40MSV2-07252013)

12.4.3.2.7. Sample -> Surrogate/ISTD Parameter

12.4.3.2.7.1. Confirm that the correct IS/SS standard # is entered in the "Surrogate Lot#" field

12.4.3.2.7.2. Example - 51970:1.163 The 51970 is the IS/SS number followed by a colon followed by the volume added (this is a fixed amount unless change to the standard delivery has occurred.)

12.4.3.2.8. File -> Save Method

12.4.3.2.9. File -> Exit

12.4.3.3. **Process and Review Curve Data**

12.4.3.3.1. If significant Column maintenance was performed, it may be beneficial to process the 20 or 50 point first to update RT's as the larger concentrations will have better spectra to confirm correct identification

12.4.3.3.2. Select Method to calibrate and process files

12.4.3.3.2.1. Compound Sublist should be "all.sub"

12.4.3.3.2.2. Sample Type change to Calib Sample

12.4.3.3.2.3. Cal Level change to appropriate level 1-7

12.4.3.3.2.4. Double check that the Q-Batch # in MiscInfo and Lab Prep Batch are correct and match

12.4.3.3.2.5. Double check that the Client SDG reflects the instrument and date

12.4.3.3.3. Review Target Data

12.4.3.3.3.1. Review each analyte of all points for correct spectrum, RT and appropriate integration

12.4.3.3.3.2. All Manual Integration of all curve points and ICV need to have Review Codes added

12.4.3.3.3.3. After reviewing all points, review each analyte point 1 -> 7 to ensure consistent RT, spectra and Integration (i.e. shoulders cropped or included, etc.)

12.4.3.4. **Review Curve in Target Method**

12.4.3.4.1. Edit Method

12.4.3.4.2. Edit Compound -> Calibration

12.4.3.4.3. Review each analyte to ensure Initial Calibration % RSD are less than 15.0%

12.4.3.4.3.1. Note analytes > 15% and re-examine target data for proper integration

12.4.3.4.4. Check that all CCC compounds are less than 30% RSD

12.4.3.4.4.1. CCC's are 11DCE, chloroform, 12DiChloropropane, toluene, ethylbenzene and vinyl chloride

12.4.3.4.4.2. Instrument maintenance must be performed to correct problem if any >30%

12.4.3.4.4.3. If RSD >15% and <30% note %RSD to record later

12.4.3.4.5. Check that all minimum relative response factors (RRF) were met for the SPCC – Chloromethane, 11DCE, bromoform are 0.1 and 1122PCA, chlorobenzene are 0.3 – if any %RSD >15 not RRF to record later

12.4.3.4.6. If %RSD >15% - Drop Upper or lower point to achieve %RSD <15

12.4.3.4.6.1. If the Report Limit (RL) for analyte is not the 1 point, can the 1 point be disabled

12.4.3.4.6.2. Can the 7 point be dropped (or 6&7 points) - ** Will require lowering Max Amount

Note: ONLY upper or lower points can be dropped, ***Never*** an intermediate point!!

12.4.3.4.6.3. Must have minimum of 5 points for Averaged RF curve

12.4.3.4.6.4. After disabling appropriate points – Click "Update Calibration" button

12.4.3.4.7. Is %RSD still >15 – Switch Curve fit to Linear Regression
12.4.3.4.7.1. Change curve fit to Linear
12.4.3.4.7.2. **CCC Compounds (11DCE, chloroform, 12dichloropropane, toluene, ethylbenzene, vinyl chloride) MUST still be <30% RSD.
12.4.3.4.7.3. Initial Calibration R^2 must be 0.990 or greater
12.4.3.4.7.4. Must have minimum of 5 points for Linear regression curve
12.4.3.4.7.5. b intercept should be as close to zero as possible
12.4.3.4.7.5.1. i.e. by dropping the 300 point does the intercept go from 0.1980442 -> 0.0681234
12.4.3.4.7.5.2. This will give less false positive hits but require linear range to be lowered to 2000 µg/L
12.4.3.4.8. If R^2 is not >0.990
12.4.3.4.8.1. Change curve fit to Quadratic
12.4.3.4.8.2. ***Must have minimum of 6 points**
12.4.3.4.8.3. R^2 must be 0.990 or greater
12.4.3.4.8.4. Like Linear regression the 300 point can be dropped (or 1 point added if RL is 5 µg/L) to achieve the intercept closest to zero, as long as 6 points remain and linear range is adjusted.
12.4.3.4.9. If calibration for compound will not pass
12.4.3.4.9.1. The instrument cannot be run for lists including these analytes
12.4.3.4.9.2. Document analytes as failing in Run logbook
12.4.3.4.9.3. Place Post-It-Note on Instrument Terminal to alert other analysts of failures

12.4.3.5. **Update Linear Range**
12.4.3.5.1. After all analyte curve fits have been checked
12.4.3.5.1.1. Compound ->Edit Compound -> Report Parms
12.4.3.5.1.2. Adjust "Max Compound Amt Limits" to reflect highest point used (300->200 if 7th point was dropped)
12.4.3.5.2. Sublists -> Update Sublists
12.4.3.5.2.1. Check the "Update Sublists QC Limits" box
12.4.3.5.2.2. Highlight first sublist and hit Enter button
12.4.3.5.2.3. Arrow down to the next sublist and hit Enter
12.4.3.5.2.4. Repeat for all Sublists
12.4.3.5.2.5. **If you fail to update all the sublists, detects above linear range will not be "a" flagged in target.
12.4.3.5.2.5.1. EpicPro used the "a" flag to switch Condition Code from "OK" to "OR"

12.4.3.6. **Lock Method**
12.4.3.6.1. Security -> Initial Calibration Locked
12.4.3.6.2. Note: Do not select "Method Locked" – This would not allow the method to be used to process data

12.4.3.7. **Verify Initial Calibration**
12.4.3.7.1. View -> Initial Calibration
12.4.3.7.2. This generates a report with calibration data that will appear on the lower tool bar
12.4.3.7.3. Print report and review
12.4.3.7.3.1. The Calibration File Names in the header match the ***correct*** files used in the curve
12.4.3.7.3.2. All Average Response Factors < 15% and at least 5 points were included
12.4.3.7.3.3. All Linear Regression >0.990 and at least 5 points were included

12.4.3.7.3.4. All Quadratic > 0.990 and at least 6 points were included
12.4.3.7.3.5. Are all low points dropped below Report Limit for that analyte
12.4.3.7.3.6. Any high points dropped verify that the Max on Column was lowered and Record max amount on the report
12.4.3.7.3.7. No midpoints of curve are missing
12.4.3.7.3.8. All CCC compounds averaged – If not is the %RSD < 30% - Record actual RSD on report
12.4.3.7.3.9. All SPCC minimum RF factors met – If not averaged, switch to Averaged in method record the RF on the report and switch curve back to appropriate curve fit
12.4.3.7.4. Manually check individual Response Factors (RF) for at least one analyte
12.4.3.7.4.1. Calculation the RF for each point in the curve of an Averaged curve fit using the following formula
12.4.3.7.4.1.1. RF = (Area of analyte*concentration of IS) / (Area of IS * concentration of analyte)
12.4.3.7.5. Save method and Exit

12.4.3.8. **Re-quantify and Uploading Curve and ICV**
12.4.3.8.1. Select Method
12.4.3.8.2. Highlight Curve and re-quantitate
12.4.3.8.3. Process ICV – Must use all.sub (or Full.sub)
12.4.3.8.4. Review ICV and check CLP.rp
12.4.3.8.4.1. All SPCC Minimum RF must be met (if analyte is linear, must hand calculate)
12.4.3.8.4.2. All CCC Analytes must be <20%
12.4.3.8.4.3. All other analytes must be <30%
Note: Up to 5% (5 Analytes for a full list spike) may be between 30-40%)
12.4.3.8.4.4. All Analytes >40% will be flagged as failing
12.4.3.8.4.4.1. Document analytes as failing in Run logbook
12.4.3.8.4.4.2. Place Post-It-Note on Instrument Terminal to alert other analysts of failures
12.4.3.8.5. Generate all files to paperless (BFB, Curve and ICV)
12.4.3.8.6. Upload all files to EpicPro (double check Q-Batch is correct prior to upload)
12.4.3.8.7. Check Q-Batch in Epic to ensure Curve, BFB, and ICV imported correctly (may take several minutes)

12.4.3.9. **MN Low Standard Verification**
12.4.3.9.1. Copy 1ppb, 5ppb, & 20ppb files into another folder (i.e. the unprocessed blank following 300ppb)
12.4.3.9.2. Paste all 3 files than Rename (example 07251305.D -> MN01-07251305.D)
12.4.3.9.2.1. This will allow original files to be un-manipulated
12.4.3.9.3. Cut files and paste back in original folder
12.4.3.9.4. Re-Quant new MN files as LCS
12.4.3.9.4.1. Sample Type = QC Control Sample
12.4.3.9.4.2. Click QC Sample Type
12.4.3.9.4.2.1. Sample Type = LCS
12.4.3.9.4.2.2. Spike List = MNLOW1.spk, MNLOW5.spk, MNLOW20.spk
12.4.3.9.5. Highlight all 3 files and Do Quick Forms – Form 3 of LCS

12.4.3.9.6. Print Form 3.s and pass on to Supervisor to update MN report limits in EpicPro

12.4.3.10. **Before proceeding with analysis of samples**

12.4.3.10.1. Check Chemstation sequence that correct Q-Batch is in BFB and CCC

12.4.3.10.2. Check that correct Method is referenced in the sequence

12.5. Sample Preparation

12.5.1. Samples

12.5.1.1. **Sample Pre-screening**

12.5.1.1.1. Samples are pre-screened using a rapid GC headspace technique. See SOP S-GB-O-001 *Sample Screening Volatile Organics Prior to Preparation* (most current revision or replacement**)** for the specifics on the pre-screening of samples.

12.5.1.2. **Water Samples**

After pre-screening, water samples typically do not require any sample preparation unless they require a dilution to bring high-level contaminants within calibration range or to minimize matrix interference. Dilutions are made following Section 12.5.1.5.1.

After analysis check the residue in the vial following analysis using pH paper. The pH should be <2. Document results in the run sequence log as <2 or >2. Footnote any sample not meeting the pH requirement. If dilutions are required, pH preservation can be verified at the time the dilution is made using the sample remaining in the original sample container.

12.5.1.3. **Soil Samples**

12.5.1.3.1. **Low concentration soils**

Samples received for low level analysis should be contained in pre-weighed VOA vials either with or without Reverse Osmosis Water (ROW) and/or sodium bisulfate preservative. NOTE: some samples may be received in coring devices (e.g. Encore™, etc.). These samples must be extruded into a VOA vial either with or without ROW and/or sodium bisulfate and a magnetic stir bar within 48 hours of sample collection. If samples are received that are greater than 10g the PM must be notified and samples will be rejected for analysis.

12.5.1.3.1.1. **Weight determination:** Prior to preparation or analysis of any soil received in a pre-weighed VOA vial, the sample weight must be determined and recorded. Accurately weigh the VOA vial to 0.01 g in the laboratory; record this amount in the sample preparation logbook. Subtract the tare weight recorded on the vial and 0.18g for each Pace Sample label that was affixed to the pre-tared vial; this will be the weight of sample in the vial.

12.5.1.3.1.2. Samples received pre-weighed in the field must be in 40 mL VOA vials and contain a magnetic stir bar, acid preservative and a

field tare weight. The analyst will compare the field tare weight to the weight of the sample before analysis. The weight of the sample should be recorded.

12.5.1.3.1.3. All samples must be extruded from the coring devices within 48 hrs. of collection. If the samples are to also be analyzed within the 48 hr criteria, no acid preservation is required. If analysis is to occur after 48 hrs. but within 14 days, the samples must be preserved with Sodium Bisulfate or if preserved with ROW, stored frozen. The ratio of Sodium Bisulfate to sample weight is 0.2g of preservative to 1g of sample.

12.5.1.3.2. **High concentration soils**

12.5.1.3.2.1. **Methanol-Preserved Samples:** Samples received in pre-weighed vials preserved with methanol must be accurately weighed in the laboratory to 0.01 g and the sample weight determined. See Section 12.5.1.4.2.1.2. Subtract the tare weight written on the VOA vial and 0.18g for each Pace Sample label that was affixed to the pre-tared vial from the weight determined in the laboratory. This will be the weight of sample in the VOA vial. The volume of methanol in the sample container should be at a 1 to 1 ratio of soil to methanol.

12.5.1.3.2.1.1. **Calculation of 1:1 ratio soil (g) to MeOH (mL).**

To calculate the amount of soil weight (g) in the sample can be calculated as follows:

Where:

$W_S = W_T - W_J - (N * W_l)$

W_s = Weight of soil in the sample (g)
W_t = Total weight of the sample including vial, cap, soil, and MeOH (g)
W_J = Weight of the jar including the vial, cap, and MeOH (g)
N = Number of Pace Sample labels
W_l = Weight of Pace Sample label affixed to the pre-tared 40mL VOA vial; which has been determined to be 0.18g

To calculate volume of MeOH to achieve the 1:1 ratio of soil weight (g) to MeOH (mL) may be calculated as follows:

Where:

$V_M = W_S - 10mL$

V_M = Volume of MeOH required to achieve 1:1 ratio of soil (g):MeOH (mL)
W_S = Weight of soil in the sample (g)
10 = Volume of MeOH initially added (mL)

12.5.1.3.2.2. **Unpreserved Samples**: Samples received in unpreserved pre-weighed vials must be accurately weighed in the laboratory to 0.01 g. NOTE: some samples may be collected and transported to the laboratory in bulk containers. An accurately weighed ≥5 gram sub-sample must be taken and added to a 40mL VOA vial. The non-compliant sample collection technique must be recorded in the preparation logbook and a qualifier added to the sample result. The samples are then preserved with 10 mL methanol within 48 hours of sample collection. To determine the sample weight: subtract the weight written on the VOA vial from the weight determined in the laboratory prior to the addition of the 10 mL methanol preservative. This will be the weight of sample in the VOA vial.

12.5.1.3.2.3. The balance is to be leveled before calibration. Calibration verification of the analytical balance is done with S-class weights. These values are to be noted in the Balance calibration logbook. The frequency of balance calibration verification is once per day before the balance is used or when the balance is moved.

12.5.1.4. **Dilutions**

12.5.1.4.1. **Water**

Dilutions on aqueous samples must be prepared in a volumetric fashion. Sample aliquots may be measured in either a volumetric pipette or syringe and brought to volume in a volumetric flask.

12.5.1.4.1.1. All steps must be performed without delays until the diluted sample is in a 40 mL VOA Vial.

12.5.1.4.1.2. Dilutions are made in gastight 50mL syringes.

12.5.1.4.1.3. Calculate the approximate volume of organic-free reverse osmosis water (ROW) added to the syringe and add slightly less than this quantity of ROW to the syringe barrel.

12.5.1.4.1.4. Inject the proper aliquot of sample using the appropriate 10µL to 5mL syringes to create the desired dilution in the 50 mL syringe. Dilute the sample to the mark with ROW. Invert, and rock back and forth three times. Repeat the above procedure for additional dilutions.

12.5.1.4.1.5. Fill a 40mL VOA vial with the diluted sample from the 50 mL syringe prepared in Section 12.5.1.5.1.4.

12.5.1.4.1.6. Place the VOA vial on the autosampler. All dilutions should keep the response of a major constituent (previously saturated peaks) in the upper half of the linear range of the curve.

12.5.1.4.1.7. The autosampler will add the internal standard and surrogate to the sample and transfer 5 mL over to the 5 mL sparge tube on the concentrator.

12.5.1.4.2. **Soil**

12.5.1.4.2.1. **Low Level Soils**

12.5.1.4.2.1.1. It will be necessary to adjust the sample weight for

quantitation purposes. Any analyte hits outside of the calibration range, 200 µg/kg, will be extracted into Methanol and analyzed under High Concentration Sample criteria.

12.5.1.4.2.2. **High Concentration Soils**

12.5.1.4.2.2.1. Dilute all samples according to the results of the screening data. A standard analytical dilution is 1:50. Add 1.0 mL of the sample extract measured with a microsyringe of appropriate volume to 49 mL of reverse osmosis water in a 50 mL syringe.

12.5.1.4.2.2.2. To make dilutions other than a standard 1:50 dilution, fill a 50 mL syringe to a volume of 49 mL with reverse osmosis water. Using a 1.0 mL syringe, inject methanol into the 50 mL syringe to bring the total volume of sample and methanol to equal 1.0 mL. Using an appropriate volume syringe, inject the sufficient amount of sample to reach desired dilution. Invert, and rock back and forth three times.

12.5.1.4.2.2.3. The 50 mL syringe contents are place into a 40 mL VOC vial by slowly deploying the plunger and injecting on the side of the vial to eliminate cavitation and loss of analytes to volatilization or sparging. Enough of the contents are injected to created a meniscus at the top of the vial that when capped will produce a no headspace sample.

12.5.1.4.2.2.4. The vial is capped and checked for headspace. If vial is free of headspace, it is ready for analysis as per Section 14.

12.5.2. Batch QC

Refer to Table 13.1 for details on Batch QC requirements.

12.5.2.1. **Method Blank**

12.5.2.1.1. **Water**

12.5.2.1.1.1. Fill a 40mL VOA vial with reverse osmosis water (ROW) and place in autosampler rack. The autosampler will add the internal standard and surrogate to the sample and transfer 5mL over to the 5mL sparge tube on the concentrator.

12.5.2.1.1.2. When leach samples are present, one leach blank must be analyzed with the analytical batch in addition to the method blank.

12.5.2.1.2. **Low Level Soil**

12.5.2.1.2.1. A method blank is prepared with 5 mL of ROW into a 40 mL VOA vial containing a disposable magnetic stir bar. The vial is placed onto the autosampler and the autosampler will add the internal standard and surrogate to the sample. The blank is preheated to 40°C and purged. The method blank must be analyzed under the same criteria as the samples.

12.5.2.1.3. **High Concentration Soil**

12.5.2.1.3.1. The method blank (extraction blank) is made by adding 10 µL of

the 2500 ppm surrogate standard in 10 mL methanol placed in a 40 mL VOA vial containing 10g of Ottawa sand. A 1.0 mL portion of this is diluted with 49 mL of ROW for a final concentration on the instrument of 50 µg/L.

12.5.2.2. **Laboratory Control Sample/Laboratory Control Sample Duplicate**

12.5.2.2.1. See Table 10.7 for spiking procedures and Table 13.1 for Batch Quality Control Criteria.

12.5.2.2.2. A Laboratory Control Sample Duplicate is required when sample volume for the Matrix Spike/Matrix Spike Duplicate is not received.

12.5.2.2.3. When EPA 624 samples are present with SW846 8260B samples, one LCS/D at 20 µg/L and one LCS/D at 50 µg/L must be analyzed to meet each method requirement. If the 20µg/L LCS/D is valid, the additional 50 µg/L LCS/D pair is not required.

12.5.2.3. **MS/MSD Samples**

12.5.2.3.1. See Table 10.7 for spiking procedures and Table 13.1 for Batch Quality Control Criteria..

12.5.2.3.2. When one to 20 EPA 624 samples are present one MS/MSD pair should be analyzed for every 20 samples (or one spiked sample per month) at a concentration of 20µg/L.

12.5.2.3.3. When Leach samples are analyzed, one MS must be analyzed per each sample matrix submitted for leaching.

13. Quality Control

13.1. Instrument Quality Control: Refer to Table 11.2 for initial and continuing calibration criteria and corrective actions.

13.2. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reverse Osmosis water (ROW)	One (1) per 20 samples or 12 hour window (whichever is most frequent)	Target analytes must be less than reporting limit. If results are reported to MDL, target analytes in MB should be non-detect	Re-analyze associated samples. ***Exceptions:*** 1. If sample ND, report sample without qualification 2. If sample result >20x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination. 3. If sample result <20x MB detects, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	Method specified compounds: Benzene, Chlorobenzene, 1,1-Dichloroethene, Toluene, Trichloroethene *OR (alternative)* Full Target List compounds	One (1) per batch of up to 20 samples	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to NELAC 2003 Chap 5 D.1.1.2.1.e	Analyze a new LCS If problem persists, check spike solution Perform system maintenance prior to new LCS run ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. Note: The State of South Carolina does not allow the use of Marginal Exceedances.
Laboratory Control Sample Duplicate (LCSD)	Method specified compounds: Benzene, Chlorobenzene, 1,1-Dichloroethene, Toluene, Trichloroethene *OR (alternative)* Full Target List compounds	One (1) per batch of up to 20 samples	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to NELAC 2003 Chap 5 D.1.1.2.1.e	Analyze a new LCSD If problem persists, check spike solution Perform system maintenance prior to new LCSD run ***Exceptions:*** 1) If LCSD rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. Note: The State of South Carolina does not allow the use of Marginal Exceedances.
Matrix Spike (MS)	Method specified compounds: Benzene, Chlorobenzene, 1,1-Dichloroethene, Toluene, Trichloroethene *OR (alternative)* Full Target List compounds	One (1) per batch of up to 20 samples, must include one TCLP MS for any analyzed in sequence	Laboratory derived limits	If LCS/LCSD and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One (1) for every 5% of all environmental samples	Laboratory Derived Limits	Report results with an appropriate footnote.

13.3. Sample Quality Control

Table 13.2 – Sample Quality Control criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	Pentafluorobenzene 1,4 Difluororobenzene 1,4-Dichlorobenzene-d4 Chlorobenzene-d5	Added to all standards, samples, spikes, control samples, and method blanks prior to analysis	**Retention Time:** RT must be ± 30 seconds from last calibration check on all samples	**Retention Time Failure:** 1. If matrix interference is NOT probable, the analytical system must be checked for source of retention time shifting. 2. Affected samples should be reanalyzed in the absence of an obvious instrument or matrix related interference.
Surrogate Standards	Dibromofluoromethane Toluene-d8 4-Bromofluorobenzene	Added to all samples, spikes, control samples and method blanks prior to analysis	Laboratory derived limits	1. Check system parameters 2. Identify and correct likely cause 3. Re-run samples ***Exceptions:*** 1. Surr rec above criteria and target compounds < RL, result may be reported with appropriate footnote. 2. Surr rec out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote.

14. Data Analysis and Calculations

14.1. Analyze Samples

14.1.1. Water Samples

14.1.1.1. Create run sequence log. Place 40 mL VOA vial containing sample (Section 12.5.1.2), or appropriately diluted 40 mL VOA vial containing sample (Section 12.5.1.5.1) onto the autosampler. The autosampler will add the internal standard and surrogate to the sample and transfer 5 mL over to the 5 mL sparge tube on the concentrator.

14.1.2. Low-level Samples

14.1.2.1. Create run sequence log. Place the already weighed 40 mL VOA vial containing the sample, stir bar and 5 mL of reverse osmosis water (ROW) or Sodium Bisulfate solution (Section 12.5.1.4.1) onto the autosampler where another 5 mL of ROW and internal standard and surrogate will be added by the autosampler. The sample is preheated to 40°C and purged. The stir bar is moving continuously during the purge cycle. This also helps in compound recovery by breaking down any clumps that may remain in the sample.

It will be necessary to adjust the sample weight for quantitation purposes. Any analyte hits outside of the calibration range, 200 µg/kg, will be extracted into Methanol and analyzed under High Concentration Sample criteria.

14.1.3. High Concentration Samples

14.1.3.1. Create run sequence log. Place 40 mL VOA vial containing sample (Section 12.5.1.4.2), or appropriately diluted 40 mL VOA vial containing sample (Section 12.5.1.5.2.2) onto the autosampler. The autosampler will add the internal standard to the sample and transfer 5 mL over to the 5 mL sparge tube on the concentrator

14.2. Data Reduction

14.2.1. Qualitative Analysis

Retention Time Comparison: The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of RT in the presence of co eluting components.

Mass Spectrum Comparison: The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.
- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.
- Compare computer-matched compounds with reference spectra to accept or reject each identification.
- All ions present in the reference spectrum that are at least 10% of the base peak must be present in the sample background-subtracted spectrum.
- The relative intensities of these ions must agree within ± 30% between the standard and sample spectra.
- While this is a good guideline, acceptance or rejection will depend upon the judgment of the analyst\

Carry-Over Protocol: Each sample must be closely evaluated to confirm that reported values are not a result of carry-over from a previous sample or QC standard. The blank(s) following the CCV or batch QC can be evaluated to determine typical amounts of carry-over to be expected from a sample with results around the mi-range of the curve (i.e. naphthalene and hexachlorobutadiene may carry over 0.5-2ppb from a 50ppb detect whereas vinyl chloride or ketones generally do not have any carry-over at the same concentration). Additionally, the blank(s) following the upper point of an ICAL can demonstrate carry-over of compounds at the upper end of the curve. Obviously, carry-over results vary from instrument to instrument and even ICAL to ICAL; therefore, when there is any question of carry over, an example of similar hits on that particular instrument's recent analysis are to be considered (i.e. a sample earlier in the sequence had benzene hit of 200ppb and the following sample was ND; therefore, it would be reasonable to assume

that a benzene detect of 1.5ppb following a sample containing 100ppb of benzene was not a result of carry-over). Every possible attempt to avoid carry-over contamination in clients' samples will be taken. This may include running instrument clean up blanks following standards that are known to carry-over or following samples that are known to have high concentrations of contaminants, or attempting to run groups of similarly concentrated samples together instead of intermittently through a sequence. When highly contaminated samples are grouped together it is to be expected that a percentage of a reported value may result from carry-over, in this case the significance of carry-over compared to reported value must be considered (i.e. a hit of PCE typically may carry-over 0.5ppb from a sample with an on-column concentration of 100ppb; therefore, a sample with concentration of 70ppb following a sample with a concentration 100ppb may contain roughly 0.5ppb of PCE resulting from carry-over which should be deemed insignificant). Similar to rules concerning Method Blank contamination, if the reported result is greater than 20 times the expected carry-over concentration, the resulting carry-over should be considered insignificant and value acceptable to report.

14.3. Quantitative Analysis – Quantitation is based on the integrated abundance of the target analyte's quantitation ion using the internal standard technique.

Raw Data Results: The GC/MS data system will calculate the concentration of each analyte as µg/L (or ng/mL). For water samples, no further calculations are necessary unless a dilution of the sample has been performed. If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

14.4. Calculation – Aqueous Sample:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

Where:

A_x= Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
A_{is} = Area of characteristic ion for the internal standard.
RF = Average Relative Response factor for compound being measured.
V_o = Volume of water purged (mL), taking into consideration any dilutions made.

14.5. Soil/ Solid calculations:

$$\textit{High}\ \text{Conc. (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

$$\textit{Low}\ \text{Conc. (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

Where:

A_x, I_s, A_{is}, RF = Same as in water and water-miscible waste above.
V_t = Volume of total extract (mL).
V_i = Volume of extract added (mL) for purging.
S_v = Volume of diluted extract.
W_s= Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

14.6. Tentatively Identified Compounds (TICs) – For some samples, identification may be desired for non-target compounds. A mass spectral library search may be conducted to attempt assignment of tentative identifications. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications.

- Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See table in Section 13.

16. Corrective Actions for Out-of-Control Data

16.1. See table in Section 13.

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

17.1. If not specifically listed in the table in Section 13, the contingencies are as follows. If there is no additional volume to perform analyses, all data will be reported as final with applicable qualifiers.

18. Method Performance

18.1. Method Detection Limit (MDL) Study: An MDL study must be conducted annually per S-GB-Q-020, *Determination of the LOD and LOQ* (most current revision or replacement) for each matrix per instrument.

18.2. Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, *Orientation and Training Procedures* (most current revision or replacement).

18.2.1. Analysis of four (4) LCS for each matrix the analyst will be performing. The concentration for low level soil and methanol soils should be at the current LCS spike concentration and the recovery is to be within the current LCS QC limits. The concentration for aqueous DOC should be at 20 µg/L and the recovery is to be within the current LCS QC limits.

19. Method Modifications

Method modifications for EPA method 8260B and EPA 624 are as follows:

- Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.
- All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.
- Procedures identified as “Best Practices” by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories.
- If a client fails to provide the method required Matrix Spike/Matrix Spike Duplicate (MS/MSD), the laboratory will analyze a Laboratory Control Spike Duplicate to demonstrate precision. The analytical batch will be qualified with the “M5” data qualifier.

Method modifications for EPA method 5035 is as follows:

- The laboratory uses a modification of SW-846 Method 5035 for medium-level volatiles in soil. The laboratory uses 10 grams of soil and 10 mL of methanol whereas the method indicates 5 grams of soil and 5 mL of methanol.

- *Note*: Samples reported to the State of South Carolina requires the use of 5 grams of soil and 5 mL of methanol.

20. Instrument/Equipment Maintenance

20.1. See current version of SOP: S-GB-Q-008 *Preventative, Routine, and Non-routine Maintenance.*

21. Troubleshooting

21.1. See most current version of the Instrument Operations Manual.

22. Safety

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

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

22.3. Equipment: Portions of the analytical instrumentation operate at high temperatures and under positive pressure. Care must be taken to minimize accidents and injuries when working on or with this equipment. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones.

The purge and trap concentrator and autosampler use gas under pressure to purge samples and, in some cases, drive the robotic assemblies. These high pressures introduce the risk of injury due to flying glass and other objects should a vessel or line rupture. Safety glasses are highly recommended at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-GB-W-001, *Waste Handling and Management* (most current revision or replacement).

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

24. Pollution Prevention

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

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.3. USEPA, SW-846, Method 8260B, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), December 1996.

25.4. USEPA, SW-846, Method 5030B, "Purge and Trap for Aqueous Samples," December 1996.

25.5. USEPA, SW-846, Method 5035A, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," Draft Revision 1 July 2002.

25.6. USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

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

26.1. Attachment I: Flow Chart

26.2. Attachment II: Client Specific Requirement Statement

26.3. Attachment III: Master Guide to Passing BFB for Agilent MSD Modes 5970-5973

26.4. Attachment IV: Agilent Document: BFB Tuning for Environmental Analysis: Three Ways to Succeed.

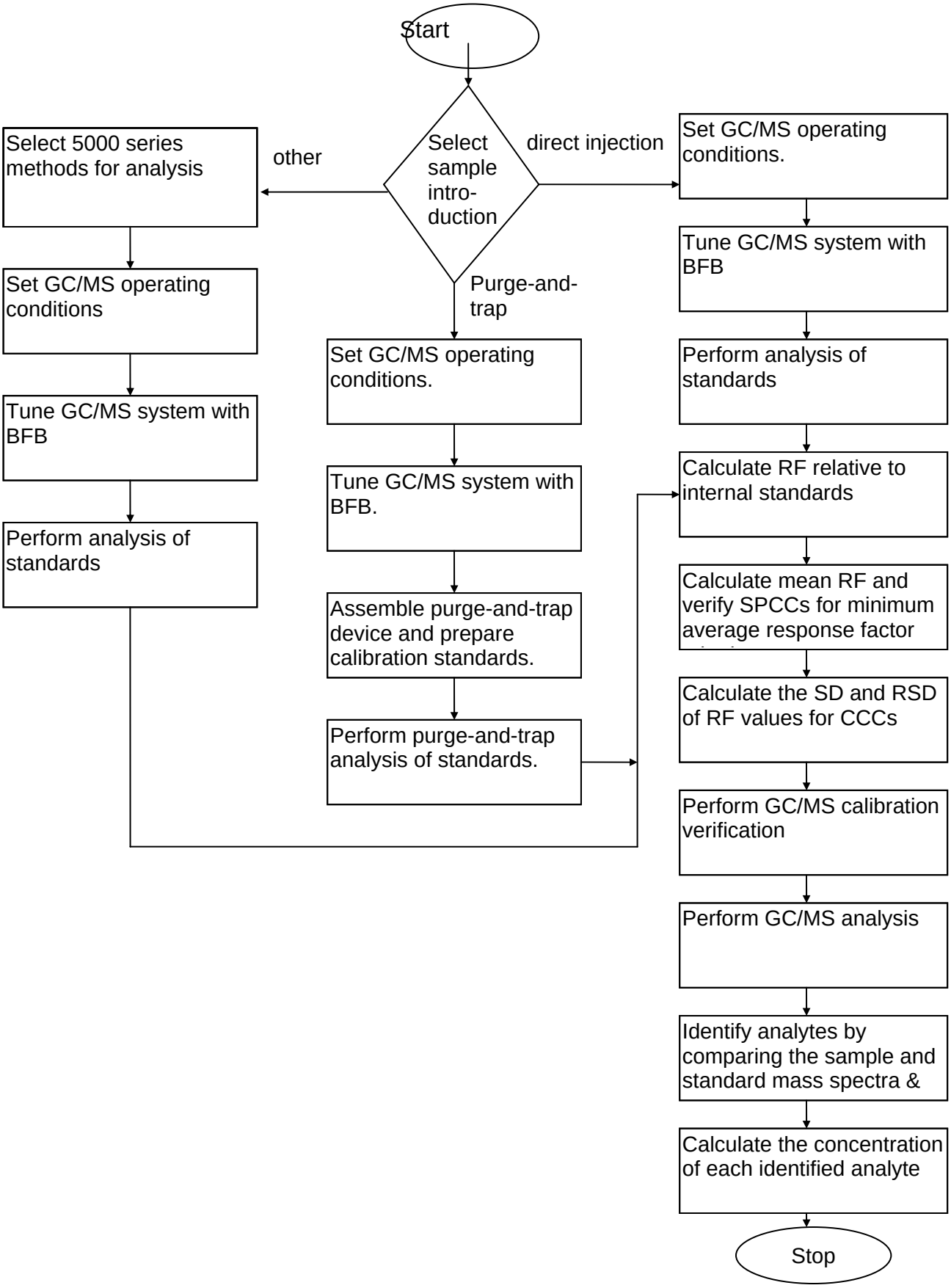
26.5. Attachment V: VOA Calibration Process

26.6. Attachment VI: VOA Calibration Checklist

27. Revisions

Document Number	Reason for Change	Date
S-GB-O-056-Rev.08	Section 2, 10.1: Added information for Nitrogen purge. Table 7.1: Updated samples to 3 vials. Table 9.1: Updated Serial Number for equipment, added 40MSVC. Tables 10.3, 10.4, 10.6, and 10.7: Updated standard information. Table 11.1: Added 1-Methylnaphthalene Section 12.4: Added Operation of the Software Systems Section 12.5.1.4: Incorporated label weight of 0.18g into determinations. Attachments V and VI: Added.	09May2014
S-GB-O-056-Rev.09	Table 7.1: Updated preservation requirement to ≤6°C from 2±4°C to match 40CFR. Table(s) 10.6, 10.7, and 11.1: Added information for CAL-3 on the water curve. Table 10.7: Added CAL 7 Curve information. Table 13.1: Added ME requirements for SC requirements. Section 25: Added Pace QM and TNI references.	02Dec2014
S-GB-O-056-Rev.10	Table 9.1: Removed 40MSV9 from instrument list; removed serial numbers from SOP. Table 10.3: Updated Stock Standards. Table 10.4: Added compounds to O2Si custom mix (changed from Restek); Removed Restek custom mix; Added compounds to 4.1 Mega Mix.	19Aug2015
S-GB-O-056-Rev.11	Throughout Document: Updated Pace Analytical Services, Inc to Pace Analytical Services, LLC Section 14.2: Added Carry-over protocols.	21Jun2017

FLOWCHART


Start
Select sample intro-duction
other
direct injection
Purge-and-trap
Select 5000 series methods for analysis
Set GC/MS operating conditions
Tune GC/MS system with BFB
Perform analysis of standards
Set GC/MS operating conditions.
Tune GC/MS system with BFB.
Assemble purge-and-trap device and prepare calibration standards.
Perform purge-and-trap analysis of standards.
Set GC/MS operating conditions.
Tune GC/MS system with BFB
Perform analysis of standards
Calculate RF relative to internal standards
Calculate mean RF and verify SPCCs for minimum average response factor
Calculate the SD and RSD of RF values for CCCs
Perform GC/MS calibration verification
Perform GC/MS analysis
Identify analytes by comparing the sample and standard mass spectra &
Calculate the concentration of each identified analyte
Stop

Attachment II:

Throughout document, reference to Client Specific requirements refers to samples analyzed following the BP Technical Requirements LaMP Revision 10.1, Canadian National Railway Services and Technical Specifications Manual.

Attachment III: Master Guide to Passing BFB for Agilent MSD Modes 5970-5973.

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Master Guide to Passing BFB for Agilent MSD models 5970-5973

The Importance of Thermal Stabilization

Before we begin discussing tuning let me make an important point. If a GC/MS has been vented, it takes quite a while for the system to thermally stabilize. So, even if you reached your ultimate pressure and all heated zones are at their setpoint and the high vacuum pump is at its setpoint, don't be fooled into thinking the mass spec has thermally stabilized. Even though the temperatures are at their setpoints, it takes several hours for the heat to fully disseminate throughout the analyzer. You can certainly run the systems prior to thermal stabilization, but don't be surprised if the system changes while you do it. Use the following guide as to how long thermal stabilization should take:

Model MSD	Typical time for thermal stabilization
5970	16 hours
5971	8 hours
5972	8 hours
5973	8 hours

Creating and Maintaining an Optimized Manual Tune File for BFB

OK, so let's assume your system has reached thermal stabilization and has passed Autotune. You now want to manually tune the system for BFB. Here is the procedure I use to take an Autotune file and generate a Manual Tune File for the MSD systems for both 524.2 and 624/8260:

Set the Oven Temperature to the temperature at which BFB elutes in your program. Since sensitivity is flow dependent, and flow is temperature dependent, we want to tune the system under the *same* conditions that BFB will experience when it elutes. Generally this temperature is around 150°C, depending on your configuration.

Change the scan range from 10-800 or 10-600 AMUs (or whatever it is in AUTOTUNE) to 10-300 AMUs. Most EPA Methods for Volatiles specify a 35-300 AMU range so 10-300 is fine.

We want to scan in the 10-29 range so we can leak check as we tune. We don't want to scan above 300 amus when we tune for BFB because that's not what the method stipulates. Set the 3 ions that are monitored from 69-219-502 to 69-131-219.

Once you have verified that no leak exists (the kind of leak where air gets sucked into the system), you can set the scan range to 35-300 (or whatever you use in your acquisition method). This isn't necessary but some analysts find it helpful. If you do this, be sure to reset the scan range to 10-300 each time you retune to check for air leaks and if none exists set it back to 35-300 amu.

At this point you need to establish in your mind the target relative abundances of 131 and 219. A good starting point would be 35-40% of each relative to ion 69.

Set the X-ray lens to maximize on ion 131 (5970, 5971, 5972). Theoretically ion 3 ions should maximize at the same point but sometimes the ramp is a bit skewed.

Our next step is to lower 219 (which should be around 60% or so from Autotune) and bring it even with 131 and to about 35-40% of ion 69 . Generally, 131 is about 20% lower than 219 in Autotune. Both of these can be achieved by doing the following:

raising the Ion Focus from at or near 0 (where it should be after Autotune) to about 30-80 Volts for 5970

raising the Entrance Lens Offset from below 8 (where it should be after Autotune) to about 15-20 for 5971, 5972, 5973.

Since raising the Ion Focus/Ent Lens Offset increases overall sensitivity, after step 4 is done we will need to *lower* the EM voltage to stay on scale. Generally, aim for between 2-4 million counts of Ion 69 adjust the EM in to keep the same abundance throughout the tuning procedure.

Do Peak width and Mass Axis calibrations. At this point, you can use the automated feature whereby the software does it for you. Later on, we can tweak it using the AMU Gain and AMU Offset if necessary.

Make minor adjustments in the Entrance Lens (5970) and Entrance Lens and/or Ion Focus (5971,2,3) to fine tune your ratios. Additionally, you can make minor adjustments on the Repeller if needed to fine tune ratios, but only do this as a last resort.

Try to keep the Repeller setting <u>constant</u> and set to whatever it sets it to in AUTOTUNE.

Often you need to go back and forth between both lenses to zero in on your target ratios. Remember to adjust the EM voltage to maintain proper abundance of ion 69.

Do Peak width and Mass Axis calibrations. Your masses obtained in Spectrum Scan (*not* Profile Scan which tells you Peak Width, not Mass Axis) should be the integer +-0.1 AMUs (i.e. 68.90-69.10 etc.). If this cannot be obtained automatically by the software, a hardware problem may exist.

Peak widths for all three ions should be between 0.47-0.54 AMUs, as close to 0.50 AMUs as possible (although in my experience 0.52 seems to be a little better). If they are not, they can be narrowed by increasing the AMU Gain and AMU offset and widened by decreasing either or both of these settings. If you cannot achieve ratios between 0.47-0.54 AMUs for all three ions, a hardware problem may exist.

For the 5971, 72 and 73s, you can also fine tune the width of ion 219 with the "219Wid" setting, although keep in mind that adjusting that also affects the 131 peak width as well.

Save the settings under a new name (or overwrite BFB.U if that file already exists) and run your BFB. It will usually pass. If not, the system must be re-tuned. Some systems require ion 131 to be greater than 219 (typically 40-35 or 35-30 , etc.); others require ion 219 to be greater than 131 (typically 40-35 or 35-30 , etc.). Adjustment of these ratios can be achieved by varying the Ion Focus and/or Entrance Lens Settings (especially the Entrance Lens). If you cannot pass BFB by having 131=219, or 131<219 by about 5-15%, or 131>219 by about 5-15%, this indicates that a problem exists. You should not have to obtain any weird abundances to make BFB pass. Generally, a system with 131 and 219 about the same abundance and both between 25-45% of 69 will pass. But since each system is unique and all will change with time and usage you must get a feel for what works best for your system.

Remember: once you have a good Tune File, you should check the tune each day and make whatever adjustments are necessary to keep ratios, abundances, and peak widths constant; this is fundamentally important in maintaining linearity and consistency in your analytical runs. You don't need to re-run Autotune each day- go directly to Manual Tune and adjust the system to look as it did the day before. Do this each day and you will be doing quite a bit to help your system stay linear.

So now we run our BFB and it will usually pass at the apex. But what if it doesn't? What if our relative ratios and peak widths of ions 69-131-219 are exactly what we think they should be and exactly what's been working for the last few months? What do we do then? We'll review the acceptance criteria for BFB (and since various methods have various criteria we will use the tightest acceptance criteria), what can fail, and how to modify your tune file to make BFB pass.

Remember: GC/MS systems are dynamic instruments: their sensitivities and responses change with time and usage, and what works today on your system may not work forever; it's essential that good GC/MS analysts understand tuning and be able to fine-tune (no pun intended) you systems to pass BFB and keep it running optimally.

Let's begin by assuming we have tuned our instrument to have all peak widths at or near 0.50+-0.05 amus, the mass axis of ions 69,131 and 219 are all +-0.1 amu, and the relative rations of 69-131-219 are 100%-35%-35% respectively. We run our BFB and it fails. We then MUST make adjustments to our Manual Tune file based on what failed, correct our ratios and/or peak widths accordingly, and rerun BFB.

I will give some guidelines to follow in modifying your tune file. If these guidelines fail to make BFB pass, a hardware problem may exist.

The chart below lists the acceptance criteria for BFB we will use in this discussion. Keep in mind that some methods and stage agencies allow you to use the Apex, The Apex + 1 scan, The Apex + 1 scan or a 3-scan average of them so be sure you're trying all the legal scans in the peak. Using scans other than the Apex and one scan to either side should not be used. Also, if you have a significant baseline you should obtain a background subtracted mass spectrum.

Acceptance criteria for 4-Bromofluorobenzene for 624/8240

Source: EPA Method 624 for 50 ng injection

Mass	Acceptance Criteria	Affected by in Tune File
50	15-40% of mass 95	ratio of 69 to 131 and 219
75	30-60% of mass 95	ratio of 69 to 131 and 219
95	Base peak, 100% relative abundance	ratio of 131 to 69 and 219
96	5-9% of mass 95	peak width of ion 131
173	<2% of mass 174	peak shape of ion 219
174	50-99.9 of mass 95	ratio of 219 to 131 and 69
175	5-9 of mass 174	peak width of ion 219
176	95-101% of mass 174	ratio of 219 to 131 and 69
177	5-9% of mass 176	peak width of ion 219

As the chart illustrates, for every criteria of BFB there is a corresponding ion in the compound PFTBA (Perflourotributylamine) which is used during tuning. So if the BFB fails for one or more criteria, we adjust the ratios and/or peak widths of the PFTBA during tuning.

If you are having problems with BFB, ALWAYS check your high vacuum pressure. The discussion that follows assumes that your ion source pressure is consistent with what it historically has been. If not, that needs to be resolved first and foremost before any of the techniques presented here can be utilized.

We will now discuss each ion and what to modify in the Manual Tune file should it fail:

Ion 50 (Acceptance criteria: 15-40% of mass 95); Affected mainly by the ratio of 69 to 131 and 219 in our tune file. Tests for adequate low-end sensitivity.

Tuning issues that cause problems with this ion:

Generally, if ion 50 fails it is because it falls under the 15% minimum percentage criterion. Occasionally it will fail because it is >40% of mass 95. I have seen many instances where ion 50 ends up below 15% of mass 95. This means that the system is not sensitive enough at the low end. To remedy this, lower the relative ratios of 131 and 219 each by about 5%. This reduction of the mid-range ends up making the low end more sensitive and will boost the amount of ion 50 that is generated. If this fails, continue to lower the relative ratios of 131 and 219. If you need to make ions 131 and 219 below 20% of ion 69 for BFB to pass I would suspect a hardware problem might exist.

If ion 75 ends up being too high (greater than 40% of ion 95), you should try raising both ions 131 and 219. This increase in the mid-range ends up making the low end less sensitive and should reduce the amount of ion 50 that is generated. If this fails, continue to raise the relative ratios of 131 and 219. If you need to make ions 131 and 219 above 50% of ion 69 for BFB to pass I would suspect a hardware problem might exist.

Hardware issues that cause problems with this ion:

The most common hardware issues that cause failure of ion 50 would be a dirty source (especially if you have elevated amounts of ion 50 AND elevated amounts of ion 75), problems with the rough pump (also for elevated amounts of ion 50) or a low-mass gain Electron Multiplier (for lower amounts of Ion 50). A dirty source is remedied by cleaning the ion source (and replacing the filaments). Problems with the rough pump can be resolved by changing the rough pump oil (be sure only to use Inland 45 oil) and/or replacing the beads in the molecular sieve filter on the rough pump (for Oil Diffusion Pump systems). If neither of these works, it's possible that the rough pump may need replacement.

Ion 75 (Acceptance criteria: 30-60% of mass 95); Affected mainly by the ratio of 69 to 131 and 219 in our tune file. Like ion 50, tests for adequate low-end sensitivity.

Tuning issues that cause problems with this ion:

Generally, if ion 75 fails it is because it exceeds the 60% maximum percentage criterion. I have never seen it fail because it is <30% of mass 95. Sometimes ion 75 does ends up above 60% of mass 95. This means that either the system is too sensitive at the low end or an indication that the source is getting dirty. To remedy this, first raise the relative ratios of 131 and 219 each by about 5%. This increase of the mid-range ends up making the low end less sensitive and will lower the amount of ion 75 that is generated. If this fails, continue to boost the relative ratio of 131 compared to 219. If this fails, try cleaning the ion source. If you need to make ion 131 and/or 219 above 60% for BFB to pass I would suspect a hardware problem exist.

Hardware issues that cause problems with this ion:
The most common hardware issues that cause failure of ion 75 would be a dirty source (especially if you have elevated amounts of ion 50 AND elevated amounts of ion 75), problems with the rough pump (also for elevated amounts of ion 75). A dirty source is remedied by cleaning the ion source (and replacing the filaments). Problems with the rough pump can be resolved by changing the rough pump oil (be sure only to use Inland 45 oil) and/or replacing the beads in the molecular sieve filter on the rough pump (for Oil Diffusion Pump systems). If neither of these work, it's possible that the rough pump may need replacement.

Note for EPA Method 524.2

2A. Ion 75 (Acceptance criteria: 30-80% of mass 95); Affected mainly by the ratio of 69 to 131 and 219 in our tune file. Like ion 50, it tests for adequate low-end sensitivity.

The EPA, in its infinite wisdom, widened the range for Ion 75 for method 524.2. I guess they figured since they're making you shoot a smaller amount of BFB (25 ng as opposed to 50 ng with 624/8260), they'll cut you some slack with the problematic ion 75. An upper limit of 80% makes it such that the source would have to be VERY dirty or some hardware problem would have to exist for it to fail.

Ion 95 (Acceptance criteria: Base peak, 100% relative abundance); Affected mainly by the ratio of 131 to 69 and 219 in our tune file.

Tuning issues that cause problems with this ion:

Generally, if ion 95 fails it is because ion 174 or 176 is the base peak. This means that ion 131 is too low and ion 219 is too high. To remedy this, raise the relative ratio of 131 and lower the relative ratio of 219 each by about 5%. This change will lower the 174/176 pair and should restore 95 to base peak status. If you need to make 131 greater than 219 by more than 15% for BFB to pass I would suspect a hardware problem might exist.

Hardware issues that cause problems with this ion:

If ion 95 fails it is because ion 174 or 176 is the base peak then the system might be running at below-ideal temperatures. In order to obtain proper ratios, the source and analyzer temperatures have to be correct. Be sure the system has thermally stabilized by allowing sufficient time (see discussion earlier in this issue). If they system has had enough time to thermally stabilize, then perhaps the analyzer is too cold. Use the following chart as a guideline:

MSD	Source temp	Quad temp	Transfer line temp
5970	200°C	same as source	250°C
5971	NA	NA	280°C
5972	NA	NA	280°C
5973	200°C to 230°C	150°C	280°C

Ion 96 (Acceptance criteria: 5-9% of mass 95); Affected mainly by the peak width of ions 69 and/or 131 in our tune file.

Tuning issues that cause problems with this ion:

Generally, if ion 96 fails it is because the peak width of ions 69 and/or 131 are not close enough to 0.50 amus. I have seen this isotope ion fail on both ends of the spectrum. If ion 96 falls below the 5% minimum, try narrowing the peak widths of ions 69 and/or 131. If ion 96 falls above the 9% maximum try widening the peak width of ions 69 and/or 131. Also, try lowering the abundance threshold and/or raising the Electron Multiplier setting.

Keep in mind that failure of this minor ion is often linked to poor peak shape in manual tune. So, even if the peak width is correct, you can still fail if the peak shapes of ions 69 and/or 131 are poor. I have seen many instances where elevated Entrance Lens settings distort the peak shape in Manual Tune. Sometimes, but not always, Entrance Lens settings above 100 mV/amu can cause distortion with the 5970, 71 and 72 and settings as low as 40 mV/amu can cause distortion with the 5973.

If this doesn't work, try changing the DC Polarity. For the 5970, this would be a small service issue as to do this one needs to swap 2 wires on the RFPA Board of the analyzer. For the 5971, 72 and 73, you can swap polarities in Manual Tune from POS to NEG (or vice versa). If you change Polarity, you'll need to do a peak width and mass axis calibration and retune the system as undoubtedly the ratios of 69-131-219 will change as well.

Hardware issues that cause problems with this ion:

If this issue can't be resolved by adjusting peak widths or changing polarities, a contaminated quadrupole and/or faulty electronics problem may exist. Usually, manual tune peak shape and corresponding isotope ratios are linked to problems with the RFPA (Radio Frequency Power Amplifier) electronics, so that would be the first thing to check.

You may also need to re-tune the RF coils to improve peak shape. This would be a service issue.

Ion 73 (Acceptance criteria: <2% of mass 174); Affected mainly by the peak shape of ion 219 in our tune file.

Tuning issues that cause problems with this ion:

This is an interesting one. Ion 173 should be absent or present in very small abundance. If it is found above the 2% of mass 174 level, it is usually because of poor peak shape in ion 219. Even if the peak widths are fine, ion 173 will fail if fronting occurs in ion 219 in Profile Scan. When tuning, you need to closely examine the peak shapes of all three ions, especially ion 219. If the peak shape of 219 is not Gaussian (symmetrical), ion 173 will be created at unacceptably high levels.

You can also try swapping the Polarity to see if peak shape improves. Also, be sure you have the Threshold set correctly in your acquisition method. It's possible that by raising the Threshold you may remedy this problem.

Hardware issues that cause problems with this ion:

The first thing to do is to clean the source, paying extra close attention to the Entrance Lens. The Entrance Lens is the component of the Ion Source that comes in contact with the quadropole, so contamination on the Entrance Lens can affect peak shape. For you 5970 users, it would be a good idea to swap Entrance Lenses if the white ceramic insulator looks excessively dirty .

Another possible remedy would be to clean the quadrupoles. (Warning: cleaning the quadrupoles is NOT considered routine maintenance as is cleaning the source and should only be done by trained personnel.)

Ion 174 (Acceptance criteria: 50-99% of mass 95); Affected mainly by the abundance of ion 219 relative to 69 and 131 in our tune file.

Tuning issues that cause problems with this ion:

I have seen this ion fail on both ends of the spectrum. If ion 174 is too large (i.e. it's the base peak), lower the relative abundances of both 131 and 219, especially ion 219. Try setting 131 about 5-10% greater than 219 in you tune file. Conversely, if ion 174 falls below 50% of mass 95, raise the relative abundances of both 131 and 219, especially ion 219. Try setting 219 about 5-10% greater than 131 in you tune file. Refer to the discussion a few pages back regarding ion 95 being the base peak.

Hardware issues that cause problems with this ion:

If ion 174 or 176 is the base peak then the system might be running at below-ideal temperatures. In order to obtain proper ratios, the source and analyzer temperatures have to be correct. Be sure the system has thermally stabilized by allowing sufficient time (see discussion earlier in this issue). If they system has had enough time to thermally stabilize, then perhaps the analyzer is too cold.

Tuning issues that cause problems with this ion:

This is a similar situation to ion 96, only ion 219 in our tune file is the key ion as opposed to 69 and/or 131. Generally, if ion 175 fails it is because the peak width of ion 219 is not close enough to 0.50 amus. I have seen this isotope ion fail on both ends of the spectrum. If ion 175 falls outside the 5-9% window, try widening or narrowing the peak width of ion 219. Try setting the peak width to 0.45 amu, then 0.50 amu, then 0.55 amu and finally 0.60 amu. You can accomplish this by raising or lowering the AMU gain and/or AMU offset. Also, adjusting the 219 Wid setting (for 5971, 2 and 3 MSDS) also can be adjusted. It's dangerous to set the peak widths much further from the 0.45-0.60
as this can cause the mass spec to mis-assign masses (i.e. it will not be able to reliably resolve one mass from another.)

You can also try swapping polarities.

If ion 175 is absent in some of the scans, you can also try changing the A/D setting (usually raising the setting helps this problem). Details of this are given in the next section.

If none of this works, faulty electronics and/or a contaminated quadrupole may exist.

Hardware issues that cause problems with this ion:

First, try cleaning the ion source.

Another possible remedy would be to clean the quadrupoles. (Warning: cleaning the quadrupoles is NOT considered routine maintenance as is cleaning the source and should only be done by trained personnel.)

Also, the rough pump plays a role in properly resolving this ion. Check the foreline pressure. For oil diffusion pump systems like the 5971, 5972 and some 5973s, this is reported on your Manual Tune report as Vacuum (expressed as millitorr). Foreline pressures above 60 mtorr can cause problems with the mass spec being unable to resolve Ion 75.

Ion 176 (Acceptance criteria: 95-101% of mass 174); Affected mainly by the abundance of ion 219 relative to 69 and 131 in our tune file.

Tuning issues that cause problems with this ion:

I have seen this ion fail on both ends of the spectrum. The problem is that there is no known remedy as far as adjustment of ratios or peak widths. The usual solution is to perform a 3-scan Enhancement (i.e. averaging of the Apex + -1 scan) or try either the Apex-1 or the Apex +1 scan. Often times a passing spectrum will result. If this happens only occasionally, then it was probably a fluke and I would just shoot BFB again-it'll probably pass. If it's a chronic problem, double check you A/D (Analog to Digital) setting (Also called Sampling rate on some systems). You might want to *increase* the A/D setting such that each scan on your peak is an average of more scans and is a more accurate representation of the true spectrum. Usually, megabore columns employ A/D of 2^3=8. Try 2^4=16 and see if the problem is solved. If you are using 2^2=4, try using 2^3=8 for your A/D.

Hardware issues that cause problems with this ion:

Often times, cleaning the Ion source will remedy this problem.

Ion 177 (Acceptance criteria: 5-9% of mass 176); Affected mainly by the peak width of ion 219 in our tune file.

Tuning issues that cause problems with this ion:

This is a similar situation to ion 175, although this ion is a lot less problematic. Generally, if ion 177 fails it is because the peak width of ion 219 is not close enough to 0.50 amus. I have seen this isotope ion fail on both ends of the spectrum. If ion 177 falls outside the 5-9% window, try widening or narrowing the peak width of ion 219. Try setting the peak width to 0.45 amu, then 0.50 amu, then 0.55 amu and finally 0.60 amu. You can accomplish this by raising or lowering the AMU gain and/or AMU offset. Also, adjusting the 219 Wid setting (for 5971, 2 and 3 MSDS) also can be adjusted. It's dangerous to set the peak widths much further from the 0.45-0.60 as this can cause the mass spec to mis-assign masses (i.e. it will not be able to reliably resolve one mass from another).

You can also try swapping polarities.

If none of this works, faulty electronics and/or a contaminated quadrupole may exist.

Hardware issues that cause problems with this ion:

First, try cleaning the ion source.

Another possible remedy would be to clean the quadrupoles. (Warning: cleaning the quadrupoles is NOT considered routine maintenance as is cleaning the source and should only be done by trained personnel.)

Summary of BFB Tuning

Usually ratios of 69-131-219 of 100%-37%-37% respectively and peak widths at 0.50 amu will cause BFB to pass...but NOT ALWAYS. Keep in mind that you need to make whatever adjustments are necessary to make BFB pass. Volatile systems are less dynamic that Semivolatile systems generally because the source stays cleaner (less contamination hits the detector on a purged sample than in a Methylene Chloride extract) so the drift is less frequent and less severe. But all GC/MS systems eventually show some change.

Attachment IV: Agilent Document: BFB Tuning for Environmental Analysis: Three Ways to Succeed.

BFB Tuning for Environmental Analysis: Three Ways to Succeed

Application

Environmental

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Abstract

The United States Environmental Protection Agency methods 524.2, 8260B, and Contract Laboratory Program Statement of Work employ purge and trap concentration of volatile compounds in water samples with analysis by gas chromatography/mass spectrometry. Each method requires the mass spectrometer to meet specific tuning criteria before proceeding to actual samples. This paper summarizes these tuning criteria, and shows three different ways that the Agilent Technologies 6890/5973 gas chromatograph/mass selective detector system can be tuned to meet them. A very simple and robust procedure is described in the Modified Autotune section. A quick reference guide for this procedure is given at the end of the paper under Modified Autotune Summary.

Introduction

If you are already familiar with 4-bromofluorobenzene (BFB) tuning and evaluation procedures, you may want to go directly to the section titled "Modified Autotune Summary" found at the end of this paper. It offers an alternative approach for tuning Agilent 6890/5973 GC/MSD systems that is routinely successful in this laboratory.

The United States Environmental Protection Agency (USEPA) has developed several methods for the analysis of volatile organic compounds (VOCs) in water samples. The three most widely used procedures all employ purge and trap (P&T) sample introduction followed by capillary column gas chromatography with mass spectral detection (P&T/GC/MS). USEPA Method 524.2 revision 4[1] is used for drinking water analysis while Method 8260B revision 2[2] is used for wastewater. The USEPA Contract Laboratory Program Statement of Work (CLP-SOW)[3] uses a similar P&T/GC/MS method for the analysis of hazardous waste.

There are many similarities among these three USEPA volatiles methods. One common requirement is that the GC/MS system must be tuned in such a way that 4-bromofluorobenzene (BFB) meets specific ion abundance criteria. This requirement helps to ensure that data are comparable between instruments of different design and

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among various laboratories. This paper summarizes USEPA method 524.2, 8260B, and CLP tuning criteria, and shows three different ways that the Agilent Technologies 6890/5973 GC/MSD system can be tuned to meet them.

Experimental

A standard containing fluorobenzene, 1,2-dichlorobenzene-d_4 and 4-bromofluorobenzene at 2.0 mg/mL was purchased from AccuStandard (New Haven, CT). A portion of this solution was diluted in methanol (B&J HPLC and pesticide grade) to a concentration of 50 ng/µL.

Standards for tune evaluation were injected by syringe or P&T into several different Agilent Technologies 6890/5973 GC/MS systems. When making syringe injections into the split/splitless inlet, a liner with a 900-µL volume was used and no more than 1.0 µL was injected to avoid over-expansion in the inlet.

Results and Discussion

Tuning Criteria

Table 1 lists the tuning criteria for USEPA methods 524.2, 8260B, and CLP-SOW. All three methods base their tuning criteria on the ion responses of BFB. All ion responses are reported relative to m/z 95, which is assumed to be the base peak even though ions 174 and 176 may be larger in the CLP-SOW method.

While many of the requirements in Table 1 are the same for all three methods, some important differences are worth noting. Method 8260B actually allows the analyst to use the tuning criteria specified in either of the other two methods. More importantly, it allows one to use "manufacturers tuning (sic) instructions" so long as it does not hurt method performance. However, many laboratories still follow the BFB tuning requirements specified in method 8260B or choose to substitute CLP-SOW tuning criteria.

Methods 524.2 and 8260 require that m/z 95 be the base peak in the BFB spectrum, which caps the m/z 174 relative abundance at 100% (relative to m/z 95). The CLP-SOW requirements allow m/z 174 to be up to 120% of m/z 95. Tuning procedures that reduce the response of m/z 174 too much may lead to lower overall sensitivity, especially for bromoform which has a quant ion of m/z 173. Conversely, maximizing this ratio, within the requirements of the method, can enhance overall sensitivity.

Automated BFB Tuning

The Agilent 5973 MSD uses perfluorotributylamine (PFTBA) for electron impact tuning because it exhibits good stability, the right volatility, and a wide range of fragment masses. However, USEPA volatiles methods evaluate the tune using BFB which produces an entirely different spectrum.

Table 1. Criteria for BFB Tuning for Three Capillary GC/MS Volatiles Methods

	Relative Abundance Criteria		
Mass (m/z)	Method 524.2	Method 8260B[a]	CLP-SOW
50	15 to 40% of 95	Same as 524.2	8 to 40% of 95
75	30 to 80% of 95	30 to 60% of 95	30 to 66 % of 95
95	Base Peak, 100%	Same as 524.2	Same as 524.2
96	5 to 9% of 95	Same as 524.2	Same as 524.2
173	<2% of 174	Same as 524.2	Same as 524.2
174	>50% of 95	Same as 524.2	50 to 120% of 95
175	5 to 9% of 174	Same as 524.2	4 to 9% of 174
176	>95 to <101% of 174	Same as 524.2	93 to 101% of 174
177	5 to 9% of 176	Same as 524.2	Same as 524.2

[a]Alternative tuning criteria may be used (for example, CLP or Method 524.2) including manufacturer's instructions provided that method performance is not adversely affected.

Therefore, automated (or manual) tuning procedures must adjust PFTBA ion responses in order to get the desired BFB response ratios. Agilent G1701CA EnviroQuant ChemStation software automates BFB tuning so that the instrument typically passes the more restrictive USEPA Method 524.2 and 8260B requirements listed in Table 1. After tuning, the analyst must inject a BFB standard by syringe or P&T to verify that the tune passes the requirements for the method in use.

Automated BFB tuning adjusts MSD source parameters so that PFTBA ion abundances meet predetermined "targets." The default PFTBA target values are set so that a subsequent BFB injection should meet the requirements for all three methods. Table 2 shows a portion of a BFB tune report that includes the target responses (as a percentage of *m/z* 69) for *m/z* 50, 69, 131, 219, 414, and 502. The actual abundances achieved by the tune are shown on the last line. When these targets are met, the Agilent 5973 MSD normally passes any of the tuning criteria listed in Table 1.

Table 2. A Portion of a Typical BFB Tune Report

Target Mass:	50	69	131	219	414	502
Target Abund (%):	1.0	100.0	45.0	55.0	2.4	2.0
Actual Tune Abund (%):	1.2	100.0	48.1	59.3	2.7	2.3

Figure 1 shows an average spectrum obtained for a 1-µL manual injection of BFB (50 ng/µL split 50:1) using the tune shown in Table 2. Agilent G1701CA EnviroQuant ChemStation Environmental Data Analysis software can evaluate the spectrum automatically and generate a report that is archived with the data file. Because BFB tuning criteria are not uniform among USEPA methods, the analyst must first specify the allowable ranges using the form shown in Figure 2. The form is accessed in Environmental Data Analysis by selecting Tuner/Edit BFB Criteria on the dropdown menu.

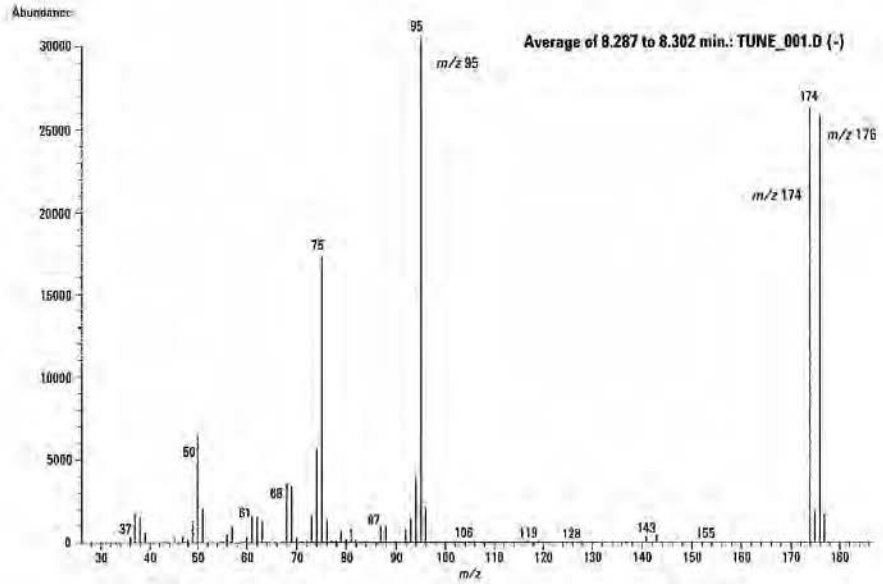

Figure 1. Average spectrum of BFB after performing a standard BFB automated target tune. One µL of a methanol solution containing 50 ng/µL of BFB was injected by hand.

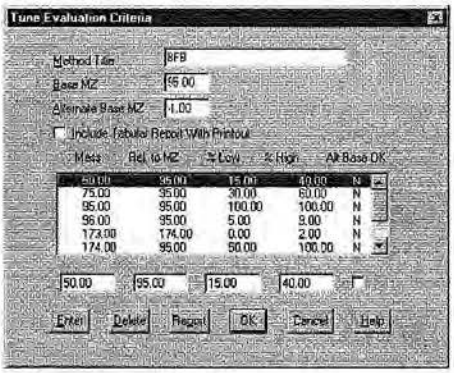

Figure 2. The Agilent G1701CA EnviroQuant ChemStation screen for entering BFB tune criteria. The user can modify the parameters to meet the requirements of the method in use. These values are used by the ChemStation for automated tune evaluation.

Having entered abundance criteria for the method in use, one can automatically assess the suitability of the tune using the EnviroQuant software (Figure 3). One can choose to "Evaluate BFB to Screen/Printer" in which case it will evaluate the current spectrum. This can be a single spectrum or an average. Alternatively, by choosing "Autofind BFB to Screen/Printer," the software automatically finds BFB in the chromatogram, averages the top three spectra and subtracts a baseline spectrum. In either case, a report such as the one in Figure 4 is generated. The most recent report is archived in the datafile.d directory in a file called tuneeval.txt.

Figure 3. Choices for automated BFB tune evaluation by the EnviroQuant software. The "Evaluate BFB..." choices use the spectrum (single or averaged) in Data Analysis window 1 for evaluation. The "Autofind..." choices automatically find the BFB peak, average the top three BFB spectra and subtract a baseline spectrum prior to evaluation.

BFB

Data File : C:\HPCHEM\1\DATA\Sep24_01\TUNE_001.D Vial: 1
Acq On : 24 Sep 2001 2:25 pm Operator:
Sample : BFB for tuning 1 uL Inst: GC/MS Ins
Misc : Multipl: 1.00
MS Integration Params: rteint.p

Method : C:\HPCHEM\1\methods\envdef.m (RTE Integrator)
Title :

AutoFind: Scans 1567, 1568, 1569; Background Corrected with Scan 1559

Target Mass	Rel. to Mass	Lower Limit%	Upper Limit%	Rel. Abn%	Raw Abn.	Result Pass/Fail
50	95	15	40	21.6	6769	PASS
75	95	30	60	56.5	17708	PASS
95	95	100	100	100.0	31317	PASS
96	95	5	9	7.1	2299	PASS
173	174	0.00	2	0.0	0	PASS
174	95	50	100	82.8	25933	PASS
175	174	5	9	7.4	1910	PASS
176	174	95	101	99.3	25747	PASS
177	176	5	9	6.6	1702	PASS

TUNE_001.D envdef.m Mon Sep 24 16:00:27 2001 MSVOC04

Figure 4. The Agilent EnviroQuant ChemStation BFB Tune Evaluation Report for the spectrum shown in Figure 1.

In this case the automated BFB tuning procedure produced a tune that passes Method 524.2 and 8260B criteria with a 174/95 ratio of 82.8%. This ratio is limited to 100% by these USEPA methods, which specify that *m/z* 95 must be the base peak. To meet these strict guidelines, one has to "de-tune" the Agilent 5973 MSD which results in somewhat lower instrument sensitivity. Laboratories may want to increase the 174/95 ratio so it more closely approaches the 100% limit of Methods 524.2 and 8260B or so that it approaches the 120% limit specified in the CLP-SOW method. Most laboratories that perform Method 8260B tune their instruments to meet the CLP-SOW requirements because the method allows laboratories to use these tune criteria and the MSD performance is closer to optimum.

In addition to the automated BFB tune, there are two procedures that can be used to improve instrument sensitivity, to meet the more liberal CLP-SOW requirements, or to create a passing tune should the standard BFB autotune fail. In this laboratory, the "Modified Autotune" procedure was found to produce tunes that routinely passed BFB criteria for any of the three methods. As shown below, changing the BFB tuning targets can also produce a passing BFB tune while enhancing the signal for bromoform.

Target Tuning

Automated BFB tuning adjusts MSD source parameters to achieve the target responses required for the method in use. This is essentially a "target tune" procedure where the initial target abundances provided by the software are designed to

meet the more restrictive 524.2 and 8260B requirements. When needed, it is easy to change the target PFTBA relative abundance criteria to produce the desired affect on the BFB ions. This is done by selecting View/Manual Tune/Set Tune Targets.

For example, consider the spectrum in Figure 1 which passed all of the tuning criteria, but which had a lower than optimum *m/z* 174 response. Experience in this laboratory has shown that increasing the relative abundance of *m/z* 174 will increase the overall sensitivity of the instrument, in particular for the bromoform response at *m/z* 173. As shown in Figure 5, the target abundances for ions 131 and 219 were each increased to 70% from their default values of 45% and 55% respectively. These choices were saved to the BFB.U tune file and a new BFB Target Tune was run. Figure 6 shows the new BFB spectrum (average of three spectra across the apex with baseline subtraction) which passes CLP-SOW criteria (Table 1) and is, therefore, satisfactory for either CLP or 8260B volatiles methods.

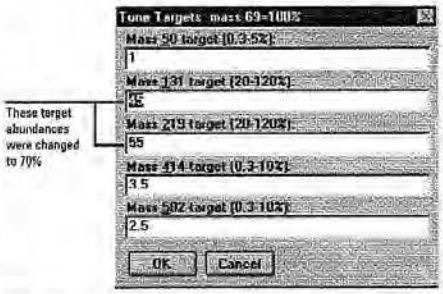

Figure 5. PFTBA target abundance values (relative to *m/z* 69) used for "target" tuning. When these abundances are saved to the BFB.U tune file, they are used by the BFB target tune algorithm.

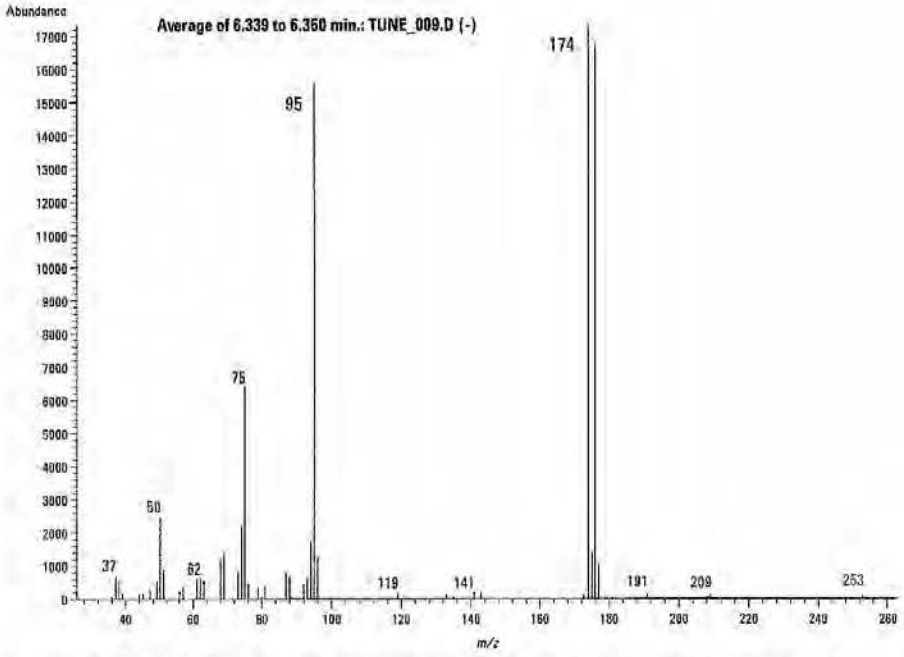

Figure 6. Average BFB spectrum obtained by changing the tune targets for *m/z* 131 and 219 to 70% (relative to *m/z* 69). This spectrum passes CLP-SOW tuning criteria.

Modified Autotune

With the convenience of automated tuning procedures available in the Agilent ChemStation software, most analysts have gladly given up the idea of manually tuning their 5973 MSDs. A combination of automated tuning with a slight manual modification has given excellent BFB results in this laboratory. The total process is easy and usually takes just a few extra minutes after the autotune is complete. The steps are described below and are summarized in a "quick reference" format in the next section.

1. From the Manual Tune portion of the software, perform an Autotune (select Tune/Autotune). This algorithm tunes the Agilent 5973 MSD for maximum sensitivity over the entire mass range and is widely used by methods that do not specify other tune criteria. This autotune emphasizes overall sensitivity by improving abundances for higher mass ions (for example, 502). As a result, the Autotune procedure typically gives an abundance for *m/z* 50 that is too low to meet 524.2 and 8260 criteria and an abundance of *m/z* 174 that may be too high, even for CLP-SOW tuning.

2. After completing the Autotune procedure, choose Edit MS Params (under the AdjParam menu item) which will display the screen shown in Figure 7.

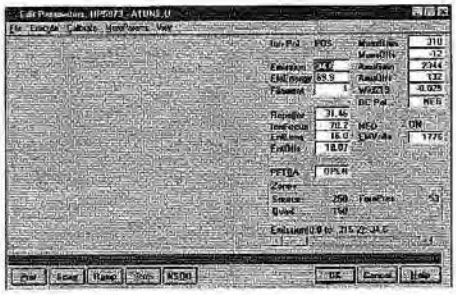

Figure 7. The Edit Parameters screen found by selecting AdjParam/Edit MS Params in the main Manual Tune window.

3. Two changes are required in the default values used for adjusting parameters in this view. First, under the MoreParams menu, choose Ramp Params and change the "Stop" value for the ion focus to 140 as shown in Figure 8. Close this window and choose AcqParams under the MoreParams window and change Mass 3 from 502 to ion 50 as shown in Figure 9. Close this window and return to the main Edit Parameters screen (Figure 7).

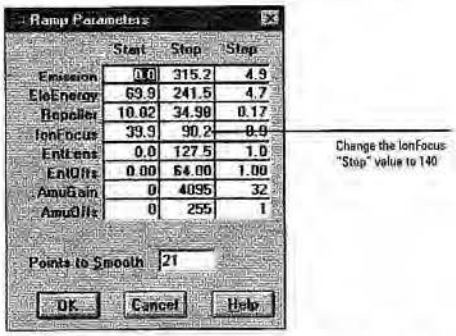

Figure 8. This window allows the user to set ranges for the various tuning parameters. The default ion focus "Stop" setpoint of 90 was set to 140.

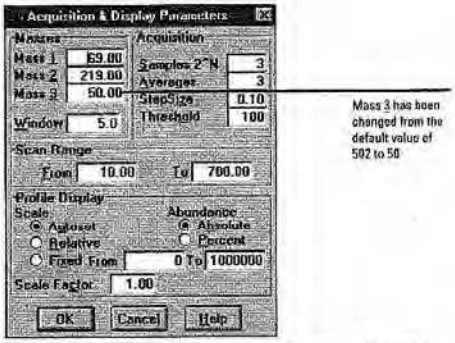

Figure 9. Acquisition and Display Parameters window. *M/z* values of 69, 219, and 50 have been chosen so that these responses can be ramped and their relative abundances displayed.

4. Highlight the IonFocus window with the cursor and then select Ramp. This gradually ramps the ion focus voltage over the specified range while monitoring the response of ions 69, 219, and 50. After about a minute, a plot of these ion responses vs. the ion focus voltage appears in the window (Figure 10).

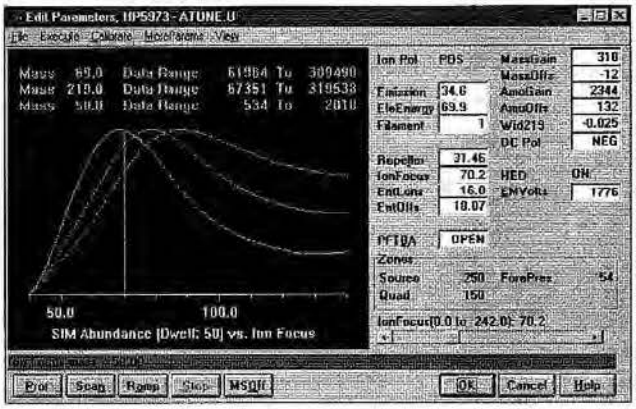

Figure 10. Abundances for ions 69, 219, and 50 while ramping the Ion Focus from 40 to 140.

5. Under the View dropdown menu item, choose Expand. This view shows the current Ion Focus setting, the abundance of m/z 69 and the relative abundances of ions 219 and 50 (Figure 11). From the plot, it is easy to see that an increase in the Ion Focus value should increase the 50:69 ratio while reducing the 219:69 ratio. These are exactly the changes that should enable the MSD to pass BFB tuning criteria.

   Note that the ion focus ramping procedure can also be performed from the main Manual Tune screen by choosing Ramp/Ramp Ion Focus on the dropdown menu.

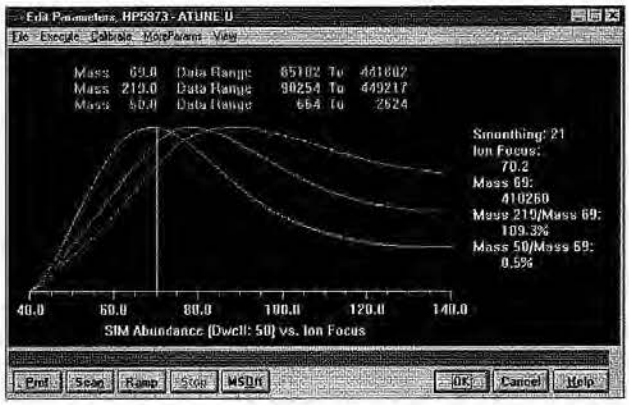

Figure 11. An expanded view of the SIM-Abundance-vs-Ion Focus plot obtained by selecting View/Expand. This view allows one to drag the vertical line to different setpoints while observing changes in the ion relative abundances.

6. The vertical line indicates the current ion focus setpoint. Use the cursor to drag this setpoint line to the right while observing the change in the 219:69 and 50:69 ratios. Agilent laboratories have had good success by setting the Ion Focus to values between 100 and 135 V. This should result in a 219:69 ratio in the 60-80% range and a 50:69 ratio that is 0.8 or greater. If tuning to meet 524.2 requirements, the 219/69 ratio should be on the low side of this range.

   An alternative to the above procedure is to select Scan in the Edit Parameters window (Figure 7) while monitoring ions 69, 219, and 50. The 219:69 and 50:69 ratios are displayed under the Relative Abundance heading and are updated with each scan. Highlight the Ion Focus setting and adjust its value using the slider bar. The effect of different Ion Focus values will be seen almost immediately in the ion ratios. These ratios will bounce around somewhat, but trends can be seen over a few scans. A good choice for the 50:69 ratio would be about 0.85.

7. Click OK and return to the Manual Tune screen. Under the Calibrate menu item, choose Adjust Abundances, which will automatically reset the electron multiplier to get ion abundances in the optimum range. Save the tune, choosing a new name for the tune file (for example, BFB1.U). Return to Instrument Control (View/Instrument Control) and be sure to select this tune file for the method used to acquire the BFB checkout chromatogram. Inject or purge an appropriate amount of BFB and evaluate the tune using the software tools provided (Figures 2 through 4). Assuming that it passes, assign this tune to the P&T/GC/MS volatiles method in use.

Figure 12 shows the spectrum (average of the three scans across the apex with baseline subtraction) for a 1-µL syringe injection (50 ng/µL split 50:1) of BFB using an ion focus value of 115 V. All other parameters (except for the electron multiplier) were set by the Autotune algorithm. This spectrum passes any of the tuning criteria listed in Table 1 but has a higher 174/95 ratio than was achieved using the standard BFB tune.

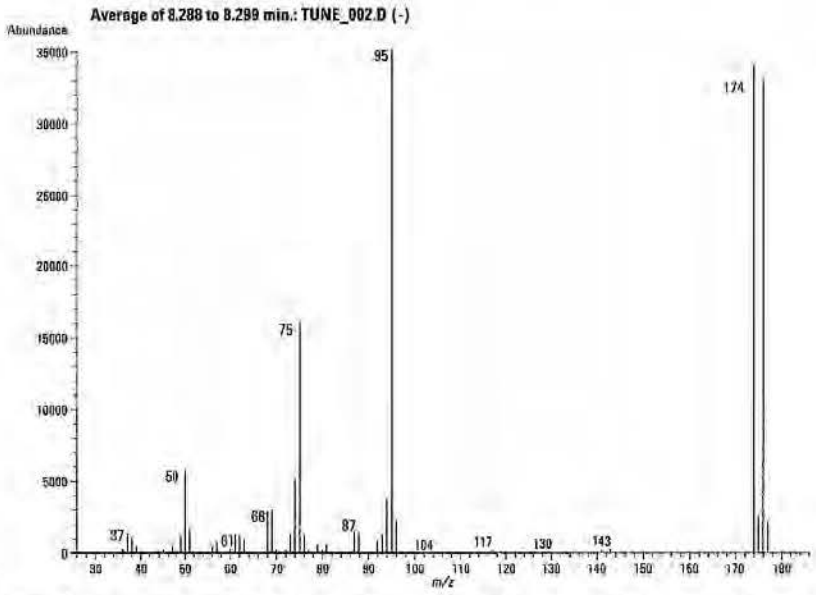

Figure 12. Average spectrum of BFB obtained after using the procedure described under Modified Autotune. After running a standard Autotune, the Ion Focus value was increased to 115 V.

The true test of a successful BFB tune is whether it holds up during repetitive VOC analyses and through normal instrument maintenance procedures. In one extreme test, the same BFB tune easily passed CLP-SOW criteria during a period when two different MSD sources were installed and four different filaments were used. On one Agilent 6890/5973 GC/MS instrument this procedure did not work until the MSD source was cleaned.

Finally, a note of caution is appropriate. While these techniques have worked well for the Agilent 6890/5973A and N GC/MSD systems, this does not imply that the same procedures are appropriate for older Agilent MSDs. Tuning frequency is dictated by the nature of the samples, choice of column and other factors such as column bleed and source cleanliness. If the source becomes too dirty, it must be cleaned in order to pass BFB tuning criteria, no matter which approach is taken.

Modified Autotune Summary

These steps summarize the procedure for modifying the standard Agilent 5973 Autotune to pass BFB tuning criteria. It is provided here as a quick reference guide for those who are already familiar with tuning procedures.

1. In the Manual Tune portion of the Agilent GC/MS ChemStation software, perform a standard Autotune.
2. In the Ramp Parameters window, change the Ion Focus Stop value to 140.
3. In the Acquisition & Display Parameters window, change ion 502 to 50.
4. In the Edit Parameters window click on Ion Focus and then on Ramp.
5. Adjust the Ion Focus value so that the 50/69 ratio is 0.8 or larger. The 219/69 ratio usually falls in the 60 to 80% range. When this PFTBA ion ratio is under 70%, the 174/95 ratio of BFB is usually under 100%.
6. In the Manual Tune window under the Calibrate menu item, adjust ion abundances.
7. Save the tune file with a new name, assign it to the method and verify that the tune passes by injecting a BFB sample according to the method requirements.

Conclusions

There are several ways to tune the Agilent 6890/5973 GC/MSD system to meet any of the USEPA BFB tuning criteria. However, factors such as source cleanliness, choice of column, flow rates and instrument-to-instrument variability make each GC/MSD system unique. Automated BFB and target tuning procedures are normally successful but the 174/95-ion ratio may not be high enough to meet laboratory needs. In our experience, the most robust and long-lasting BFB tunes were generated by the procedure outlined above under Modified Autotune. The procedure takes just a few minutes to complete.

References

1. *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry,* Method 524.2, revision 4.1, U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Cincinnati, OH (1995).
2. *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS),* Method 8260B, revision 2 (1996).
3. *USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM04.2,* USEPA Contract Laboratory Program, Office of Emergency and Remedial Response.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

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Agilent Technologies

Attachment V

Pace Analytical Services, Inc
1241 Bellevue Street Suite 9
Green Bay, WI 54302
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Fax: 920 469 8827

VOA Calibration Process

Epic Pro

Make Q-Batch

- Batching -> New Batch -> Queue = MSV
- Click Empty Batch icon on taskbar
- Highlight QC Rule -> F9 -> type MSV
- Select appropriate QC Rule (i.e. MSV water) – Select OK – F10 to save
- Record Q Batch #

Create Standards

- System -> Utility -> Clone Standard by Event
- Select Event (111 = MeOH soil curve, 115 = Water/LLsoil curve) Select OK
- Double Click on standard event
- Review Standard composed of – Find/Replace if necessary
- Update expiration date to 7 days from creation – F10 to Save
- Operations -> Standard Log -> Enter – Record Standard #'s

Chemstation

Create Chemstation methods

- Tune MS, Save Tune file as date (i.e. 072513.u)
- Update both DBFB and Curve method to use new tune file
- Save Curve method as date (i.e. W072513.m)

Set up Sequence

- Load pre-existing curve sequence if available
- Change old method to the new method & copy through all files (DBFB remains the same)
- Change Q-Batch# in BFB, Curve and ICV files

Start Analysis

- Run minimum of 2 BFB injections to ensure the tune is optimized
- Retune or adjust as needed, repeat 2 more BFB
- Analyze a 2 blanks to verify the system is clean and IS areas within range
- First IS, pentafluorobenzene should be between 300,000 – 550,000 area counts
- Raise or lower EM as necessary – You ***Must*** reanalyze BFB if voltage was adjusted
- Reanalyze blanks to ensure correct voltage and proceed w/ analysis of curve

Target

Create Method

- Rename existing method to new name matching Chemstation method (i.e. W072513.m)
  Note: if other data in Directory was processed w/ old method a copy of that method must remain in directory as well.
- To avoid excessive file size, Audit trail in method should be reset at a minimum of annually
  The ***ONLY*** time an audit trail may be rest is prior to calibrating the instrument.
  Note: The Audit trail will remain intact in previous days folder.
  Double click into method folder, highlight the .audit file and delete

Edit Method

- Security -> Method unlocked
- Global -> Calibration – click "update Curve Parameters" to averaged
- File -> Zero Calibration
- Compound ->Edit Compound -> Calibration
  Review all analytes to ensure all necessary points are enabled
  Are any 300 points dropped? If so, mark them enabled and make note of these to change the "Max Compound Amount Limit" after the curve has been run.
- Reports -> Tabular –> "Print Custom Report" –click "Select Format"
  On toolbar a "Select" icon will appear
  Click on ManIntprepost.mac – click "Open"
  Note: It is necessary to do this ***Every*** time a calibration is zeroed, even if the macro shows up in this field as the link to the macro that was lost when the calibration was zeroed.
- Sample -> Default Sample
  Change "Lab Prep Batch" field to the new Q-Batch #
  Change "Client SDG" to be the instrument and date (i.e. 40MSV2-07252013)
- Sample -> Surrogate/ISTD Parameter
  Confirm that the correct IS/SS standard # is entered in the "Surrogate Lot#" field
  Example – 51970:1.163 The 51970 is the IS/SS number followed by a colon followed by the volume added (this is a fixed amount unless change to the standard delivery has occurred.)
- File -> Save Method
- File -> Exit

Process and Review Curve Data

- If significant Column maintenance was performed, it may be beneficial to process the 20 or 50 point first to update RT's as the larger concentrations will have better spectra to confirm correct identification
- Select Method to calibrate and process files
  Compound Sublist should be "all.sub"
  Sample Type change to Calib Sample
  Cal Level change to appropriate level 1-7
  Double check that the Q-Batch # in MiscInfo and Lab Prep Batch are correct and match
  Double check that the Client SDG reflects the instrument and date

- Review Target Data
  - Review each analyte of all points for correct spectrum, RT and appropriate integration
  - All Manual Integration of all curve points and ICV need to have Review Codes added
  - After reviewing all points, review each analyte point 1->7 to ensure consistent RT, spectra and Integration (i.e. shoulders cropped or included, etc.)

Review Curve in Target Method

- Edit Method
- Edit Compound -> Calibration
- Review each analyte to ensure Initial Calibration %RSD are less than 15.0%.
  - Note analytes >15% and re-examine target data for proper integration
- Check that all CCC compounds are less than 30% RSD
  - CCC's are11DCE, chloroform, 12DiChloropropane, toluene, ethylbenzene and vinyl chloride
  - Instrument maintenance must be performed to correct problem if any >30%
  - If %RSD >15% and <30% note %RSD to record later.
- Check that all minimum relative response factors (RRF) were met for the SPCC – Chloromethane, 11DCE, bromoform are 0.1 and 1122PCA, chlorobenzene are 0.3– if any %RSD >15 note RRF to record later.
- If %RSD > 15 – Drop Upper or lower point to achieve %RSD < 15
  - If the Report Limit (RL) for analyte is not the 1 point, can the 1 point be disabled
  - Can the 7 point be dropped (or 6 & 7 points) – **Will require lowering Max Amount
  - Note: ONLY upper or lower points can be dropped, ***NEVER*** an intermediate point!!
  - Must have minimum of 5 points for Averaged RF curve
  - After disabling appropriate points – Click "Update Calibration" button
- If %RSD still > 15 – Switch Curve fit to Linear Regression
  - Change curve fit to Linear
  - **CCC Compounds (11DCE, chloroform, 12dichloropropane, toluene, ethylbenzene, vinyl chloride) MUST still be <30% RSD.
  - Initial Calibration R^2 must be 0.990 or greater
  - Must have minimum of 5 points for Linear regression curve
  - b intercept should be as close to zero as possible
    - i.e. by dropping the 300 point does the intercept go from 0.1980442 -> 0.0681234
    - This will give less false positive hits but require linear range to be lowered to 200ug/L
- If R^2 is not > 0.990
  - Change curve fit to Quadratic
  - ***Must have minimum of 6 points**
  - R^2 must be 0.990 or greater
  - Like Linear regression the 300 point can be dropped (or 1 point added if RL is 5ug/L) to achieve the intercept closest to zero, as long as 6 points remain and linear range is adjusted.
- If calibration for compound will not pass
  - The Instrument cannot be run for lists including these analytes
  - Document analytes as failing in Run logbook
  - Place Post-It-Note on Instrument Terminal to alert other analysts of failures

Update Linear Range

- After all analyte curve fits have been checked
  - Compound->Edit Compound->Report Parms
  - Adjust "Max Compound Amt Limits" to reflect highest point used (300->200 if 7th point was dropped)
- Sublists -> Update Sublists
  - Check the "Update Sublists QC Limits" box
  - Highlight first sublist and hit Enter button
  - Arrow down to the next sublist and hit Enter
  - Repeat for all Sublists
  - **If you fail to update all the sublists, detects above linear range will not be "a" flagged in target
    - Epic Pro uses the "a" flag to switch Condition Code from "OK" to "OR"

Lock Method

- Security -> Initial Calibration Locked
- Note: Do not select "Method Locked" – This would not allow the method to be used to process data

Verify Initial Calibration

- View -> Initial Calibration
- This generates a report with calibration data that will appear on the lower tool bar
- Print report and review
  - The Calibration File Names in the header match the ***correct*** files used in the curve
  - All Average Response Factors < 15% and at least 5 points were included
  - All Linear Regression > 0.990 and at least 5 points were included
  - All Quadratic > 0.990 and at least 6 points were included
  - Are all low points dropped below Report Limit for that analyte
  - Any high points dropped verify that the Max on Column was lowered and Record max amount on the report
  - No midpoints of curve are missing
  - All CCC compounds averaged – If not is the %RSD < 30% - Record actual RSD on report
  - All SPCC minimum RF factors met – If not averaged, switch to Averaged in method record the RF on the report and switch curve back to appropriate curve fit
- Manually check individual Response Factors (RF) for at least one analyte
  - Calculate the RF for each point in the curve of an Averaged curve fit using the following formula
  - RF = (Area of analyte *concentration of IS) / (Area of IS *concentration of analyte)
- Save method and Exit

Re-quantify and Uploading Curve and ICV

- Select Method
- Highlight Curve and re-quantitate
- Process ICV – Must use all.sub (or Full.sub)

- Review ICV and check CLP.rp
  - All SPCC Minimum RF must be met (if analyte is linear, must hand calculate)
  - All CCC Analytes must be <20%
  - All other analytes must be <30%
    - Note: Up to 5% (5 Analytes for a full list spike) may be between 30-40%)
  - All Analytes > 40% will be flagged as failing
    - Document analytes as failing in Run logbook
    - Place Post-It-Note on Instrument Terminal to alert other analysts of failures
- Generate all files to paperless (BFB, Curve and ICV)
- Upload all files to Epic Pro (double check Q-Batch is correct prior to upload)
- Check Q-Batch in Epic to ensure Curve, BFB and ICV imported correctly (may take several minutes)

MN Low Standard Verification

- Copy 1ppb, 5ppb & 20ppb files into another folder (i.e. the unprocessed blank following 300ppb)
- Paste all 3 files than Rename example (07251305.D -> MN01-07251305.D)
  - This will allow original files to be un-manipulated
- Cut files and paste back in original folder
- Re-Quant new MN files as LCS
  - Sample Type = QC Control Sample
  - Click QC SampleType
    - Sample Type = LCS
    - Spike List = MNLOW1.spk, MNLOW5.spk, MNLOW20.spk
- Highlight all 3 files and Do Quick Forms – Form 3 of LCS
- Print Form 3's and pass on to Supervisor to update MN report limits in Epic Pro

Before proceeding with analysis of samples

- Check Chemstation sequence that correct Q-Batch is in BFB and CCC
- Check that correct Method is referenced in the sequence

Attachment VI

Pace Analytical Services, Inc
1241 Bellevue Street Suite 9
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Phone: 920 469 2436
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VOA Calibration Review Checklist

Method:	SW846 8260B
Instrument:	
Q-Batch:	
HBN:	

Comments: Check box if there is an issue and document what was done.

	Prior to Running Curve	*Comments:*
☐	IS/SS filled with Fresh standard and primed	
☐	Sparge tube/sipper tube clean or replaced	
☐	Replace Injection Port Septa if necessary	
☐	Instrument was tuned and new unique Tune file was created (i.e. 072513.u)	
☐	DBFB method was updated to use current tune file	
☐	Water method was updated to use current tune file and saved as the date (i.e. W072513.m)	
☐	Correct Q-Batch entered in sequence	
☐	Correct standards entered in sequence	
☐	Correct Method entered in sequence	

	Prior to Processing Curve in Target	*Comments:*
☐	Method renamed to match Chemstation Method name	
☐	Method Unlocked and Zeroed	
☐	All point enabled (if 300 point was previously dropped)	
☐	All compounds curve fit re-set to Averaged	
☐	Manual Integration Macro selected	
☐	Q-Batch entered in Method and BFB default sample in the Lab Prep Batch field	

	Prior to Processing Samples	*Comments:*
☐	Initial Calibration Report reviewd by another Analyst	
☐	Curve and ICV Passed - all failures recorded in logbook and note placed on instrument terminal	
☐	Sublist all updated to reflect linear ranges if 7th points were added or dropped	
☐	Files uploaded and generated to paperless	
☐	Q-Batch reviewed in EpicPro to assure properly imported	
☐	MN Low Standard re-quanted and Quick Forms generated	
☐	Correct Q-Batch and Method are in new sequence	

Issues: Write any and all out of control issues below:

☐ Labtrack was issued _____

☐ Supervisor was notified _____

To the best of my knowledge, all of the above information is correct and all supporting documentation has been provided.

Analyst: _____ **Date:** _____

Reviewer: _____ **Date:** _____

F-GB-O-140-Rev.00 (26March2014)
Pace Analytical - Green Bay Laboratory

STANDARD OPERATING PROCEDURE

SETAFLASH CLOSED-CUP FLASHPOINT

Reference Methods: SW-846 Method 1020B ASTM D 3278-78

Local SOP Number:	S-GR-I-005-rev.00
Effective Date:	Date of Final Signature
Supersedes:	S-GR-I-18124-rev2.0
SOP Template Number:	SOT-ALL-Q-001-rev.13

APPROVALS

Garrett Ern — Laboratory General Manager — 4/11/2018 — Date

Lucy Delany — Laboratory Quality Manager — 04/12/18 — Date

David R. Osborne — Laboratory Department Manager — 4/12/18 — Date

PERIODIC REVIEW

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

Signature	Title	Date

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

TABLE OF CONTENTS

1. Purpose/Identification of Method

1.1. This procedure is applicable to the flashpoint of liquid waste samples. The procedure, while not technically applicable, is also used to determine the flashpoint of solid waste samples. Flashpoints reported from the analysis of solid waste samples will be qualified.

1.2. This procedure is not applicable to waste samples that are difficult to homogenize where a representative aliquot cannot be analyzed in the tester.

2. Summary of Method

2.1. A small sample aliquot is heated at a low, constant rate while a flame is intermittently directed into the cup at regular intervals to check for a vapor flash.

2.2. The flashpoint is the lowest temperature at which application of the flame ignites vapors above the sample and a flash is observed.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved with the analytical process.

3.2. **Parameters**: Flashpoint applicable range 68 - 200° F

4. Applicable Matrices

4.1. Non Aqueous Liquid

4.2. Solid – Method Modification

4.3. Water

5. Limits of Detection and Quantitation

5.1. Limits of Detection (LOD/MDL) and Limits of Quantitation (LOQ/PWL) are listed in the Laboratory Information Management System (LIMS) and are available by request from the Quality Manager.

6. Interferences

6.1. Use the actual ambient air pressure of the laboratory at the time of testing to calculate adjusted flashpoint.

6.2. Solid samples must be homogeneous and representative to give an accurate result. If not, narrate that a representative and/or homogeneous sample could not be evaluated.

6.3. Do not open containers unnecessarily or make sample transfers at a temperature within 30° F of the flashpoint. Do not mix solid samples excessively to minimize the loss of volatile materials.

6.4. Use the draft-free box during the flashpoint determination to minimize drafts across the flashpoint tester.

6.5. Care must be taken to assure that all test conditions are consistent. These conditions include the size of the flame, the rate of temperature increase, the frequency of dipping the flame into the sample vapor and observation of the flash itself.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Collect and store samples in glass bottles with PTFE-lined lids.

7.2. Transport and store samples at 0 - 6° C until the time of analysis.

7.3. Shake liquid waste samples just prior to removing a sample aliquot.

7.4. Do not mix and/or homogenize solid waste samples unless it can be done quickly within the sample container without the risk of losing entrained volatiles. Test at least two representative aliquots from within the sample.

7.5. No sample aliquot shall be placed in the tester cup that exceeds 30° F below the sample's expected flashpoint.

8. Definitions

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

8.2. **Term** – Definition (or explanation of acronym)

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

9.1. Koehler Rapid Tester Model K16502, Closed-cup

9.2. ASTM Thermometer No. 9F Range 20 - 230° F, 287 mm

9.3. Barometer, verified annually

9.4. Syringe, 2 ±0.1 mL capacity

Note: Test the syringe for accuracy using an analytical balance and water. Maintain a record of the testing.

10. Reagents and Standards

10.1. Reference standard, p-xylene, 99%+, anhydrous. Two separate source standards are required.

Note: Do not store p-xylene in the hood. Store in a flammables cabinet.

11. Calibration and Standardization

11.1. Not applicable to this SOP.

12. Procedure

12.1. Use the thermometer reading, not the LED readout for the temperature of the testing unit.

12.2. Determine the p-xylene flashpoint by adding 2.0 mL (using provided syringe) through the entry port and determining the flashpoint based on the procedure. Repeat. When the unit is properly operating, the average flashpoint will be 81 ±1.5° F.

12.3. If the value lies outside this window, verify all operating conditions and repeat the test. If the average is still outside the acceptance window, contact the area supervisor.

12.4. Do not analyze samples unless an acceptable p-xylene test can be made.

12.5. Determine the second source p-xylene flashpoint by adding 2.0 mL (using provided syringe) through the entry port and determining the flashpoint based on the procedure. Repeat. When the unit is properly operating, the average flashpoint will be 81 ±1.5° F.

12.6. Thoroughly inspect, clean and dry all parts of the tester cup and cover assembly before testing a sample. Be sure to remove all cleaning solvent.

12.7. Check to see that the tester temperature is at or below 68° F. Add 2.0 mL of liquid sample through the injection port with the syringe. For solids, use approximately 2 g of sample.

12.8. For the first determination, switch the tester on and adjust the target temperature to ramp to by depressing the red preset button while turning the black knob. This is helpful for checking the calibration and when the flashpoint temperature is approximately known. Otherwise, set to 210° F. Light the flame.

12.9. Allow the temperature to reach 68° F then check for a flash by applying the flame for a second.

12.9.1. If a flash is observed as evidenced by a large blue flame appearing and propagating itself across the surface of the sample, report the flashpoint as less than 68° F.

Note: Do NOT confuse the bluish halo that sometimes surrounds the test flame with a true flashpoint.

12.9.2. If no flash is observed, allow the temperature to rise 9° F and check again.

12.9.3. Repeat the test flame every 9° F until a flash is observed or until 210° F is reached.

12.9.4. If a flash is not observed at 210° F, report the flashpoint as greater than 200° F.

12.10. Allow the tester to cool, clean the cup then inject a new aliquot of the sample. DO NOT retest the first sample aliquot.

12.11. Bring the tester to the temperature of the last interval before the flash was observed then test for a flash every 1° F until a flash is observed.

12.12. Record this last observation as the observed sample flashpoint.

12.13. When enough sample is available, repeat the 1° F determination with a fresh aliquot. The result of the duplicate analysis must be within 3° F of the initial analysis. If this criterion is not met, qualify the result as estimated.

13. Quality Control

13.1. Run each sample in duplicate using the 1° F frequency test. The duplicate must be within 3° F of the first result. If this criterion is not met, repeat the duplicate once to determine which result to report. If still not within 3° F of the first result or the first duplicate, qualify the result as estimated.

13.2. A p-xylene standard (LCS) from a source other than the accuracy check standard must be analyzed in duplicate with each batch of up to 20 samples. The average value must be 81 ±1.5° F. If this criterion is not met, all samples analyzed in the batch must be re-analyzed or qualified as estimated.

13.3. Notify the area supervisor if the second-source p-xylene standard fails. Perform the LCS analysis at the beginning of the analytical batch.

13.4. All flashpoint thermometers must be calibrated against a NIST-certified thermometer prior to their initial use and thereafter on an annual basis.

14. Data Analysis and Calculations

14.1. Observe and record the ambient barometric pressure at the time of the test in mm of mercury. When the pressure differs from 760 mm, correct the flashpoint as follows:

[F + [0.06 (760 - P)]] = Corrected Flashpoint

Where:

F = observed flashpoint, °F

P = ambient barometric pressure, mm mercury

Note: The corrected flashpoint needs to be reported only if the corrected flashpoint is greater than 1° F from the observed flashpoint.

14.2. Report the first 1° F result if a flashpoint is observed between 68° F and 200° F. Otherwise, report <68° F or >200° F as appropriate.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Record all measurements made.

15.2. All solid sample flashpoints must be qualified as follows:

"SW-846 method 1020 is not designed to be used for solid waste matrices. The reported flashpoint should not be used to determine the hazardous waste characteristic of ignitability"

16. Corrective Actions for Out-of-Control Data

16.1. Corrective actions for out-of-control quality control parameters include what is described in Section 13.0, Section 14.0, and Section 15.0.

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

17.1. If no additional sample volume to perform re-analyses is available, all data will be reported as final with applicable qualifiers. If necessary, an official case narrative will be prepared by the Quality Manager or Project Manager.

18. Method Performance

18.1. Before the analysis of actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC). While IDCs are not instrument dependent, one is required on each instrument used in sample analysis to demonstrate the instrument's ability to generate acceptable accuracy and precision. Annually, a Continuing Demonstration of Capability (CDC) is required.

18.1.1. Initial Demonstration of Capability

18.1.1.1. Analyze four 2.0 mL aliquots of p-xylene. The average value must be 81 ±1.5° F.

18.1.1.2. Input results to the IDC spreadsheet located on the laboratory intranet library.

18.1.1.3. If the acceptance window is not met, locate and correct the source of the problem and repeat the study.

18.1.1.4. Repeated failure will confirm a general problem with the procedure. If this occurs, locate and correct the source of the problem and repeat the study.

18.1.1.5. Samples may not be analyzed by any analyst or on any instrument until the initial demonstration of capability study has been successfully completed.

18.1.1.6. Give a copy of all IDC spreadsheets and raw data to the Quality Assurance department.

18.1.2. Continuing Demonstration of Capability (CDC)

18.1.2.1. A CDC must be performed annually.

19. Method Modifications

19.1. Not applicable to this SOP.

20. Instrument/Equipment Maintenance

20.1. Thoroughly clean and dry all parts of the flashpoint tester cup between samples. Additional cleaning when necessary can be accomplished with solvents such as methylene chloride which are capable of removing oil and stubborn material.

20.2. Visually inspect the flashpoint tester prior to use to insure proper mechanical functionality.

20.3. All maintenance activities must be documented in the maintenance log.

21. Troubleshooting

21.1. For additional information on system maintenance and troubleshooting refer to the instrument manual.

22. Safety

22.1. Wear a laboratory coat and approved safety glasses while in the laboratory. In addition, disposable gloves must be worn whenever samples or reagents are handled.

22.2. Follow all instructions outlined in the Laboratory Safety Manual and Chemical Hygiene Plan.

22.3. For laboratory waste disposal, refer to the applicable laboratory waste disposal procedure.

22.4. The total toxicity and/or carcinogenicity of reagents used in this procedure have not been precisely defined. Treat all chemicals as a potential health hazard. Reduce exposure to the lowest possible level by adherence to established safety policies.

22.5. Safety Data Sheets are maintained on the MSDSOnline website of all chemicals used in this procedure. https://msdsmanagement.msdsonline.com/company/c0ce0b0a-17d3-4f3c-afc6-25352729b299/

22.6. Waste samples can be highly toxic and varied. Treat any exposure as a potential danger and immediately decontaminate the exposure. Clean waste-contaminated personal protective equipment before using again.

22.7. Bring all safety issues to the attention of the Area Supervisor and/or Health and Safety Officer.

23. Waste Management

23.1. Consult the appropriate Safety Data Sheet (MSDS) for questions concerning chemical disposal.

23.2. Follow all instructions for specific laboratory waste disposal requirements.

23.2.1. The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations.

23.2.2. Samples at pH <2, or pH >12, are hazardous and must be handled and disposed of as hazardous waste, or neutralized and disposed of in accordance with all federal, state, and local regulations. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the responsibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance is also required with any sewage discharge permits and regulations.

23.2.3. Many analytes in this procedure decompose above 500 °C. Low-level waste such as absorbent paper, tissues, and plastic gloves may be burned in an appropriate incinerator. Gross quantities of neat or highly concentrated solutions of toxic or hazardous chemicals should be packaged securely and disposed of through commercial or governmental channels that are capable of handling these types of wastes.

23.3. To minimize the environmental impact and costs associated with chemical disposal, order and use only the minimum amount of material required.

24. Pollution Prevention

24.1. Maintain an inventory of all chemicals used in the laboratory to monitor their use.

24.2. Never dispose of laboratory chemicals without first referencing appropriate written instructions of disposal for that particular material. Conserve the use of chemicals where applicable.

24.3. Comply with all environmental laws associated with chemicals in the laboratory.

25. References

25.1. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, 3rd Edition, Final Update IIIB, Revision 2, November, 2004, Method 1020B, "Setaflash Closed-Cup Method for Determining Ignitability"

25.2. American Society for Testing Materials (ASTM) Standard, ASTM D 3278-78, "Flashpoint of Liquids by Setaflash Closed Tester", December, 21, 1978

25.3. SOP GR-15-102, *Laboratory Waste Disposal*, latest revision

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: Batch Worklist Report Example

26.2. Attachment II: Electronic Prep Log Workbench Example

27. Revisions

Document Number	Reason for Change	Date
SOT-ALL-Q-001-rev.11	Sections 1, 7, 9, 11, and 26: changed name of sections. Created new sections 4, 5, 14, 15, 16, 17, 19, 20, and 21 to comply with TNI 2009 Standard and DoD 2010 QSM. Added section 3.2 to emphasize operations role in reviewing and revising method SOPs. Section 12.2.2: removed list of sections and added reference to section 12.2.3 Section 12.2.3: reorganized and revised to account for new sections and reorganization of SOP. General: added SQM and SGM as applicable due to management structure changes. Sections 23 and 24: separated from one combined section.	18May2012
SOT-ALL-Q-001-rev.12	Sections 12.2.3.9, 12.2.3.12, 12.2.3.26: revised language for clarity and to match actual practice.	01Sep2014
SOT-ALL-Q-001-rev.13	Cover page: revised the footer language and removed the uncontrolled document numbering line. General: made administrative edits that do not affect the policies or procedures within the document. Section 8.9: revised definition of uncontrolled document. Sections 12.1.1, 12.2.1, and 12.7.1: removed requirement for Director of Quality to sign Corporate SOPs. Sections 12.2.3.13 and 12.2.3.27: reworded for clarity. Section 12.2.3.19: added general guidelines for method modifications. Section 12.2.5: added paragraph regarding Corporate administrative SOPs. Section 12.4.2: added section on SOP-Method-Practice review process. Section 12.4.3: changed language to intent of TNI requirement for signatories. Section 18: added standard language. Sections 25.3, 25.4: revised and made into red text.	10Feb2017
SOT-ALL-Q-001-rev.13	Used this as a template for revising S-GR-I-18124-rev2.0	11Apr2018

Attachment I: Batch Worklist Report Example

Batch Worklist

PASI Grand Rapids Laboratory

Pace Analytical

Queue WET Wet Chemistry | **QC Rule** 1020 W: 1020 Flash Point, Closed Cup | **Min Due** 3/29/2018 08:06:00 AM
Batch 4611 | **HBN** 18849 | **Created** 3/27/2018 03:59:12 PM | **Min Hold** 4/10/2018 11:59:00 PM
Status RE | **Analyst** Evan Boggs | **Other**

Pos	Lab ID	Type	CC	Location	Container ID	Storage	Due Date	Hold Date	Analytical Due Date	Collected	Sample ID	Original Sample
1	75002	BLANK	OK				03/28/2018	04/24/2018 23:59			BLANK for HBN 18849 [WET/4611] In-house QC Account	
	*Reportable Compounds: flpt											
2	75005	DUP	OK				03/28/2018	04/13/2018 23:59		03/15/2018	Milky Liquid Waste(72290DUP) In-house QC Account	469631002
	*Reportable Compounds: flpt											
3	75003	LCS	OK				03/28/2018	04/24/2018 23:59			LCS for HBN 18849 [WET/4611] In-house QC Account	
	*Reportable Compounds: flpt											
4	75004	LCS	OK				03/28/2018	04/24/2018 23:59			LCS for HBN 18849 [WET/4611] In-house QC Account	
	*Reportable Compounds: flpt											
5	469391001	PS	OK	MI	469391001 AG3U1/1	C1-DD4	03/29/2018	04/10/2018 23:59		03/13/2018	UIC Pfizer 469391	
	*Reportable Compounds: flpt						JFlag Cmps? N	Matrix: Water				
6	469598001	PS	OK	MI	469598001 BP1U1/2	RECEIVING	03/29/2018	04/13/2018 23:59		03/16/2018	Non-Haz Liquid Advanced Resource Recovery 469598	
	*Reportable Compounds: flpt						JFlag Cmps? N	Matrix: Solid				
7	469631001	PS	OK	MI	469631001 WPDU1/1	C1-B5	03/29/2018	04/13/2018 23:59		03/16/2018	Garage Oil Clean Harbors (Ford) 469631	
	*Reportable Compounds: flpt						JFlag Cmps? N	Matrix: Non Aqueous Liquid				

Attachment II: Electronic Prep Log Workbench Example

Prep Log Report

Batch Information: WET_18849_FLASH

Template Version: F-GR-I-056-Rev.00 (15Jun2017)

Analysis Method	EPA 1020B	Instrument	46WET6	Analyzed By	EB1	Thermometer ID	281
Correction Factor (F)	0	Barometric Pressure (mm Hg)	739	Corrected Barometric Pressure Factor (F)	1.2668	Acceptance Range:	LCS 79.5-82.5 F, Dup +/- 2 Deg F
Reviewed By	IDT	Reviewed By Date	03/30/2018 12:25	Batch Notes			

Sample Information:

QC Rule	Sample Type	Lab Sample ID	Select	Run Date/Time	Matrix	Initial Temp. (F)	Observed Flashpoint (F)	Confirmation Flashpoint (F)	Difference (F)	Flashpoint (F)	Sample Notes	1020-SPK (mL)
1020 W	BLANK	75002	Y	03/27/2018 15:15:00	Water	68	>200	>200		>200		
1020 W	LCS	75003	Y	03/27/2018 15:44:00	Water	68	80	80	0.00	81.27		3305 (1)
1020 W	LCS	75004	Y	03/27/2018 15:55:00	Water	68	80	80	0.00	81.27		3305 (1)
1020 W	PS	469631001	Y	03/27/2018 16:10:00	Non Aqueous Liquid	68	>200	>200		>200		
1020 W	DUP	75005	Y	03/27/2018 16:51:00	Non Aqueous Liquid	68	>200	>200		>200		
1020 W	PS	469631002	Y	03/27/2018 17:22:00	Non Aqueous Liquid	68	>200	>200		>200		
1020 W	PS	469391001	Y	03/27/2018 17:58:00	Water	68	>200	>200		>200		
1020 W	PS	469598001	Y	03/27/2018 18:37:00	Solid	68	>200	>200		>200		

Standard Notes:

3305: WET 1020-SPK 2mL of standard

Pace Analytical Services, LLC
1700 Elm Street SE, Suite 200
Minneapolis, MN 55414

Phone: 612-607-1700
Fax: 612-607-6444

STANDARD OPERATING PROCEDURE

PREPARATION AND ANALYSIS OF SAMPLES FOR THE DETERMINATION OF DIOXINS AND FURANS

Reference Methods: USEPA Method 8290/8290A/1613B/DLM2.0

Local SOP Number:	S-MN-H-001-Rev.29
Effective Date:	Date of Final Signature
Supersedes:	S-MN-H-001-Rev.28

APPROVALS

Laboratory General Manager — Date: 19 JUN 2018

Laboratory Quality Manager — Date: 15 Jun 2018

PERIODIC REVIEW

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

Signature	Title	Date

This is **COPY#** 15 Distributed on **01Oct2018** by LAB1 and is ____ **CONTROLLED**

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SECTION **PAGE**

1. Purpose/Identification of Method

1.1. The purpose of this standard operating procedure is to describe the preparation, analysis, processing, and reporting of samples for the determination of dioxins and furans using USEPA Method 8290, 8290A, 1613B and DLM2.0.

2. Summary of Method

2.1. For every project, all field samples and QC samples (LCS, LCSD, MB, MS, MSD- here-to-fore referred to collectively as "QC") must be spiked and treated exactly the same. Stable isotopically labeled analogs of 15 of the polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are added to each sample. Samples containing coarse solids are prepared for extraction by grinding or homogenization. Water samples are extracted in separatory funnels or by solid phase extraction. Soils and other finely divided solids are extracted using Soxhlet or microwave assisted extraction apparatus. Note that, in this document, CDD and CDF mean chlorinated dibenzo-p-dioxin and chlorinated dibenzofuran. The prefixes to those acronyms are P for poly, T for tetra, Pe for penta, Hx for hexa, Hp for hepta and O for octa.

2.2. After extraction, $^{37}Cl_4$-labeled 2,3,7,8-TCDD is added to each extract to measure the efficiency of the cleanup process. Sample cleanup may include back extraction with acid and/or base, alumina, silica gel, and activated carbon chromatography.

2.3. Samples are spiked with two labeled recovery standards that are used to determine the portion of the analytes and internal standards that survived the extraction and enrichment processes. The extracts are then analyzed using high resolution gas chromatography/high resolution mass spectrometry to determine the concentration of PCDDs and PCDFs present in the samples.

2.4. The accuracy of the method can be affected by matrix interferences, especially for non-isotope dilution analytes.

2.5. Pace Analytical will comment all deviations from the SOP in the final narrative to be included with each project. Generally, deviations that are not specifically addressed in the SOP will trigger a re-extraction. Exceptions will generally only be allowed after discussion with the client, however for OHIO VAP, the SOP must be followed. PLEASE NOTE: For Ohio VAP, only 1613B, and 8290A are used.

3. Scope and Application

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method or non-analytical process.

3.2. **Parameter**s: This SOP applies to the dioxin and furan compounds listed in Attachment IV

3.3. For Ohio VAP, if requirements specified in this SOP are not able to be met, Pace Analytical will narrate any potential bias or justification for reporting in the project narrative on the final report. Additional narratives are provided as needed on a case by case basis in the event of the following occurrences: instrument failure, limited sample volume, report revisions or matrix interferences.

3.4. All references contained in this SOP with regards to spiking volumes, standard concentrations and instrument configuration are based on recommended parameters and may be subject to change based on instrument technology and application.

4. Applicable Matrices

4.1. This SOP is applicable to water, sludge, soil, fly ash, tissue, food/food oil and waste materials. This method can be applied to most other matrices as well.

Note: Per Ohio VAP OAC Rule 3745-300-01 (A) this method applies to "environmental media", including soil, sediment, surface water, and ground water. Environmental media also include naturally occurring transitional zones between soil, sediment, surface water or ground water, such as bedrock, soil gas, and air.

5. Limits of Detection and Quantitation

5.1. The reporting limits (LOQ) for all analytes for this method correspond to the concentration of the CS-1 (0.5-5 pg/uL) and are calculated based on the amount of sample used for the determination. All current MDLs are listed in the LIMS and are available by request from the Quality Manager.

6. Interferences

6.1. Most samples analyzed for PCDD/PCDF content contain other organic compounds that interfere with or contaminate the mass spectrometric instrumental system. Therefore, after initial extraction, extracts are taken through the cleanup steps outlined in the "Extract Enrichment/Clean Up" section of this procedure. Exceptions to performing the optional clean up steps of acid/base and carbon column cleanup steps may be made with consultation of the laboratory manager and are usually limited to water matrices. The acid clean-up procedure is used to remove lipids in tissue samples and must not be omitted for this matrix.

6.2. Matrix interferences may be caused by contaminants (particularly chlorinated biphenyl ethers) co-extracted from the sample and vary considerably from source to source. These biphenyl ethers rearrange in the mass spectrometer source to form dibenzofurans.

6.3. Some samples may contain levels of interfering compounds that overload the analyte clean up columns. Consult the laboratory manager for alternate procedures should this occur.

6.4. Rigorous glassware cleaning techniques must be used and method blank data must be monitored to evaluate the effectiveness of the glassware cleaning techniques.

6.5. HPLC grade solvents must be used for extractions. Solvents having new lot numbers must be screened for contamination prior to use by analyzing a solvent blank by the applicable analytical methods.

6.6. Raw data from all blanks, samples, and spikes are evaluated for interferences. Determine if the source of interferences is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

6.7. If chromatographic interferences are present (specifically, matrix components that interfere with the determination of PCDDs or PCDFs), the area from the least affected signal of the pair is used along with the theoretical ratio to determine the area of the second ion. These values are then used to calculate the estimated maximum concentration that is then reported as the estimated maximum possible concentration (EMPC).

6.8. Some interference may be reduced by analysis of a dilution of the extract.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Table 7.1 – Sample Collection, Preservation, Shipment and Storage

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Glass container (see section 7.2). One liter of water samples containing less than or equal to 1% solids should be extracted. Reduced/elevated volumes are used when high level samples are anticipated or to match project requirements. Aqueous or solid samples containing greater than 1% solids must be considered as solids.	If residual chlorine is present, 80 mg of sodium thiosulfate is typically added to the sample at the time of collection to neutralize the chlorine.	Maintain samples at <6ºC under darkness from the time of collection until extraction.	See section 7.4.
Solid	Glass container (see section 7.2). Sufficient volume is typically extracted to provide a dry weight of 10 grams (except for tissue samples and other samples noted to be reported on an as received basis).	n/a	Maintain samples above freezing but <6ºC under darkness from the time of collection until extraction. Ohio VAP	See section 7.4.

			samples must be stored Frozen at less than -10°C under darkness as tissues, per method 1613B. Pace has determined that there is no impact on samples stored at temperatures up to <6°C and for practical reasons applies this to solid samples other than Ohio VAP.	
Tissue	Glass container (see section 7.2).	n/a	Stored frozen at ≤-10°C under darkness.	See section 7.4.
Oil	Glass container (see section 7.2). One hundred milligram aliquots are typically used for waste oil-based samples. Twenty-gram aliquots are typically used for food oil samples.	n/a	Maintain samples at <6°C under darkness from the time of collection until extraction.	See section 7.4.

7.2. Sample bottles - 1 Liter glass amber bottles for liquids that contain less than 1% solids; 500 milliliter (mL) wide mouth (or smaller) glass amber bottles for solid and sludge. All bottles are purchased pre-cleaned from the vendor. If glass amber bottles are not available, samples must be protected from the light. All bottles should have Teflon lined caps. Laboratory cleaned bottles may be substituted for pre-cleaned bottles. Lab cleaned bottles should be detergent washed, then solvent rinsed and baked at 500°C for the minimum of three hours.

7.3. One gram or smaller aliquots are typically extracted for waste samples and samples suspected to contain high analyte levels. Sample amounts extracted for food samples containing fat are typically based on the lipid content of the sample. Non-fat foods and all feeds are based on the raw sample weight.

7.4. For method 8290 and 8290A, samples are typically extracted within 30 days of sample collection and the extract analyzed within 45 days of extraction. For DLM, shorter hold times apply, see Attachment VIII. For Method 1613B, samples are typically extracted within one year of sample collection and the extract analyzed within 40 days of extraction. Some states have implemented shorter extraction hold times. Exceeding hold times between collection and extraction or extraction and analysis do not necessarily invalidate the results. Whenever samples are analyzed after the holding time expiration date, the results must be considered to be minimum concentrations and identified as such. For Ohio VAP, this may only be done when the lapse of holding time is outside of the lab's control, and it must be narrated for potential bias.

7.5. All sample extracts are stored in the extract freezer at < or equal to -10 °C in darkness until analysis. Extracts are warmed to room temperature and vortexed before analysis.

7.6. Criteria for Acceptance/Rejection of Samples

7.6.1. Samples are to be rejected if information allowing determination of the applicable test and client information cannot be obtained.

7.6.2. If sample integrity has been compromised, the client must be contacted for instructions and permission to proceed with analysis. The client's comments and instructions are documented as part of routine laboratory policy.

8. Definitions

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

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

9.1. Table 9.1 – Equipment and Supplies

Description	Supply	Fisher, or Equivalent (for reagents)
Solvent	Acetone - Optima (4bottle/cs)	A929-4
Solvent	Methanol - Optima (4bottle/cs)	A454-4
Solvent	N-Nonane, 99% 100mL	AC129111000
Solvent	N-Tridecane, 99+% 100mL	AC139511000
Acid	Sulfuric Acid 2.5L (6bottle/cs)	A300S-212
Solvent	Hexane, Ded. Lots (4bottle/cs)	H306-4
Solvent	Me.Chloride, Ded. Lots (4bottle/cs)	D151-4
Solvent	Toluene, Ded. Lots (4bottle/cs)	T291-4
Acid	GW: Nitric Acid (6bottle/cs)	A509P212
Solvent	Ethyl Ether Annhydrous 1L	EI38-1
Solvent	HPLC Grade Cylcohexane	C620-1
Solvent	HPLC Grade Iso-Octane	
Sodium Thiosulfate	Used to treat residual chlorine	Fisher Scientific or equivalent replacement
Dispenser	25-100ml dispenser for SF	13-688-75
Containers	12 dram Vials (3 pk/cs)	03-339-26H
Containers	250 mL Disp. Glass Jars (24jar/cs)	NC9199987
Containers	40mL Clear Vial w/cap (80vial/cs)	NC9879693
Containers	500mL Glass Jar (12jar/cs)	NC9941118
Containers	8oz. Clear Centrifuge Jar (96JARS/CS))	NC0475499
Containers	Bottle 1L amber (12bottle/cs)	05-719-91
Containers	DW: 60mL Clear Vial (72vial/cs)	05-719-398
Containers	GW: Versa-Clean (12bottle/cs)	04-342
Containers	12ml Standard Vials	03-340-60c
Containers	200ml Kimble Chase Kimble Vol Flask	10-212C
Funnels	Case of 300ml Buchner Funnels	10-358-22L
Containers	2.5L amber, precleaned for DRBC.	Various Vendors.
Funnels	250 ml Funnel for SPE (47mm)	13-645-089
Funnels	1000 ml Funnel for SPE (47mm)	13-645-090
Beakers	Polypropylene Disp. 250ml beakers (lipids)	01-291-5
Syringes	50ml Syringe DISP. For Silica and Alumina	1481736
Syringes	25ml Syringe DISP for DW Silica	148268
Containers	Vials with insert for 8280	03-376-407
Containers	Amber jars for Silica Media	NC9941126
Containers	2L C and G containers- for TIP WASTE	NC9204036
Centrifuge tubes	50ml centrifuge tubes	06-0443-18
Cleaning	GW: Acetone - Hist. 20L saftin	A16S-20
	hawkins Sodium Bicarbonate	14422
	Chromerge	C577-12
	Bin for glassware cleaning, select color	60086
	Lid for Bins	60962
Extraction	Whatman Thimbles - L 43X123mm 25/pk	09-656H
	Sand - QC Standard Ottawa 2.5KG	SX0075-3
	PTFE Boiling Stones - 450g	09-191-20
	Round Botton standalone 500mls	07-250-079
	Tongue Depressors 6in by 3/4in	11-700-556
	Soxhlet extraction apparatus	Fisher Scientific or equivalent
	Microwave Extraction System	CEM MARS 5
	Heating Mantles for Soxhlet apparatus	Fisher Scientific or equivalent

	Dean Stark Apparatus	K585151-0035
	1000ml Separatory Funnel with Teflon stop cocks	Fisher Scientific or equivalent
Cleanup	Glass Wool, silane treated, Supelco	2-0411
	Celite, Supelco	20199-U
	Glass Tubing 12mm X 4ft	11-362G
	Glass Tubing 20mm X 4ft	11-362N
	Glass Tubing 15mm X 4ft	11-362J
	Alumina (50-200 mesh) ICN	NC9983739
	Silica Gel (100-200mesh) 2.5kg	S679-212
	Glass Wool - Regular 1lb	11-388
	3 chamber snyder column	NC9207667
	Sodium Sulfate Annhydrous	S415-200LB
	Florisil, 60-100 mesh/Reagent Gr.	220752-1KG
Pippetters	10uL Tips(10pk/cs)	13-707-64
	Monstr-Pipette (8pk/cs)	22-378893
	Pipet - Disp. 5 3/4" (4box/cs)	13-678-20B
	Pipet - Disp. 9" (4box/cs)	13-678-20D
	Tips 0-200 uL	02-681-135
	50-1000 tipsuL	222491954
	Bulbs for Small Pipettes (2.25inch)	03-448-22
	Bulbs for Small Pipettes (1.5inch)	03-448-21
Needles	N Evap needles	NC9433071
Filters	DW: Glass Fiber Filter (100/pk)	09-873DD
Funnels	Funnel - 60mm Disposable (100/cs)	05-555-6
	Large POWDER FUNNEL 110-150 4/PK	10-500-3
	Funnels - Disp. Powder for H2Os (36/cs)	10-500-1
Balance	0.01g and 0.0001g	Fisher Scientific or equivalent
Drying oven	Up to 400 degrees C	Fisher Scientific or equivalent
Centrifuge	For samples in extraction lab	Fisher Scientific or equivalent
Avalon	Data Processing System for HRMS	
Capillary Column	DB 225 30m 0.25mm ID 0.25u	J&W
Capillary Column	DB 5 60m 0.25mm ID 0.25u	J&W
HRMS	High Resolution Mass Spec equipped with a GC HP Agilent 6890 or equivalent	Auto Spec or equivalent
Avalon	Data processing and reporting software	Avalon, see master software list for current version

10. Reagents and Standards

10.1. Table 10.1 – Reagents and Standards

Reagent/Standard	Concentration/Description	Requirements/Vendor/Item #
Acidic Silica gel	30% w/w, thoroughly mix 44.0g of concentrated sulfuric acid with 100.0 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw-cap.	Fisher Scientific or equivalent
Basic Silica gel	Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw cap.	Fisher Scientific or equivalent
Canola oil	Canola oil, or equivalent, for Oil quality control sample matrix,	Local grocery store
Primary Ical Stock Standards	Wellington #EPA-1613CS1 thru EPA-1613CS5 (or equivalent) The CS3 is CS3WT, and also includes the CPM and window defining isomers.	#EPA-1613CS1 thru EPA-1613CS5; CS3WT
ICV Stock Standard	Stock solution used as a Second Source- 400-4000ng/L, in Nonane	Cambridge(Cerriliant) EDF-7999-10X

Internal Standard Stock Standard	Labeled standards use for quantitation of Natives- stock is at 100ng/mL in Nonane	1613/8290 Internal is cat# EDF-8999 (or equivalent) from Cambridge
Native Stock Standard	Native used in LCS and Spikes- Stock is at 40-400ng/mL in Nonane	cat# EPA-1613STOCK from Wellington
Recovery Stock Standard	Labeled Standards used to quantify recovery of "internal standards" in Nonane, 2000ng/mL	cat# 1613-ISS from Wellington
Cleanup Standard	Labeled standard used for quantitation of cleanup efficiency- stock is at 50ng/mL in Nonane	1613 Cleanup is cat# MCDD-2378 from Wellington

10.2. Table 10.2 - Working Standard Dilutions and Concentrations

Standard	Standard(s) Amount	Solvent	Solvent Volume	Final Total Volume	Final Concentration
Sodium hydroxide (NaOH)	40 g	Reagent water	~1 L	1 L	1N
Potassium Phosphate, monobasic (KH_2PO_4)	68.05 g	Reagent water	~1 L	1 L	0.5 M

10.3. Standards and working solutions are prepared from or compared to certified standards or purchased as certified premixed standards. All standards are valid for 1 year from date opened (or prepared). All standards are stored per manufacturer instructions until opened. Opened standards are stored in glass bottles at <6ºC. The standards must be stored at any refrigerator or freezer temperature (not to exceed 6ºC) sufficient to maintain standard/solvent volume for nonane, Acetone, or tridecane. Standards may be re-verified by comparison to a valid native analyte solution. The final concentrations determined for any solution being re-verified must be within 20% of the expected concentrations for that solution.

10.4. The preparation of standards and working solutions is thoroughly documented in the appropriate standards notebook. Such documentation allows the traceability of each solution to a certified, purchased solution.

10.5. Preparation of Primary Stock Solution of Internal Standards

NOTE: Identification # denotes the next sequential number assigned to the vial upon receipt in the Dioxin Stock Standard Tracking Logbook.

Compound	Conc (mircrogram/milliliter (µg/mL))
2,3,7,8-TCDD-$^{13}C_{12}$	1.0
2,3,7,8-TCDF-$^{13}C_{12}$	1.0
1,2,3,7,8-PeCDD-$^{13}C_{12}$	1.0
1,2,3,7,8-PeCDF-$^{13}C_{12}$	1.0
2,3,4,7,8-PeCDF-$^{13}C_{12}$	1.0
1,2,3,4,7,8-HxCDD-$^{13}C_{12}$	1.0
1,2,3,6,7,8-HxCDD-$^{13}C_{12}$	1.0
1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	1.0
1,2,3,6,7,8-HxCDF-$^{13}C_{12}$	1.0
1,2,3,7,8,9-HxCDF-$^{13}C_{12}$	1.0
2,3,4,6,7,8-HxCDF-$^{13}C_{12}$	1.0
1,2,3,4,6,7,8-HpCDD-$^{13}C_{12}$	1.0
1,2,3,4,6,7,8-HpCDF-$^{13}C_{12}$	1.0
1,2,3,4,7,8,9-HpCDF-$^{13}C_{12}$	1.0
OCDD-$^{13}C_{12}$	2.0

10.5.1. Using an Eppendorf pipette, add 1000 µL of primary stock into a pre-rinsed 50 mL volumetric flask and bring to volume with Acetone to prepare the 2000 ng/mL (40ng/mL OCDD-13C12)

solution. Alternately, combine the purchased Wellington stock solutions (1 mL each) and bring to 10 mL with Acetone to prepare the 100 ng/mL (200 ng/mL OCDD-13C12) solution.

10.5.2. Vortex the vial for at least 1 minute after bringing to room temperature.

10.5.3. After sonication, transfer the solution noted above into a pre-rinsed vial and label. Identification must include: ID# and log #, $^{13}C_{12}$ primary stock solution of internal standard, preparation date, expiration date and preparer's initials.

10.5.4. Seal vial with Teflon tape and store in standards freezer at-18°C ± 2°C.

10.5.5. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.6. Preparation of Internal Standard Spiking Solution

10.6.1. Allow the stock standard to reach room temperature before using. Vortex for ~10 seconds before taking an aliquot.

10.6.2. Prior to extraction, 100 µL of this solution is added to each sample, MB, LCS, LCSD and all other reportable QC in the batch.

10.7. Preparation of Primary Native Standard Spiking Solution

Compound	Concentration (µg/mL)
2,3,7,8-TCDF	0.40
2,3,7,8-TCDD	0.40
1,2,3,7,8-PeCDD	2.0
1,2,3,7,8-PeCDF	2.0
2,3,4,7,8-PeCDF	2.0
1,2,3,4,7,8-HxCDD	2.0
1,2,3,6,7,8-HxCDD	2.0
1,2,3,7,8,9-HxCDD	2.0
1,2,3,4,7,8-HxCDF	2.0
1,2,3,6,7,8-HxCDF	2.0
1,2,3,7,8,9-HxCDF	2.0
2,3,4,6,7,8-HxCDF	2.0
1,2,3,4,6,7,8-HpCDD	2.0
1,2,3,4,6,7,8-HpCDF	2.0
1,2,3,4,7,8,9-HpCDF	2.0
OCDF	4.0
OCDD	4.0

10.7.1. This is a purchased solution in nonane (Wellington, or equivalent).

NOTE: One vendor source and standards prepared from the source are used for the ICAL. The other vendor source and standards diluted from it are used as an independent validation of all standards purchased and therefore may stand as an ICV if one is required.

10.7.2. The native stock standard comes in a vial with approximately 1.2 mL present. After an ampule is cracked open, put the remaining volume in a crimp top amber vial.

10.7.3. NOTE: Identification - # denotes the next sequential number assigned to the standard from the HRMS Standard Preparation Logbook.

10.7.4. Store in standards refrigerator at <6°C.

10.7.5. Record all standard preparation information in Dioxin Stock Standard Preparation Logbook.

10.8. Preparation of Native Spiking Solution

10.8.1. Allow it to reach room temperature before using. Vortex for ~10 seconds before taking an aliquot.

10.8.2. Add 0.250 mL of native stock standard to a pre-rinsed 20 mL volumetric flask and bring to volume with Acetone to prepare this 5-5-50 ng/mL solution..

10.8.3. Vortex for ~30 seconds to ensure homogenization and transfer into 2 dram vials. Identification must include: Native Spiking Solution ID# ,log #, preparation date, expiration date and preparer's initials.

10.8.4. Note: Identification FS-N-# full scan native - # denotes the next sequential number assigned to the standard from the HRMS Standard Preparation Logbook.

10.8.5. Store in the standards refrigerator at <6°C until ready to use.

10.8.6. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.8.7. Prior to extraction, add 40uL to "spiked" QC samples (LCS, LCSD, MS, MSD).

10.9. Preparation of Cleanup Standard Primary Stock

Compound	If Conc. is µg/mL	Amt. Added (µL)	Final Conc. (µg/mL)
$^{37}Cl_4$ 2,3,7,8-TCDD	50	200	1.0

10.9.1. The 50 µg/mL solution is purchased in nonane (Cambridge or equivalent). Vortex the vial, allow the solution to reach room temperature and add 200 µL of the solution to a pre-rinsed 10 mL volumetric flask. Bring to volume with Acetone to prepare this 1 µg/mL solution.

10.9.2. Transfer the Cleanup stock standard to a 2 dram vial with color coded tape. Identification must include: $^{37}Cl_4$ Cleanup Standard: Primary Stock ID# log #, preparation date, expiration date and preparer's initials.

10.9.3. NOTE: Identification - # denotes the next sequential number assigned to the standard from the HRMS Standard Preparation Logbook.

10.9.4. Seal vials with Teflon tape and store in the standards refrigerator at <6°C.

10.9.5. Record all standards preparation information in HRMS Standard Preparation Logbook.

10.10. Preparation of $^{37}Cl_4$ Cleanup Standard Secondary Stock

10.10.1. Vortex the standard and allow it to reach room temperature.

10.10.2. Using an Eppendorf pipette, add 1 mL of cleanup stock standard into a pre-rinsed 25 mL volumetric flask. Bring to volume with Acetone to prepare this 40 ng/mL solution.

10.10.3. Vortex for ~ 30 seconds, transfer to 2 dram vials. Identification must include: ID# (BCl4-#), log #, vial numbers, preparation date, expiration date and preparer's initials.

10.10.4. NOTE: Identification - # denotes the next sequential number assigned to BCl4 standard from the HRMS Standard Preparation Logbook.

10.10.5. Store in standards refrigerator at <6°C.

10.10.6. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.11. Preparation of $^{37}Cl_4$ Cleanup Standard Spiking Solution

10.11.1. Vortex and allow it to reach room temperature.

10.11.2. Using an Eppendorf pipette, add 2 mL of $^{37}Cl_4$ Cleanup stock standard into a pre-rinsed 100 mL volumetric flask and bring to volume with toluene to prepare this 800 pg/mL.

10.11.3. Sonicate or Vortex for five minutes and transfer to pre-rinsed 6 dram vials. Identification must include ID# , log #, vial number, preparation date, expiration date and preparer's initials.

10.11.4. NOTE: Identification - # denotes the next sequential number assigned to thestandard from the HRMS Standard Preparation Logbook.

10.11.5. Vortex and store in standards refrigerator at <6°C.

10.11.6. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.11.7. 250 µL of this solution is added to each sample between extraction and enrichment.

10.12. Preparation of $^{13}C_{12}$ Recovery Standard Primary Stock

Compound	Conc. (µg/mL)
1,2,3,4-TCDD-$^{13}C_{12}$	2.0
1,2,3,7,8,9-HxCDD-$^{13}C_{12}$	2.0

10.12.1. This solution is purchased at a concentration of 2.0 µg/mL from CIL or Wellington.

10.13. Preparation of $^{13}C_{12}$ Recovery Standard Spiking Solution

10.13.1. Sonicate or Vortex the $^{13}C_{12}$ Primary Recovery Standard for five minutes and allow it to reach room temperature before using.

10.13.2. Using an Eppendorf pipette, add 1 mL of $^{13}C_{12}$ Recovery stock standard into a pre-rinsed 10 mL volumetric flask. Bring to volume with Acetone to prepare this 200 ng/mL solution.

10.13.3. Vortex, transfer to 2-dram vials labeled with tape. Identification must include: ID# , log #, vial numbers, preparation date, expiration date and preparer's initials.

10.13.4. Note: Identification - # denotes the next sequential number assigned to the standard from the HRMS Standard Preparation Logbook.

10.13.5. Store in standards refrigerator at <6°C.

10.13.6. Record all standard preparation information in HRMS Standard Preparation Logbook.

10.13.7. 10 µL of this solution is added to each sample during the final concentration of the extract.

10.13.8. This solution may otherwise be purchased as a prepared mix from Wellington Laboratories or equivalent.

10.14. Initial Calibration Solutions

10.14.1. These solutions are purchased from CIL or Wellington.

PCDD/PCDF	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,7,8,9-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100

$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

10.14.2. The CS-3 is also available with the window defining and column resolution isomers in the same solution (See Quality Control Section).

10.14.3. Perfluorokersosene is used as the tuning and lock mass generating solution during the course of the analysis.

11. Calibration and Standardization

11.1. Table 11.1 – Calibration and Standardization

Calibration Metric	Parameter/Frequency	Criteria	Comments
Initial Calibration (ICAL)	Following proper tuning and documentation (see section 14,) prior to analyzing samples, the instrument is calibrated by analyzing a series of five standard solutions, one of which is at or below the reporting limit. The ICAL is performed when the continuing calibration solution is replaced by one from a different lot or when the continuing calibration does not pass the method specified criteria with minor maintenance or tuning. Initial calibrations must also be performed with any significant changes to the analytical system, including major maintenances or column changes. Initial calibrations are generated using standard solutions containing target native and labeled	A signal to noise ratio of >10:1 is required for each isomer. Ratios must be within 15% of theoretical values. Any outliners are flagged in Avalon. Initial calibration relative standard deviations must be less than 20% for the native and labeled isomers. (35% for labeled analytes in 1613B and DLM2.0) RSE - Percent error between the calculated and expected amounts of an analyte should be ≤ 30% for all standards. For some data uses, ≤ 50% may be acceptable for the lowest calibration point.	Additional standards are analyzed to demonstrate chromatographic resolution and stability of the ICAL. These consist of the continuing calibration solution described above, and a purchased solution (Wellington 5TDWD or equivalent) containing the isomers required to demonstrate the chromatographic resolution of the 2,3,7,8-TCDD (25% valley) and the presence of the first and last eluting isomers of each congener class. A solution (Wellington EPA-1613-CS3WT) is available and incorporates all of the above components into a single solution. Determination of calibration function acceptability is done in addition to, the response factor evaluation for determining a successful ICAL. If these criteria fail, the instrument should be evaluated and corrected for problems in the system. The ICAL should be re-analyzed. Ohio VAP samples must be re-analyzed if curve is found to be outside of control limits after the

	PCDD/PCDF compounds. Response factors are calculated and averaged for each compound. These averages are used for quantification and for comparison to the daily continuing calibration. In addition, for Ohio VAP, the RSE or Relative Error must be calculated for each calibration level, per PACE Calibrations SOP S-MN-L-148 (or equivalent replacement). **No points may be dropped from this 5 point curve**.		samples were shot. Before this re-analysis, a valid curve must be produced.
Initial Calibration Verification (ICV)	The initial calibration must be verified by analyzing a standard that is from a secondary vendor than the ICAL standards.	±10% of Continuing calibration range.	Sample analysis must not proceed without successful second source verification. Should this verification fail, the fault must be determined and either the curve, the verification, or both must be reanalyzed.
Continuing Calibration Verification (CCV)	At the beginning and end of each 12-hour shift on days when initial calibrations are not performed. The ending CCAL is not required for Method 1613B.	For 8290/8290A - must yield response factors within ±20% (natives) to 30% (labeled) of the initial calibration. An additional 5% is allowed for the ending CCAL, with appropriate flags. See For DLM2.0, the ranges for both the beginning and ending calibrations are within ±20% (natives) to 35% (labeled) of the initial calibration. For Method 1613B, the statistical ranges are described in Attachment V.	Calibration must be verified prior to sample analysis. If the criteria are not met, the samples may be evaluated to determine the impact to the data results and preliminary results may be issued. If the samples appear to be the cause of an ending calibration verification failure, the results may be reported with appropriate flags. For Ohio VAP, samples must be bracketed by CCV meeting criteria or corrective actions must be performed with repeat analysis of samples so that CCV (continuing calibration verification) criteria pass. When the CCV Fails with a High bias, the data may be reported if the samples associated are showing non-detect for the affected analytes.
Internal Standard	Internal standards are spiked into each extract (sample, and QC) prior to extraction in order to monitor the level of recovery that is achieved for each individual sample.	For methods 8290/8290A - acceptable recoveries range from 40 to 135% for the internal standards unless a deviation is due to variation in instrument response as a result of analytical interferences. The acceptance ranges for Method 1613B and DLM2.0 are described in Attachment V.	If used, results outside the target range must be flagged. The analysis may be repeated based on project requirements. See section For Ohio VAP, the corrective actions listed in 11.1.4.1 apply.

11.1.1. Percent valley between 2,3,7,8-TCDD and any other peak in the column performance check must be <25%, relative to the height of 2,3,7,8-TCDD prior to the analysis of sample extracts. For DLM2.0 an acceptable column performance mix is also required at the end of each analytical sequence.

11.1.2. All peaks for a given PCDD/PCDF level of chlorination must elute within the window(s) set up for that particular class (determined from the window defining mix that contains first and last eluting isomers).

11.1.3. Native compounds must elute within ±2 seconds of the expected elution time relative to the elution times of the corresponding internal standards.

11.1.4. Internal Standards

11.1.4.1. Since the method is based on isotope dilution, the accuracy of native congener determinations is generally not affected when an internal standard recovery falls outside the target range. In general, samples will be considered acceptable with up to three internal standards outside of the target range provided the signal to noise ratio of those standards is greater than or equal to 10:1. If more than 3 recoveries exceed established limits, the data may still be acceptable, but the analyst must use his/her discretion as to how to proceed. Any accepted exceedance must be narrated. If the failures are readily attributable to the analysis (not the extraction), the extract is re-analyzed.

Note: For Ohio VAP, samples with failing internal standards must be re-analyzed to confirm failures. Re-extraction may be necessary if failures are repeated. Failures in the laboratory QC will result in re-extraction of the associated batch.

Note: For South Carolina, samples with failing internal standards must be re-analyzed to confirm failures. Re-extraction may be necessary if failures are repeated. All failures must be flagged in the data reports.

11.1.4.2. If recoveries are outside of the target range and it appears that matrix interferences are the cause, samples can be diluted or processed through further clean-up steps and re-analyzed. If recoveries are still outside of the target ranges, the data are reported with flags or the samples are re-extracted.

11.1.5. Prior to each analytical sequence, the resolution of the mass spectrometer is verified to be 10,000 or greater. Hardcopies of the reference peaks are printed at the beginning and end of each analytical shift where possible.

11.1.6. The resolving power of the DB-5MS chromatographic column is checked daily using a standard solution containing 2,3,7,8-TCDD and the adjacent TCDD isomers. When second column confirmations are performed, the DB-225 (or equivalent) column resolution is checked using a standard solution containing 2,3,7,8-TCDF and the adjacent TCDF isomers. Acceptable performance is achieved when 2,3,7,8-TCDD or 2,3,7,8-TCDF is resolved from the adjacent isomers by a valley of 25% or less.

11.1.6.1. WIDNR require all positive detections to be confirmed by using the process defined in 11.1.6.

11.1.7. The group times for the selected-ion-monitoring data acquisitions are also checked daily by analyzing the column performance mix that contains the first and last eluting isomers of each congener class. In this way one is assured of collecting data representative of the total PCDD/PCDF content and the 2,3,7,8-substituted isomers are suitably resolved. The isomers described above are also available as part of the CS-3 calibration solution (EPA 1613 CS3 WT).

12. Procedure

12.1. Glassware Cleaning – See SOP S-MN-O-465 for full details on cleaning options

12.1.1. Wash and Kiln

12.1.1.1. Hand wash all glassware with Liquinox soap and water solution per the manufacturers suggestion

12.1.1.2. Rinse with regular water minimum of three times to remove soap

12.1.1.3. Rinse with DI water three times.

12.1.1.4. Bake at 500 C for minimum 3 hours.

12.1.2. Microwave extraction cells receive a modified cleaning. The cells are washed with soap and water, rinsed with 1:1 nitric acid, and rinsed with water and acetone.

12.1.3. Water Glassware Pre-extraction

12.1.3.1. Rinse all the separatory funnels three times with MeCl. Add ~60 mL MeCl to each separatory funnel, cap and rotate on the tumbler for two minutes for each rotation. Vent each rotation to release the pressure.

12.1.3.2. Drain the rinse solvent into each round bottom receiving vessel, swirl to rinse the inside of each vessel.

12.1.3.3. All round bottoms and concentration glassware will have been rinsed with MeCl during the cleaning cycles and be ready for use.

12.1.4. Microwave Cell Pre-extraction

12.1.4.1. Pre-rinse the cell with acetone and twice with hexane

12.1.4.2. Place 50 mL of Acetone:toluene 10:90 in the clean MARS cell (a disposable glass liner may be used to expedite cleaning of the cell- however solvent should be reduced by 10mls if liner is used.)

12.1.4.3. Blank the system with the same solvent to be used for extraction using the "Blank" program for extraction.

12.1.5. Soxhlet/Dean Stark Glassware Pre-extraction

12.1.5.1. Place 300 mL of toluene in the extractor along with approximately 5-8 Teflon boiling chips into the boiling flask.

12.1.5.2. Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1-2 drops of toluene per second must fall from the condenser tip into the receiver. Extract the apparatus for 3 hours.

12.1.5.3. After pre-extraction, disassemble the apparatus. Refill the apparatus with 200-250 mL fresh extraction solvent.

12.2. Preparation Prior to Sample Extraction

12.2.1. Aqueous samples containing one percent solids (or less) are extracted in separatory funnels.

12.2.1.1 Visually inspect each sample by holding up and looking through the glass container, if there is no visible sediment in the sample, treat the samples as it is <1% solid. If there is greater than 0.5 cm sediment present, determine the percent solids.

12.2.1.2 If upon pouring the sample in the separatory funnel, the sample is thick, viscous, or has notable suspended solids present, determine the percent solids before proceeding further.

12.2.2. In samples expected or known to contain high levels of the PCDDs and /or PCDFs, the smallest sample size representative of the entire sample should be used, and the extract diluted, if necessary.

12.2.3. Determination of Percent Solids

12.2.3.1. Weigh 5-10 grams (g) of sample to three significant figures into a tared weighing vessel.

12.2.3.2. Dry overnight (minimum of 12 hours) at 110 ± 5°C and cool in a desiccator. Reweigh.

12.2.3.3. % Solids = $\frac{\text{Wt dried sample (g)} \times 100}{\text{Wt wet sample (g)}}$

12.2.3.4. Data are recorded electronically and printed out as needed.

12.2.4. Grinding, Homogenization, and Blending

12.2.4.1. Prior to spiking, samples with particle size greater than 1 mm are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix dependent.

12.2.4.2. In general, hard particles can be reduced by grinding with a metal bar. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or by blending.

12.2.4.3. The grinding, homogenization, or blending procedures must be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

12.2.4.4. Tissue samples, certain papers and pulps, slurries and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process. This process is often carried out at our Pace Analytical Services Green Bay laboratory.

12.3. Aqueous Samples- less than 0.5cm settled at the bottom of the jar (<1% Solids)

12.3.1. Preparation

12.3.1.1. Weigh the sample in the bottle to ± 1 g on a top loading balance. Record this weight.

12.3.1.2. Use appropriate indicator paper to verify the presence of residual chlorine and pH< 9. If there is residual chlorine is present treat with 80 mg Sodium Thiosulfate. If the pH is >9 add sufficient volume of sulfuric acid to get the pH between 7-9. Record the information on the extraction logs.

12.3.1.3. Spike 20 µL of the internal standard spiking into the bottle. Cap the bottle and mix by carefully shaking for 2 minutes. Allow equilibration for 1 hour.

12.3.1.4. For each batch set up QC according to section 13 by placing 1.0 L aliquots of reagent water in clean 1 L 1L Amber bottle. Spike as described in section 13.1. Allow equilibration for 1 hour with the samples.

12.3.1.5. For Wisconsin Samples

12.3.1.5.1. If there is any visible sediment (or other particulate), the sample water must be filtered with a glass fiber filter.

12.3.1.5.2. The filter will be extracted via soxhlet independently of the remaining water (which must be processed as stated above.)

12.3.1.5.3. The two extracts should be combined at concentration and proceed through cleanup as normal.

12.3.1.6. Samples with >1% solids (more than 0.5cm settled at bottom of jar) are processed as described in section 12.5 However, the results are reported based on the total sample weight extracted and are considered as a water matrix.

12.3.2. Sample Extraction by Microsteam Distillation (2L) (not to be used for Ohio VAP)

12.3.2.1. Add 5mls of DI water to the microsteam concentrator, followed by 5mls of Iso-Octane. Place 3-5 glass beads into the top of the concentrator. These will fall halfway and be stopped by the catch barbs inside.

12.3.2.2. At the vent of the concentrator, place a plug of glass wool.

12.3.2.3. Place raw sample into 2L round bottom. Using silicate boiling stones, heat until rolling boil and reduce the power to 60% to hold boil without overheating the apparatus.

12.3.2.4. Once sample is boiling, extract for 3 hours and then turn of the mantle and allow everything to cool for at least 30 minutes.

12.3.2.5. Drain the extraction solvent and water remaining in the concentrator into a 60ml vial. Rinse the apparatus three times with Iso-ocatane (approximately 5 mls each), collecting the rinsates into the 60ml vial each time. Try to cover the entire inside of the apparatus. Remove and allow to cool for 5 minutes.

12.3.2.6. Decant the water using a small glass pipette, leaving behind the entire amount of Iso-Octane, and proceed with sample cleanup.

Note: Microsteam distillation is not approved for South Carolina. A separatory funnel method must be used in place of this method.

12.3.3. Sample Extraction by Separatory Funnel

Note: Aqueous samples originating in North and South Carolina must be extracted using separatory funnel extraction.

12.3.3.1. Quantitatively transfer sample into a separatory funnel with three 35 mL rinses of $MeCl_2$. Weight empty container for use in the determination of the amount of sample extracted.

12.3.3.2. Extract by shaking the separatory funnel, venting any backpressure for a minimum of 2 minutes.

12.3.3.3. If an emulsion layer forms, allow it to dissipate, or use mechanical such as centrifuge or chemical (salt,, ethanol etc.) means to break the emulsion. Once the emulsion is broken, continue the extraction.

12.3.3.4. After the extraction allow the layers to separate.

12.3.3.5. Remove the methylene chloride layer. Repeat the extraction two times with fresh aliquots of 100 mL of methylene chloride, combining the three solvent portions.

12.3.3.6. Transfer the methylene chloride through a 10 cm plug of sodium sulfate prebaked at 400 °C for 4 hours and glass wool to 500ml boiling flask. Assemble the round bottom flask and Snyder column. Add 30-50 mL Toluene through the Snyder column. Concentrate to approximately 10 mL using heating mantle.

12.3.3.7. Remove and allow to cool for 5 minutes.

12.3.3.8. Rinse Snyder column down into the flask with three 2 mL portions of hexane and proceed with sample cleanup (12.12).

12.4. Solid Phase Extraction (SPE)

12.4.1. Assemble the Solid Phase Extraction apparatus as follows:

12.4.1.1. Center an unused 47 mm Octadecyl (C18) extraction disk onto the metal screen on top of the port.

12.4.1.2. Center a 47 mm fiberglass filter paper directly over the extraction disk.

12.4.1.3. Place the glass funnel on top and secure with screw thread clamp. Ensure that the pump and SPE unit are connected to the solvent waste collection satellite at this point. Turn on the vacuum pump.

12.4.2. Rinse the disk by adding approximately 30 mL of methylene chloride.

12.4.3. Turn the valve so that it is open to the filtration apparatus and allow the methylene chloride to thoroughly saturate the disk. Do not let the disk go dry.

12.4.4. Open the valve(s) by moving the port handles to the waste position and allow half the methylene chloride to pass through. Once approximately half has passed through close the valve(s) by moving it back to its center position.

12.4.5. Open the valve to allow the remainder of the methylene chloride to be pulled through the disk. Close the valve when the disk appears dry.

12.4.6. Next add approximately 50 mL methanol to the funnel.

12.4.7. Again pull the methanol into the disk by vacuum and allow to sit for one to two minutes.

12.4.8. Turn the vacuum on again to pull most of the methanol through the disk. Do not allow the disk to go dry. Leave a small layer of methanol on top of the disk. If the disk does go dry, repeat the methylene chloride conditioning step 12.4.3.

12.4.9. Displace the methanol by rinsing the disk with one 50 mL aliquot of distilled water. Dump the methanol portion into a flammable waste container. Allow the water to penetrate the disk and let stand for one to two minutes. Then pull the remainder through the disk

being careful to leave a layer of water on top. If the disk goes dry at this stage, repeat the previous steps beginning with the methylene chloride conditioning step 12.4.3.

12.4.10. Switch the tubing to the pump and SPE unit so that the unit is now connected to the water waste satellite. To extract the sample, carefully invert the sample container so that it rests on top of the funnel and allow the water to be pulled through the disk at the approximate rate of 100 mL per minute. If the sample is received in a wide mouth bottle, carefully pour approximately 200 mL at a time without letting the disks go dry.

12.4.11. Remove the sample container and allow the disk to remain under vacuum for approximately 30 seconds.

12.4.12. Screw on appropriate labeled 40ml vials to each port.

12.4.13. Rinse the sample container with 2 – 3 mL (1 large pipette worth) acetone and then pour onto the disk.

12.4.14. Open the valve(s) by moving the port valve handle(s) to the elute position and allow all the acetone to pass through the disk into the collection vial.

12.4.15. Rinse the bottle with 10 mL methylene chloride and pour onto the disk.

12.4.16. Open the valve(s) by moving the port valve handle(s) to the elute position so that approximately half the methylene chloride passes through the disk and into the collection vial and then let stand for 1.5-2 minutes.

12.4.17. Pull the remainder of the methylene chloride through the disk and collect into the collection vial.

12.4.18. Repeat steps 12.4.15-12.4.17, allowing the disk to stand under solution for no less than 1½ – 2 minutes each time.

12.4.19. Remove the 60 mL vials from the ports and empty the waste satellites appropriately. If no solvents have passed into the water waste satellites the water waste may be dumped down the drain.

12.4.20. Rinse the filtration apparatus with aliquots of toluene and acetone, respectively. For additional cleaning, the funnel may be washed with soap and water and then rinsed with acetone, toluene, and acetone aliquots, respectively.

12.4.21. Pipette the water layer off the top of each SPE sample extract.

12.4.22. Concentrate the SPE sample extract to approximately 1 mL on the nitrogen blow down units.

12.4.23. Concentrate the sample to almost dryness on the blow down unit and add 1 – 2 mL of hexane to complete the solvent exchange.

12.4.24. If the sample does go dry on the N-evap, then place the sample in a sonicator for 15 minutes and vortex to ensure that the analytes are in solution.

12.4.25. Add the appropriate amount of cleanup standard to the sample extract as with Separatory funnel, and proceed to cleanup.

Note: For South Carolina SPE, this method is not approved.

12.5. Aqueous Samples containing >1% Solids (more than 0.5cm of settled sediment at the bottom of the sample jar)

12.5.1. Preparation

12.5.1.1. Review the percent solids information to determine the sample size sufficient to provide 10 g equivalent dry weigh sample. Weigh a well-mixed aliquot of each into a clean beaker, pre-extracted thimble or glass jar. In certain cases, i.e., sludge or waste matrices, this amount may be modified to a smaller aliquot to provide more workable extracts.

12.5.1.2. The sample may be separated using a centrifuge, and the liquid fraction decanted. With this procedure, the correct sample amount is first transferred into a different container for centrifuging. After centrifuging, the entire solid portion is mixed with sodium

sulfate and transferred into a Soxhlet extraction thimble. If centrifuged, rinse any particulate off the sides of the secondary sample container with small quantities of methylene chloride.

12.5.1.3. Save aqueous phase. Measure the volume of the water, if greater than 100 mL of water is present, extract it in a separatory funnel or by SPE and combine with the solid extract, otherwise discard aqueous phase)

12.5.1.4. Spike with 20 µL of the internal standard spiking solution. Allow the sample to stand for 1 hour after spiking prior to moving on with extraction.

12.5.1.5. For each batch set up QCaccording to section 13.1 by weighing 10g aliquots of clean sand into clean beakers or glass jars. Spike as described in 13.1. Allow the QC to stand for 1 hour after spiking prior to moving on with extraction.

12.5.1.6. Extract the sample:

12.5.1.6.1. Fill the soxhlet with toluene to the neck of the soxhlet, allow it to drain into the round bottom flask. Turn on the mantle and reflux for 16-24 hours. Check the apparatus for foaming frequently during the first two hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

12.5.1.6.2. If applicable, drain the water from the receiver at 1-2 hours and 8-9 hours, or sooner if the receiver fills with water. Continue to reflux the sample for the 16-24 hours. Cool and disassemble the apparatus.

12.5.1.7. Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration.

12.5.1.8. Concentrate to approximately 5-10 mL. Remove and allow to come to room temperature (approximately 5 minutes).

12.5.1.9. Rinse Snyder column down into the flask with ~5 mL portions of hexane.

12.5.1.10. If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes (12.12), combine with the filtrate in a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup (12.12).

12.6. Soil/Solid by Microwave Assisted Extraction

Note: Solid samples originating in South Carolina must be extracted using Soxhlet extraction. Do not use MAE for South Carolina samples.

12.6.1. Blank extract the MAE vessels with 90:10 Toluene:Acetone

12.6.2. Weigh a 10-gram aliquot (dry weight) of the homogenized sample and place into a microwave extraction cell. If the sample material is wet, it may be dried with the addition of hydromatrix after the sample has been weighed.

12.6.3. Spike the sample with 20 µL of the internal standard spiking solution. Allow the samples to stand for 1 hour prior to proceeding with extraction.

12.6.4. For each batch, set up QC according to section 13.1 by weighing 10g aliquots of clean sand into clean microwave cells. Spike as described in 13.1. Allow the QC to stand for 1 hour prior to proceeding with extraction.

12.6.5. Add 50 mL of Acetone:toluene 10:90 to the extraction cell, insert the Teflon plug and the cap. Seal the screw on cap tightly.

12.6.6. Insert the cells into the microwave and run using the "1613" program. The program is as follows:

Power				
Max	**%**	**Ramp**	**Degrees C**	**Hold Time (min)**
800w	80	10:00	125	20
1600w	100	10:00	150	50

12.6.7. After extraction program is complete (approximately 2 hours) sonicate the cells for a minimum of 20 minutes.

12.6.8. Carefully open each cell containing the extracted sample and collect the solvent extract.

12.6.9. Rinse the cell and sample material twice with 10 mL of hexane, combining the hexane with the original solvent extract.

12.6.10. The Acetone must be removed from the extract prior to cleanup.

12.6.11. The solvent layer is ready for silica column cleanup (12.12)

12.7. Soil/Solid Samples by Soxhlet

12.7.1. Preparation

12.7.1.1. Weigh a 10-gram aliquot (dry weight) of the homogenized sample, and place into a Soxhlet thimble. If the "solid" sample contains >90% moisture, treat like the waters >1% solids in 12.5. If the sample material is wet, but less than 90% moisture, dry it by mixing with extracted anhydrous sodium sulfate before adding to the Soxhlet thimble. If the sample is extracted using Soxhlet Dean-Stark apparatus (with toluene,) no sodium sulfate should be added.

12.7.1.2. Spike the sample aliquot with 20 µL internal standard spiking solution. Allow the samples to stand for 1 hour before proceeding to extraction.

12.7.1.3. For each batch set up QC according to 13.1 by weighing 10g aliquots of clean sand into clean Soxhlet thimbles or clean beakers. Spike as described in 13.1. Allow the QC to stand for 1 hour before proceeding to extraction.

12.7.2. Sample Extraction

12.7.2.1. Place the prepared sample in the thimble into the Soxhlet extractor. The Dean-Stark attachments maybe utilized in place of the sodium sulfate drying step.

12.7.2.2. Add 300 mL of toluene and reflux for a minimum of 16 hours. Reflux at a rate of three cycles per hour. If applicable, drain the water from the receiver as needed.

12.7.2.3. Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

12.7.2.4. Concentrate to approximately 10 mL. Remove and allow cooling for 5 minutes.

12.7.2.5. Rinse Snyder column down into the flask with three 2 mL portions of hexane.

12.7.2.6. If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes (12.12), transfer the extract to a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup (12.12).

12.8. Preparation and Extraction of Fly Ash Samples

12.8.1. Weigh a 10g aliquot of the homogenized sample and an equivalent amount of anhydrous sodium sulfate into a clean beaker. Mix well. NOTE: If high levels are expected, a smaller (1 gram) aliquot may be extracted. If the sample is extracted using Soxhlet Dean-Stark apparatus (with toluene,) no sodium sulfate should be added.

12.8.2. Spike the sample aliquot with 20 µL of the internal standard spiking solution. Allow the samples to stand for 1 hour before proceeding with extraction.

12.8.3. For each batch set up QC according to 13.1 by weighing 10g aliquots of clean sand into clean Soxhlet thimbles or clean beakers. Spike as described in 13.1. Allow QC to stand for 1 hour before proceeding with extraction.

12.8.4. Place each prepared fly ash sample into a thimble and place in the Soxhlet apparatus.

12.8.5. Add 300 mL toluene and extract for 16 hours, maintaining three cycles per hour.

12.8.6. Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

12.8.7. Concentrate to approximately 10 mL. Remove and allow cooling for 5 minutes.

12.8.8. Rinse Snyder column down into the flask with ~5 mL portions of hexane.

12.8.9. If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes (12.12), transfer the extract to a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup (12.12).

12.9. Milk and Milk Product Samples

12.9.1. Accurately measure a 100 mL aliquot of milk and transfer to a 2 liter separatory funnel.

12.9.2. Spike the sample aliquot with 20 µL of the internal standard spiking solution. Allow the samples to stand for 1 hour before proceeding with extraction.

12.9.3. For each batch set up QC according to 13.1 by 100 mL aliquots of de-ionized water into clean separatory funnels. Spike as described in 13.1. Allow the QC to stand for 1 hour before proceeding with extraction

12.9.4. Add 300 mL of 1.5M potassium oxalate solution and 600 mL of de-ionized water to each sample in the separatory funnel.

12.9.5. Gently shake the separatory funnel for 8-10 minutes.

12.9.6. Add 150 mL of 1:1:1 ethanol/ether/hexane to the sample and shake gently for 3-4 minutes.

12.9.7. Allow the layers to separate 15-20 minutes.

12.9.8. Collect the milk (bottom layer) and emulsion layers in a clean 2 L beaker. (The emulsion layer can be reduced by adding small volumes (10-30 mL) of the 1:1:1 solvent mixture to the separatory funnel after separation of the layers).

12.9.9. Transfer the clear organic layer directly to a Kuderna-Danish concentrator and set aside.

12.9.10. Transfer the milk and emulsion back to the separatory funnel and repeat the extraction two more times. Combine the organic layers to the K-D flask and save the emulsion layer in a 500 mL separatory funnel.

12.9.11. After the final extraction, rinse the 2 L separatory funnel with 60 mL of the 1:1:1 solvent mixture and add to the K-D flask.

12.9.12. Concentrate the extract to 2 mL and allow cooling.

12.9.13. Quantitatively transfer the extract into the separatory funnel containing the emulsion and add 80 mL hexane.

12.9.14. Perform the acid washes and cleanup (12.12) as described. For milk samples, acid cleanup is not considered optional.

NOTE: The first acid wash should not be shaken. Slowly pour the first 50 mL of sulfuric acid into the separatory funnel and allow separation for 15 minutes. Drain the acid and perform the remaining washes in the normal manner.

12.10. Preparation of Tissue Samples (Environmental)

12.10.1. If the sample is supplied as whole fish or fillets, grind the sample using a meat grinder or blender.

12.10.2. Weigh a 10 (use 20 grams if EU requirements apply) gram aliquot of the homogenized sample into a clean beaker. Mix in enough extracted anhydrous sodium sulfate to dry the sample (usually approximately twice the tissue weight. Quantitatively transfer the sample into a clean Soxhlet thimble and top with extracted glass wool.

12.10.3. Spike the sample aliquot with 20 µL of the internal standard spiking solution. Allow the samples to stand for 1 hour before proceeding with extraction.

12.10.4. For each batch set up QC according to 13.1 by weighing 10 g aliquots of clean tuna or reference oil matrix and place each aliquot into a Soxhlet thimble. Spike as described in 13.1. Allow the QC to stand for 1 hour before proceeding with extraction

12.10.5. Store any remaining sample in the freezer at approximately -18°C.

12.10.6. If the sample is extracted using Soxhlet Dean-Stark apparatus (with toluene,) no sodium sulfate should be added.

12.10.7. Place the loaded thimble into the Soxhlet apparatus.

12.10.8. Add 250 mL of hexane/methylene chloride (1:1 v/v) and reflux for a minimum of 18-hours.

12.10.9. Alternatively, the sample can be extracted using Soxhlet Dean-Stark apparatus and toluene. No sodium sulfate is used with this option.

12.10.10. Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. Add 30-50 mL toluene through the Snyder column, allow it to drain into the round bottom flask.

12.10.11. Concentrate to approximately 10 mL. Remove and allow cooling for 5 minutes.

12.10.12. Rinse Snyder column down into the flask with three 2 mL portions of hexane.

12.10.13. Perform the acid washes and cleanup as described (12.12). For tissue and food samples, acid cleanup is not considered optional. The column acid wash procedure may be preferable to the separatory funnel procedure.

NOTE: The first acid wash should not be shaken. Slowly pour the first 50 mL of sulfuric acid into the separatory funnel and allow separation for 15 minutes. Drain the acid and perform the remaining washes in the normal manner.

12.10.14. Concentrate to 1 mL using KD and N-evap apparatus and proceed with sample cleanup.

12.11. Preparation of Oil Based Food Product Samples

12.11.1. Canola oil or equivalentis used as the reference matrix for oil based food and feed matrices.

12.11.2. Weigh out a 10-gram aliquot (use 20 grams if EU requirements apply) of the oil based sample into a clean 8 ounce soil jar and spike the aliquot with the internal standard spiking solution.

12.11.3. Spike the other aliquot(s) with 20 µL of the internal standard spiking solution and with 10 µL of the native spiking solution (20 uL of a 2x dilution is also acceptable) This (they) serve(s) as the laboratory control spike(s). If matrix spikes are prepared with the extraction batch, only one laboratory spike is required. If included, matrix spikes are prepared in the same manner as laboratory spikes except using sample material rather than reference matrix..

12.11.4. For each batch set up QC according to 13.1 by weighing 10-gram aliquots of the canola oil reference matrix and place each aliquot into a clean beaker. Spike as described in 13.1. Allow the QC to stand for 1 hour before proceeding with extraction

12.11.5. Spike one reference sample with 20 µL of the internal standard spiking solution. This aliquot serves as the method blank. Allow the samples to stand for 1 hour before proceeding with extraction.

12.11.6. Add 50 mL of hexane to the sample. Gently shake to mix the oil and solvent, allow the sample to sit for 1 hour to dissolve the oil into solution..

12.11.7. Proceed to “Super Carbon First” enrichment (12.12).

12.12. Extract Enrichment/Cleanup Procedures

12.12.1. Back Extraction with Acid – Micro scale

NOTE: This enrichment step is optional. It is used on extracts based on appearance and color. If the extract is cloudy, emulsive, or multi-layered, this back extraction is employed. It is also used when the extract is not clear or if the sample appears particularly dirty (i.e. multi-layer, sludge-like) or contains various organic materials (i.e. milk, fish, vegetation, etc.). Most samples undergo this procedure, including all QC samples in associated batch.

12.12.1.1. Spike each extract with 50µL of the clean-up standard..

12.12.1.2. Quantitatively transfer H2O and Soxhlet extracts with 15 mL of hexane to 40 mL vials.

12.12.1.3. Partition the extract against 2-3 mL concentrated sulfuric acid. Agitate the samples for two minutes with periodic venting into a hood. Remove and discard the acidic bottom layer. Emulsions may be broken down by mechanical or chemical means.

12.12.1.4. Repeat 12.12.1.3, the acid washing, until no color is visible in the aqueous layer, to a maximum of four washings.

12.12.1.5. Acid waste is collected and stored in labeled containers for disposal. Use caution when handling.

12.12.1.6. Repeat step 12.12.1.3, but substitute buffer solution (100 mL 0.5 M KH2PO4).

12.12.1.7. Concentrate extract to approximately 1 mL on the N-evap and proceed with column cleanup. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS!

12.12.2. Back Extraction with Acid – Macro scale

NOTE: This enrichment step is optional. It is used on extracts based on appearance and color of the extract is cloudy, emulsive, or multi-layered, this back extraction is employed. It is also used when the extract is not clear or if the sample appears particularly dirty (i.e. multi-layer, sludge-like) or contains various organic materials (i.e. milk, fish, vegetation, etc.). If samples undergo this procedure, all QC samples in associated batch must go through the same process at least once.

12.12.2.1. Spike the extract with 50 µL of the cleanup standard.

12.12.2.2. Quantitatively transfer concentrated extracts to an 8 oz flint glass jar with 50ml of N-Hexane.

12.12.2.3. Quantitatively transfer and partition the extract in 50 mL concentrated sulfuric acid. Agitate briefly with periodic venting into a hood. Remove and discard the aqueous bottom layer. Emulsions may be broken down by mechanical or chemical means.

12.12.2.4. Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.

12.12.2.5. Acid waste is collected and stored in labeled containers for disposal. Use caution when handling. Repeat step 12.12.2.3 but substitute DI water, as needed.

12.12.3. "Super Carbon First" Column

12.12.3.1. Bake the Carbon at 130ºC for 4- 6 hours. .

12.12.3.2. Prepare carbon/Celite packing by mixing 18% (by weight) 100–400 mesh active carbon (Pre-extracted in Soxhlet with Toluene overnight) and 82% (by weight) Celite. Mix thoroughly.

12.12.3.3. The column is prepared using 18mm tubing in one foot increments. These are designed to be used only once, and discarded after use.

12.12.3.4. Insert a silanized glass wool plug at one end (~2" from the end of the column) and pack with ~1/2 inch of Celite followed by 3.0 g of the carbon/Celite mixture. Cap the end with a silanized glass wool plug. Note: Tap the column between layers to level out the resins.

12.12.3.5. Rinse the column "clean (Celite)" side up with 30 mL of hexane. The flow rate must be less than 0.5 mL/minute. If the flow rate is greater than 0.5 mL/min, discard the column. Discard the rinses.

12.12.3.6. While the column is still wet with hexane, quantitatively transfer the sample extract to the top of the column and rinse the jar with two 10 mL aliquots of hexane. If necessary use a 3rd 10 mL hexane rinse to completely transfer the sample to the column. Note: Add the sample and rinses slowly using sonication or vortexing as needed to keep the sample dissolved.

12.12.3.7. Collect the hexane containing the sample matrix as waste, periodically rinsing the bottom of the column with fresh hexane to remove any residual oil matrix from the column.

12.12.3.8. Elute the column with 30 mL Methanol. Follow this elution with 10 mL Hexane, discard in waste collection.

12.12.3.9. Carefully turn the column upside down and elute the PCDDs and PCDFs with 60 mL of toluene.

12.12.3.10. Evaporate the toluene to near dryness, add 5-10 mL of hexane and spike the sample with 50 uL cleanup standard before proceeding to the silica column and alumina column cleanups described below.

12.12.4. Silica Column

12.12.4.1. Vertically clamp a disposable glass column, 15 mm ID x 35 cm. Rinse with hexane, air dry, and place a pre-extracted silanized glass wool plug into bottom.

12.12.4.2. Pack the column in the following order (bottom to top): 1 g neutral silica, 2 g basic silica, 4 g acidic silica, 2 g neutral silica and 2 g sodium sulfate. Between each layer, tap the column to settle the silica. Wet column with 15-20 mL hexane after all layers are added, allow this to drain into the alumina column in (12.12.5) if doing the stacked columns Plug the end of the column with a septum when it starts dripping. Check the column for channeling. If channeling is observed, discard the column. DO NOT allow the column to go dry.

12.12.4.3. Spike the extract with the cleanup standard, if it has not already been added in 12.12.3.10.

12.12.4.4. Quantitatively transfer the sample extract onto the column using two 2 mL rinses of hexane. Break off the tip of the column containing the septum. Elute until the solvent just covers the silica. Do NOT let the column go dry.

12.12.4.5. Elute the column with 80 mL hexane onto the alumina column in 12.12.5 if doing stacked columns.

12.12.4.6. Jumbo-silica columns are prepared using three times the amount of the silica noted above in each layer of the column. Larger macro-silica columns may be prepared using nine times the amount of the silica noted above in each layer of the column. These columns are prepared in drying tubes and are eluted with approximately 300 mL or 500 mL of hexane, respectively.

12.12.5. Alumina Column

12.12.5.1. Pack a silanized glass wool plug into the bottom of a disposable glass column (15 mm ID x 35 mm). Pack the column in the following order: 4 g of prebaked (400 °C for 4 hour) anhydrous sodium sulfate, 7 g of neutral alumina, and 4 g of anhydrous sodium sulfate to cover the alumina. Between layers, tap the top of the column gently to settle the adsorbents.

12.12.5.2. Elute with 15-20 mL hexane from 12.12.4.2. Discard the eluate. Check the column for channeling. If channeling is present, discard the column. DO NOT TAP A WETTED COLUMN AND DO NOT LET THE COLUMN GO DRY.

12.12.5.3. The 80 mL sample from 12.12.4.5 is eluted into the alumina column. Disassemble and dispose of the silica column then elute with 40 ml of 60% (v/v) methylene chloride in hexane. Collect this fraction in a 12 dram vial.

12.12.5.4. Concentrate the extract to near dryness using an N-evap apparatus.

12.12.5.5. Solids stack the alumina column on top of the below carbon column and continue the cleanup process.

12.12.6. Carbon Column

12.12.6.1. Bake the Carbon at 130°C for 4- 6 hours.

12.12.6.2. Prepare carbon/Celite packing by mixing 18% (by weight) 100-400 mesh active carbon (pre-extracted in soxhlet with acetone overnight) and 82% (by weight) Celite. Mix thoroughly.

12.12.6.3. Prepare a 15 mm glass tube about one foot in length.

12.12.6.4. Insert a silanized glass wool plug at one end and pack with 1 cm of Celite followed by ~1 g of the carbon/Celite mixture. Cap the end with a silanized glass wool plug.

12.12.6.5. Rinse the column "clean (Celite)" side up sequentially with 10-15 mL hexane. The flow rate must be less than 0.5 mL/minute. If the flow rate is greater than 0.5 mL/minute, discard the column. Discard the rinses.

12.12.6.6. While the column is still wet with hexane, allow the samples elute from 12.12.5.3, dispose of the solvent and remove the alumina column.

12.12.6.7. Turn the column upside down and elute the PCDDs and PCDFs with 15 mL of toluene. Proceed to Final Extract Transfer.

12.13. Final Extract Preparation

12.13.1. Extract Transfer

12.13.1.1. Concentrate the extract under a gentle stream of nitrogen to a volume of less than 1 mL. Do NOT blow the sample so the portions of the solvent "ride" up the sides of the glass vial. The temperature of the N-Evap bath must be <42°C

12.13.1.2. Add 10 µL of tridecane using a calibrated Eppendorf pipette to an autosampler vial to act as a keeper solvent.

12.13.1.3. Quantitatively transfer the extract to the autosampler vial. Rinse the original vial with less than 1 mL of methylene chloride/hexane (60:40 V:V). Transfer rinsate to the auto-sampler vial. Repeat the rinse of the auto-sampler vial with two additional aliquots (<1 mL) of methylene chloride/hexane. Then blow down extract to the level of the 10 uL keeper solvent.

12.13.1.4. Add the 10 µL of recovery standard to the extract with a calibrated Eppendorf pipette for a final volume of 20 µL and cap. Vortex each of the sample vials.

12.13.1.5. Transfer the extracts to the analytical laboratory for analysis. Extracts must be stored in the dark at < or equal to -10°C.

13. Quality Control

13.1. Table 13.1 – Quality Control

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Spike 100 µL of the internal standard spiking solution into one reference matrix. Note: When setting up method blanks, the glassware used must be varied randomly amongst the sets used for sample extraction.	One method blank is typically prepared with each twenty samples of any given matrix.	A method blank or solvent blank must be analyzed between standards and samples to demonstrate lack of PCDD/PCDF carryover. Method blanks are treated like samples in the analytical sequence. For DLM2.0 the method blank associated with a given sample must be analyzed at the beginning of the same sequence as the sample. For Ohio VAP:	If the method blank contains significant PCDDs/PCDFs, find and correct the source of the problem. If the contamination appears to be instrument related, correct the problem, analyze a solvent blank, and reanalyze the method blank before proceeding with samples. If the contamination appears to be from the extraction or enrichment steps, the analysis of samples may continue. If the sample shows similar contamination it must be re-extracted, if possible. All associated sample results must be qualified for method blank contamination when any analyte is detected in the method blank at 10% or more of the sample concentration. If the method blank shows no contamination above the reporting level calibration solution, analysis of samples may continue. However, all associated sample results must be qualified for method blank contamination when any analyte is detected in the method blank at 10% of

			< RL at a minimum For Wisconsin- per NR149, and subsequent discussion: the laboratory can use the highest of any of the following values for HRMS: • One-third the concentration of the lowest standard in the initial calibration • Five percent of the regulatory limit • Ten percent of the measured concentration in the sample	more of the sample concentration ***Exception:*** For Ohio VAP all associated samples must be re-extracted if the blank shows detections >/= RL under any circumstances.) See Attachment VIII for special DLM2.0 method blank requirements.
Laboratory Control Sample (LCS)/ Laboratory Control Sample Duplicate (LCSD)	Spike 100 µL of internal standard spiking solution and 40 of the native spiking solution into the remaining reference matrix. Note: For Ohio VAP, LCSD is not analyzed,	At a minimum, one laboratory control spike is prepared with each batch of samples (up to 20) of any given matrix. For batches that DO NOT have sufficient sample volume to perform an MS/Sample duplicate or MS/MSD set, a laboratory control spike duplicate must be performed to show precision. NOTE: Only one laboratory control spike is required when an MS/Sample duplicate or MS/MSD set are prepared in the same batch.	For method 8290/8290A, control limits are set at 70-130%. The ranges for Method 1613B are provided in Attachment V. DLM2.0 also utilizes the 1613B ranges. If an LCSD was required, the RPD value must also be calculated.	Recoveries of up to 2 native analytes outside the expected control limits are allowed (provided it is a random event) with a detailed explanation of data impact in the narrative section of the final report. For OHIO VAP, all analytes of interest must meet QC criteria, or be re-analyzed/re-extracted. Additionally, for Ohio VAP samples, if the outlier is an analyte of interest and corrective actions do not result in acceptable data, the samples must be re-extracted. If re-extraction is not possible due to depleted sample volume, then contact the client for further instructions. The client may want to re-submit the sample or have the lab qualify the data and narrate as appropriate. Accuracy of the standard spiking solutions must, at a minimum, be verified quarterly by comparison of the solutions to certified native materials obtained from a second source or batch. If the recoveries are not within the control limits, data must be evaluated to determine the impact on the associated samples. If it is determined that the instrument may be the cause of the outlier, the QC must be reanalyzed to confirm results as well as any associated samples that may have been impacted by the instrumentation failure. If it is determined that the cause is due to poor extraction, all associated samples must be re-extracted and reanalyzed or qualified accordingly. LCS failures biased high may still be used if samples were non-detect for the analytes in question.
Matrix Spike Duplicate (MSD) or Matrix Spike (MS) /Sample Duplicate (DUP) (Method 8290 only	Place the appropriate amount of the client supplied duplicate sample into clean apparatus. Spike 20 µL of internal standard	One matrix spike/spike duplicate set must be prepared with the extracted sample batch (up to 20 samples) when sufficient sample volume is supplied. (If insufficient sample volume is	For Method 8290/8290A, the recovery limits of the native PCDD/PCDF analytes in the spiked samples range from 70 -130% and 20% RPD. For Method 1613B, use the laboratory spike (OPR) limits from	Recoveries of selected analytes outside the acceptable range do not invalidate the data but provide information, which is used by the laboratory to monitor recovery trends and to assure optimization of the method. This is particularly true of MS/MSD recoveries where native PCDD/PCDF are subject to the effects of the sample source. Data must be qualified accordingly on the final report. If native recoveries in the MS/MSD indicate a laboratory method performance problem (i.e. >2 recoveries are

unless specified)	spiking solution and 10 µL of the native spiking solution (or 20uL of a 2x dilution) into the client-supplied duplicate samples (if supplied). If there is insufficient sample volume for MS/MSD or MS/Sample Duplicate see 13.1.1. Note: MS/MSD is optional for Ohio VAP.	available, refer to Section 13.1.1). Matrix spikes are not performed for DLM2.0 since approved results forms are not available.	attachment V.	outside the acceptance limits, but the original sample does not appear to be the cause), analysis of the associated batch samples must be suspect until corrective action is taken to determine the root cause of the problem, and the problem is negated. Accuracy of the standard spiking solutions must, at a minimum, be verified quarterly by comparison of the solutions to certified native materials obtained from a second source or batch. For Minnesota Admin Contract clients – all MS/MSD failures require reanalysis of the MS/MSD and the original sample. If it is still out of control, investigate and document the cause in the associated narrative as well as qualifying appropriately. Recoveries impacted by elevated sample levels (>2 times the spike level) are not required to be within the acceptance range.

13.1.1. For each batch (up to 20 samples) to be extracted in the same 12 hour shift, place two aliquots of the reference matrix into clean apparatus (See extraction sections for reference matrix type). One reference matrix must serve as the method blank and the other must be a laboratory control sample (LCS) spiked with 40uL of 5-150ng/mL native analyte solution, and 100ul of Internal standard solution at 20-40mg/ml . Include one additional aliquot of reference matrix if insufficient sample volume to perform an MS/Sample duplicate or MS/MSD is found. This aliquot must serve as a laboratory control spike duplicate (LCSD- spiked as the LCS above) for the batch to show precision. Note: Only one lab control spike is required when an MS/Sample duplicate or MS/MSD set is prepared in the same batch.

13.2. Extraction Corrective Action (Does not apply for Ohio VAP)

13.2.1. If a laboratory error occurs during the extraction process that results in the loss of an extract prior to final concentration and transfer of the sample, a new aliquot may be re-extracted and added to the original batch. The new aliquot must be set up within 12 hours of the set up of the first sample in the extraction batch or it must be put into a new batch. This may include a QC aliquot.

13.2.2. Make note of any error and corrective action on the extraction sheet. Include times of laboratory error and re-set up of the aliquot.

13.3. Reporting and Review

13.3.1. Reports are generated using the Avalon software package. Reporting options are chosen to match the requirements for individual clients.

13.3.2. Units/Significant Figures

13.3.2.1. Values are reported to two significant figures. Aqueous samples are routinely reported in units of pg/L and solid matrices are reported in ng/kg. Other units are available upon request.

13.3.3. Data Qualifiers/Flags - The information typically reported is summarized below.

13.3.3.1. Base Report

13.3.3.1.1. Case narrative including client name, address, project information, introduction,sample information, and discussion of results.

13.3.3.1.2. Copies of chain of custody documents and analytical requests

13.3.3.1.3. Sample Analysis Results

13.3.3.2. Full Report

13.3.3.2.1. Those items listed in base report summary

13.3.3.2.2. Raw data including sample, QC sample and standards

13.3.3.2.3. Selected ion current profiles (chromatograms)

13.3.3.2.4. Communications records

13.3.3.2.5. Extraction and login forms

13.3.3.2.6. Instrument resolution checks

13.3.3.2.7. Calibration Results

13.3.4. Levels of Review

13.3.4.1. Each sample work-up must be rechecked for work-up, header information and data entry accuracy. The results of this review are recorded on the raw data sheet.

13.3.4.2. All data generated during analysis are peer reviewed and a review checklist is completed. The project manager reviews the data prior to inclusion in the final report.

13.3.5. Data Archiving or Filing

13.3.5.1. All analytical results are stored in Avalon.

13.3.5.2. After reporting, the complete project file is archived in the permanent chemistry archive.

14. Data Analysis and Calculations

14.1. Sample Analysis

14.1.1. Introduce PFK into the batch inlet and tune the instrument to a resolution of ≥ 10,000 (M/ΔM, 10% valley) using a PFK peak within the analysis mass range (M/Z 331 or 381). Tuning is accomplished by adjusting the various instrument voltages displayed on the tune pages in the "AutoSpec" window to maximize both signal strength and resolution (peak width). If the scan width is set to 200 ppm, a peak crossing the 5% y axis at 50% of the displayed width will be considered 10,000 resolution. If peak shape and intensity appear reasonable, tuning may just be a matter of optimizing each of the variable lens voltages as fine tuning. If irregularities are present, consult with an experienced analyst. Print, sign and date a copy showing the reference peak resolution. This record is scanned into Avalon. Note: The instrument can be programmed to centroid and obtain static resolution printouts at any time during the course of the run. Using this ability, one may either obtain the first functional group in its entirety, or all functional groups. The choice is left to the operator, but may be client directed. As the system is inherently pre-disposed to hysteresis, it is critical that the "Cycle magnet through zero" radio box be checked on each individual function. If this is not done, it is likely that function one of the next run will be largely lost. Subsequent injections will not suffer any consequence however.

14.1.2. Typical Operating conditions include:

Trap current:	500 µA
Electron Energy:	32 ± 5 eV (40 ± 5 eV for Thermo instruments)
Source Temperature:	270 °C
Emission/Trap Ratio:	≤ 3
Accelerating Voltage:	8000 eV (5000 eV for Thermo instruments)

14.1.3. Once the tune objectives have been met, the Waters instruments need to complete a selected ion calibration to ensure proper operation. Open the "experiment calibration" window and ensure that "dioxfur" is selected as the experiment file. Next, start the calibration and check the box on the right hand side to center the reference peak. All reference peaks bracketing the quantitation masses need to be at least 10,000 resolution. Once the peak is centered, choose the "next" button. Repeat this centering and continuing process until all five mass groupings have been completed.

14.1.4. Once the mass calibration is complete, change to the "MassLynx" window and enter the analytical information (filename, sample ID, etc.) onto the table. The tables are saved according to an instrument date code. For example, table U130102A would be instrument "U" from year

2013, month 01 and day 02. The A signifies the first run sequence from that day. A second sequence would be U130101B. Sample filenames follow the same format and have a sequential number added to the end of the code. For example U130101A_01 would be the first injection from that sequence.

14.1.5. The first injection of the sequence is typically the calibration standard (that also contains the column resolution and window defining isomers). This is generally followed by laboratory spikes and matrix spikes if they are available. Next a blank (instrument or method) is run. Some type of blank must be analyzed between the calibration standard and non-spiked sample extracts. Method blanks are considered the same as sample extracts and may be analyzed either after spikes or with the sample extracts if an instrument blank was included in the sequence. The sample extracts are next followed by the ending calibration standard. Note: If the sequence is running at a time when staff are present, it is advantageous to check the calibration standards and blank promptly so corrective action can be taken if they do not meet the criteria in Table 11.1 and Table 13.1.

14.2. Qualitative Analysis

14.2.1. Samples are queued as discussed in the data processing section of this SOP. In order for a peak to be accepted as a PCDD/PCDF isomer, the following criteria must be met:

14.2.1.1. Intensity ratios must be within 15% of the theoretical value.

14.2.1.2. The signal to noise of the peak versus the background noise must be >2.5:1.

14.2.1.3. No PCDF peak may have a co-eluting peak in the mass window monitored for polychlorinated diphenylethers.

14.2.1.4. The peak elutes within the retention time determined from the analysis of the column performance window mix standard.

14.3. Data Processing

14.3.1. Data is collected using MassLynx Version 4.0 or Xcalibur Version 2.0 software. The software is run on personal computers running Microsoft Windows XP.

14.3.2. The raw data files are imported into the Avalon (Version 3.0) data processing program for integration. Information on how to use Avalon is available in the Avalon manual that can be accessed on the HRMS group computers. Also, since the DB-5MS capillary column gives partial resolution of 2,3,7,8-TCDF isomer (typically 30-40% valley or less), second column confirmation analyses are only performed if co-elution is exhibited or based upon project requirements. If 25% valley is achieved no further confirmation is required.

14.3.2.1. The confirmation is required for all samples exhibiting positive detections for 2,3,7,8-TCDF for samples from WIDNR.

14.3.3. Note that the window mixture does not need to be queued. Visually inspect the chromatographic data to ascertain the elution times of the first and last eluting isomers of each congener class and chromatographic resolution.

14.3.4. With the elution time information recorded, adjust the method file times so that the group changes occur at points between the elution time of the last isomer of a given class and the first isomer of the following class. The first PeCDF isomer is monitored in Group 1 with the group change set approximately 30 seconds later.

14.4. Calculations

14.4.1. Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for each congener using Equation 1.

Equation 1

$$\%RSD = \frac{SD}{\overline{X}} x100$$

Where:
RSD = Relative standard deviation.

SD = Standard deviation of average RFs for a compound
$\overline{X}$ = Mean of 5 initial RFs for a congener

14.4.2. The standard deviation is calculated following Equation 2.

Equation 2

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_1 - \overline{RF}\right)^2}{n-1}}$$

Where:
RF_1 = Each individual response factor
$\overline{RF}$ = Mean of the Response Factor
n = The total number of values

14.4.3. Calculate the percent difference using Equation 3.

Equation 3

$$\%Difference = \frac{RF_1 - RF_c}{RF_1} x100$$

Where:
RF_1=Average response factor from initial calibration.
RF_c=Response factor from current verification check standard

14.4.4. The PCDD/PCDF isomers (native or labeled) are quantified by comparison of their responses to those of the corresponding/appropriate labeled standard. Relative response factors are calculated from analyses of standard mixtures containing representatives of each of the PCDD/PCDF congener classes at five concentration levels, and each of the internal and recovery standards at one concentration level. The PCDD/PCDF response factors are calculated by comparing the sum of the responses from the two ion masses monitored for each chlorine congener class to the sum of the responses from the two ion masses of the corresponding isotopically labeled standard. The formula for the response factor calculation is:

Equation 4

$$Rf = \frac{Aa \times Qs}{As \times Qa}$$

Where:

Rf = Response factor
Aa = Sum of integrated areas for analyte
Qs = Quantity of labeled standard
As = Sum of integrated areas for labeled standard
Qa = Quantity of analyte

14.4.5. The levels of PCDD/PCDF in the samples are quantified using the following equation:

Equation 5

$$C = \frac{An \times Qis}{Ais \times W \times Rf}$$

Where:

C = Concentration of target isomer or congener class
An = Sum of integrated areas for the target isomer or congener class
Qis = Quantity of labeled internal standard added to the sample
Ais = Sum of integrated areas for the labeled internal standard
W = Sample amount (dry weight for soil samples)
Rf = Response factor

14.4.6. The levels of interferences in samples are quantified using the following equation:

Equation 6

$$EMPC = \frac{An \times Qis}{Ais \times W \times Rf}$$

Where:
EMPC = Estimated Maximum Possible Concentration of target isomer
An = Sum of integrated areas for the target isomer (Note that the signal from the ion that yields the lowest concentration is used to calculate the secondary signal using the theoretical isotope ratio.)
Qis = Quantity of labeled internal standard added to the sample
Ais = Sum of integrated areas for the labeled internal standard
W = Sample amount (dry weight for soil samples)
Rf = Response factor

14.4.6.1. An Estimated Detection Limit (EDL), based on the signal to noise ratio of the noise level of the ion of interest versus the appropriate standard, is calculated for each sample and isomer. The equation used for calculating the EDL is:

Equation 7

$$EDL = \frac{Hn \times Qis \times 2.5}{His \times W \times Rf}$$

Where:
EDL = Estimated Detection Limit
Hn = Sum of noise heights for target isomer
Qis = Quantity of labeled internal standard added to the sample
His = Sum of signal heights from labeled internal standard
W = Initial sample weight or volume
Rf = Response factor

Note: If a signal is present which does not meet the ion ratio requirement but is greater than 2:5:1 S/N, the 2.5 factor is omitted for that ion mass.

14.4.7. A quantitation limit equal to the concentration of the lowest calibration standard is used for this method and is calculated as follows:

Equation 8

$$QL = \frac{C \times V}{W}$$

Where:
QL = Quantitation Limit
C = Concentration of lowest level standard
V = Volume of final extract
W = Initial sample weight (dry weight for soil samples) or volume

14.4.7.1. Isomers present below the QL are reported as not detected at the QL. If the calculated EDL is above the QL for any given isomer, the signal to noise based EDL is reported for that isomer. If requested by a client, the EDL values may be be reported for all analytes. Any positive values below the concentration of the lowest calibration standard must be flagged "J" as estimated values.

14.4.7.2. The recovery of the 2,3,7,8-TCDD-$^{37}Cl_4$ enrichment efficiency standard and each $^{13}C_{12}$-labeled internal standard, relative to either 1,2,7,8-TCDD-$^{13}C_{12}$ or 1,2,3,7,8,9-HxCDD-$^{13}C_{12}$, is calculated using the following equation:

Equation 9

$$\%R = \frac{Ais \times Qrs \times 100}{Rfr \times Ars \times Qis}$$

Where:
%R = Percent recovery of labeled internal standard
Ais = Sum of integrated areas of labeled internal standard
Qrs = Quantity of recovery standard
Ars = Sum of integrated areas of recovery standard
Rfr = Response factor of the specific labeled internal standard relative to the recovery standard
Qis = Quantity of the labeled internal standard added to the sample.

14.4.8. Calculate the %Difference using Equation 10.

Equation 10

$$\%Difference = \frac{RF_1 - RF_c}{RF_1} x100$$

Where:
RF_1=Average response factor from initial calibration.
RF_c=Response factor from current verification check standard

14.4.9. Calculate the %recovery using Equation 11 and the RPD using Equation 12.

Equation 11

$$\text{Percent Recovery} = \frac{C_q}{C_a}(100)$$

Where,
C_q=Quantitated concentration of compound *x* in ppbv;
C_a=Actual concentration of compound *x* in ppbv.

Equation 12

$$RPD = \frac{|R1-R2|}{\frac{R1+R2}{2}}(100)$$

where,
R1=result for sample 1
R2=result for sample 2

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See tables in section 11 & 13.

16. Corrective Actions for Out-of-Control Data

16.1. See tables in section 11 & 13.

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

17.1. If not specifically listed in the table in section 11 & 13, the contingencies are as follows. If there is no additional sample volume to perform re-analyses, all data will be reported as final with applicable qualifiers. If necessary, an official case narrative will be prepared by the Quality Manager, Project Manager or analytical staff. For Ohio VAP, if requirements specified in this SOP are not met, Pace Analytical will narrate any potential bias or justification in the project narrative on the final report. Additional narratives are provided as needed. Pace may have the need to narrate potential bias in the event of instrument failure, limited sample volume, report revisions or matrix interferences.

18. Method Performance

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

18.2. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually (per the method) per S-MN-Q-269 – Determination of Limit of Detection and Limit of Quantitation (or equivalent replacement) for each matrix per instrument.

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-MN-Q-279 - Training and Employee Orientation (or equivalent replacement).

18.4. **Periodic performance evaluation (PE)** samples are analyzed to demonstrate continuing competence per SOP S-MN-Q-258 – Proficiency Testing Program (or equivalent replacement). Results are stored in the QA office.

19. Method Modifications

19.1. 8290/8290A Table of Modifications

8290 section	8290A section	Method	Pace SOP
1.2	1.2	8280 Analyses	High level samples are not automatically analyzed by Method 8280.
2.7	2.7	Standards	Method 1613/DLM2.0 standards are substituted for those described in Method 8290.
3.4/4.2	4.4	Second column confirmations	Confirmations are not performed unless specifically required for a project. (Required for Wisconsin Samples)
11.3.1	5.5.1	Samples weighed in hood	Sample may be homogenized in a hood and weighed outside of the hood
7.5	11.5	Chromatographic columns	The sizes for some columns may vary from those listed
4.3.27	6.3.27	Rotary evaporator for concentration	Other options used for concentration
4.2	6.2	DB-5 column specified	May substitute a DB-5MS column
5.2	7.3.3	Silica activated at 180 C	May be activated at 400 C
7.5	11.5	Acid or basic silica options	Neutral silica may be substituted
5.7	7.8	Column performance mix	May be combined with CS-3
7.6	11.6	GC program	The GC program does not match the one in the method
7.8.4.1	11.8.4.1	Minimum retention time	Shorter retention times may be used due to advances in chromatographic columns. This does not apply to DLM2.0.
7.4.5.2	11.4.5.2	Aqueous percent solids	Percent solids determinations are not performed on samples obviously containing less than 1% solids.
7.4.5.1	11.4.5.1	Marking bottle volumes	Since weights are used for sample calculations, the sample volume is not marked.
7	11	Solvent volumes for extraction	Volumes used for sample extraction may vary from those in the method.
7.3.3	8.7	Lipid determination	Lipids may otherwise be determined as described in attachment IX
7.5	11.5	Extract cleanup	Cleanup column preparation and elution volumes were modified from those

			described in this method.
8.4	--	Laboratory performance	QC outliers may sometimes be flagged and reported depending on project requirements.
3.0	4.0	Interferences	The presence of interferences may be flagged and narrated.
7.9.3	--	Dilution	Samples with levels above the calibration range may be diluted.

19.2. 1613B Table of Modifications

1613B Method	**Pace SOP**
2.1.1.2+ Particulate filtered	Particulate is separated by centrifuge
2.1.2+ SDS used for extraction	Soxhlet is optional substitute for SDS
4.2.2 Glassware washing	Glassware wash sequence is modified
4.2.4 Pre-extraction with toluene	Methylene chloride is an optional substitute for toluene
5.3.1 Samples weighed in hood	Sample are homogenized in a hood and weighed outside of the hood
6.1.1 Bottles are cleaned	Pre-cleaned bottles are an optional substitute
6.7 GPC cleanup	GPC is not currently available at this facility
6.7.4 Chromatographic columns	Some column size varies from those listed
6.8 Rotary evaporator for concentration	Other options used for concentration
6.9 DB-5 column specified	Optionally substitute a DB-5MS column
7.5 Silica activated at 180 C	Silica activated at 400 C
7.5 Acid or basic silica options	Neutral silica is an optional substitute
7.15 Column performance mix	Optionally combined with CS-3
8.2 Solids stored frozen	Stored at 0-6 C
9.5.1 Order of analysis	Blanks are treated like samples and analyzed at any point in a sequence. Some type of blank must be analyzed before samples to demonstrate that the system is clean.
10.1.1 GC program	The GC program does not match the one in the method
10.2.4 Minimum retention time	Advances in chromatographic columns allow shorter retention times.
11.2.1 Aqueous percent solids	Percent solids determinations are not performed on samples obviously containing less than 1% solids.
11.4.2 Marking bottle volumes	Since weights are used for sample calculations, the sample volume is not marked.
12.1 Solvent volumes for extraction	Some sample extraction volumes vary from those in the method.
12.4.1.9 Lipid determination	Lipids are otherwise determined and described in the Lipid Determination SOP.
13. Extract cleanup	Cleanup column preparation and elution volumes were modified from those described in this method. The columns more closely resemble those from Method 8290A.
15. Laboratory performance	Depending on project requirements, QC outliers are sometimes flagged and reported.
16.5 Second column confirmations	Confirmations are not performed unless specifically required for a project.
16.6/18.3 Interferences	The presence of interferences is flagged and narrated (usually per functional group.)
17.5 Dilution	Samples with levels above the calibration range are diluted.
17.6.1.4.1 Reporting limit	Results below the calibration range are reported and flagged as estimated.

19.3. Any modifications made for DLM2.0 need to be approved by the client prior to sample analysis.

20. Instrument/Equipment Maintenance and Troubleshooting

20.1. There is no set schedule for the maintenance listed in this section. It is performed on an as needed basis. Regular preventative maintenance is performed by Pace employees or by the instrument manufacturer. If the instrument needs to be vented, do the following in this order: close the analyzer isolation valve, turn off the source ion gauge, close the source isolation valve, close all source rough pump valves, and allow air into the source chamber through the bleed valve while watching vacuum gauges to ensure leakage does not occur. If any leakage is seen, close the bleed valve and open the main roughing pump valve. Determine the cause of the problem and correct.

20.2. The rough pump oil must be changed if the pump fails to produce a vacuum lower than 10^{-1} mbar or if the pump oil becomes excessively dark. To do so, turn off the ion gauge, isolate and turn off the diffusion pump and allow it to cool. When the diffusion pump is cool, isolate and turn off the rough pump. Now drain the oil into a waste container and recap the drain. Add oil up to the full line and turn

on the pump. When the gurgling sound stops, open the valve to pump on the instrument. After several minutes, turn on the diffusion pump. Wait another 10-15 minutes and turn on the ion gauge. If it is a source linked pump, the source needs to be evacuated.

20.3. Helium gas is used as the carrier gas for HRMS instruments. When this cylinder pressure falls below 500 psi, the tank must be replaced.

20.4. The chromatographic column used for these analyses is the DB-5MS in a 60 meter length. As with any column, these degrade in time. Once this degradation reaches the point where EPA Method 8290 criteria are not met, the column needs to be replaced. Similar results are required for the DB-225 confirmation column.

20.5. The injector liner and baseplate require periodic cleaning or replacement. This maintenance is performed either as a preventative measure or when analyte response factors indicate that injector maintenance is required. A low response factor for the heavier labeled analytes is a typical indicator that injector maintenance is required.

20.6. Air leaks are a common source of problems in mass spectrometry. If the system seems unstable or shows arching, the first step is to check for air leaks. This is done by comparing the signal at m/z 28 to historic levels or by monitoring the mass of a gas or solvent that is then applied to potential leaking locations. Correct any leaks before proceeding to other measures.

20.7. Source/ion volume cleaning is also be done either as a preventative measure or to correct issues with instrument operation. Source cleaning is performed when tuning parameters no longer offer the desired effect, when arcing occurs, or for a number of other reasons. Instructions for removing, cleaning and reassembly of the source are provided in the instrument operation manuals.

20.8. All maintenance must be documented. Routine maintenance, such as injector maintenance, ion volume cleaning, etc. is recorded in the instrument run log. Other 'major' maintenance is documented in the maintenance log that is also incorporated into the log book.

21. Troubleshooting

21.1. Refer to section 20.

22. Safety

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

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

22.3. The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Therefore, all PCDDs and PCDFs must be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and who understand the risks associated with this procedure.

22.4. Neat PCDDs and PCDFs require the use of respirators and are <u>not</u> to be handled in the laboratory.

22.5. All samples analyzed at the Minnesota laboratory are held until analytical results have been reported. Samples containing PCDD/PCDFs above the allowable levels are labeled, segregated, and disposed of by personnel trained in handling toxic waste. Similarly grossly contaminated waste items including pipette tips and other laboratory equipment are segregated, collected in lined waste containers, properly labeled, and disposed of in accordance with hazardous waste regulations.

22.6. Laboratory staff must wipe down a representative area of specified fume hoods at least annually using pre-sterilized gauze and hexane. These wipes must be analyzed according to this method to ensure that

good laboratory practices are observed at all times. The results of the wipes must be archived for reference.

23. Waste Management

23.1. All laboratory waste are managed and disposed in accordance with all federal, state, and local laws and regulations. Procedures for handling waste generated during this analysis are addressed in S-MN-S-003 - Waste Handling and Management (or equivalent replacement).

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

24. Pollution Prevention

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

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. Department of Defense (DoD) Quality Systems Manual- most current version.

25.5. USEPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Method 8290, September 1994.

25.6. USEPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Update 4, Method 8290A, February, 2007.

25.7. USEPA Method 1613: Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS (September 1997, Revision B).

25.8. USEPA Analytical Services Branch: Analysis of Chlorinated dibenzo-p-dioxins (CCDs) and Chlorinated Dibenzofurans (CDFs), Method DLM2.0, May 2005.

25.9. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Online, July 2014, Revision 4, Method 8000D.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. ATTACHMENT I – Dioxin Extraction Worksheet (example)

26.2. ATTACHMENT II – GC Program (example)

26.3. ATTACHMENT III – MS Acquisition Program (example)

26.4. ATTACHMENT IV – Method 8290 Analyte List

26.5. ATTACHMENT V – 1613B Acceptance Criteria

26.6. ATTACHMENT VI – Food and Feed Extraction Amounts

26.7. ATTACHMENT VII - Theoretical Ion Abundance Ratios and QC limits

26.8. ATTACHMENT VIII – Additional Requirements for DLM2.0

26.9. ATTACHMENT IX - Process for Lipid Determination

27. Revisions

Document Number	Reason for Change	Date
S-MN-H-001Rev.28	Updated to LLC throughout document Removed uncontrolled	6Jul2017

	Added "Copies without a distribution number below are considered uncontrolled" to the statement of copyright. Table 9.1 - Updated Updated 10.3/10.6.2/10.8.2/10.9.1/10.10.2/10.13.2/12.12.1.1/12.12.2.1/ 12.12.3.1/12.12.3.10/14.4.9	
S-MN-H-001Rev.29	2.1: Added first sentence "For every project, all field…exactly the same" 2.5: Added notes at end "however for OHIO VAP…are used." Added Sections 3.3 and 3.4. Table 7.1: Added to Solid row, Storage column two sentences at end about Ohio VAP. 7.4: Added last sentence for Ohio VAP. 7.5: Added "or equal to" and "in darkness" Table 9.1: Removed Butanol row, updated typos, and added "(for reagents" to Fisher column heading. Updated from Butanol to Acetone in the following Sections: 10.3, 10.8.2, 10.9.1, 10.10.2, 10.13.2. Updated to a new Section 10.5.1. 10.5.3: Updated to "After sonication, transfer the solution noted above into a pre-rinsed vial…" from "pipette the compounds noted above into a pre-rinsed 2-dram vial…" Removed Sections 10.6.2 through 10.6.7. 10.6.2: changed 20uL to 100uL, added "MB, LCS...in the batch" 10.7.1: Added "and therefore may stand as an ICV if one is required." Edited 10.8.2 volumes and concentration. Added Section 10.8.7. Converted Section 10.9 to a table format. Table 11.1, ICAL row: Added clarifications for Ohio VAP, added RSE paragraph in criteria, added "determination of calibration….." in Comments. 11.1.4.1: Added "Failures in the laboratory QC will result in re-extraction of the associated batch" to the first Note. Added 12.3.1.5 and all subsections for WI. 12.5.1.5: edited to just abbreviation for QC. 12.13.1.5: edited to "at < or equal to" instead of "at approximately" Table 13.1: MB row Component column to "Spike 100 uL…" instead of 20, LCS row Component column to "Spike 100uL…" instead of "20" "and 40uL of the native instead of 10uL (or 20uL of 2x dilution)". Also clarified Ohio VAP requirements. MB row Acceptance Criteria column added "For Wisconsin…." 13.1.1: Added the following "spiked with 40uL of 5-150ng/mL native analyte solution, and 100ul of Internal standard solution at 20-40mg/ml" and "spiked as the LCS above" for the LCSD. 17.1: Added "For Ohio VAP…" sentences at the end. Added reference 25.9.	07Aug2017

ATTACHMENT I – Dioxin Extraction Worksheet (example)

Dioxin | **Water** | **Sep Funnel** | **EB-15245**

QC Matrix Lot #: _____
Time of Spiking: _____
Balance: 10BAL2

Extract Solvents:
Toluene Lot # _____
Hexane Lot # _____
MeCl Lot # _____

Extraction On (Date/Time): 08/27/14 14:00
Extraction Off (Date/Time): 08/27/14 20:00

Standards	Name/ID	Amount	Initial	Witness	Expiration Date
Internal Std.	FS-I-9966-126	20	KH	CMB	07/18/15
Native	FS-N-9966-133	20	KH	CMB	08/07/15
Cl37 Std.	DWCL4-9966-135	250	MF		07/24/15
Recovery	FS-R-9966-136	10	MF		08/20/15
Tridecane	A0341780	10	MF		
Others	FS-I-9966-131	20			08/05/15

#	Sample ID	Internal Standards	Native Standards	Full Bottle Weight	Empty Bottle Weight	pH/ResCl Check	pH Adjusted	Glassware Set	Location	Comments
1	BLANK-41752	x		1492.1	509.3					Extraction QC
2	LCS-41753	x	x	1494.2	509.0					Extraction QC
3	LCSD-41754	x	x	1503.1	509.4					Extraction QC
4	10278321001	x		1106.5	412.0				Rcving	
5	10278610001	x		1573.6	512.7				Rcving	
6	10278439001	x		1387.7	439.0				Rcving	
7	10278508001	x		1487.7	490.8				Rcving	
8	10278821002	x		1378.5	417.5				10/C10 29	
9	10278998001	x		1384.6	417.2				Rcving	
10	10278808001	x		1433.3	438.5				Rcving	
11	10278808002	x		1423.4	438.4				Rcving	
12	10278808003	x		1436.8	438.8				Rcving	
13	10278808004	x		1442.4	439.2				Rcving	
14	10278846001	x		1558.1	567.3				Rcving	
15	10278978001	x		1573.2	514.6				10/C10 29	
16	10278841001	x		1133.9	390.6				Rcving	
17	10278841002	x		1384.6	391.6				Rcving	
18	10278938001	x		1423.3	436.5				Rcving	
19	10278938002	x		1404.4	431.0				Rcving	
20	92213407002A	x		1362.5	406.6					

Relinquished By: M Felea
Received By: _____
Date: _____

F-MN-H-045-Rev.01, 29May2014

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EB-15245

Batch Notes:

Silica
Initials: TDP
Date: 8/28/2014
Neutral Batch: 1
Basic Batch: 1
Acid Batch: 1
Hexane Lot #: 141255
Dispenser: _____

Acid Base
Sulphuric Acid Lot #: _____
Base Batch: _____

Alumina
Initials: MF
Date: 8/29/2014
Alumina Lot #: 31
Hexane Lot #: 141255
Dispenser: Q193
60% Batch: 1591
Dispenser: HRBT-011

Carbon
Initials: _____
Date: _____
Hexane Lot #: _____
Dispenser: _____
50% Batch: _____
Dispenser: _____
75% Batch: _____
Dispenser: _____
Toluene Lot #: _____
Dispenser: _____
Methanol Lot #: _____
Dispenser: _____

Florisil
Initials: _____
Date: _____
Florisil Lot #: _____
Hexane Lot #: _____
Dispenser: _____
6% Batch: _____
Dispenser: _____

2 of 2

ATTACHMENT I – Dioxin Extraction Worksheet (example)

Dioxin	Tissue	Soxhlet	EB-15250

QC Matrix Lot #:
Time of Spiking:
Balance: 10BAL2

Extract Solvents:
Toluene Lot #
Hexane Lot #
MeCl Lot #

Extraction On (Date/Time): 08/27/14 00:45
Extraction Off (Date/Time):

Standards	Name/ID	Amount	Initial	Witness	Expiration Date
Internal Std.	FS-I-9966-131	20	TDP		
Native	FS-N-9966-133	20	TDP		
Cl37 Std.	DWCL4-9966-135	250	MF		07/24/15
Recovery					
Tridecane					
Others					

#	Sample ID	Internal Standards	Native Standards	Extracted mL or g	Glassware Set	Location	Comments
1	BLANK-41766	x		62.4			Extraction QC
2	LCS-41767	x	x	60.5			Extraction QC
3	LCSD-41768	x	x	60.2			Extraction QC
4	10278349001	x		61.2		Rcving	
5	4099994001	x		20.7		Rcving	
6	4099994002	x		20.1		Rcving	
7	4099994003	x		20.1		Rcving	
8	4099994005	x		16.4		Rcving	
9	4099994006	x		7.2		Rcving	
10	4099994007	x		21.5		Rcving	
11	4099996001	x		20.0		Rcving	
12	4099996002	x		20.2		Rcving	
13	4099996003	x		20.3		Rcving	
14	4099996004	x		14.8		Rcving	
15	4099996005	x		20.6		Rcving	
16	4099996006	x		20.5		Rcving	
17	4099996007	x		20.6		Rcving	
18	4099996008	x		20.4		Rcving	

Relinquished By: Received By: Date:

F-MN-H-046-Rev.00, 16May2014

1 of 2

Batch Notes: EB-15250

Silica
Initials MF
Date 9/3/2014
Neutral Batch 10667-2N
Basic Batch 10667-2B
Acid Batch 10667-2A
Hexane Lot # 141255
Dispenser Q193

Alumina
Initials MF
Date 9/4/2014
Alumina Lot # 31
Hexane Lot # 141255
Dispenser Q193
60% Batch 1592
Dispenser HRBT-011

Carbon
Initials
Date
Hexane Lot #
Dispenser
50% Batch
Dispenser
75% Batch
Dispenser
Toluene Lot #
Dispenser
Methanol Lot #
Dispenser

Florisil
Initials
Date
Florisil Lot #
Hexane Lot #
Dispenser
6% Batch
Dispenser

Acid Base
Sulphuric Acid Lot #
Base Batch

Be sure to include Witness initials, and Expiration dates. This sheet is just an example, but is not in fact complete.

ATTACHMENT II – GC Program (example)

Inlet Method Report MassLynx 4.1 **Page 1 of 2**

Method File: C:\MassLynx\Default.pro\Acqudb\dioxfur
Last Modified: Tuesday, October 13, 2009 12:12:43 Central Daylight Time

Printed: Tuesday, October 13, 2009 12:33:55 Central Daylight Time

HP6890 GC Column 1

Column Length(m)	30.00
Column Diameter(um)	250.00
Film Thickness(um)	0.25
Carrier Gas	HELIUM
Mode	Constant Pressure
Inlet	Front Inlet

HP6890 GC Column 2

Column Length(m)	60.00
Column Diameter(um)	250.00
Film Thickness(um)	0.25
Carrier Gas	HELIUM
Mode	Constant Flow
Inlet	Back Inlet

HP6890 GC Oven Parameters

Maximum Oven Temp(°C)	350.0
Equilibrium Time(min)	0.3

HP6890 GC Oven Ramp

Initial Temperature(°C) 180.0

Time At initial temperature(mins) 3.00

Time(min)	Rate(°C/min)	Temp(°C)
20.0	12.0	226.0
3.5	6.0	320.0
0.0	0.0	24.0
0.0	0.0	24.0
0.0	0.0	24.0
0.0	0.0	24.0

HP6890 GC Pressure 1

Initial Pressure(kPa) 0.1

Time(min)	Rate(kPa/min)	Final Pres(kPa)
0.0	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0

HP6890 GC Flow 2

Initial Flow(ml/min) 1.0

Time(min)	Rate(ml/min^2)	Final Flow(ml/min)
0.0	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0

HP6890 PTV Inlet Cryogenic Parameters

Cryo Cooling Enabled
Ambient Temperature(°C) 40.0

Back Inlet
Split/Splitless: Splitless Mode

Initial Temperature(°C)	280.0
Initial Pressure(kPa)	1.0
Purge Pressure(kPa)	20.0
Purge Time(min)	1.00

ATTACHMENT III - MS Acquisition Program (example)

AutoSpec Experiment Report Page 1

Experiment File: c:\masslynx\default.pro\acqudb\dioxfur.exp

Printed : Thu Jan 13 10:26:46 2005

Name	Default Experiment
Creation Time	Thu 13 Jan 2005 10:06:51
Instrument Identifier	Autospec
Version Number	1.0
Duration (min)	46.0
Solvent Delay Divert Valve Enabled	0
Number Of Functions	5

Function 1 : Voltage SIR, Time 12.00 to 29.20, Mass 303.90 to 409.80 EI+

Type	Voltage SIR			
Data Format	Centroid			
Ion Mode	EI Mode			
Polarity	Positive			
Parameter File	C:\Masslynx\Default.pro\ACQUDB\M488MW1_10K.ipr			
Start Mass	303.9			
End Mass	409.8			
Start Time (min)	12.0			
End Time (min)	29.2			
Scan Time (sec)	915.0			
InterScan Time (sec)	0.1			
Scans To Sum	1000000			
Number of channels	15			
Channel 0 Mass	303.901600	50.00	15.00	
Channel 1 Mass	305.898700	50.00	15.00	
Channel 2 Mass	315.941800	50.00	15.00	
Channel 3 Mass	317.938900	50.00	15.00	
Channel 4 Mass	318.979200	50.00	15.00	
Channel 5 Mass	318.979200	50.00	15.00	LM
Channel 6 Mass	319.896500	50.00	15.00	
Channel 7 Mass	321.893600	50.00	15.00	
Channel 8 Mass	327.884700	50.00	15.00	
Channel 9 Mass	331.936700	50.00	15.00	
Channel 10 Mass	333.933800	50.00	15.00	
Channel 11 Mass	339.859700	50.00	15.00	
Channel 12 Mass	341.856700	50.00	15.00	
Channel 13 Mass	375.836400	20.00	15.00	
Channel 14 Mass	409.797400	20.00	15.00	

Function 2 : Voltage SIR, Time 29.20 to 34.80, Mass 339.86 to 409.80 EI+

Type	Voltage SIR
Data Format	Centroid
Ion Mode	EI Mode
Polarity	Positive
Parameter File	C:\Masslynx\Default.pro\ACQUDB\M488MW2_10K.ipr
Start Mass	339.9
End Mass	409.8
Start Time (min)	29.2
End Time (min)	34.8
Scan Time (sec)	840.0
InterScan Time (sec)	0.1
Scans To Sum	1000000
Number of channels	12

ATTACHMENT III (Continued)

AutoSpec Experiment Report Page 1

Experiment File: c:\masslynx\default.pro\acqudb\dioxfur.exp

Printed : Thu Jan 13 10:26:46 2005

Name	Default Experiment
Creation Time	Thu 13 Jan 2005 10:06:51
Instrument Identifier	Autospec
Version Number	1.0
Duration (min)	46.0
Solvent Delay Divert Valve Enabled	0
Number Of Functions	5

Function 1 : Voltage SIR, Time 12.00 to 29.20, Mass 303.90 to 409.80 EI+

Type	Voltage SIR			
Data Format	Centroid			
Ion Mode	EI Mode			
Polarity	Positive			
Parameter File	C:\Masslynx\Default.pro\ACQUDB\M488MW1_10K.ipr			
Start Mass	303.9			
End Mass	409.8			
Start Time (min)	12.0			
End Time (min)	29.2			
Scan Time (sec)	915.0			
InterScan Time (sec)	0.1			
Scans To Sum	1000000			
Number of channels	15			
Channel 0 Mass	303.901600	50.00	15.00	
Channel 1 Mass	305.898700	50.00	15.00	
Channel 2 Mass	315.941800	50.00	15.00	
Channel 3 Mass	317.938900	50.00	15.00	
Channel 4 Mass	318.979200	50.00	15.00	
Channel 5 Mass	318.979200	50.00	15.00	LM
Channel 6 Mass	319.896500	50.00	15.00	
Channel 7 Mass	321.893600	50.00	15.00	
Channel 8 Mass	327.884700	50.00	15.00	
Channel 9 Mass	331.936700	50.00	15.00	
Channel 10 Mass	333.933800	50.00	15.00	
Channel 11 Mass	339.859700	50.00	15.00	
Channel 12 Mass	341.856700	50.00	15.00	
Channel 13 Mass	375.836400	20.00	15.00	
Channel 14 Mass	409.797400	20.00	15.00	

Function 2 : Voltage SIR, Time 29.20 to 34.80, Mass 339.86 to 409.80 EI+

Type	Voltage SIR
Data Format	Centroid
Ion Mode	EI Mode
Polarity	Positive
Parameter File	C:\Masslynx\Default.pro\ACQUDB\M488MW2_10K.ipr
Start Mass	339.9
End Mass	409.8
Start Time (min)	29.2
End Time (min)	34.8
Scan Time (sec)	840.0
InterScan Time (sec)	0.1
Scans To Sum	1000000
Number of channels	12

ATTACHMENT III (Continued)

AutoSpec Experiment Report Page 3

Experiment File: c:\masslynx\default.pro\acqudb\dioxfur.exp

Printed : Thu Jan 13 10:26:46 2005

Channel 0 Mass	380.976000	50.00	20.00	
Channel 1 Mass	380.976000	50.00	20.00	LM
Channel 2 Mass	407.781800	50.00	20.00	
Channel 3 Mass	409.778800	50.00	20.00	
Channel 4 Mass	415.000000	30.00	20.00	
Channel 5 Mass	417.825000	50.00	20.00	
Channel 6 Mass	419.822000	50.00	20.00	
Channel 7 Mass	423.776700	50.00	20.00	
Channel 8 Mass	425.773700	50.00	20.00	
Channel 9 Mass	430.000000	30.00	20.00	
Channel 10 Mass	435.816900	50.00	20.00	
Channel 11 Mass	437.814000	50.00	20.00	
Channel 12 Mass	479.716500	50.00	20.00	

Function 5 : Voltage SIR, Time 43.00 to 46.00, Mass 429.97 to 513.68 EI+

Type	Voltage SIR
Data Format	Centroid
Ion Mode	EI Mode
Polarity	Positive
Parameter File	C:\Masslynx\Default.pro\ACQUDB\M488MW5_10K.ipr
Start Mass	430.0
End Mass	513.7
Start Time (min)	43.0
End Time (min)	46.0
Scan Time (sec)	875.0
InterScan Time (sec)	0.1
Scans To Sum	1000000

Number of channels	13			
Channel 0 Mass	429.972800	50.00	15.00	
Channel 1 Mass	430.972800	50.00	15.00	LM
Channel 2 Mass	430.972800	50.00	15.00	
Channel 3 Mass	441.742800	50.00	15.00	
Channel 4 Mass	443.739800	50.00	15.00	
Channel 5 Mass	453.783000	50.00	15.00	
Channel 6 Mass	455.780100	50.00	15.00	
Channel 7 Mass	457.737700	50.00	15.00	
Channel 8 Mass	459.734700	50.00	15.00	
Channel 9 Mass	465.000000	80.00	15.00	
Channel 10 Mass	469.777900	50.00	15.00	
Channel 11 Mass	471.774900	50.00	15.00	
Channel 12 Mass	513.677500	50.00	15.00	

ATTACHMENT IV - Method 8290 Analyte List

Compound	CAS Registry No.[3]
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin (PeCDD)	40321-76-4
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	39227-28-6
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	57653-85-7
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin (HxCDD)	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin (HpCDD)	35822-46-9
1,2,3,4,5,6,7,8-Octachlorodibenzo-*p*-dioxin (OCDD)	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	51207-31-9
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	57117-41-6
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	57117-31-4
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	70648-26-9
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	72918-21-9
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	60851-34-5
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	55673-89-7
1,2,3,4,5,6,7,8-Octachlorodibenzofuran (OCDF)	39001-02-0
Total Tetrachlorodibenzo-*p*-dioxin (TCDD)	41903-57-5
Total Pentachlorodibenzo-*p*-dioxin (PeCDD)	36088-22-9
Total Hexachlorodibenzo-*p*-dioxin (HxCDD)	34465-46-8
Total Heptachlorodibenzo-*p*-dioxin (HpCDD)	37871-00-4
Total Tetrachlorodibenzofuran (TCDF)	55722-27-5
Total Pentachlorodibenzofuran (PeCDF)	30402-15-4
Total Hexachlorodibenzofuran (HxCDF)	55684-94-1
Total Heptachlorodibenzofuran (HpCDF)	38998-75-3

[3] Chemical Abstract Service Registry Number

ATTACHMENT V – 1613B Acceptance Criteria

A. Acceptance Criteria for Performance Tests When All CDDs/CDFs are Tested[1]

CDD/CDF	Test Conc. (ng/mL)	s (ng/mL)	IPR[2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3-12.9	6.7-15.8	7.8-12.9
2,3,7,8-TCDF	10	2.0	8.7-13.7	7.5-15.8	8.4-12.0
1,2,3,7,8-PeCDD	50	7.5	38-66	35-71	39-65
1,2,3,7,8-PeCDF	50	7.5	43-62	40-67	41-60
2,3,4,7,8-PeCDF	50	8.6	36-75	34-80	41-61
1,2,3,4,7,8-HxCDD	50	9.4	39-76	35-82	39-64
1,2,3,6,7,8-HxCDD	50	7.7	42-62	38-67	39-64
1,2,3,7,8,9-HxCDD	50	11.1	37-71	32-81	41-61
1,2,3,4,7,8-HxCDF	50	8.7	41-59	36-67	45-56
1,2,3,6,7,8-HxCDF	50	6.7	46-60	42-65	44-57
1,2,3,7,8,9-HxCDF	50	6.4	42-61	39-65	45-56
2,3,4,7,8,9-HxCDF	50	7.4	37-74	35-78	44-57
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65	35-70	43-58
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56	41-61	45-55
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63	39-69	43-58
OCDD	100	19	89-127	78-144	79-126
OCDF	100	27	74-146	63-170	63-159
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	20-175	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	22-152	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	21-227	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	21-192	76-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	13-328	77-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	21-193	85-117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-163	85-118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	19-202	76-131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	21-159	70-143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	17-205	74-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	37	29-136	22-176	73-137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	25-166	72-138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	21-158	78-129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28-141	20-186	77-129
$^{13}C_{12}$-OCDD	200	95	41-276	26-397	96-415
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4	3.1-19.1	7.9-12.7

[1] All specifications are given as concentration in the final extract assuming a 20-µL volume.
[2] s = standard deviation of the concentration
[3] X = average concentration

ATTACHMENT V – 1613B Acceptance Criteria (Continued)

B. Acceptance Criteria for Performance Tests When Only Tetra Compounds are Tested [1]

CDD/CDF	Test Conc. (ng/mL)	s (ng/mL)	IPR[2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.7	8.7-12.4	7.3-14.6	8.2-12.3
2,3,7,8-TCDF	10	2.0	9.1-13.1	8.0-14.7	8.6-11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	35	32-115	25-141	85-117
$^{13}C_{12}$-2,3,7,8-TCDF	100	34	35-99	26-126	76-131
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.4	4.5-13.4	3.7-15.8	8.3-12.1

C. Labeled Compound Recovery in Samples When All CDDs/CDFs are Tested

CDD/CDF	Test Conc. (ng/mL)	Labeled Compound Recovery (ng/mL)[1]	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25-164	25-164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24-169	24-169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25-181	25-181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24-185	24-185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21-178	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32-141	32-141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	28-130	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26-152	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26-123	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29-147	29-147
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	28-136	28-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23-140	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28-143	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26-138	26-138
$^{13}C_{12}$-OCDD	200	34-313	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5-19.7	35-197

[1] All specifications are given as concentration in the final extract assuming a 20-µL volume.
[2] s = standard deviation of the concentration
[3] X = average concentration

ATTACHMENT V – 1613B Acceptance Criteria (Continued)

D. Labeled Compound Recovery in Samples When Only Tetra Compounds are Tested

CDD/CDF	Test Conc. (ng/mL)	Labeled Compound Recovery (ng/mL)[1]	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	31-137	31-137
$^{13}C_{12}$-2,3,7,8-TCDF	100	29-140	29-140
$^{37}Cl_4$-2,3,7,8-TCDD	10	4.2-16.4	42-164

[1] All specifications are given as concentration in the final extract assuming a 20-µL volume.
[2] s = standard deviation of the concentration
[3] X = average concentration

ATTACHMENT VI – Food and Feed Extraction Amounts

Food and Feed Extraction Amounts, 10 µL Final Volume

Food or Feed Type	EU Limit	Target PQL	Amount	Weight Basis
Meat, Ruminants	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Meat, Poultry	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Meat, Pig	0.6 pg/g	0.12 pg/g	35 grams	Lipid
Meat, Liver	4.0 pg/g	0.8 pg/g	10 grams	Lipid
Fish, Muscle	3.0 pg/g	0.6 pg/g	15 grams	Lipid
Milk/Milk Products	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Eggs/Egg Products	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Oils & Fats, Ruminants	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Oils & Fats, Poultry	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Oils & Fats, Pigs	0.6 pg/g	0.12 pg/g	35 grams	Lipid
Oils & Fats, Mixed	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Vegetable Oil	0.5 pg/g	0.1 pg/g	40 grams	Lipid
Fish Oil	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Fruits	0.4 pg/g	0.08 pg/g	100 grams	Total
Vegetables	0.4 pg/g	0.08 pg/g	100 grams	Total
Cereals	0.4 pg/g	0.08 pg/g	100 grams	Total
Feed Materials, Plant	0.5 pg/g	0.1 pg/g	80 grams	Total
Minerals	0.5 pg/g	0.1 pg/g	80 grams	Total
Animal Fat, Incl. Milk & Eggs	1.2 pg/g	0.24 pg/g	34 grams	Total
Animal Products	0.5 pg/g	0.1 pg/g	80 grams	Total
Fish Oil	4.5 pg/g	0.9 pg/g	10 grams	Total
Fish	1.0 pg/g	0.2 pg/g	40 grams	Total
Compound Feedstuffs	0.4 pg/g	0.08 pg/g	100 grams	Total
Pet Food	1.5 pg/g	0.3 pg/g	28 grams	Total

ATTACHMENT VII - Theoretical Ion Abundance Ratios and QC limits

Theoretical Ion Abundance Ratios and QC Limits				
Number of Chlorine Atoms	**M/Z's Forming Ratio**	**Theoretical Ratio**	**QC Limit[1] Lower**	**Upper**
4[2]	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
5[3]	M/(M+2)	0.61	0.52	.70
6	(M+2)/M+4)	1.24	1.05	1.43
6[4]	M/(M+2)	0.51	0.43	0.59
7	(M+2)/(M+4)	1.05	0.88	1.20
7[5]	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

1 QC limits represent ±15% windows around the theoretical ion abundance ratios.

2 Does not apply to the clean up standard ($^{37}Cl_4$-2,3,7,8-TCDD)

3 used for native PeCDD only

4 used for $^{13}C_{12}$-HxCDF Only

5 used for $^{13}C_{12}$-HpCDF Only

ATTACHMENT VIII – Additional Requirements for DLM2.0

Requirements for DLM2.0 Projects*

Samples must be extracted within 10 days of collection, except for CWA and SDWA waters which are extracted within 7 days. The hold time from extraction to analysis is 30 days.

Retention times from each continuing calibration determination must be within 15 seconds of those from the initial calibration.

The retention time for 1,2,3,4-TCDD must be greater than 25 minutes.

Blank levels must be less than the CS1 concentration, except for OCDD and OCDF that must be less than three times higher than in the CS1.

Sample extracts with concentrations above the calibration range must be diluted to bring the analytes within the calibration range. This does not apply to OCDD or OCDF. The dilutions must be made using the internal standard spiking solution.

Dilutions must be less than 20X. If analytes remain above the calibration range after dilution, the sample extraction must be repeated using a smaller sample aliquot.

Re-extract the affected sample if any internal standard recoveries or isotope ratios are outside target ranges. The ranges are those from Method 1613B.

The criterion for an acceptable initial calibration is that native analytes have relative standard deviations of less than 20%. The range is extended to 35% labeled analytes.

The criterion for an acceptable initial calibration is that native analytes have response factors within 20% of the initial calibration curve. The range is extended to 35% labeled analytes.

The LCS recovery criteria are the statistical ranges from Method 1613, however, up to 3 compounds are allowed to have recoveries outside the specified ranges.

Both the column performance mix and continuing calibration must be run at the beginning and end of each analytical sequence and must pass all method requirements. The ending standard analyses must be injected within 12 hours of the sequence start time.

The method blank must be run in each analytical before any of the associated samples. If samples are analyzed in multiple sequences, the associated method blank is analyzed in each sequence.

* Some of these requirements were also noted in the body of this SOP.

ATTACHMENT IX - Process for Lipid Determination

Option 1: Lipid Determination through Soxhlet Extraction

- Tare 40 mL vials using a four-place balance. Record these tare weights in the percent lipids logbook.
- Record the initial weights used to set up the samples for extraction in the percent lipids logbook.
- After Snyder concentration of extracts, transfer extracts to tared 40 mL vials per applicable method SOP.
- Concentrate the transferred extracts in tared 40 mL vials using a nitrogen evaporator until all solvent has evaporated and only lipid is remaining.
- Record final weights of vials and lipids measured using a four place balance in percent lipids logbook.

Option 2: Lipid Determination Using Methylene Chloride

- Accurately weigh out a 10-gram aliquot of sample material using an analytical balance. Record the weight to four places in the lipids logbook (see Attachment I). Use 10% corn oil mix for the laboratory spike matrix.
- Combine sample aliquot with sodium sulfate and stir until the mixture is free flowing (typically 40-60 grams of sodium sulfate are required).
- Set up the glass column and place a plug of glass wool at the bottom. Check that the stopcock is in the closed position.
- Quantitatively transfer the sample/sodium sulfate mixture to the glass column.
- Add 90-mL of methylene chloride to the column and assure the entire sample has been saturated with the solvent. Allow the column to stand for 10 minutes.
- Weigh a 150 mL glass beaker (or equivalent) using an analytical balance and record the tare weight to four places in the lipids logbook under TW. Place the tared glass beaker under the glass column.
- Open the stopcock to allow the methylene chloride to elute from the column at a rate of approximately one drop per second.
- Allow the methylene chloride in the beaker to evaporate to dryness under ambient conditions.
- Reweigh the beaker containing the dried residue on an analytical balance. Record the final weight (FW) to thousandths in the lipids logbook.

QC Requirements

1. This process requires an analytical balance calibrated to the nearest 0.001 gram
2. One method blank is required with each batch of up to 20 samples. Use solvent only for the method blank to insure the process is free from possible contamination
3. Two laboratory control samples, or one LCS and one Sample Duplicate are required for each batch of lipid determination. Use 10 grams of tissue reference material for the LCS/LCSD.

Appendix B
Field Operating Procedures

APPENDIX B

Field Operating Procedures

Appendix B presents the following CH2M (CH2M) field operating procedures (FOPs) to perform the field investigation within the Munger Landing site in the St. Louis River Area of Concern in Duluth, Minnesota.

FOP Number	Title
FOP-01	Global Positioning System Procedures
FOP-02	Sediment Sampling Vessel Operation and Station Positioning
FOP-03	Recording Field Information on Mudpuppy II
FOP-04	Vibracore Boat Sediment Sampling
FOP-05	Manual Coring Methods
FOP-06	Sediment Surface Dredge (Ponar) Sampling
FOP-07	Mudpuppy II Decontamination Procedures
FOP-08	Geotechnical Field Testing
FOP-09	Field Equipment Cleaning and Decontamination Procedures
FOP-10	Sample Handling, Packaging, and Shipping
FOP-11	Documentation and Chain-of-Custody Procedure
FOP-12	Field Logbook

FIELD OPERATING PROCEDURE-01

Global Positioning System Procedures

Organization: CH2M	Revision: 0	Date: April 2018

Purpose

This FOP provides guidelines for the collection of horizontal coordinates during field activities using a global positioning system (GPS) unit. Accurate surveys of sampling locations and boundaries are necessary in order to determine precise spatial reference points for characterization of site conditions and evolution of the site conceptual model.

Scope

The method described for the collection of horizontal coordinates is applicable to a Trimble R6 GPS receiver or comparable GPS receivers. The Minimum vertical and horizontal accuracies of ± 0.2 foot and ±0.5 feet respectively for this project. To achieve real-time data with a minimum of 1 meter accuracy with no post-processing of data using GPS Pathfinder Office, the following criteria must be met:

- Minimum number of satellites = 4
- Maximum Position Dilution of Precision (PDOP) = 6
- Minimum Signal to Noise Ratio (SNR) = 4
- Minimum elevation = 15 degrees

If any of the above criteria cannot be met because of weather conditions, time of day, or obstructions of the sky such as buildings or foliage resulting in a less than submeter accuracy, the following should be performed:

- Mark the location on the applicable aerial photograph or map and estimate the distance from two known locations and note in the field logbook so that, at a minimum, a general location position can be obtained. The location should also be marked using a weighted buoy or wooden lathe and an additional attempt made prior to demobilizing the field effort.

Equipment and Materials

- Trimble R6 GPS receiver or comparable GPS receiver and compatible data logger
- Field logbook
- Buoy with anchor and rope
- Aerial photograph or map of sampling area

Procedures and Guidelines

1. Assemble and turn on unit in accordance to manufacturer's instructions.
2. Verify that the GPS horizontal datum is set to the World Geodetic System of 1984 or the Universal Transverse Mercator Zone 16, North American Datum of 1983 (NAD83) and the vertical datum is set to North American Vertical Datum of 1988 (NAVD88).
3. Sampling locations will be reported in latitude/longitude and referenced to the World Geodetic System of 1984 or the Universal Transverse Mercator Zone 16, NAD83, with a Minimum vertical and horizontal accuracies of ± 0.2 foot and ±0.5 feet, respectively. Elevations should be referenced to International Great Lakes Datum 1985 (IGLD85).

4. Verify that the GPS is referenced to known survey control monuments (*x*, *y*, and *z*) surrounding the project site within the level of accuracy specified prior to field activities and upon return.
5. Place the GPS antenna over the location where coordinates are to be collected and record coordinates in the field logbook and/or log coordinates into the GPS receiver. If locations are to be logged into the receiver, readings must be collected every 5 seconds for a period of 1 minute (see manufacturer instructions on position logging). The data files recorded for each position must be named including both the sample location identification and date recorded.
6. Download the data from the GPS unit to a personal computer daily record in the field logbook or appropriate field form as they are collected.

Reference

U.S. Environmental Protection Agency (EPA). 2008. *USEPA Interim Guidance for Developing Global Positioning System Data Collection Standard Operating Procedures and Quality Assurance Project Plans, Revision 1.0.* February.

Key Checks and Items

- Charge and check batteries daily.

FIELD OPERATING PROCEDURE-02

Sediment Sampling Vessel Operation and Station Positioning

Organization: CH2M	Revision: 0	Date: February 2018

Precise positioning of station locations is required to meet the sampling goals. Both accuracy (the ability to define position) and repeatability (the ability to return to a sampling station) are essential. Positioning for all surveys will be achieved using a global position system (GPS) capable of locating stations with an accuracy and repeatability of plus or minus 1 meter.

Equipment and Materials

- Sampling and support vessels. Sampling vessel should be equipped with anchors or spuds, a motor, GPS, and applicable health and safety equipment indicated in the health and safety plan (HASP)
- Cellular phone
- Personal protection equipment (rubber or latex gloves, boots, personal flotation device, etc.) as specified in the HASP
- Items needed to document data collection activities, including a field logbook, field forms, and an indelible waterproof pen
- GPS unit

Positioning of the Sampling Vessel

1. Prior to daily departure of the sampling vessel, the sampling crew will be informed of the planned sampling locations and the number of samples required at each location. The sampling team will verify that the GPS is referenced to known survey control monuments (*x*, *y*, and *z*) surrounding the project site prior to departure from the dock or launch ramp and upon returning after sampling activities.
2. Vessel navigation and positioning will be accomplished using GPS methodology.
3. The GPS system antenna will be in a “transit” mount, which will allow it to be removed and manually repositioned over the sampling point to acquire final “as-sampled” *x*, *y* position measurements.
4. After the sampling vessel is anchored or spudded, the sampling team will measure and record the water depth to the top of sediment as detailed in field sampling plan.
5. The above information will be recorded on the sample log form prior to acquisition of the sample. The sample log will also be annotated with the exact sampling location coordinates, date, time, weather and water surface conditions, as well as any relevant other information associated with the acquisition of each sample.

FIELD OPERATING PROCEDURE-03

Recording Field Information on Mudpuppy II

Organization: Cetacean Marine, Inc.	Revision: 1	Date: April 2018

TABLE OF CONTENTS

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes procedures to collect and record field information on board the Research Vessel (R/V) *Mudpuppy II* and associated recording equipment to minimize equipment and user error.

2.0 APPLICABILITY/SCOPE

U.S. EPA's sediment sampling vessel, the R/V *Mudpuppy II*, is utilized by U.S. EPA and Great Lakes partners to sample sediments in rivers, harbors and inland lakes within the Great Lakes watershed. In an effort to prevent unnecessary error in the use of geographical positioning system (GPS) equipment and recording of sample information, Cetacean Marine has developed this SOP for recording field information onboard the R/V *Mudpuppy II*. This SOP should be followed by all project participants supporting the collection of samples on the R/V *Mudpuppy II*. Project participants should refer to the project-specific quality assurance project plan (QAPP) and field sampling plan (FSP) for detailed sampling procedures and requirements.

3.0 DEFINITIONS

DRS	Data Reporting Standard
FSP	Field Sampling Plan
GLLA	Great Lakes Legacy Act
GLNPO	Great Lakes National Program Office
GPS	Global Positioning System
QAPP	Quality Assurance Project Plan

R/V	Research Vessel
SOP	Standard Operating Procedure

4.0 SUMMARY OF METHOD/PROCEEDURE

In order to reduce the possibility of error in collecting field information while sampling on the R/V *Mudpuppy II*, a system of redundancy and procedural guidelines has been established. Field data are hand written in the vessel's log and on field data sheets. In addition, a digital copy of position data is recorded on the vessel's computer. The digital position data file also includes field data that are input by the user at the time of sample collection. This method provides 3 source documents should a discrepancy arise.

5.0 PERSONNEL QUALIFICATION/RESPONSIBILITIES

The Vessel operation contractor should be trained on the use of the navigation system, including the GPS unit and associated hardware. EPA Chief Scientists should attend a standard R/V *Mudpuppy II* introduction training (i.e. attend an annual shakedown or shadow and experienced employee), which includes the use of the data dictionary function in Terra Sync.

6.0 EQUIPMENT AND SUPPLIES

The R/V *Mudpuppy II* uses a Trimble Pro XRS GPS, coupled to a laptop computer running Trimble Terra Sync (V5.41) software to collect position data and GPS Pathfinder Office (V5.6) to post process position data. The vessel also has a dedicated log book. Field data reporting forms are generated for the survey based on information needed.

7.0 REAGENTS AND STANDARDS

N/A

8.0 HEALTH AND SAFETY CONSIDERATIONS

N/A

9.0 INTERFERENCES

Poor satellite geometry due to angle of elevation or physical obstructions (buildings, trees, bridges) can have a significant adverse effect on the accuracy of the position recorded.

10.0 PROCEDURE

At the beginning of each Great Lakes Legacy Act (GLLA) sampling event, the *Mudpuppy II* crew will make the following observations using the vessel's GPS unit:

1. Measure and record latitude and longitude at 2 horizontal control points and record on GPS daily check sheet.

2. Measure and record elevation at 2 vertical control points and record on GPS daily check sheet.
3. Calculate displacement between known position/elevation of control points with observed position/elevation and record on GPS daily check sheet.
4. Establish 3 reference points. Record latitude, longitude, elevation and physical description for each reference point on GPS daily check sheet.

The following site information should be collected and recorded by the Captain in the ship's log each day of sampling:

a. Time departing dock (ship time, military)
b. Start time (ship time, military)
c. End time (ship time, military)
d. Date (mm/dd/yyyy)
e. Cruise from
f. Cruise to
g. Weather (e.g., clear, overcast, rain, snow, hazy, fog, partly cloudy, mostly cloudy) and sea conditions (e.g., windspeed, wave height, other observations)
h. GPS reference station readings (It is recommended that reference station GPS readings are taken each day. Sample locations may not allow for visiting all reference station locations on any given day).

The following site information should be collected and recorded at each sampling station:

1. Vessel's Log Book(filled out by Captain):
    a. Station ID
    b. Anchored/Tied off/Drifting
    c. Time arrived at station (shiptime, military)
    d. Coordinates using primary GPS (degrees, decimal minutes)
    e. Water depth (feet and inches.
    f. Probe depth (feet)
    g. Core tube length/Ponar (feet)
    h. Depth of core penetration (feet)
    i. Length of recovered core (inches)
    j. Comments (e.g., bottom type, reason for moving station, problems encountered, GPS issues)

2. Field Information Form (filled out by EPA, contractor or State personnel):

   Note: Refer to site specific QAPP and FSP for details about required information to be recorded for each sample and example field information form. Great Lakes Legacy Act surveys are to record minimum field data elements as specified in the Great Lakes Legacy Act (GLLA) Data Reporting Standard (DRS). Examples of information to be recorded on the field information form include:

   a. Station ID
   b. GPS coordinates
   c. Type of sample (routine, duplicate, equipment blank)
   d. Sample ID
   e. Date of sample
   f. Time of sample
   g. Sample technique (core, ponar, box core)
   h. Water depth
   i. Probe depth
   j. Depth of penetration
   k. Sample coordinates
   l. Core tube length
   m. Refusal?
   n. Length of recovered core
   o. Percent recovery
   p. Sheen/odor observations.
   q. Sediment color/consistency
   r. Field crew names (first and last name, affiliation)
   s. Other locational information observations.
   t. Sub-sample parameters/collection depths

3. Data dictionaries (filled out by Captain, EPA, contractor or State personnel):

   Each sample location (feature) collected using Terra Sync will have a number of optional data fields that can be added to the electronic record of sample position. Each type (grab, vibracore, probe etc.) of feature will have different data fields. Data fields may replicate data recorded in the Ship's log or field data sheets.

11.0 WASTE MANAGEMENT

N/A

12.0 DATA AND RECORDS MANAGEMENT

Ship logs will be retained indefinitely at R/V *Mudpuppy II* warehouse in Bay City, MI. The entire log book or a particular survey can be scanned and e-mailed upon request at any time. Project files (which include position and data dictionary fields) from Terra Sync and Pathfinder Office will be kept on the *Mudpuppy II* computer and backed up to an external hard drive. Project files may be downloaded and transferred via e-mail or USB flash drive to EPA upon request. EPA will store the project files as part of the electronic project record according to the appropriate EPA retention schedule.

The Support contractor will typically scan any loose data sheets and attach them to the final data summary report submitted to EPA. The electronic record will be stored and maintained according to their contract requirements.

13.0 QUALITY CONTROL & QUALITY ASSURANCE

The GLLA DRS's Locational Data Checklist and Metadata Recording Form must be used for GLLA projects. This form specifies the following data collection requirements:

1. Settings:
   a. Minimum of four satellites
   b. Positional dilution of precision (PDOP) ≤ 6
   c. Satellite elevation ≥ 15 degrees above the horizon
   d. A minimum signal-to-noise ratio based on the model recommendations
2. Record:
   a. Datum
   b. Any variations from standard settings (see note below)
   c. Any environmental anomalies (tall buildings, bridges) affecting accuracy
   d. GPS unit specifications
   e. Data correction method used
   f. Final post-processed accuracy of data

The Captain will attempt to sample an impacted station at a different time, but if the interference is unavoidable, the sampling crew will make note of the issue in the hard copy and electronic records

14.0 REFERENCES

U.S. EPA. March 2010. *Great Lakes Legacy Act Data Reporting Standard*, Version 1.0. Great Lakes National Program Office.

15.0 ATTACHMENTS

Great Lakes Legacy Act Data Reporting Standard Locational Data Checklist and Metadata Recording Form.

Great Lakes Legacy Act Data Reporting Standard GPS Daily Check.

U.S. EPA Great Lakes National Program Office
Locational Data Checklist and Metadata Recording Form

This document accompanies *GLNPO's Great Lakes Legacy Act Data Reporting Standard*, Version 1.0, March 2010, which provides detailed data reporting guidance for project data including required electronic data deliverables (EDD). In addition to the EDD and project field forms, project participants are required to complete this checklist at the end of each sampling event. Copies of completed forms should be submitted to the GLNPO Project Lead.

Contact Information

Contact Name: _____ Phone Number: _____

Affiliation: _____ E-mail Address: _____

Study Information

Project Title: _____

Site Name: _____

Sampling Start Date: _____ Sampling Stop Date: _____

Preparation Activities (please confirm each activity in the boxes to the right)

1. Sampling staff are trained in GPS Field Data Collection and have familiarized themselves with the GPS unit used for this project (certified training recommended). ☐

2. Determined window of satellite availability. http://www.trimble.com/planningsoftware_ts.asp ☐

3. Established at least two control points for both vertical and horizontal accuracy. ☐
   For assistance locating control points visit http://www.ngs.noaa.gov/cgi-bin/datasheet.prl or http://www.geocaching.com/mark/. This may not be feasible if the GPS unit is mounted to a vessel. *

4. Located 3 reference points. * ☐

Data Collection Activities (please confirm each activity in the boxes to the right)

1. GPS unit was configured to collect data only when the following requirements were met:
   a. A minimum of four satellites ☐
   b. Position dilution of precision (PDOP)<=6 ☐
   c. Satellite elevation >=15° above the horizon ☐
   d. A minimum signal-to-noise ratio (refer to GPS user manual for recommendation) ☐

2. Collected point data based on the nearest base station's logging interval. ☐

3. Collected point data for a period of at least 1 minute per location. ☐

4. Reported locational data in WGS 84 or NAD 83 (please specify_____). ☐

Please provide an explanation if a box was not checked for any of the responses above and specify deviations (include sample IDs if applicable):

_____

_____

_____

*Collect these points on at least the first day of sampling. Collecting on each sampling day is recommended. Record on page 2.

GPS Unit Specifications

GPS Brand and model number: _____

Model accuracy: _____

Data Processing

Which of the following best describes any data correction that may have been performed:

☐ real-time correction - specify type _____ ☐ post processed differential correction - provide base station id and location _____

☐ no correction ☐ other, please specify _____

Quality Information

Describe any difficulties in collecting locational data: _____

_____

List final post-processed accuracy of the data: _____

Data Collector:

Confirm required information has been provided.

_____ _____

Signature Date

GLNPO Project Lead:

Confirm required information has been provided.

_____ _____

Signature Date

U.S. EPA Great Lakes National Program Office
GPS Daily Check

Collect these data on at least the first day of sampling. Collecting on each sampling day is recommended.

Project Title: _____

Date: _____

Horizontal Control Point 1

Benchmark ID: _____ Time: _____

Established Latitude: _____ Measured Latitude: _____

Established Longitude: _____ Measured Longitude: _____

Displacement (include UOM): _____

Horizontal Control Point 2

Benchmark ID: _____ Time: _____

Established Latitude: _____ Measured Latitude: _____

Established Longitude: _____ Measured Longitude: _____

Displacement (include UOM): _____

Vertical Control Point 1

Benchmark ID: _____ Time: _____

Established Elevation: _____ Measured Elevation: _____

Displacement (include UOM): _____

Vertical Control Point 2

Benchmark ID: _____ Time: _____

Established Elevation: _____ Measured Elevation: _____

Displacement (include UOM): _____

Reference Point 1

Time: _____

Physical/Locational description: _____

Measured Latitude: _____ Measured Longitude: _____

Reference Point 2

Time: _____

Physical/Locational description: _____

Measured Latitude: _____ Measured Longitude: _____

Reference Point 3

Time: _____

Physical/Locational description: _____

Measured Latitude: _____ Measured Longitude: _____

SUMMARY OF CHANGES FOR

***R/V MUDPUPPY II* - QMP-SOP'S**

(WITH REQUIRED SIGNATURES*)

RECORDING FIELD INFORMATION				**SOP # 108**
Rev #	**Date**	**Preparer** **PRINT / SIGN**	**Approver (COR)** **PRINT / SIGN**	**Approver (RRS I Section Chief)** **PRINT / SIGN**
1	April 2018	Harry Rogers 	Mary Beth Giancarlo 	Scott Cieniawski 

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FIELD OPERATING PROCEDURE-04

Vibracore Boat Sediment Sampling

Organization: Cetacean Marine, Inc.	Revision: 2	Date: April 2018

TABLE OF CONTENTS

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes procedures in using the vibracoring system to obtain sediment cores on board the Research Vessel (R/V) *Mudpuppy II*.

2.0 APPLICABILITY/SCOPE

This SOP describes the equipment and supplies used for the Vibracoring system sample collection. The vibracoring system consists of the vibracore head, core tube, underwater electrical cable coming from the surface support platform to the vibracore head, and control box located between the underwater cable and the power source.

This SOP should be followed by all project participants supporting the collection of samples using the vibracoring system. Project participants should also refer to the project-specific quality assurance project plan (QAPP) and field sampling plan (FSP) for detailed sampling procedures and requirements. The information in this SOP is adapted from EPA SOP #2016, *Sediment Sampling* (U.S. EPA, 1994).

3.0 DEFINITIONS

FSP	Field Sampling Plan
GLLA	Great Lakes Legacy Act
GLNPO	Great Lakes National Program Office
GPS	Global Positioning System
QAPP	Quality Assurance Project Plan
R/V	Research Vessel
SOP	Standard Operating Procedure

4.0 SUMMARY OF METHOD/PROCEDURE

The vibracore head has a core tube clamp and an internal vibrator motor. The vibracorer applies thousands of vibrations per minute to help penetrate the sediment. When the core tube is inserted in the core tube clamp, the vibracorer is lowered to 6" above the water body and then turned on. As soon as the core tube touches the sediment, the sediment and water interface to create a slurry due to the vibrations between the core tube and sediment. This eases the entry of the core tube into the sediment.

5.0 PERSONNEL QUALIFICATION/RESPONSIBILITIES

Training for using the vibracoring system to obtain sediment samples on board the R/V *Mudpuppy II* involves shadowing a trained sampler and taking samples under supervision of the trainer. Personnel have an opportunity to learn how to use many of the samplers during the sampling season. In addition, all project participants should attend a standard R/V *Mudpuppy II* introduction training.

6.0 EQUIPMENT AND SUPPLIES

This section provides physical details of the vibracorer and presents a description of the equipment and supplies commonly required for sample collection.

6.1 Detailed Equipment Description

The vibracorer for the R/V *Mudpuppy II*, a Rossfelder P3C Vibracore (P3C) (Figure 1), operates at the following specifications:

Weight of vibracore head:	150 lbs
Power setting:	Medium = 5.0 kW, 8.0 amps
Force:	Centrifugal force at 60 Hz, medium power setting, produces a force of 20 kilonewtons
Vibrations per minute:	3450 vibrations per minute at 60 Hz
Water depth capability:	125 feet (based on R/V *Mudpuppy II* winch capacity)
Core tube type:	4 inch diameter metal or polycarbonate tubes

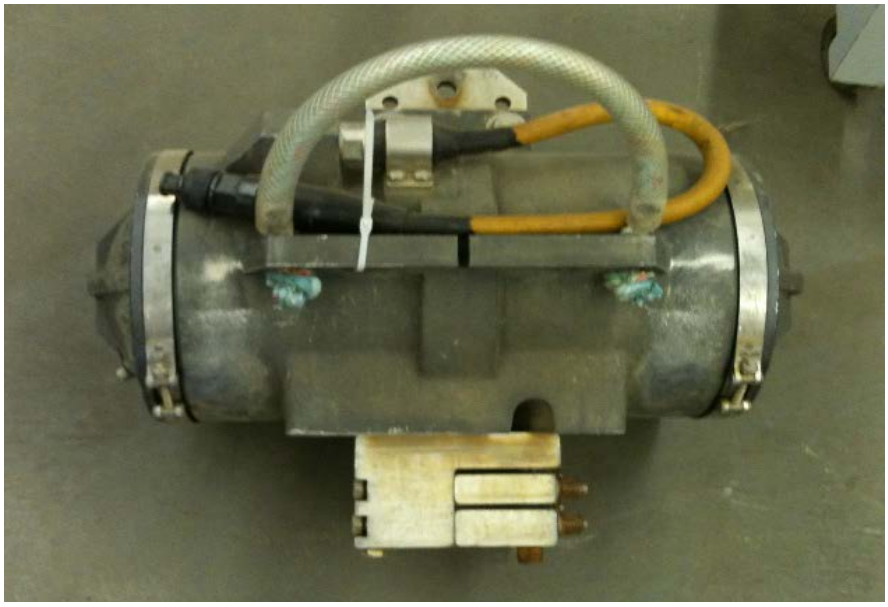

Figure 1. Vibracore sampler

6.2 Equipment List

The following equipment and supplies are required for the collection of a long core sediment sample at a typical sampling location, and are available on the R/V *Mudpuppy II* unless otherwise stated.

- Rossfelder P3C Vibracore
- Polycarbonate core tubes
- Underwater electrical cable
- Control box/power source
- Wrench
- Hydraulic articulating crane with winch
- Eggshell core catcher
- 20’ aluminum tube
- Stainless steel or aluminum rivets
- Stainless steel nose cone
- Chisel, Drill, Punch, Push rod
- Duct tape
- Cap
- Hand sledge, Hammer
- Polycarbonate liners
- Extractor flange
- Hand saw
- Rivet jig
- Riveter

7.0 REAGENTS AND STANDARDS

N/A

8.0 HEALTH AND SAFETY CONSIDERATIONS

At all times personnel should comply with the policies and procedures within the GLNPO *Safety, Health and Environmental Compliance Manual* (U.S. EPA, 2016*)* as this manual takes precedence over the SOP requirements. At a minimum, project participants must wear: a hard hat with face shield, safety glasses, a life jacket, steel-toed boots, and rubber gloves or leather gloves to operate the sampler. The power cable should not be bent, twisted, pinched or stepped on.

9.0 INTERFERENCES

Refer to the Rossfelder P3C Vibracore Manual.

10.0 PROCEDURE

10.1 Instrument or Method Calibration and Standardization

N/A

10.2 Sample Collection

The following sampling procedure is used to collect sediment samples up to 15 feet in length (disposable polycarbonate core tubes) using the vibracoring system on the R/V *Mudpuppy II*, after securing the vessel as instructed by the captain. Project participants should refer to the project-specific QAPP and FSP for any additional sample collection procedures.

1. Record sample location using global positioning system (GPS).
2. Measure and record water depth.
3. Install eggshell core catcher using 4 aluminum peel-back rivets (if not already done).
4. Using the winch, vertically lift the vibracore head so that the vibracore head is suspended just off of the bow of the sampling vessel.
5. Insert the core tube into the core tube clamp, making sure that the tube is contacting the top of the clamp..
6. Hold core tube in place while tightening the clamp around the core tube using a socket or a wrench.
7. With the winch, lower the entire assembly until the core nose is just above the sediment surface, as indicated by the markings on the power cable. Turn on the power to the vibracore head.

8. Slowly lower the vibracorer by keeping 6-10 inches slack of cable at a time. The power cable is marked in 1-ft increments. Monitor the core tube penetration by feeling for slack in the cable, watching the winch cable and listening to vibracorer. Keep track of penetration depth by counting the markings on the power cable.
9. Once the vibracorer ceases to penetrate the sediment :(i.e., the unit stops lowering, the cable remains slack or the vibracorer head starts to tip over) or the core tube has penetrated its entire length, turn off power to the vibracore head. **NOTE:** Care must be taken to ensure the vibracore head is not embedded in the sediment.
10. Using the winch, remove the core from the sediment surface.
11. Lift the entire assembly out of the water. Rise off core tube as it is being raised. Lower entire assembly until the sediment/water interface is about eye level..
12. Drill hole at sediment/water interface to decant water from tube.
13. Tie a clove hitch around the core tube.
14. Remove and lower the core tube onto the processing table. (This applies to 10' and shorter tubes. 15' and 20' tubes are laid on the deck on the port side of the boat.)
15. Measure the retrieved sediment, cut core tube to length, cap and tape ends of core tube.
16. Rinse the vibracorer off with site water, making sure to rinse the inside of the core clamp and check valve. Further decontamination should be performed in accordance with the site specific QAPP and FSP.

Steps to Obtain Sediment Cores of Twenty Feet in Length Using the Vibracorer

The following procedure is used to collect sediment samples 20 feet long using the vibracore system on the R/V Mudpuppy II. When sediment thickness is greater than 15 feet, cores up to 20 feet can be collected using outer-tube/liner/nosecone system. The change in methodology is necessary because at lengths over 15 feet, polycarbonate tubes (alone) do not transfer enough energy to the tip of the tube. What typically happens is that the core tube stops penetrating and the body of the core tube takes on a cyclonic movement that causes increased mixing of the core contents. Using an aluminum outer tube coupled with a thin wall polycarbonate liner, sufficient energy is transferred to the tip to collect 20 foot cores.

1. Use the rivet jig to mark rivet hole locations at one end of the aluminum outer tube.
2. Drill 3/16" holes where marked.
3. Slide a thin wall polycarbonate liner into the aluminum tube, leaving 6 inches of liner exposed at the end of the aluminum tube where the rivet holes are located.

4. Slide a stainless steel nose cone (with stainless core catcher attached) into the core liner until it bottoms out.
5. Slide the nose cone and liner (together) into the aluminum tube until it bottoms out and rotate the nose cone until the rivet holes line up.
6. Rivet the nose cone to the aluminum tube using 3/16" stainless steel rivets.
7. Making sure the liner stays completely seated on the nose cone, cut off the extra liner from the top of the tube assembly with a hand saw.
8. Continue taking the core as with a disposable polycarbonate tube.
9. After removing the core tube from the vibracorer head, lay the core tube down on the port side of the vessel, slowly decanting the water out the top of the tube.
10. Drill out the center of each rivet using a 3/16" drill bit.
11. Using a hammer and chisel, knock the heads off of the rivets and push the body of the rivet through the outer tube using a punch.
12. Keeping them together, slide the liner and nose cone out of the aluminum tube. If the liner does not easily slide out of the outer tube, the extractor flange and hand sledge can be used to drive them out from the top of the core.
13. Once the liner has slid out about a foot, the nose cone can be removed and the bottom of the core liner capped.
14. Slide the outer tube all the way off of the liner towards the top of the tube.
15. Wash sediment off the outside of the liner.
16. Measure the retrieved sediment, cut core tube to length, cap and tape ends of core tube.
17. Rinse the nose cone and outer core tube (inside and out) with site water.

10.3 Sample Handling and Preservation

Project participants should refer to the project-specific QAPP and FSP for details on specific sample handling and preservation procedures.

10.4 Sample Preparation and Analysis

N/A

10.5 Computer Hardware and Software to be Used

Project participants should refer to the project-specific QAPP and FSP for any computer hardware and software needed.

10.6 Troubleshooting

Refer to the Rossfelder P3C Vibracore Manual.

10.7 Data Acquisition, Calculations, and Data Reduction

Project participant should refer to the project-specific QAPP and FSP for any data acquisition, calculations or data reduction procedures.

10.8 Data Review and Acceptance

N/A

11.0 WASTE MANAGEMENT

Excess samples should be disposed of overboard. For further details, refer to the project specific QAPP and FSP.

12.0 DATA AND RECORDS MANAGEMENT

All Great Lakes Legacy Act (GLLA) projects must follow GLNPO's *GLLA Data Reporting Standard* (U.S. EPA, 2010). Other sediment projects should refer to reporting requirements outlined in their project-specific QAPP.

13.0 QUALITY CONTROL & QUALITY ASSURANCE

For specific quality control and quality assurance procedures, project participants should refer to the project-specific QAPP and FSP. At a minimum:

- If the first attempt at sample collection is not successful and discarded, project participants should adjust sample location so that the next attempt does not collect discarded material. Alternatively, the contents of the core can be discarded along the sides of the vessel to avoid contaminating subsequent attempts if moving sample location is not an option.
- All data must be documented according to the project-specific QAPP and FSP specifications.
- All instrumentation must be calibrated (when applicable), operated, and maintained in accordance with instructions as supplied by the manufacturer unless otherwise specified.
- All project participants must follow the sample handling, labeling, preservation and shipping procedures described in the project-specific QAPP and FSP.
- The sampler must be emptied and cleaned in between sample collection according to the procedures in this SOP and in the project-specific QAPP and FSP.

14.0 REFERENCES

Rossfelder P3C Vibracore Manual, Oct 1999.

U.S. EPA. November 1994. *Sediment Sampling,* SOP#2016, Rev. 0.0. Office of Solid Waste and Emergency Response, Environmental Response Team. http://www.dem.ri.gov/pubs/sops/wmsr2016.pdf

U.S. EPA. May 2016. *Safety, Health and Environmental Compliance Manual.* Great Lakes National Program Office.

U.S. EPA. March 2010. *Great Lakes Legacy Act Data Reporting Standard,* Version 1.0. Great Lakes National Program Office.

15.0 ATTACHMENTS

N/A

SUMMARY OF CHANGES FOR

***R/V MUDPUPPY II* - QMP-SOP'S**

(WITH REQUIRED SIGNATURES*)

VIBRACORE				**SOP # 103**
Rev #	**Date**	**Preparer** **PRINT / SIGN**	**Approver (COR)** **PRINT / SIGN**	**Approver (RRS I Section Chief)** **PRINT / SIGN**
2	April 2018	Harry Rogers 	Mary Beth Giancarlo 	Scott Cieniawski 

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FIELD OPERATING PROCEDURE-05

Manual Coring Methods

Organization: CH2M	Revision: 0	Date: May 2016

Purpose

This outline describes the collection of manual sediment cores over depth using polycarbonate core tubes.

Scope

The manual sediment coring procedures describe the use of core tubes for collection of unconsolidated sediments in shallow waters (<8 feet). Operator manuals, if available, should be consulted for specific details.

Equipment and Materials

- Polycarbonate Core tubes (3" outer diameter [OD]), 8' in length
- Global Positioning System (GPS) with +/- 1 meter accuracy
- Core tube caps
- Core drivers (3")
- Hack saw (2)
- Nylon climbing rope ¼" OD (50')
- Tape measure
- Duct tape
- Log book
- Sample containers, as appropriate
- Personal protective equipment (disposable gloves, boots, hip/chest waders, etc.)

Procedures and Guidelines

1. Field personnel will enter river downstream of sample location and proceed upstream to the sample location to prevent contamination of non-sampled areas.
2. Document location using Global Positioning System (X and Y coordinates).
3. Assess the water depth to the top of the sediment using a surveyor's rod and record in field forms or log book.
4. The amount of core tube needed for a sample is determined by adding the water depth to the sediment depth, plus an additional 2 to 3 feet to assist in core tube extraction.
5. The core tube is lowered to the sediment/water interface. After contact with the sediment, the core tube is gently pushed into the soft sediment to reduce compaction. A core driver is then placed over the core barrel and gently driven into the clay substrate until refusal. The amount of compaction allowed will determine the size core tube to be used. The smaller the diameter of the tube the greater the compaction.

6. Once the core tube is driven to refusal, the barrel is filled to the top with water, capped, and sealed with duct tape. Climber's rope is wrapped around the core tube to assist in extraction. The core tube is then extracted by pulling up on the rope. Once the tube is loose and brought near the water surface, a cap is placed on the bottom of the core tube under water.
7. Sediment cores will be kept in an upright position for an adequate amount of time that allows for the settling of fine-grained particles at the sediment/water interface. After allowing for settling, the water column within the core liner will be drained to no less than 4 inches above the sediment while in a vertical position. Once the excess water is drained, the top of core will be capped, sectioned to manageable lengths (approximately 4 to 5 feet), labeled, and stored upright in preparation for transfer to the onshore staging area for logging and final sample processing by CH2M.
8. Record the sample location on a project map for each specific site or zone. Survey the sample location.
9. Follow the site safety plan designed for the specific nature of the site's sampling activities and locations.
10. Decontaminate all sampling implements and protective clothing according to prescribed procedures.

Key Checks and Items

- Start downstream, work upstream.
- Log exact locations using permanent features or GPS.
- Beware of hidden underwater hazards.

FIELD OPERATING PROCEDURE-06

Sediment Surface Dredge (Ponar) Sampling

Organization: Cetacean Marine, Inc	Revision: 2	Date: April 2018

SOP-MP 102 Standard Operating Procedure for Using the Standard and Petite Ponar and Petersen Grab On Board the Research Vessel Mudpuppy II

Rev. 2 4-18

TABLE OF CONTENTS

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes procedures in using the Standard & Petite Ponar and Peterson grabs to obtain sediment grab samples on board the R/V *Mudpuppy II*.

2.0 APPLICABILITY/SCOPE

This SOP describes the equipment and supplies used for the Standard & Petite Ponar and Peterson grabs to obtain sediment grab samples and steps for sample collection using the Standard & Petite Ponar and Peterson grab. The Standard Ponar consists of a center pivot, tapered scooped edges, heavy-duty hinges, scoop, underlip, stainless steel screen, and a pinch-pin (Figure 1). The Peterson grab consists of a clamshell pivot, tapered scoop edges, and a safety pin lock (Figure 2). The Petite Ponar consists of a center pivot for low-bottom disturbance with removable top screens, self-releasing pinch-pin, heavy duty hinges, and is designed for hand line operation especially since it is half the weight of a Standard Ponar (Figure 3).

This SOP should be followed by all project participants supporting the collection of samples using the Standard & Petite Ponar and Peterson grabs. Project participants should refer to the project-specific quality assurance project plan (QAPP) and field sampling plan (FSP) for detailed sampling procedures and requirements. The information in this SOP is adapted from EPA SOP #2016, *Sediment Sampling* (U.S. EPA, 1994).

3.0 DEFINITIONS

FSP	Field Sampling Plan
GLLA	Great Lakes Legacy Act

GLNPO	Great Lakes National Program Office
GPS	Global Positioning System
QAPP	Quality Assurance Project Plan
R/V	Research Vessel
SOP	Standard Operating Procedure

4.0 SUMMARY OF METHOD/PROCEDURE

To collect a sample, the sampler (with line attached) is cocked by inserting a pinch-pin (ponars) or raising the cocking bar in to position (Petersen). The sampler is then raised above the deck to keep tension on the pinch pin or locking bar. The sampler should then be lowered into the water until it has reached the sediment. The pinch-pin will pop out (or cocking bar drop) and the sampler should then be closed. The sampler should be brought on board and the water decanted.

5.0 PERSONNEL QUALIFICATION/RESPONSIBILITIES

Training for using the Standard & Petite Ponar and Peterson grabs on board the R/V *Mudpuppy II* involves shadowing a trained sampler and taking samples under supervision of the trainer. Personnel have an opportunity to learn how to use any of the grab samplers at a sampling event during the sampling season. In addition, all project participants should attend a standard R/V *Mudpuppy II* introduction training.

6.0 EQUIPMENT AND SUPPLIES

This section provides physical details of the equipment and presents a description of the equipment and supplies commonly required for sample collection.

6.1 Detailed Equipment Description

The Standard Ponar consists of a center pivot, tapered scooped edges, heavy-duty hinges, scoop, underlip, stainless steel screen, and a pinch-pin (Figure 1). It has a scoop volume of 8.2 liters, can hold 25lbs, and a sampling area of 229 mm by 229 mm (9 inches by 9 inches). The maximum depth of collection is 3.5 inches.
Reference the 1725-F10 Standard Ponar user manual for specifications on the unit.

Figure 1. Standard

The Peterson grab consists of a clamshell pivot, tapered scoop edges, and a safety pin lock (Figure 2). It has a scoop volume of 9.89 liters and a sampling area of 305 mm x 305 mm (12 inches by 12 inches). The maximum depth of collection is 5.5 inches. Operation requires winch and crane due to its working weight. The Petersen grab is used for sand, gravel, and/or clay sediments or for collecting large-volume samples.

Figure 2. Peterson Grab

The Petite Ponar consists of a center pivot for low-bottom disturbance with removable top screens, self-releasing pinch-pin, heavy duty hinges, and is designed for hand line operation especially since it is half the weight of a Standard Ponar (Figure 3).). It has a scoop volume of 8.2 liters and a maximum depth of collection of 2.75 inches.
Please reference the 1728-G30/G40 Petite Ponar user manual for specifications on the unit.

6.2 Equipment List

The following equipment and supplies are required for the collection of a single sediment sample at a typical sampling location, and are available on the R/V *Mudpuppy II* unless otherwise stated.

- Standard Ponar, petite Ponar or Petersen grab
- Crane mounted hydraulic winch equipped with synthetic line or steel cable (not needed for petite Ponar)
- Nylon line for petite Ponar
- Stainless steel pan or bowl
- Stainless steel spoons and spatulas

7.0 REAGENTS AND STANDARDS

N/A

8.0 HEALTH AND SAFETY CONSIDERATIONS

At all times personnel should comply with the policies and procedures within the GLNPO *Safety, Health and Environmental Compliance Manual* (U.S. EPA, 2016*)* as this manual takes precedence over the SOP requirements. At a minimum, project participants must wear: A hard hat with shield, safety glasses, a life jacket, steel-toed boots, and rubber gloves or leather gloves to operate the sampler. Personnel should never place their hands inside the Standard Ponar, Petite Ponar or Pertersen grabs while they are cocked as serious injury could occur. Make sure a safety pin is inserted in the grabs prior to reaching into grabs to remove sediment.

9.0 INTERFERENCES

Refer to the section entitled Maintenance in the 1725-F10 Standard Ponar and 1728-G30/G40 Petite Ponar user manuals for steps in maintaining ponars on board the R/V *Mudpuppy II*. Since the Petersen grab is galvanized, not stainless steel, it should not be used for sampling sediments that will be analyzed for metals

10.0 PROCEDURE

10.1 Instrument or Method Calibration and Standardization

N/A

10.2 Sample Collection

The following sampling procedure is used to collect sediment samples with the Standard Ponar, Petite Ponar and Peterson grab samplers on the R/V *Mudpuppy II*, after securing the vessel as instructed by the captain. Project participants should refer to the project-specific QAPP and FSP for any additional sample collection procedures.

1. Record sample location using global positioning system (GPS).
2. Measure and record water depth.
3. Securely fasten the cable or line to the grab.
4. Insert the pinch-pin (tripping device) into ponar. Note that the pinch-pin has a spring wrapped around it. Hold ponar grab at the shackle to avoid getting fingers and hands pinched.
5. After inserting the pinch-pin into grab, lift the grab with the winch. Lifting the ponar will secure the pinch-pin in place. For the Petersen grab, lift the cocking bar upward and pull up on the lifting cable by hand so that the cocking bar catches in the cocking notch. Lifting the ponar or Petersen grab will secure the pinch pin or locking bar in place.
6. Winch the grab into the water body until grab has reached sediment bottom. Pull sharply on the winch cable to ensure the pinch pin/cocking bar releases.
7. Record the latitude and longitude.
8. Pull in on the cable by hand to close the grab.
9. Hoist the grab out of the water to approximately waist height in front of the boat.
10. Decant the water from grab and lower grab into Stainless steel pan or bowl.
11. Empty sediment from the grab by lifting the weights or pushing down on the lifting bars. Insert the safety pin into the grab. Use a stainless steel spoon or spatula to dislodge sediment stuck to the inside of the grab. Alternately, the screens of the Ponar can be removed and the sediment accessed through the top of the closed ponar. Use a stainless steel spoon to remove desired sediment from grab.
12. If not already done, insert the safety pin into the grab. Winch (standard Ponar and Petersen grab) or lift (petite Ponar) the grab and put the grab back into its place on the deck.
13. Follow sample collection, sample handling and preservation, safety and waste handling per QAPP and site safety plan.
14. Rinse the grab with site water after using. Decontaminate the grab according to the site specific QAPP and FSP.

10.3 Sample Handling and Preservation

Project participants should refer to the project-specific QAPP and FSP for details on specific sample handling and preservation procedures.

10.4 Sample Preparation and Analysis
N/A

10.5 Computer Hardware and Software to be Used

Project participants should refer to the project-specific QAPP and FSP for any computer hardware and software needed.

10.6 Troubleshooting
Refer to the 1725-F10 Standard Ponar and 1728-G30/G40 Petite Ponar user manuals.

10.7 Data Acquisition, Calculations, and Data Reduction
Project participants should refer to the project-specific QAPP and FSP for any other data acquisition, calculations or data reduction procedures.

10.8 Data Review and Acceptance
N/A

11.0 WASTE MANAGEMENT

Excess samples should be disposed of overboard. For further details, refer to the project specific QAPP and FSP.

12.0 DATA AND RECORDS MANAGEMENT

All Great Lakes Legacy Act (GLLA) projects must follow GLNPO's *GLLA Data Reporting Standard* (U.S. EPA, 2010). Other sediment projects should refer to reporting requirements outlined in their project-specific QAPP.

13.0 QUALITY CONTROL & QUALITY ASSURANCE

For specific quality control and quality assurance procedures, project participants should refer to the project-specific QAPP and FSP. At a minimum:

- If the first attempt at sample collection is not successful and discarded, project participants should adjust sample location so that the next attempt does not collect discarded material. Alternatively, the contents of the ponar can be discarded along the sides of the vessel to avoid contaminating subsequent attempts if moving sampling location is not an option.
- All data must be documented according to the project-specific QAPP specifications.
- All instrumentation must be calibrated (when applicable), operated, and maintained in accordance with instructions as supplied by the manufacturer unless otherwise specified.
- All project participants must follow the sample handling, labeling, preservation and shipping procedures described in this SOP and the project-specific QAPP and FSP.

- The sampler must be emptied and cleaned in between sample collection according to the procedures in this SOP and in the project-specific QAPP and FSP.

14.0 REFERENCES

User manual 1725-F10 Standard Ponar User Manual **http://wildco.com/download/bottom-sampling-equipment/031680%201725-F10%20Standard%20Ponar%20Grab.pdf**

User manual 1728-G20 Petite Ponar User Manual **http://wildco.com/download/bottom-sampling-equipment/24-1728%201728-G30%201728-G40%20petite%20ponar.pdf**

U.S. EPA. November 1994. *Sediment Sampling,* SOP#2016, Rev. 0.0. Office of Solid Waste and Emergency Response, Environmental Response Team. http://www.dem.ri.gov/pubs/sops/wmsr2016.pdf

U.S. EPA. May 2016. *Safety, Health and Environmental Compliance Manual.* Great Lakes National Program Office.

U.S. EPA. March 2010. *Great Lakes Legacy Act Data Reporting Standard,* Version 1.0. Great Lakes National Program Office.

15.0 ATTACHMENTS

N/A

SUMMARY OF CHANGES FOR

***R/V MUDPUPPY II* - QMP-SOP'S**

(WITH REQUIRED SIGNATURES*)

PONAR & PETERSON GRAB				**SOP # 102**
Rev #	**Date**	**Preparer** **PRINT / SIGN**	**Approver (COR)** **PRINT / SIGN**	**Approver (RRS I Section Chief)** **PRINT / SIGN**
2	April 2018	Harry Rogers 	Mary Beth Giancarlo 	Scott Cieniawski 

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FIELD OPERATING PROCEDURE-07

Mudpuppy II Decontamination Procedures

Organization: Cetacean Marine, Inc	Revision: 2	Date: April 2018

SOP-MP 107 Standard Operating Procedure for the Decontamination of the Research Vessel Mudpuppy II Between Sediment Surveys to Prevent Transport of Contaminants, Invasive Species, and Waterborne Pathogens.

Rev. 2 4-18

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1.0 PURPOSE

In an effort to prevent the transport of contaminants, invasive plant and animal species, and/or waterborne pathogens between various water bodies, the U.S. EPA Great Lakes National Program Office (GLNPO) has adopted standard operating procedures (SOPs) for decontamination of the Research Vessel (R/V) *Mudpuppy II* and sampling equipment between sediment surveys.

2.0 APPLICABILITY/SCOPE

U.S. EPA's sediment sampling vessel, the R/V *Mudpuppy II*, is utilized by U.S. EPA and its Great Lakes partners to sample sediments at numerous rivers and harbors, and some inland lakes, within the Great Lakes watershed. Rarely the use of the R/V *Mudpuppy II* is requested outside the Great Lakes basin. This SOP applies only to the R/V *Mudpuppy II* and the equipment that are normally operated on the vessel. This SOP does not apply to other research vessels or equipment that is brought on by other partners.

3.0 DEFINITIONS

AIS	Aquatic Invasive Species.
Decontamination	The process of removing chemical contaminants and killing attached AIS.

4.0 SUMMARY OF METHOD/PROCEDURE

This SOP describes the procedures that the R/V *Mudpuppy II* crew will follow to decontaminate the R/V *Mudpuppy II* and associated sampling equipment after a sediment sampling event is completed and before launching into a different water body. The

Standard procedure for preventing transport of AIS by boat is "clean, drain, dry". This includes cleaning the vessel of all visible plant, sediment and animal materials, draining all bilges and tanks and allowing the boat to air dry for a minimum of 5 days before placing it into another water body. If the boat cannot be dried for the full time, if AIS is identified, or if the vessel has water in it that cannot be proven to be free of AIS, disinfection should take place. Since the R/V Mudpuppy II may need to be used for emergencies with little notice, the vessel will be decontaminated each time it comes out of the water, unless the vessel will be put back into the same water body in short order and is not transported away from that water body.

Federal, State and local laws restrict the transport of aquatic invasive species, sediment and water. For this reason, some of the procedures listed below are required to be completed prior to leaving the launch site. If a decontamination site is locally available, immediate decontamination should be performed. Otherwise, decontamination will be performed when returning to the vessel's home port.

5.0 PERSONNEL QUALIFICATION/RESPONSIBILITIES

The R/V *Mudpuppy II* crew (i.e. Captain and Marine Technician) must read, be familiar with, and comply with the requirements of this SOP. Specialized training is not required for decontamination of the vessel and/or equipment; however, new staff will be supervised by experienced staff.

6.0 EQUIPMENT AND SUPPLIES

The following supplies are necessary for decontaminating the R/V *Mudpuppy II* between sediment surveys:

- Potable water source and hose
- Wash water storage tank
- Hot water pressure washer
- Low pressure attachment for pressure washer
- Undercarriage attachment for pressure washer
- Non-alkaline/phosphate free soap
- Stiff bristled brush (long handle)
- Soft bristled brush (long handle)
- Soft bristled hand brush
- Low pressure diffuser for pressure washer
- Outboard flushing ears
- Wet/dry vacuum
- Containment pad and berm
- 12 volt transfer pump

- 55 gallon drum
- 5 gallon bucket
- 12 volt battery
- Confined space ventilator fan
- Cloth rags or heavy duty paper towels
- Infrared thermometer

7.0 REAGENTS AND STANDARDS

N/A

8.0 HEALTH AND SAFETY CONSIDERATIONS

At a minimum, wear steel-toed boots, safety goggles, and heat resistant rubber gloves or leather gloves while decontaminating the R/V *Mudpuppy II*.

9.0 INTERFERENCES

N/A

10.0 PROCEDURE

Prior to loading boat on trailer, scrub visible sediment from deck using stiff bristle brush. Scrub visible sediment from hull of boat using soft bristle brush. Rinse with site water. This will most likely take place at the location of the final sampling station as part of the station decontamination.

1. Prior to leaving launch site, remove all visible vegetation from boat and trailer.
2. Prior to leaving launch site, raise bow of boat and discharge bilge water via bilge pump (do this far enough away from the ramp so that bilge water will not run into surface water).
3. Prior to leaving launch site, vacuum out remaining bilge water (dump vacuum away from surface water, preferably on gravel or grass).
4. Prior to leaving launch site, vacuum water out of deck tie-down pockets (dump vacuum away from surface water, preferably on gravel or grass).
5. Prior to leaving launch site, release wash-down pump pressure by opening sprayers.
6. Prior to leaving launch site, open generator, air conditioner, and wash-down pump sea-cocks.
7. Prior to leaving the launch site, clean out sea strainers and vacuum out water. Dispose of material from strainers in trash receptacle.
8. Prior to leaving launch site, remove filter nets on tray table and dispose of material in trash receptacle.
9. Fill power washer water storage tank with potable water. Add water to tank when the level is reduced to 50%. If municipal water supply is capable of providing a

minimum flow of 5 gallons per minute, the water supply can be attached directly to the power washer.

10. Establish a containment area around boat for purposes of decontamination. Pump wash water from containment area to storage tank for later use, or to municipal WTP if permitted to do so. This will usually occur at the home facility. In the event of decontamination at another facility, follow procedures in place at that location.
11. Pay out anchor lines, scrub anchors and chains with hand brush and soap. Rinse with 140 degree low pressure water. Make sure the tubing on the anchor is void of sediment, cleaning out with high pressure spray if necessary.
12. Fill drum with 140 degree water and place anchor and anchor line in drum. Allow to sit in drum for a minimum of 2 minutes.
13. As the anchor lines are soaking, clean the anchor rests and anchor lockers of any residual plant material and sediment. Scrub area with phosphate free/non-alkaline soap and hand brush, rinse rests and lockers down for a minimum of 10 seconds with 140 degree low pressure water (be careful not to soak the 12 volt switches inside of the anchor lockers).
14. Spray the anchor lines with high pressure 140 degree water as they are brought back into the anchor lockers. Use of a commercially available rope cleaner with 140 degree wash water is an acceptable alternative.
15. Scrub bulkheads and decks that are accessible only when on the boat. Start with the pilot house roof and work down using phosphate free/non-alkaline soap and a stiff bristle brush for decks and a soft bristle brush for bulkheads. Rinse bulkheads with 140 degree low pressure spray and decks with 140 degree high pressure spray.
16. Remove the bilge hatch covers and wipe off the seals and mating surfaces. Rinse with 140 degree low pressure spray for at least 10 seconds. Dispose of rags in solid waste receptacle.
17. Remove intake strainers and rinse with 140 degree low pressure water for at least 10 seconds. Replace strainers.
18. Attach low pressure hose to wash down pump valves and run them with 120 degree water for a minimum of 2 minutes. Cool the pumps down by running with cold water for 30 seconds.
19. If air conditioner valve was opened at any time while in the water, attach low pressure hose to air conditioner valve and run with 120 degree water for a minimum of 2 minutes. Cool the air conditioner down by running with cold water for 30 seconds
20. Attach low pressure hose to generator valve and run with 120 degree water for a minimum of 2 minutes. While the generator is running, pay out all the winch line into a bucket of 120 degree water and let sit for a minimum of 2 minutes. Cool generator down by running with cold water for 30 seconds.
21. Remove oil absorbent pads from bilge and discard.
22. Using low pressure 120 degree water, rinse the bilges for at least 2 minutes. Pump out rinse water with bilge pump and vacuum out the remaining water.

23. Attach flushing ears to each outboard and run for a minimum of 2 minutes using low pressure 120 degree water. Cool outboards down by running with cold water for 30 seconds.
24. Scrub the outside of the hull and outboards with non-alkaline/phosphate free soap using a soft bristle brush. Rinse with 140 degree low pressure spray for at least 10 seconds.
25. Using 140 degree high pressure water, spray all areas of the vessel below the water line to remove any attached organisms. Use an undercarriage attachment to spray down the bottom of the vessel.
26. Rinse all surfaces of the trailer with 140 degree low pressure spray for a minimum of 10 seconds. Follow up with 140 degree high pressure spray to remove any attached organisms. Use undercarriage attachment for hard to reach areas.
27. Store vessel with bilge hatches open to allow them to dry, if time allows. Use of forced ventilation will speed up dry time if needed. Replace oil absorbent pads (with new) when dry.
28. Clean all sampling equipment with non-alkaline/phosphate free soap and hand brush. Rinse with 140 degree low pressure spray for at least 10 seconds.
29. Fill out decontamination record and keep on board in case of inspection.

11.0 WASTE MANAGEMENT

All sediment, plant and animal material removed from vessel must be disposed of in trash receptacle, do not place back into water. Used oil absorbent pads that do not contain free liquid may be disposed of with solid waste. Oil pads that contain free liquid must be disposed of in accordance with federal, state and local laws.

12.0 DATA AND RECORDS MANAGEMENT

Decontamination/disinfection check lists shall be kept for 3 years at the home port office.

13.0 QUALITY CONTROL & QUALITY ASSURANCE

Use infrared thermometer to routinely check water temperature.

14.0 REFERENCES

Michigan Department of Natural Resources. December 9, 2014. *Invasive Species Decontamination for Field Operations in Michigan.*

Minnesota Department of Natural Resources. June, 2013. *Aquatic Invasive Species (AIS) Decontamination Handbook for Lake Service Providers.*

National Oceanic and Atmospheric Administration. *Preventing Invasive Species: Cleaning Watercraft and Equipment*

15.0 ATTACHMENTS

R/V Mudpuppy II Decontamination Record.

R/V MUDPUPPY II DECONTAMINATION RECORD

Last waterbody visited: _____ Date pulled out: _____

Prior to leaving launch ramp:

Visible AIS when pulled out? Yes/No

Visible sediment removed from boat? Yes/No

All vegetation removed from boat and trailer? Yes/No

Bilge water removed from boat? Yes/No

Water removed from deck pockets? Yes/No

Wash down pumps drained? Yes/No

Sea-cocks open for transport? Yes/No

Strainers cleaned and drained? Yes/No

Tray table nets removed and debris discarded in trash? Yes/No

At decontamination site:

Location of decontamination? _____

Date of decontamination? _____

Decontamination of vessel with non-alkaline/phosphate free soap performed? Yes/No

Anchor lines soaked in 140 degree water for at least 2 minutes? Yes/No

Anchor lockers cleaned out and flushed with 140 degree water? Yes/No

Anchor lines pressure washed prior to stowing in lockers? Yes/No

Decks and interior bulkheads rinsed with 140 degree water for at least 10 seconds? Yes/No

Deck power washed with 140 degree high pressure water? Yes/No

Hatch seals and surfaces cleaned and rinsed with 140 degree water? Yes/No

Intake strainers rinsed with 140 degree water for at least 10 seconds? Yes/No

Wash down pumps run with 120 degree water for at least 2 minutes? Yes/No

Air conditioner flushed with 120 degree water for at least 2 minutes? Yes/No

Generator run with 120 degree water for at least 2 minutes? Yes/No

Winch cable soaked in 120 degree water for at least 2 minutes? Yes/No

R/V MUDPUPPY II DECONTAMINATION RECORD

Oil absorbent pads removed from bilge and discarded? Yes/No

Bilges rinsed with 120 degree water for at least 2 minutes and pumped out? Yes/No

Outboard engines run on flushing ears with 120 degree water for at least 2 minutes? Yes/No

Exterior of vessel rinsed with 140 degree low pressure water for at least 10 seconds? Yes/No

Exterior of vessel sprayed with 140 degree high pressure water? Yes/No

Bottom of vessel sprayed with 140 degree high pressure water and undercarriage attachment? Yes/No

All surfaces of trailer rinsed with 140 degree low pressure water for at least 10 seconds? Yes/No

All surfaces of trailer sprayed with 140 degree high pressure water? Yes/ No

Vessel stored with hatches open for a minimum of 5 days? Yes/No Passive dry time: _____

Bilge areas force ventilated with fan? Yes/No Ventilated dry time: _____

Bilges dry at time of mobilization for next survey? Yes/No Date of mobilization: _____

New oil absorbent pads placed in bilge? Yes/No

Sampling equipment decontaminated with non-alkaline/phosphate free soap? Yes/No

Sampling equipment rinsed with 140 degree low pressure water for at least 10 seconds? Yes/No

Comments:_____
_____
_____
_____
_____
_____
_____

Signature: _____ Date: _____

SUMMARY OF CHANGES FOR

***R/V MUDPUPPY II* - QMP-SOP'S**

(WITH REQUIRED SIGNATURES*)

CLEANING MPII BETWEEN SEDIMENT SURVEYS				**SOP # 107**
Rev #	**Date**	**Preparer** **PRINT / SIGN**	**Approver (COR)** **PRINT / SIGN**	**Approver (RRS I Section Chief)** **PRINT / SIGN**
2	April 2018	Harry Rogers 	Mary Beth Giancarlo 	Scott Cieniawski 

* Pls attach a PDF signature next to your name and return to the Originator for publication. For this to work going forward, the document must be kept in PDF Format

FIELD OPERATING PROCEDURE-08

Geotechnical Field Testing

Organization: CH2M	Revision: 0	Date: May 2016

Purpose and Scope

The purpose of this procedure is to provide a guideline for the use of pocket penetrometers and miniature vane shear (Torvane) devices for the estimation of undrained shear strengths of cohesive soil samples in the field.

Equipment and Materials

- Pocket Penetrometer
- Miniature Vane Shear Device (with Standard, Large, and Small Vanes)

Procedures and Guidelines

Pocket Penetrometer

1. Slide the ring (if present) on the barrel of the penetrometer down against the handle (zero position).
2. The surface of the cohesive soil to be tested should be relatively flat. The sample may be trimmed as needed to create a flat surface as long as the sample remains intact (not disturbed).
3. Grip the handle of the penetrometer so that the scale is visible and push the tip of the penetrometer into the soil so that the groove marked on the tip is even with the level of the soil.
4. Read the scale to determine the estimated unconfined compressive (shear) strength. If the ring is present, the reading should be taken from the lower side of the ring – side closest to the handle. The direct-reading scale (in tons/ft^2 or kg/cm^2) corresponds to equivalent unconfined compressive strength.
5. To minimize errors, take several readings near each other and discard those readings that may vary significantly from the majority and average of the readings.
6. Record all penetrometer readings on the sediment logs at the appropriate depth. Discarded readings should be lined out.

Miniature Vane Shear (Torvane)

1. Mount the desired vane to the unit and make sure it is secure.
    a. The standard vane should be used in the stress range of 500-2,000 psf (0.2-1 kg/cm^2) for fully saturated, medium to stiff cohesive soils
    b. The large vane should be used in the stress range of 0-500 psf (0-0.2 kg/cm^2) for remolded samples or soft cohesive soils
    c. The small vane should be used in the stress range of 4,000+ psf (2.0 kg/cm^2) for very stiff to hard cohesive soils
2. Align the “0” on the inner dial on top of the unit with the mark on the outer ring using a counter-clockwise rotation while holding the outer ring.

3. The surface of the cohesive soil to be tested should be at least two inches in diameter and relatively flat. The sample may be trimmed as needed to create a flat surface as long as the sample remains intact (not disturbed).
4. Press the unit into the sample until the vane blades are completely covered.
5. While maintaining constant pressure, rotate the outer ring of the unit until failure occurs. At failure, the soil will shear within the vanes and the device will spin back to the starting position. The outer ring should be rotated at a constant rate so that failure of the sample occurs within 5 to 10 seconds.
6. Release the outer ring, slowly, once failure has occurred. The mark on the outer ring will remain in place indicating the shear value at failure.
7. Record the shear value at failure. One revolution of the outer ring corresponds to a shear value of 1 kg/cm^2. Multiply readings by 0.2 when using the large vane and by 2.5 when using the small vane. Only one test is required per depth interval.
8. Record Torvane readings on sediment logs at the appropriate depth.

References

ASTM WK27337 – New Test Method for Pocket Penetrometer Test

ASTM D4648 – Standard Test Method for Laboratory Miniature Vane Shear Test for Saturated Fine-Grained Soil

Key Checks and Preventative Maintenance

- Prior to each use, make sure that the equipment is clean and dry.
- Protect the equipment from inclement weather and vandalism.

FIELD OPERATING PROCEDURE-09

Field Equipment Cleaning and Decontamination Procedures

Organization: CH2M	Revision: 0	Date: October 2016

Purpose

This field operating procedure (FOP) provides a general guideline for decontamination of reusable field sampling equipment. Personnel decontamination procedures are not addressed in this FOP. For a detailed list of personnel decontamination procedures, please refer to the Health and Safety Plan (HASP).

Scope

The methods for decontaminating reusable sampling equipment are discussed in the following sections.

Materials

- Health and safety equipment (as required in the HASP)
- Potable water
- Distilled water
- Non-phosphate soap
- Appropriate cleaning solvent (for example, methanol or acetone)
- Rinse collection plastic containers (5 gallon buckets)
- Brushes
- Garbage bags
- Spray bottles

Procedures and Guidelines

1. Disposable sampling equipment (core liners, aluminum pans, sampling utensils, etc.) should be used when possible.
2. Follow the health and safety procedures specified in the health and safety plan.
3. All non-disposable sampling equipment will be decontaminated on arrival at the site and prior to each use.
4. If a sediment grab sampler is implemented it should be decontaminated as follows:
    - In accordance with U.S. Environmental Protection Agency direction received on November 20, 2012, the Petite Ponar dredge sampler will be decontaminated by triple rinsing within the river at the location of sampling. The rinse water will be returned to the river.
    - If site conditions are observed (oily, sheen, etc.), then non-disposable equipment will be rinsed by adding a surfactant to the water, and the decontamination fluid will be containerized.
5. If drilling tools are implemented they should be decontaminated before the onset of drilling and between boring locations. Decontamination will include, but is not limited to, rods, split spoons or similar samplers, coring equipment, auger bolts, augers, and casing.

6. The following decontamination procedures should be followed for non-disposable sampling devices and equipment:
    - Wash with non-phosphate detergent and potable water.
    - Rinse with distilled water.
    - Rinse equipment with solvent (methanol or acetone) if equipment comes in contact with oil or grease.
    - Rinse with distilled water.

Attachments

None

Key Checks and Preventive Maintenance

Effectiveness of decontamination procedures will be monitored by collecting equipment blank samples, as specified in the FSP and/or QAPP.

FIELD OPERATING PROCEDURE-10

Sample Handling, Packaging, and Shipping

Organization: CH2M	Revision: 0	Date: May 2016

Purpose

This procedure delineates protocols for the packing and shipping of samples to the laboratory for analysis.

Scope

This procedure is applicable for all samples collected and prepared for analysis at an offsite laboratory. There are also additional procedures for analysis at an onsite laboratory.

Equipment and Materials

- Waterproof hard plastic coolers
- Plastic resealable bags
- Plastic garbage bags
- Absorbent packing material (not vermiculite)
- Inert cushioning material (not vermiculite)
- Ice
- Chain-of-custody forms
- custody seals
- Airbills and shipping pouches (for example, FedEx)
- Clear tape
- Strapping tape
- Mailing labels

Procedures and Guidelines

Prepare Bottles for Shipment

1. Arrange decontaminated sample containers in groups by sample number.
2. Check that sample container lids are tight.
3. Arrange containers in front of assigned coolers.
4. Affix appropriate adhesive labels to each container. Protect label with clear tape.
5. Enclose each sample in a clear, resealable plastic bag and ensure sample labels are visible.

Prepare Coolers for Shipment

1. For samples that will be dropped off at an onsite laboratory, these steps may be skipped. Sample bottles can be delivered to the onsite laboratory in a cardboard box or resealable plastic bag with the signed chain-of-custody form. They must then be transferred to the laboratory refrigerator.
2. Tape drains shut, inside and out.
3. Affix “This Side UP” labels on all four sides and “Fragile” labels on at least two sides of each cooler.

4. Place mailing label with laboratory address on top of the coolers.
5. Place inert cushioning material (for example, bubble wrap, preformed poly-foam liner) in the bottom of the cooler. Do not use vermiculite.
6. Place appropriate chain-of-custody records with corresponding custody seals on top of each cooler.
7. Place the samples inside a garbage bag and tie the bag.
8. Double bag and seal loose ice in resealable plastic bags to prevent melting ice from leaking and soaking the packing material. Place the ice outside the garbage bags containing the samples. Place sufficient ice in cooler to maintain the internal temperature at 4 degrees Celsius (°C) (±2°C) during transport.
9. Fill cooler with enough absorbent material and packing material to prevent breakage of the sample bottles and to absorb the entire volume of the liquid being shipped.
10. Sign each chain-of-custody form (or obtain signature) and indicate the time and date the cooler was custody sealed.
11. Seal the laboratory copies of the chain-of-custody forms in a large resealable plastic bag and tape to the inside lid of the cooler. Retain the chain-of-custody forms. Each cooler must contain a chain-of-custody form (or forms) that correspond to the contents of the cooler.
12. Close lid and latch.
13. Peel custody seals carefully from backings and place intact over lid openings (right front and left back). Cover seals with clear protection tape.
14. Tape cooler shut on both ends, making several complete revolutions with strapping tape. **Do not** cover custody seals.
15. Relinquish to carrier (for example, FedEx). Place airbill receipt inside the mailing envelope and send to sample documentation coordinator, along with the other documentation.

High-concentration Samples or Nonaqueous Phase Liquid Samples

When shipping high-concentration samples or samples of nonaqueous phase liquid, the CH2M dangerous goods shipping handbook should be consulted for reference. In addition, the CH2M dangerous goods shipping coordinator, Rob Strehlow, can be contacted at the Milwaukee, Wisconsin, equipment warehouse (414-257-4615) for assistance. This does not apply for samples delivered to an onsite laboratory.

Key Checks and Items

None.

FIELD OPERATING PROCEDURE-11

Documentation and Chain-of-Custody Procedure

Organization: CH2M	Revision: 0	Date: September 2018

Purpose

This procedure provides a definition of "custody" and describes protocols for documenting the transfer of custody from one party to the next (for example, from the site to the laboratory). A documented custody trail is established using sample tags and a chain-of-custody form that uniquely identifies each sample container, and who has possession of it from the sample's origin to its final destination. The chain-of-custody form also describes the sampling point, date, time, and analysis parameters.

Scope

Sample personnel should be aware that a sample is considered to be in a person's custody if the sample meets the following conditions:

- It is in a person's actual possession.
- It is in view after being in a person's possession.
- It is locked up so that no one can tamper with it after it has been in physical custody.

When samples leave the custody of the sampler, the cooler must be custody-sealed and possession must be documented.

Data generated from using this procedure may be used to support the following activities: site characterization, risk assessment, and evaluation of remedial alternatives.

Equipment and Materials

- Scribe-generated chain-of-custody
- Scribe-generated sample container labels

Procedures and Guidelines

Chain-of-Custody Forms

The chain-of-custody form must contain the following information:

- CASE NUMBER/CLIENT NUMBER: If a Contract Laboratory Program (CLP) laboratory is used, enter the case number provided by EPA's Regional Sample Control Center (RSCC). If the CLP is not used, enter the Statistical Analysis System (SAS) number provided by CH2M's sample and analytical coordinator.
- EPA REGION: Enter Region "5."
- CERCLIS ID: If applicable.
- SPILL ID: If applicable.
- SITE NAME/STATE: "Munger Landing"/St. Louis River Area of Concern.

- PROJECT LEADER: Enter the CH2M site manager's name.
- ACTION: Choose "Site Characterization."
- SAMPLING CO.: "CH2M."
- SAMPLE NO.: This is the unique number that will be used for sample tracking. For Central Regional Laboratory (CRL) and CLP laboratories, this number is taken from a block of numbers assigned by the EPA RSCC. For non-CRL and non-CLP laboratories, the CH2M sample and analytical coordinator will assign this number.
- MATRIX: Describes the sample media (such as surface water).
- SAMPLER NAME: The name of the sampler or sample team leader.
- CONCENTRATION: Low (L), low/medium (M), or high (H).
- SAMPLE TYPE: "Grab" or "Composite."
- ANALYSIS: This indicates the analyses required for each sample.
- PRESERVATIVE: Document what preservative has been added to the sample (for example, "HCl," "Ice Only," "None").
- STATION LOCATION: This is the CH2M station location identifier.
- Sample Collect Date/Time: Use military time.
- QC TYPE: This is for field quality control (QC) only, and includes field duplicate, field blanks, equipment blanks, and trip blanks.
- DATE SHIPPED: The date that samples are relinquished to the shipping carrier.
- CARRIER NAME: This is the carrier used for shipping samples (for example, "FedEx").
- AIRBILL: Air bill number used for shipping (if samples are hand delivered to their destination, "Hand-delivered" should appear in this field).
- SHIPPED TO: This is the laboratory name and full address, including the laboratory contact. If the contact is not known, use "Sample Custodian."
- CHAIN OF CUSTODY RECORD fields: The sampler's signature must appear in the "Sampler Signature" and the "Relinquished By" fields. The date and time (military time) must also be included. If additional personnel were involved in sampling, their signatures should appear in the "Additional Sampler Signature(s)" field.
- Although the samples are "relinquished" to the shipping carrier, the shipping carrier does not have access to the samples as long as the shipping cooler is custody sealed. Consequently, the shipping carrier does not sign the chain-of-custody form.
- SAMPLE(S) TO BE USED FOR LABORATORY QC: This identifies which samples are to be used for matrix spike (MS)/matrix spike duplicate (MSD) analyses.
- Indicate if shipment for case is complete: Use "Y" or "N."
- CHAIN-OF-CUSTODY SEAL: There is usually a minimum of two seals per shipping container.

Sample Labels

Each sample container will be identified with a uniquely numbered sample label. Each label will contain the following information:

- The unique sample number for sample tracking
- CH2M station location (the sample identifier)
- Date of sampling
- Time the sample was collected (in military time)
- All parameters for which the sample will be analyzed
- Preservative used (if any)
- Sample matrix (such as sediment)
- Identification when sample is intended to be used by the laboratory for MS/MSD

Attachments

- Attachment 1: Example Chain-of-Custody Form
- Attachment 2: User Manual for Scribe Sampling

Key Checks and Items

- All sample containers must be properly tagged.
- Each cooler must have a chain-of-custody form and the samples in the cooler (as identified by the sample tags) must match what is on the chain-of-custody form.
- Each chain-of-custody form must be properly relinquished (signature, date, time).
- The shipping cooler must be custody sealed in at least two places.

FOP-11 Attachment 1
Example Chain-of-Custody Form

USEPA CLP Organics COC (LAB COPY)
DateShipped: 6/10/2010
CarrierName: FedEx
AirbillNo: 12365478900

CHAIN OF CUSTODY RECORD
Site #: Demo
Case #: 99999
Cooler #: 0022

No: CLP Chain-0001
Lab: ABC Special Lab
Lab Contact: Mr. John J. Chemist
Lab Phone: 555-111-2222

Organic Sample #	Matrix/Sampler	Coll. Method	Analysis/Turnaround	Tag/Preservative/Bottles	Station Location	Collected	Inorganic Sample #	For Lab Use Only
Y0000	Soil/ START	Grab	BNA, VOA	1002, 1003 (4)	SS-0002	06/09/2010 08:00		
Y0001	Soil/ START	Grab	BNA, VOA	1004, 1005 (4)	SS-0003	06/09/2010 08:00		
Y0002	Soil/ START	Grab	BNA, VOA	1006, 1007 (4)	SS-0004	06/09/2010 08:00		
Y0003	Soil/ START	Grab	BNA, VOA	1008, 1009 (4)	SS-0005	06/09/2010 08:00		
Y9999	Soil/ START	Grab	BNA, VOA	1000, 1001 (4)	SS-0001	06/09/2010 08:00		

Special Instructions:

Shipment for Case Complete? N

Samples Transferred From Chain of Custody #

Analysis Key: BNA=CLP TCL Semivolatiles, VOA=CLP TCL Volatiles

Items/Reason	Relinquished by	Date	Received by	Date	Time	Items/Reason	Relinquished By	Date	Received by	Date	Time

FOP-11 Attachment 2
User Manual for Scribe Sampling

Part 1

Part 1 – Quick Start Guide

Scribe captures sampling, observational, and monitoring field data. It can import and export electronic data and can be configured for use with hand held computers. Scribe requires Windows 98 Second Edition or higher, 50 MB free disk space, a Pentium processor and 64 MB RAM. Scribe contains a demo project, which may be opened and used as a demo tool.

Starting a New Project

The first time Scribe is opened, the New Project Wizard starts, and helps create the first project.

New Project Wizard Screen

Click **Next** to display the "Project Information" screen.

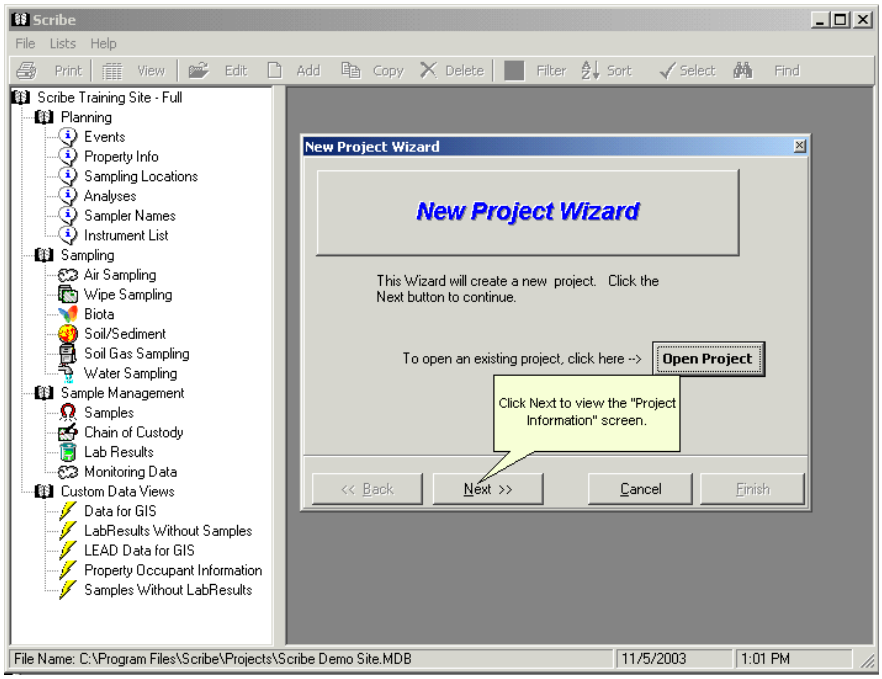

Figure 1 New Project Wizard screen

Project Information Screen

Enter the official EPA Site Name.

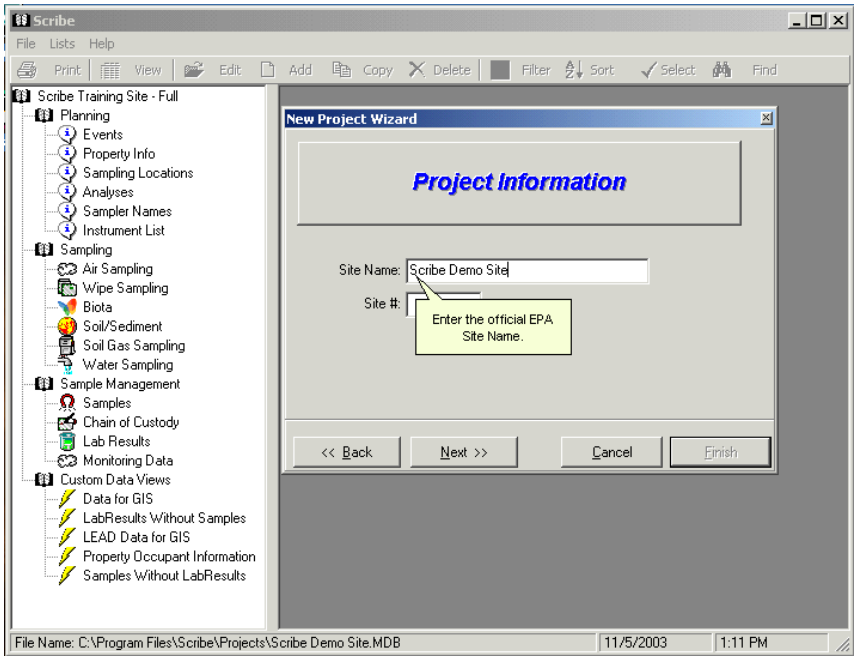

Figure 2 Project Information screen – Site Name

Enter the official EPA Site Charge number

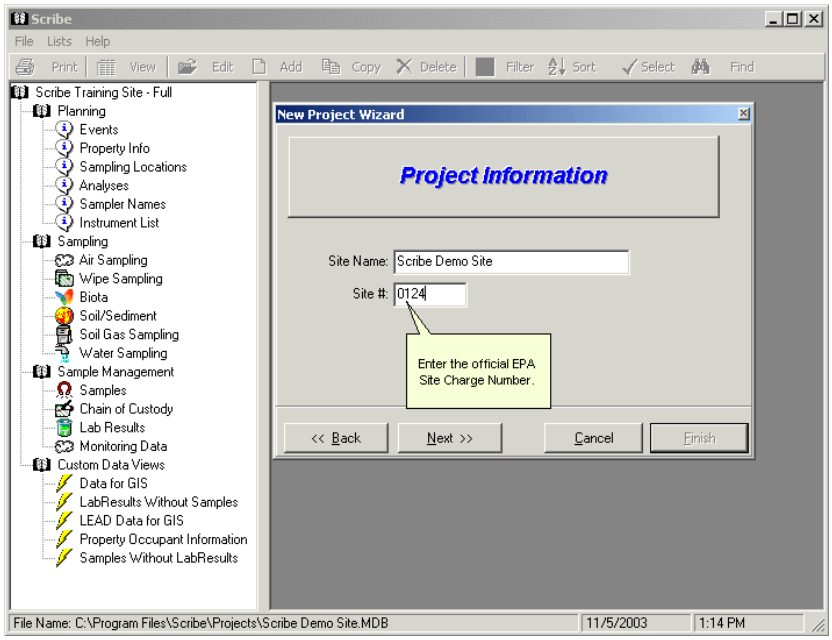

Figure 3 Site Information screen – Site #

Click **Next** to display the "Project File Path" screen.

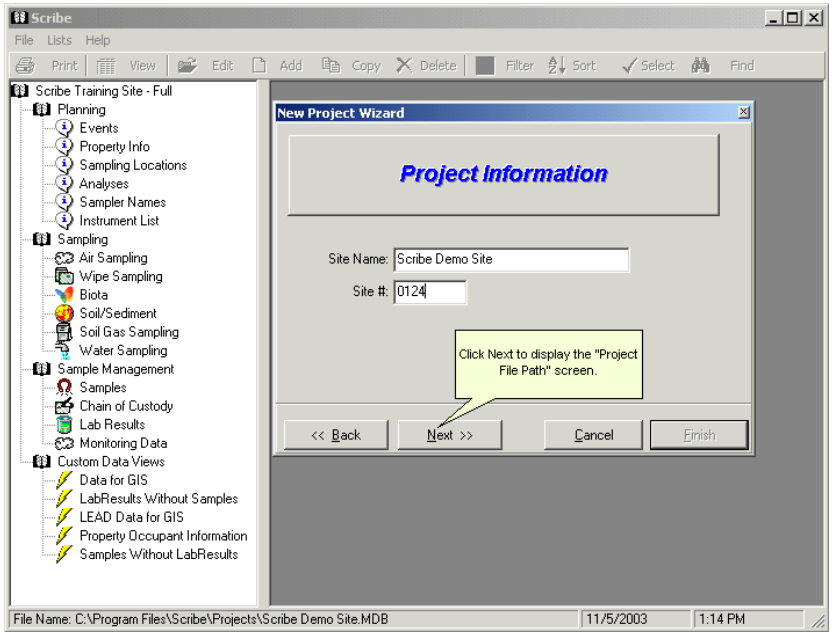

Figure 4 Project Information screen – Next

Project File Path Screen

The "Project File Path" screen displays a default location and filename for the project database.

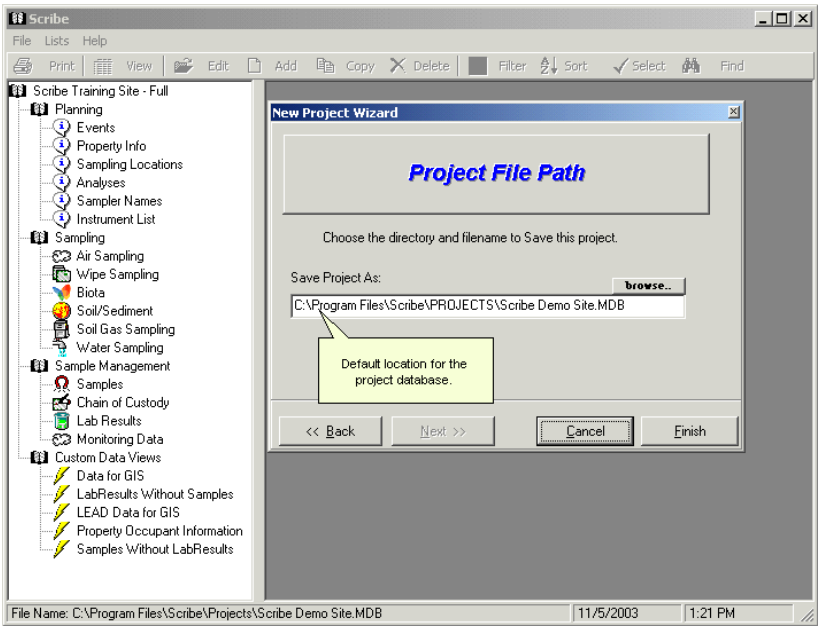

Figure 5 Project File Path screen

Click **Finish** to accept default path and filename to complete creation of the new project.

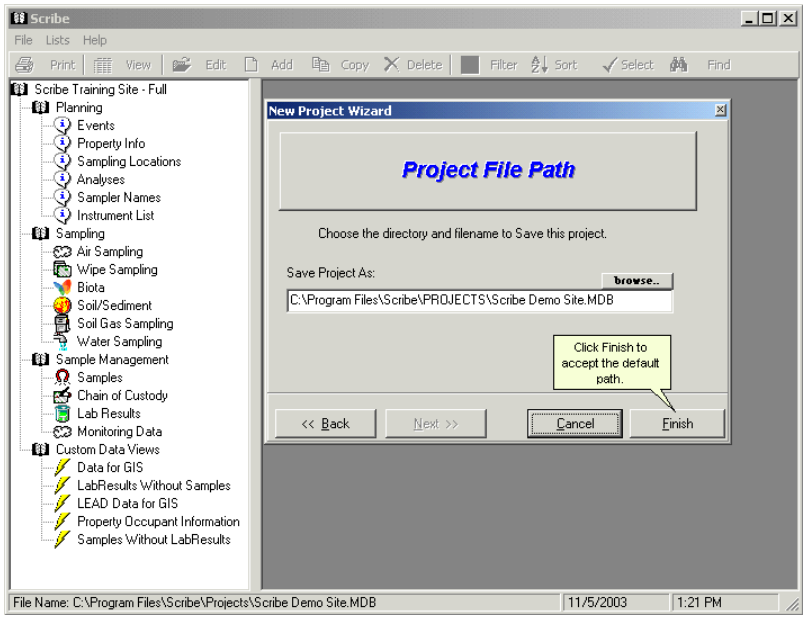

Figure 6 Project File Path - Finish

Site Info Screen

The New Project Wizard closes and the "Site Info" screen displays. Completing the information on this screen is not required but recommended.

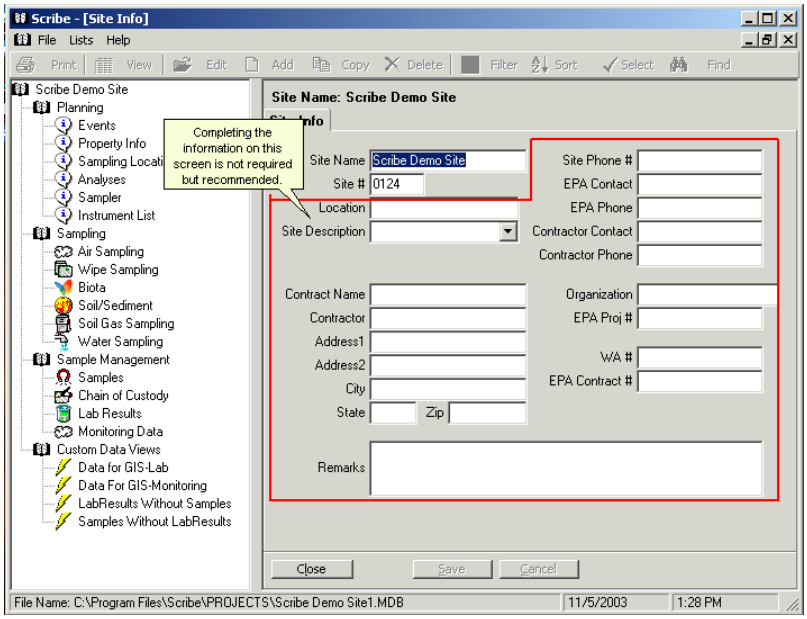

Figure 7 Site Info screen

Click one of the "Sampling" tasks in the "Navigation Pane" (e.g. Soil/Sediment).

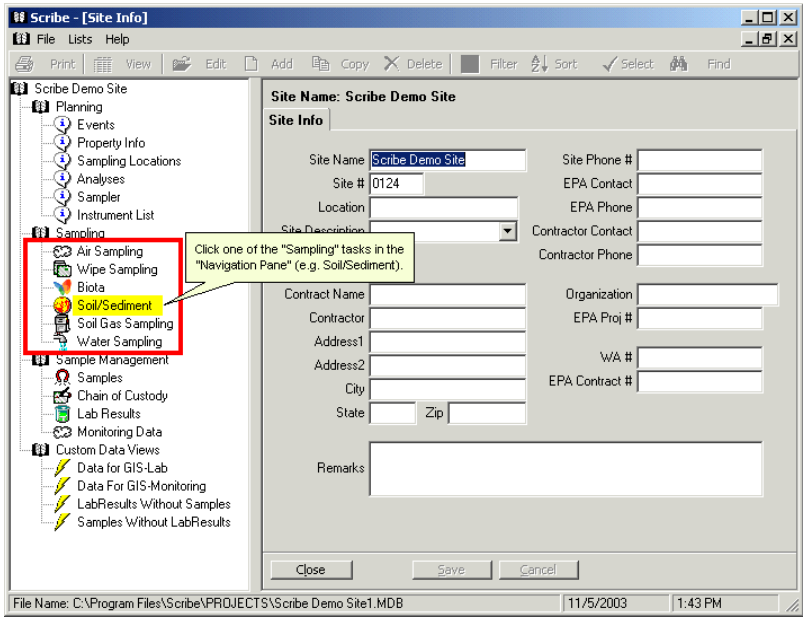

Figure 8 Site Info – Soil/Sediment Task

The "Soil/Sediment" screen with "Summary" tab displays.

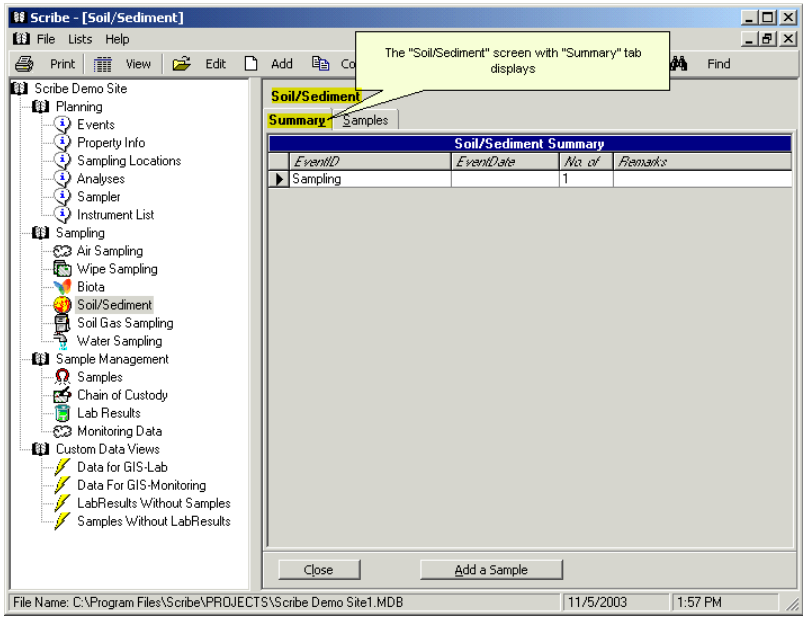

Figure 9 Soil/Sediment – Summary Tab

Click on the "Samples" tab.

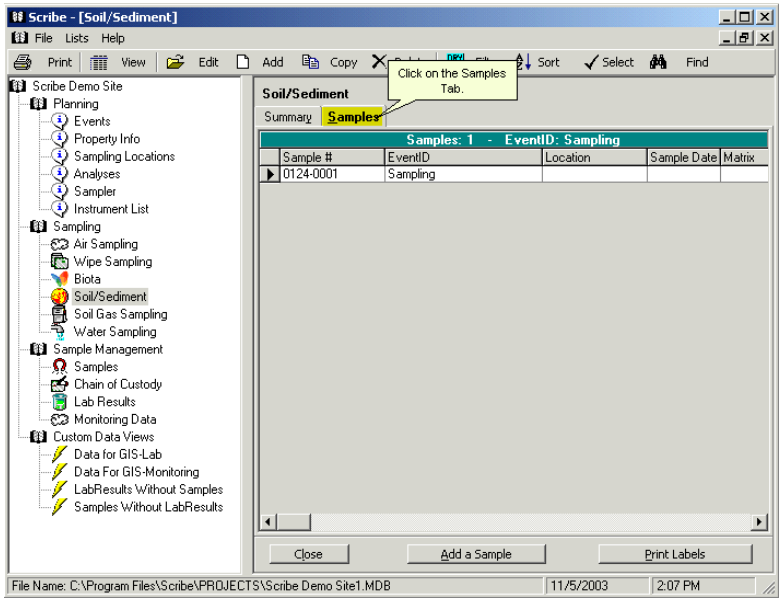

Figure 10 Click on Samples Tab

To add a Sample, Click **Add a Sample** to display the Sample Details screen.

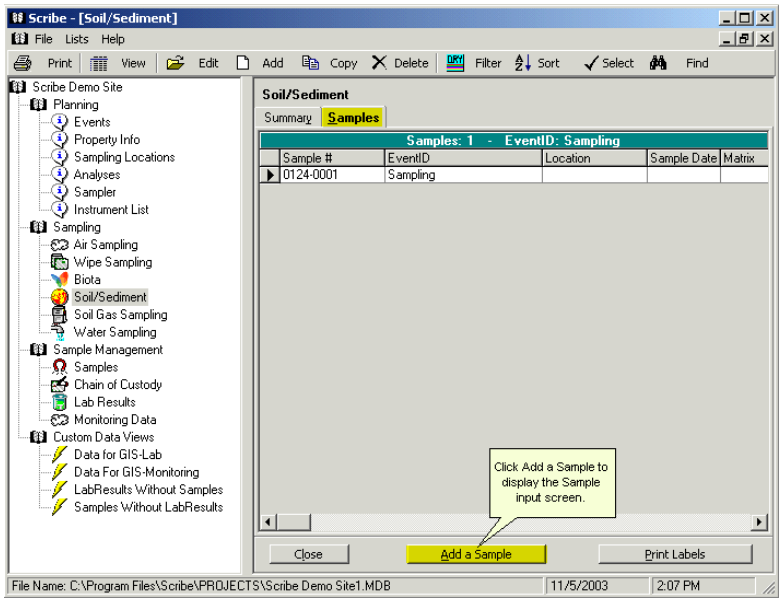

Figure 11 Soil/Sediment – Add a Sample Button

Copy a sample by right clicking on the sample and selecting **Copy** from the popup. The copied sample is added to the end of the list.

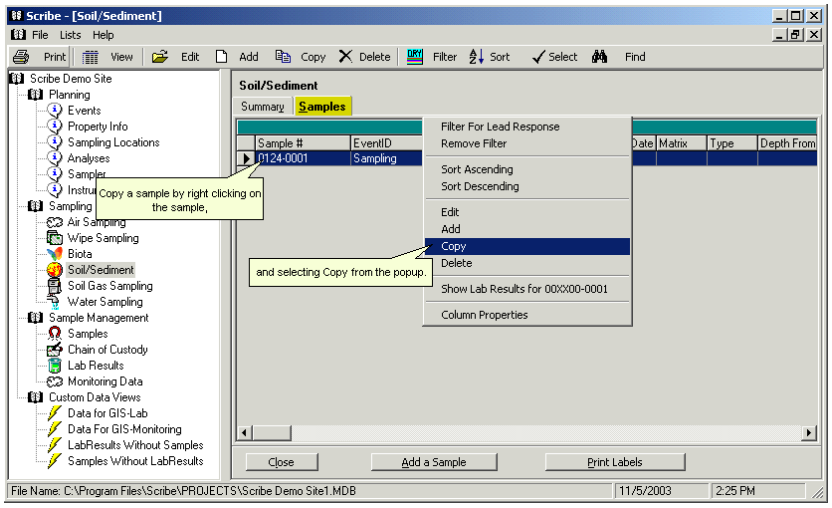

Figure 12 Copy a Sample

Only the "EventID" and "Sample #" fields are required in the Sample Details screen. Select from a list of default values for each field by clicking the down arrow next to the field or enter a value directly in the field.

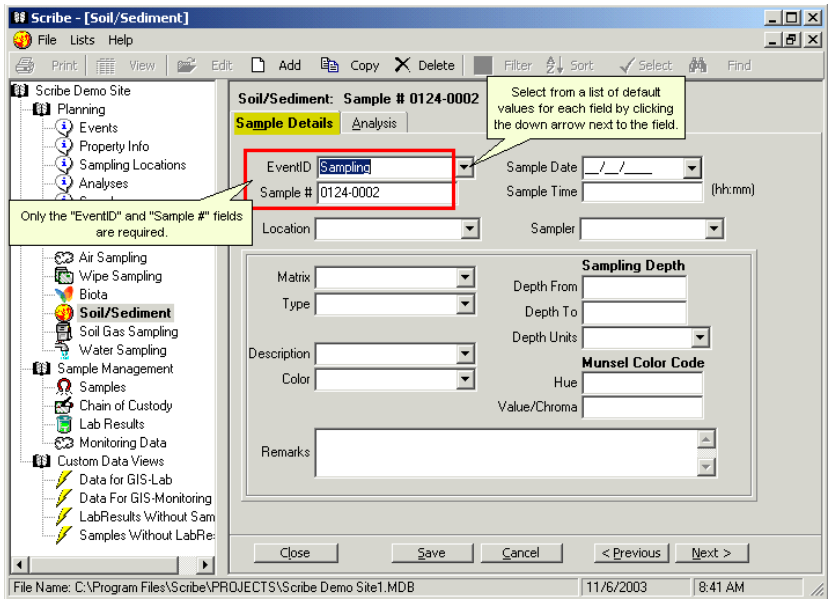

Figure 13 Sample Input screen - Sample Details Tab

Click the "Analysis" tab.

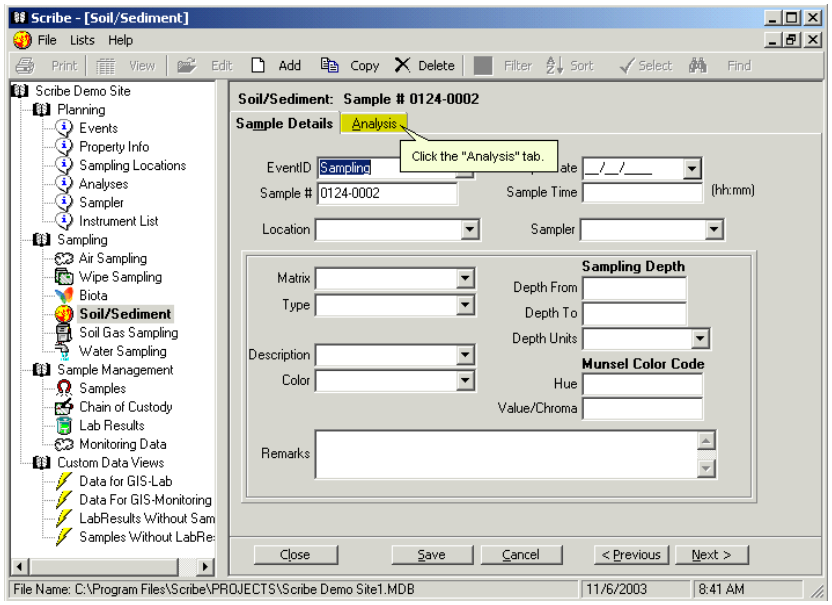

Figure 14 Sample Input screen – Click Analysis Tab

A Sample cannot be assigned to a chain unless Analysis information is provided. Some fields display a dropdown arrow when selected. Clicking on the drop down arrow displays a drop down menu.

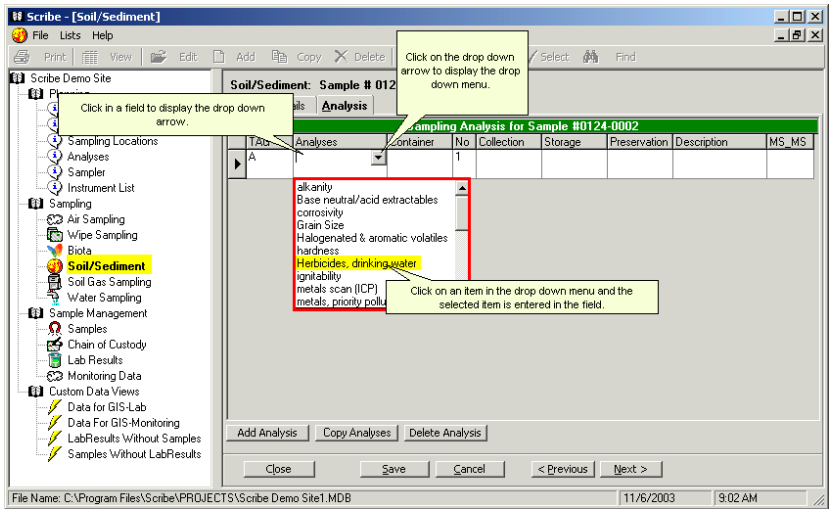

Figure 15Adding a Sample - Analysis Tab – Completing Fields

Click **Add Analysis** to add a new analysis. Fill in necessary fields. Notice that the "Tag" field automatically increments and the number field is filled in on the new record.

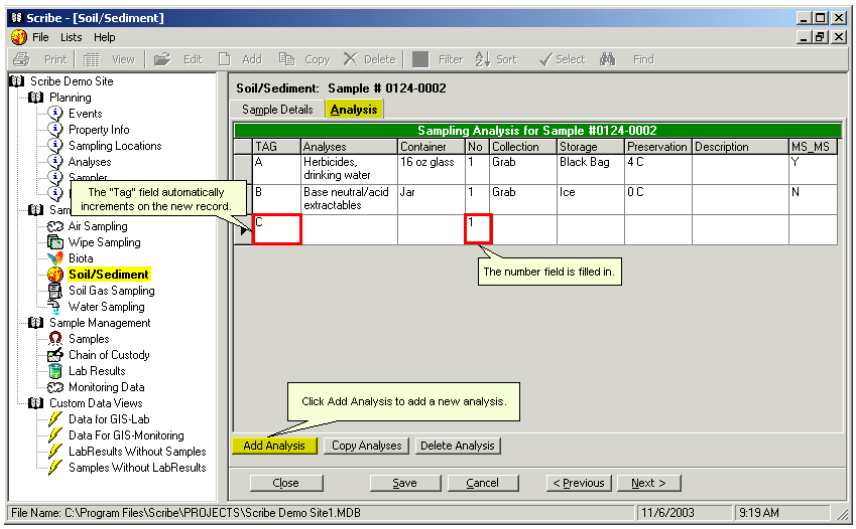

Figure 16 Add Analysis Button

Click **Save**.

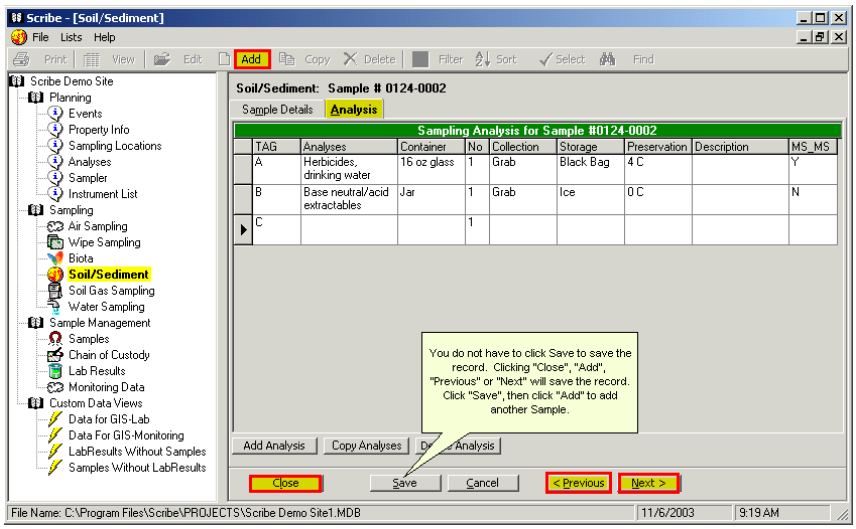

Figure 17 Analysis Tab – Save Button

Hi-light an analysis then click **Copy Analysis** to copy the selected analysis. The "Tag" field automatically increments, but all other fields are copied from the hi-lighted field.

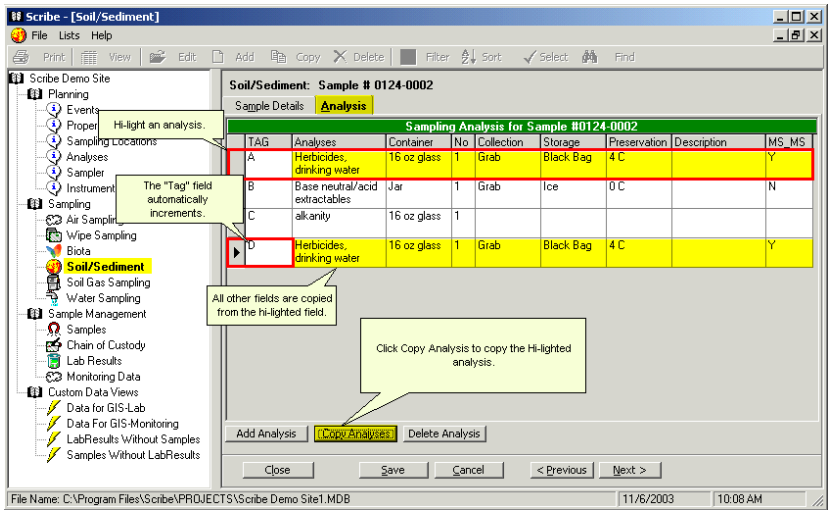

Figure 18 Copy Analysis

Click **Close**.

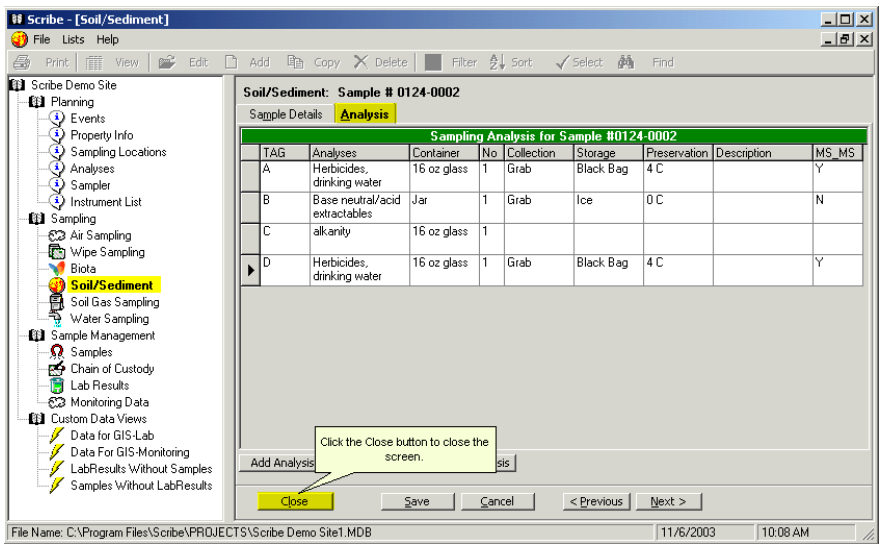

Figure 19 Analysis Tab – Close Button

All samples shown on the screen are printed. **Filter** selects or deselects items to display for printing. Print specific samples by Clicking **Filter** to display the "Basic Filter." Click **More** to display the "Advanced Filter".

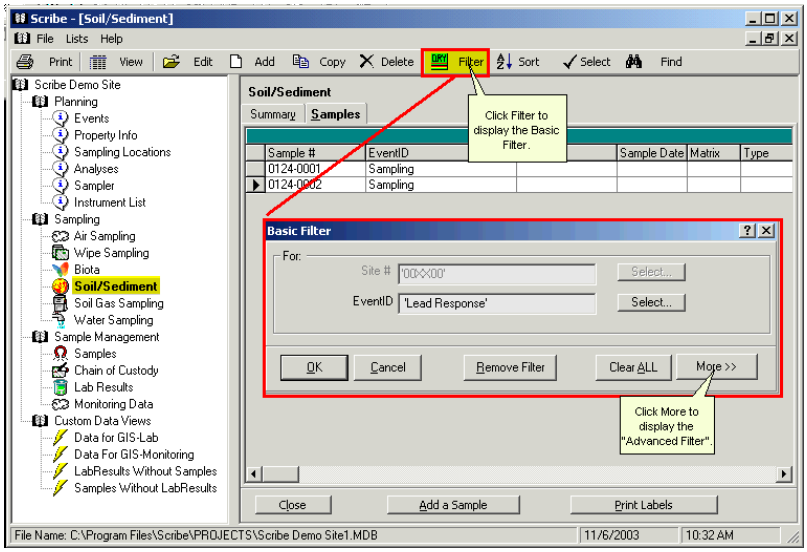

Figure 20 Basic Filter

Click **Select** and "drop down arrows" to select items in each of the "Advanced Filter" fields. Click **OK** to filter samples.

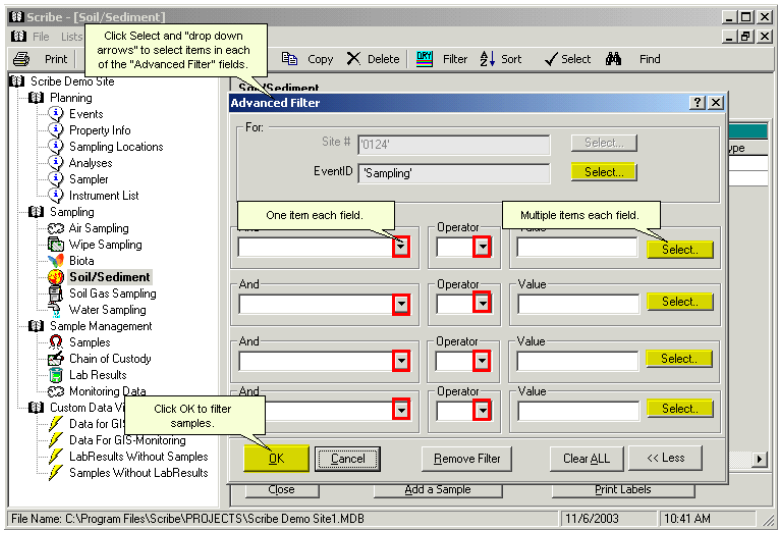

Figure 21 Advanced Filter

Click **Print Labels**.

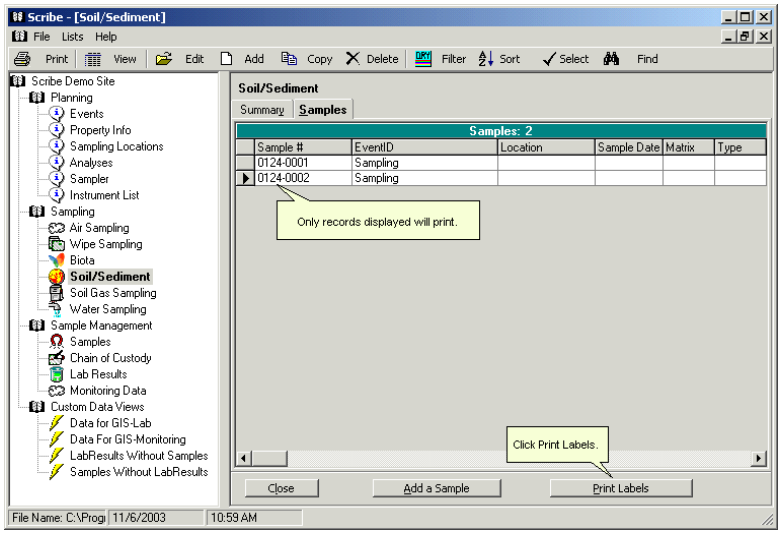

Figure 22 Print Labels Button

Click **Label Setup**.

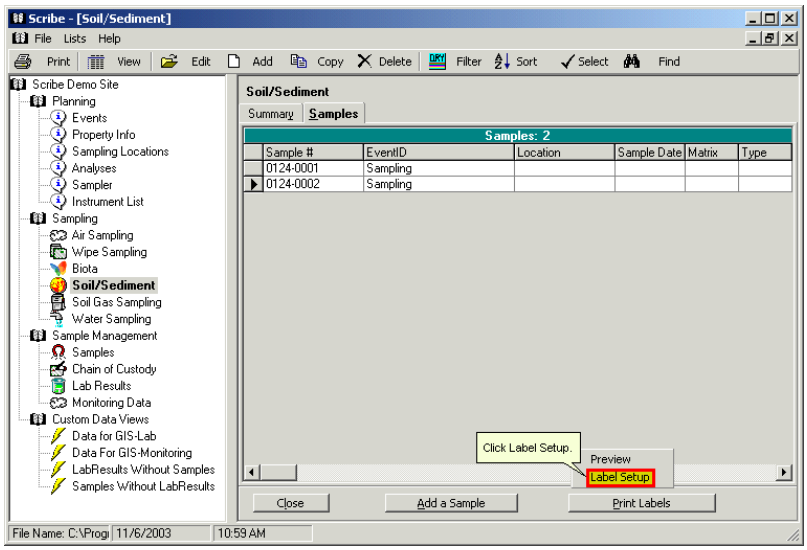

Figure 23 Label Setup Popup

Select the desired Label from the default list and click **Next**.

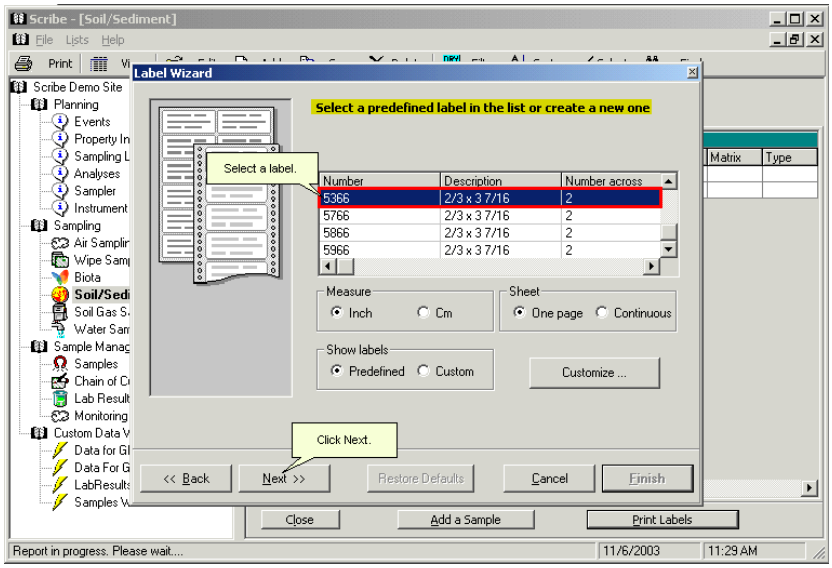

Figure 24 Label Wizard

Add, delete and organize label fields from this screen. Change the design or accept the default, then click **Next**.

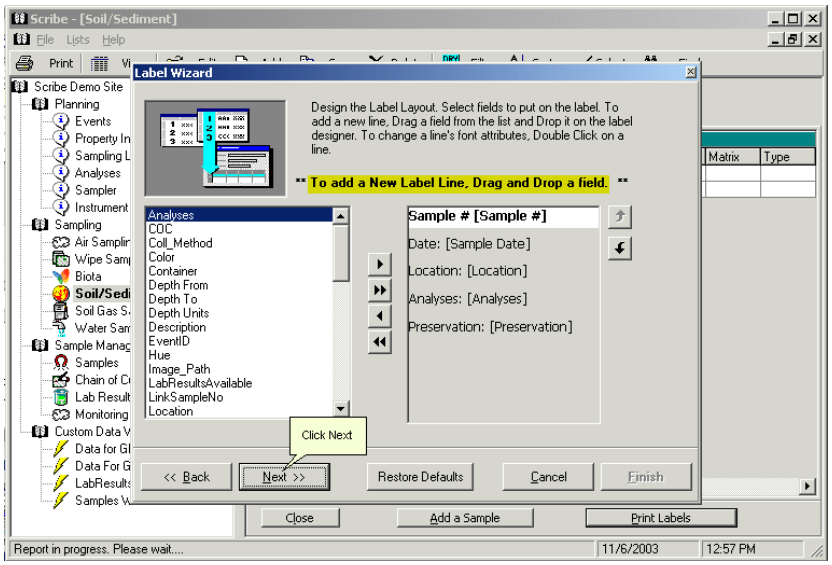

Figure 25 Label Wizard - Add, Delete and Organize Fields

Enter the "Label Number" from which to start printing then click **Finish** to display the "Preview" screen.

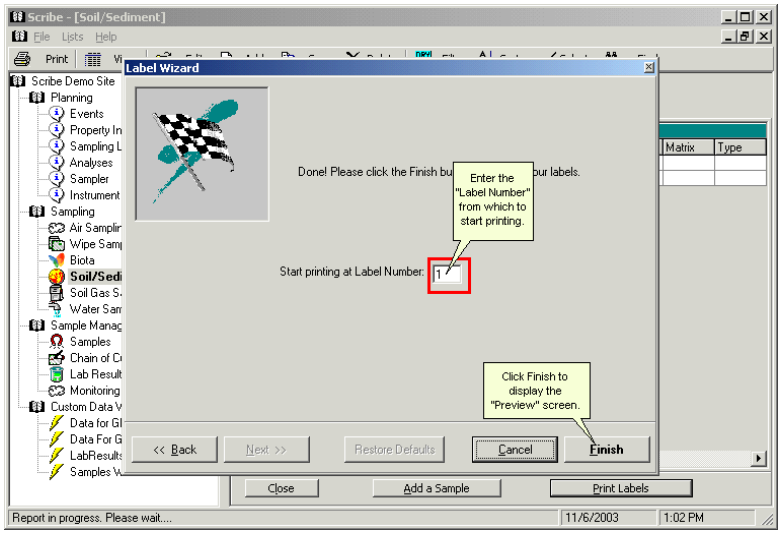

Figure 26 Start Printing at Label Number

The preview screen shows how the label will look when printed. Click **Print All** to print all the labels.

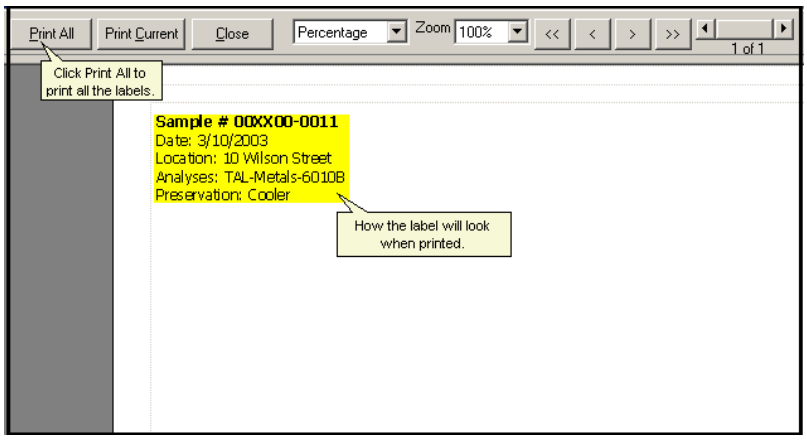

Figure 27 Label Print Preview

Select "Chain of Custody" in the "Navigation Pane".

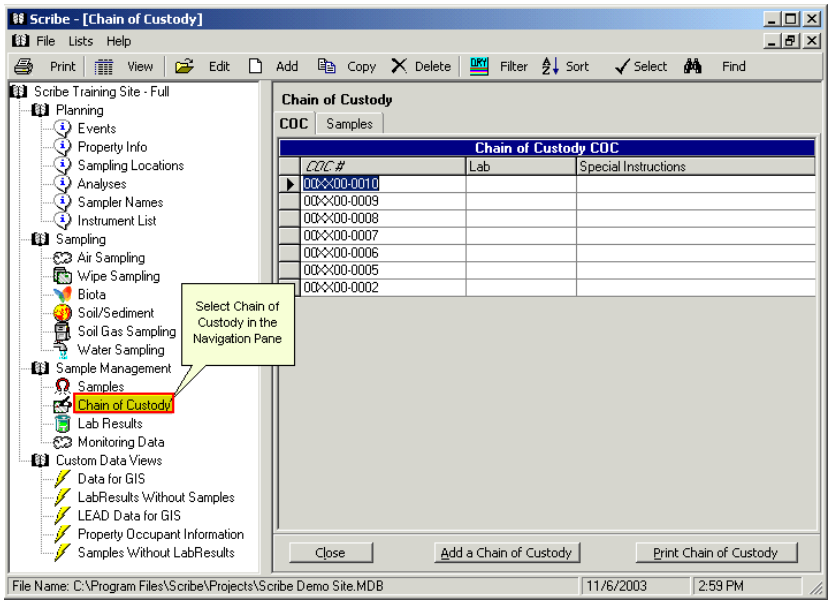

Figure 28 Chain of Custody – Navigation Pane

Click **Add a Chain of Custody**.

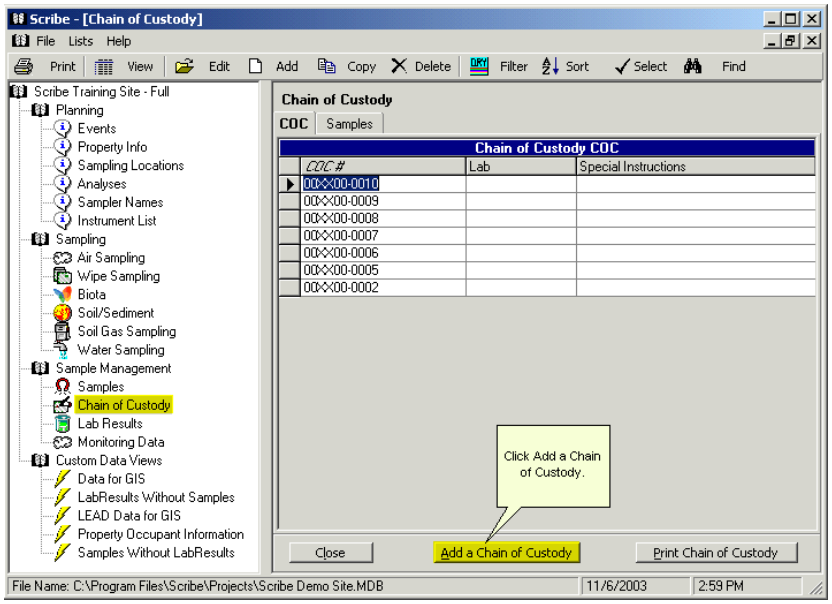

Figure 29 Add a Chain of Custody button

The "COC Details" screen displays. "COC #" is the only required. We recommend you complete the other fields because Lab info will print in the header of the Chain of Custody. I.e. Contact Name, Cooler #, Contact Phone #, Lab, and Lab Phone. Field.

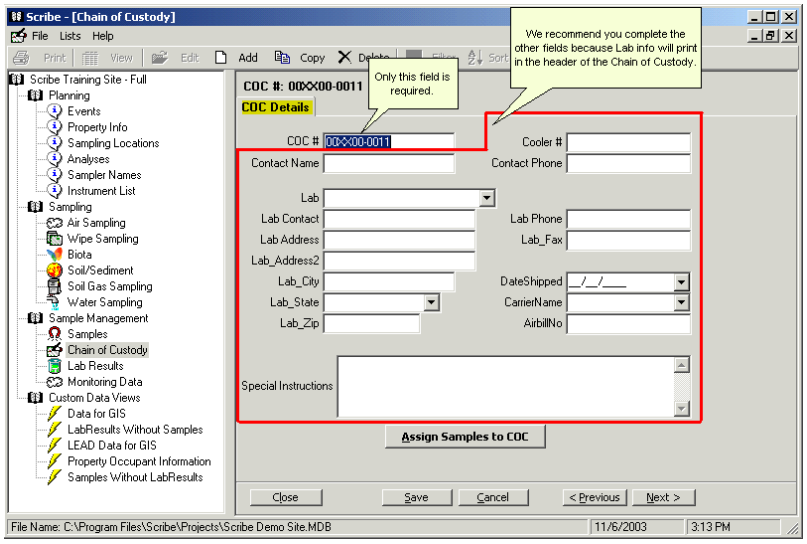

Figure 30 COC Details – Enter COC#

Click **Assign Samples to COC**.

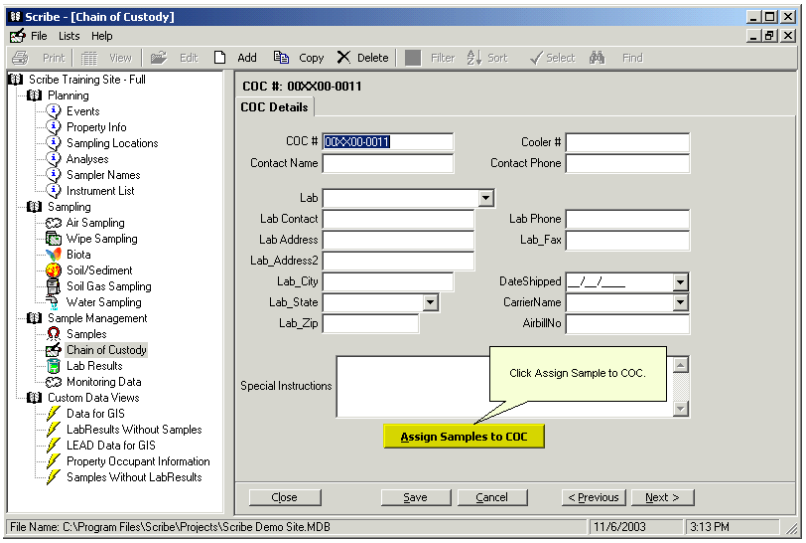

Figure 31 COC Details – Assign Sample to COC

The "Chain of Custody Screen" appears.

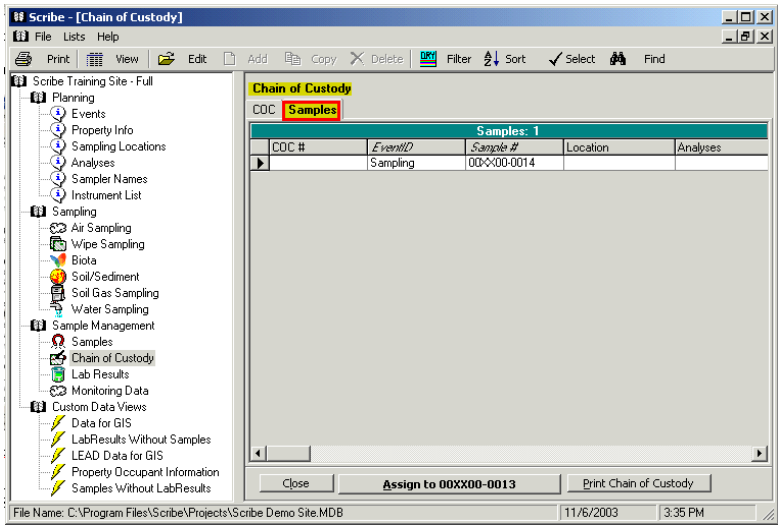

Figure 32 COC Samples Tab

Select Samples to assign to the Chain of Custody. Hi-light multiple samples by holding down the **Shift** key or **Ctrl** key while clicking on the samples.

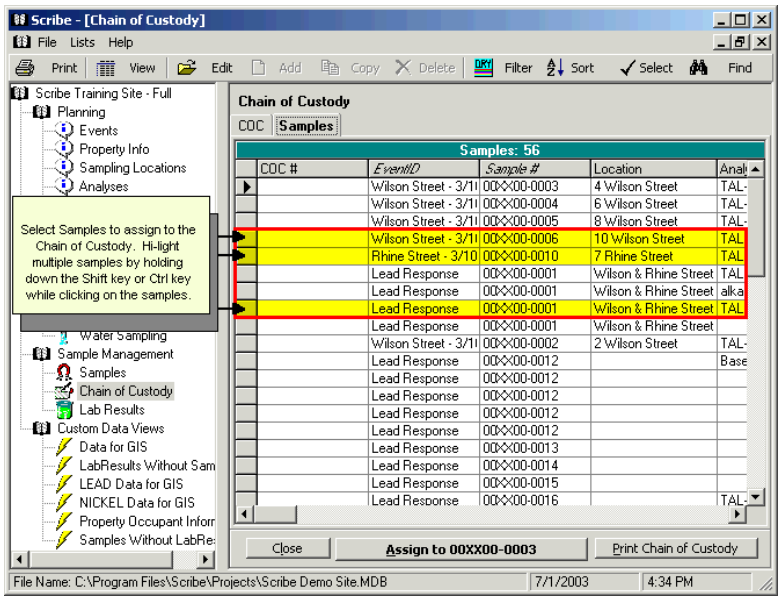

Figure 33 Select Samples to Assign to COC.

Click **Assign to … .**

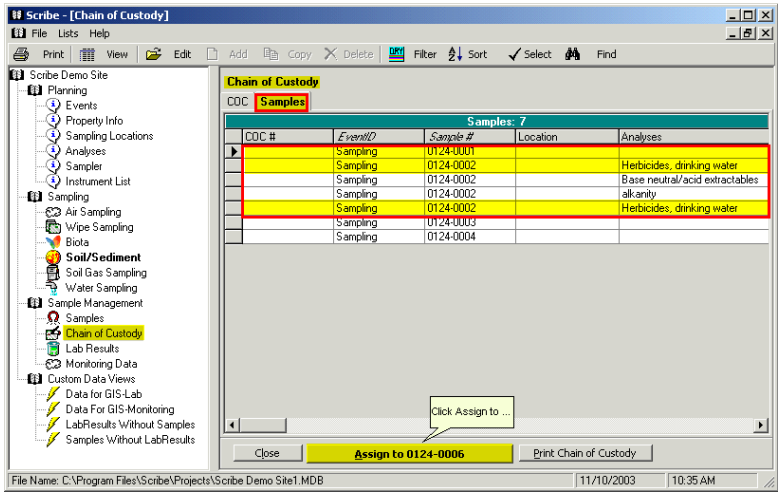

Figure 34 Chain of Custody – Assign to… Button

Click **Yes**.

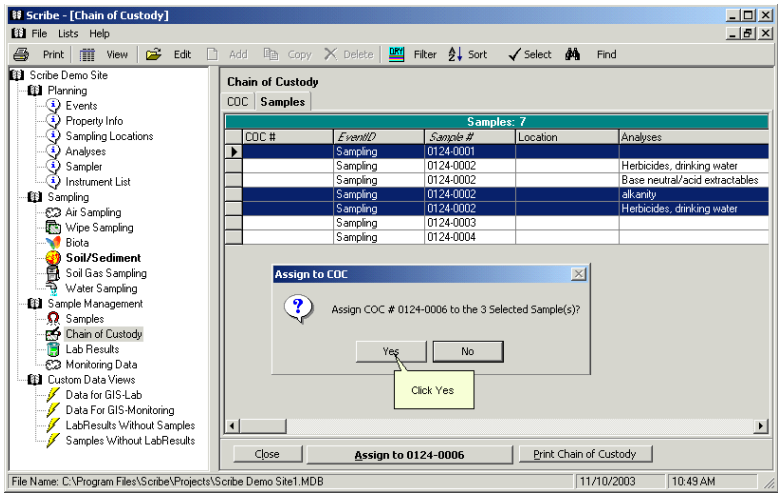

Figure 35 Assign to COC – Yes/No

Click **Print Chain of Custody**.

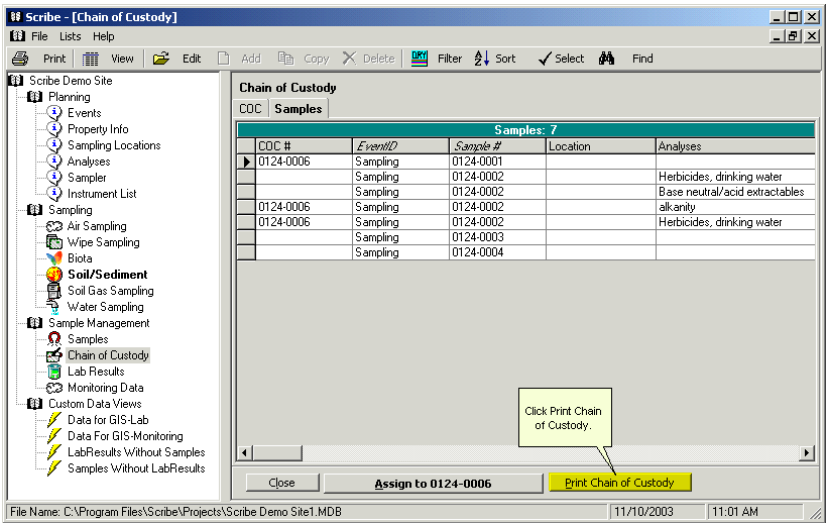

Figure 36 Print Chain of Custody Button

Click **Preview**.

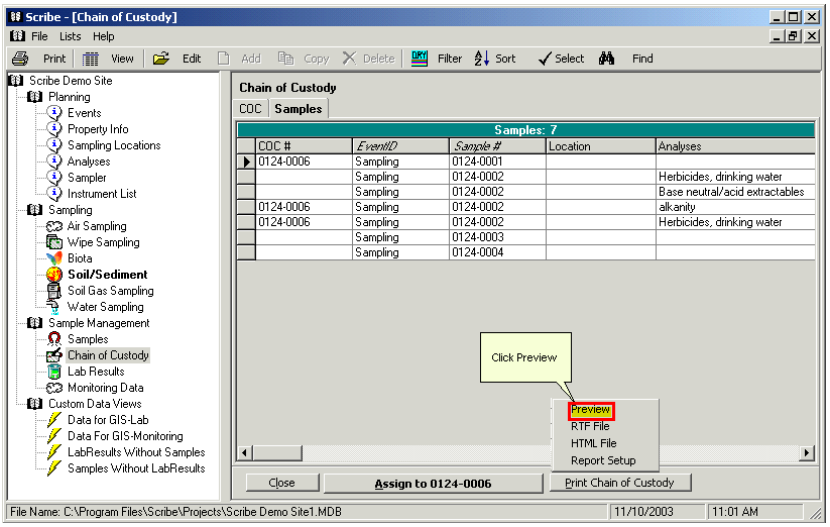

Figure 37 Chain of Custody - Preview

The default "Chain of Custody Record" report displays. Click **Print All** to print the report or **Close** to exit without printing.

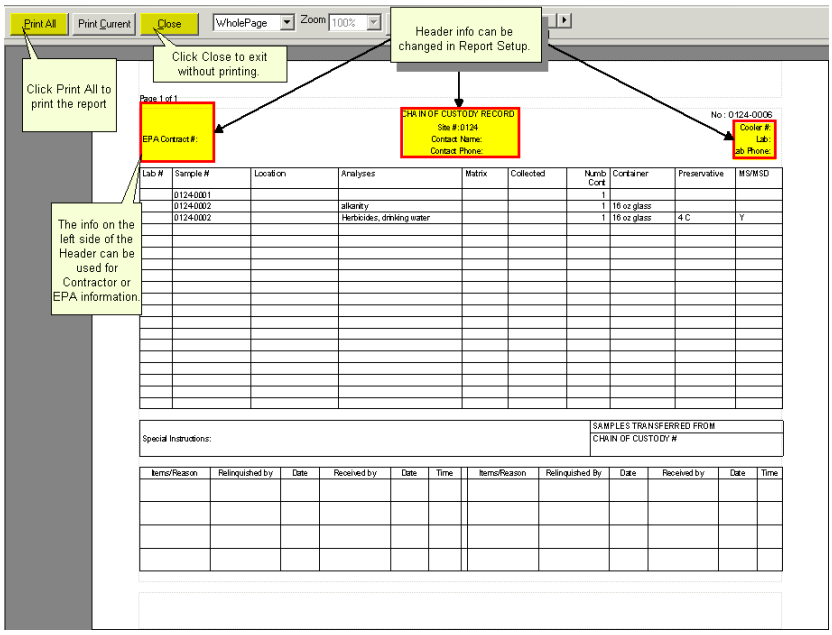

Figure 38 Chain of Custody Record Report Print Preview

You can modify the Report Header by Clicking **Report Setup** from the Popup menu.

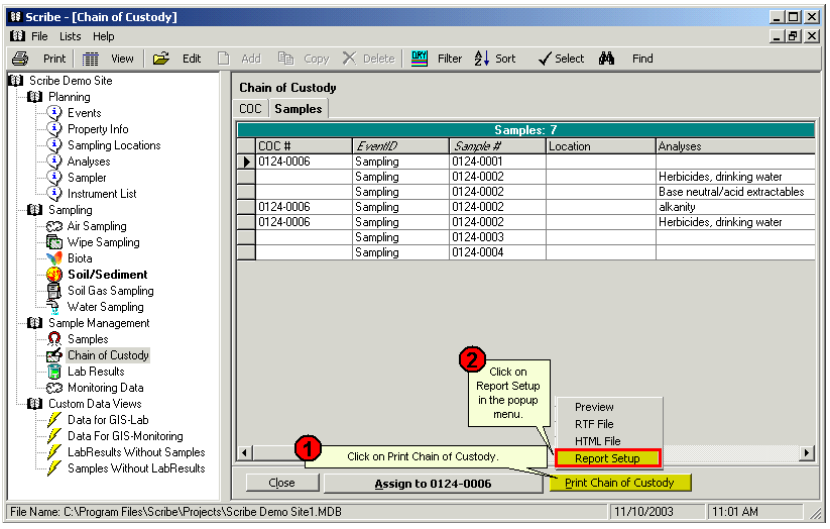

Figure 39 Select Report Setup

The Report Header screen allows you to customize the Chain of Custody Report Header. Click in the field you wish to change and type in the info. If the field has a drop down arrow, click on the drop down arrow then select an item from the drop down menu. The left side of the Header can be used for Contractor or EPA information. The info in Report Header screen will print on all future Chains for this project.

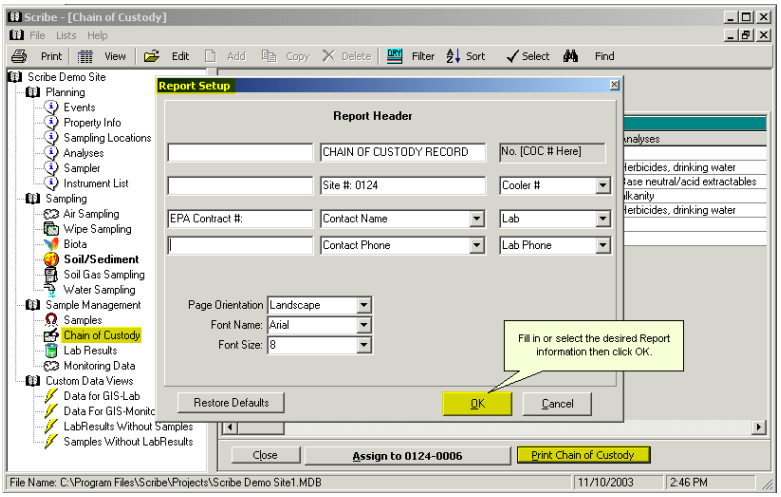

Figure 40 Change Report Header

This completes the Quick Start Guide. For more information on any feature discussed in this guide, refer to Part 2, Field Use Basics, which presents extensive information on the use of this database.

FIELD OPERATING PROCEDURE-12

Field Logbook

Organization: CH2M	Revision: 0	Date: May 2016

Purpose

The purpose of this FOP is to delineate protocols for recording field survey and sampling information in a field logbook.

Scope

Data generated from the use of this FOP may be used to support the following activities: site characterization, risk assessment, and evaluation of remedial alternatives.

Equipment and Materials

Field logbook
Indelible waterproof ink pen

Procedures and Guidelines

All information pertinent to a field survey or sampling effort will be recorded in a bound field logbook that will be initiated at the start of the first onsite activity. The field logbook will consist of a bound notebook with consecutively numbered pages that cannot be removed. The outside front cover of the logbook will contain the project (site) name and the specific activity (for example, remedial design sampling). The inside front cover will include the following:

- The name of the person to whom the logbook is assigned
- Logbook number
- Project name
- Project start date
- Project end date

Each page will be consecutively numbered, dated, and initialed. All entries will be made in indelible ink, and all corrections will consist of line-out deletions that are initialed and dated. If only part of a page is used, the remainder of the page should have an “X” drawn across it. At a minimum, entries in the logbook will include the following:

- Time of arrival and departure of site personnel, site visitors, and equipment
- Instrument calibration information, including make, model, and serial number of the equipment calibrated
- Field observations (such as sample description, weather, unusual site conditions or observations, and sources of potential contamination)
- Detailed description of the sampling location, including a sketch or field map markup
- Details of the sample site (for example, coordinates [*x*, *y*], water elevation [*z*], casing diameter and depth, integrity of the casing)

- Sampling methodology and matrix, including distinction between grab and composite samples
- Names of samplers and crew members
- Start or completion time of sample collection activities
- Field measurements (such as water depths, sediment probe depths)
- Type of sample (such as sediment)
- Number, depth, and volume of sample collected
- Field sample number
- Requested analytical determinations
- Sample preservation
- Quality control samples
- Sample shipment information including chain-of-custody form number, carrier, date, and time
- Health and safety issues (including level of personal protective equipment)
- Signature and date by personnel responsible for observations

Sampling situations vary widely. No general rules can specify the extent of information that must be entered in a logbook. Records should, however, contain sufficient information so that someone can reconstruct the sampling activity without relying on the collector's memory. The field team leader will keep a master list of all field logbooks assigned to the sampling crew.

Attachments

None.

Key Checks and Items

None.

Appendix C
Field Forms

SEDIMENT CORE LOG

STATION ID:

PAGE: **OF**

PROJECT :	Munger Landing Sediment Characterization	SURFACE ELEVATION (FT AMSL):	
PROJECT NUMBER :		WATER DEPTH (FT) :	
CONTRACTOR :	R/V Mudpuppy II vessel	SEDIMENT PROBE THICKNESS (FT):	
EQUIPMENT :		X - COORDINATE :	
LOGGER :		Y - COORDINATE :	
DATE :		CHEMICAL ANALYSIS:	___Dioxin/Furan ___PCB ___Mercury
START :	END :		___MethyMercury ___TOC ___Archive

DEPTH BELOW SURFACE (FT)				**SEDIMENT DESCRIPTION**	**COMMENTS**			
	PENETRATION (FT)							
		RECOVERY (FT)						
			#/TYPE	SEDIMENT TEXTURE, COLOR, RELATIVE DENSITY OR CONSISTENCY, & STRUCTURE	PID	POCKET PEN	T-VANE	SAMPLE ID

NOTES:

U.S. EPA Great Lakes National Program Office
Locational Data Checklist and Metadata Recording Form

This document accompanies *GLNPO's Great Lakes Legacy Act Data Reporting Standard* , Version 1.0, March 2010, which provides detailed data reporting guidance for project data including required electronic data deliverables (EDD). In addition to the EDD and project field forms, project participants are required to complete this checklist at the end of each sampling event. Copies of completed forms should be submitted to the GLNPO Project Lead.

Contact Information

Contact Name: _____ Phone Number: _____

Affiliation: _____ E-mail Address: _____

Study Information

Project Title: _____

Site Name: _____

Sampling Start Date: _____ Sampling Stop Date: _____

Preparation Activities (please confirm each activity in the boxes to the right)

1. Sampling staff are trained in GPS Field Data Collection and have familiarized themselves with the GPS unit used for this project (certified training recommended). ☐

2. Determined window of satellite availability. http://www.trimble.com/planningsoftware_ts.asp ☐

3. Established at least two control points for both vertical and horizontal accuracy. For assistance locating control points visit http://www.ngs.noaa.gov/cgi-bin/datasheet.prl or http://www.geocaching.com/mark/. This may not be feasible if the GPS unit is mounted to a vessel. * ☐

4. Located 3 reference points. * ☐

Data Collection Activities (please confirm each activity in the boxes to the right)

1. GPS unit was configured to collect data only when the following requirements were met:
   a. A minimum of four satellites ☐
   b. Position dilution of precision (PDOP)<=6 ☐
   c. Satellite elevation >=15° above the horizon ☐
   d. A minimum signal-to-noise ratio (refer to GPS user manual for recommendation) ☐

2. Collected point data based on the nearest base station's logging interval. ☐

3. Collected point data for a period of at least 1 minute per location. ☐

4. Reported locational data in WGS 84 or NAD 83 (please specify_____). ☐

Please provide an explanation if a box was not checked for any of the responses above and specify deviations (include sample IDs if applicable):

_____

_____

_____

*Collect these points on at least the first day of sampling. Collecting on each sampling day is recommended. Record on page 2.

GPS Unit Specifications

GPS Brand and model number: _____

Model accuracy: _____

Data Processing

Which of the following best describes any data correction that may have been performed:

☐ real-time correction - specify type _____ ☐ post processed differential correction - provide base station id and location _____

☐ no correction ☐ other, please specify _____

Quality Information

Describe any difficulties in collecting locational data: _____

_____

List final post-processed accuracy of the data: _____

Data Collector:

Confirm required information has been provided.

_____ _____

Signature Date

GLNPO Project Lead:

Confirm required information has been provided.

_____ _____

Signature Date

U.S. EPA Great Lakes National Program Office
GPS Daily Check

Collect these data on at least the first day of sampling. Collecting on each sampling day is recommended.

Project Title: _____

Date: _____

Horizontal Control Point 1

Benchmark ID: _____ Time: _____

Established Latitude: _____ Measured Latitude: _____

Established Longitude: _____ Measured Longitude: _____

Displacement (include UOM): _____

Horizontal Control Point 2

Benchmark ID: _____ Time: _____

Established Latitude: _____ Measured Latitude: _____

Established Longitude: _____ Measured Longitude: _____

Displacement (include UOM): _____

Vertical Control Point 1

Benchmark ID: _____ Time: _____

Established Elevation: _____ Measured Elevation: _____

Displacement (include UOM): _____

Vertical Control Point 2

Benchmark ID: _____ Time: _____

Established Elevation: _____ Measured Elevation: _____

Displacement (include UOM): _____

Reference Point 1

Time: _____

Physical/Locational description: _____

Measured Latitude: _____ Measured Longitude: _____

Reference Point 2

Time: _____

Physical/Locational description: _____

Measured Latitude: _____ Measured Longitude: _____

Reference Point 3

Time: _____

Physical/Locational description: _____

Measured Latitude: _____ Measured Longitude: _____

PID (MiniRae) Calibration Log Sheet
Munger Landing
Minnesota and Wisconsin

Revision: 00	Date: October 2018

Date/Initials	Project Number	PID Number (S/N)	Calibration Gas Lot No. (100 ppm isobutylene)	Calibration Readings (zero/span)	Comments

IDW Tracking Log - Drum Contents Log
Munger Landing
Minnesota and Wisconsin

Revision: 00	Date: October 2018

Date/Initials	Inspector Name	Contents Matrix	Origin of Waste (e.g., Sample Loc ID)	RCRA Hazardous (known or pending analysis)?	Accumulation Start Date	Accumulation End Date	Notes

ch2m

IDW Storage Area - Inspection Log
Munger Landing
Minnesota and Wisconsin

Revision: 00	Date: October 2018

Date/Initials	Inspector Name	Container Type	Leaking (Y/N)	Uncovered (Y/N)	Bulging / Rusting (Y/N)	Labeled (Y/N)	Secondary Containment (Y/N)	Comments

ch2m

IDW Tracking Log - Container Delivery and Pickup
Munger Landing
Minnesota and Wisconsin

Revision: 00	Date: October 2018

Date/Initials	Container Type (Drum/Roll Off)	Service Provider	Date Container Pick up or Drop off	# Containers	IDW type (decon water, sediment, PPE)	IDW Sample ID (if applicable)	Notes

Appendix D
EPA Sample Summary Table

ID	Lat_DD	Long_DD	Group	Reason - Category	Intervals	PCB	*Analyze*	*Hold*	Dioxin	*Analyze*	*Hold*	HG	*Analyze*	*Hold*	MeHG	Analyze	Hold	TOC	Analyze	Hold	State	Basis	Notes
1	46.7053629	-92.202794	1	Outet	4	4	*2*	*2*	4	*2*	*2*	4	*2*	*2*	2	*2*	-	4	*2*	*2*	WI	Confrim PCB & Dioxin at SLR 16-UR22	PCB 1.8 ppm, Hg 1.1 ppm, Dioxin 42 ppt 0.5 to 2 feet, 584.3 to 582.3 ft MSL
2	46.7052348	-92.2027281	1	Outlet	4	4	*2*	*2*	4	*2*	*2*	4	*2*	*2*	2	*2*	-	4	*2*	*2*	WI	Confrim SLR 16-UR22	PCB 1.8 ppm, Hg 1.1 ppm, Dioxin 42 ppt 0.5 to 2 feet, 584.3 to 582.3 ft MSL
3	46.7047681	-92.2027014	1	Outlet	4	4	*2*	*2*	4	*2*	*2*	4	*2*	*2*	2	*2*	-	4	*2*	*2*	WI	PCB Dioxin Extent	No dioxin in BW17, DF detects here though UR26, middle slip clean
4	46.7052792	-92.2038301	2	DS Footprint Confirmation	4	-	-	-	4	*2*	*2*	-	-	-	-	-	-	4	*2*	*2*	MN	Deeper flow channel limited data	PCB ND in 2 intervals at 042 and 067, No PCB data at BW14-001, north end of dredged slip
5	46.704792	-92.2037666	2	DS Footprint Confirmation	3	3	*2*	*1*	3	*2*	*1*	-	-	-	-	-	-	3	*2*	*1*	WI	Extent in Wisconsin - PCB & dioxin	No PCB or surface dioxin at 024. 042 PCB ok - No dixon data
6	46.7048005	-92.204346	2	DS Footprint Confirmation	4	-	-	-	4	*2*	*2*	-	-	-	-	-	-	4	*2*	*2*	MN	Deeper flow channel (10 ft hole) - no data	No PCB at 024, no surface dioxin at 024 (0.15 to 0.3 m is clean)
7	46.7045198	-92.2050517	2	DS Footprint Confirmation	4	-	-	-	4	*2*	*2*	4	*2*	*2*	-	-	-	4	*2*	*2*	MN	Deeper flow channel (9 ft hole) - no data	No PCB at 039, No dioxin at 039,
8	46.704031	-92.2044483	2	DS Footprint Confirmation	3	3	*2*	*1*	3	*2*	*1*	3	*2*	*1*	2	*2*	-	3	*2*	*1*	WI	Extent in Wisconsin	No data
9	46.7039499	-92.2053116	3	Hotspot Delineation	4	-	-	-	4	*2*	*2*	4	*2*	*2*	-	-	-	4	*2*	*2*	MN	Confrim BW14-11 limiited vetrtical	No dioxin at 011, No surface PCB - Only 1 PCB spanning two depth bins (0.34 to 0.59 m) map shows 2
10	46.7036026	-92.2056585	3	Hotspot Delineation	4	4	*2*	*2*	4	*2*	*2*	4	*2*	*2*	-	-	-	4	*2*	*2*	MN	Confirm hotspot extent	Surface dioxin 292 PPT at 045, no PCB at 045, 85 PPT dioxin at 032 (0.15 to 0.47m)
11	46.7034635	-92.2063489	3	Hotspot Delineation	3	3	*2*	*1*	3	*2*	*1*	3	*2*	*1*	-	-	-	3	*2*	*1*	MN	Confirm hotspot extent	
12	46.702927	-92.2052324	3	Hotspot Delineation	3	3	*2*	*1*	3	*2*	*1*	2	*2*	-	2	*2*	-	3	*2*	*1*	WI	Extent in Wisconsin - Step out from 032	032 Dioxin 85 PPT (0.15 to 0.47), no surface DF at 0.32
13	46.7029483	-92.2064011	3	Hotspot Delineation	3	3	*2*	*1*	3	*2*	*1*	-	-	-	-	-	-	3	*2*	*1*	MN	Confirm hotspot extent	
14	46.7022278	-92.2064325	3	Hotspot Delineation	3	3	*2*	*1*	3	*2*	*1*	-	-	-	-	-	-	3	*2*	*1*	MN	Confirm hotspot extent	
15	46.7022705	-92.205495	3	Hotspot Delineation	4	4	*2*	*2*	4	*2*	*2*	-	-	-	-	-	-	4	*2*	*2*	WI	Extent in Wisconsin - Step out from 047	047 PCB Surf ok, 0.956 PPM bottom, dioxin surf 18 PPT, bottom 118 PPT
16	46.7015177	-92.2057697	3	Hotspot Delineation	4	4	*2*	*2*	4	*2*	*2*	4	*2*	*2*	2	*2*	-	4	*2*	*2*	WI	Extent in Wisconsin - Step out from 049	049 PCB >MEC, Dioxin Surf = 22 PPT, 204 PPT (0.15 to 0.39 m)
17	46.7004423	-92.2070818	3	Hotspot Delineation	3	3	*2*	*1*	3	*2*	*1*	-	-	-	-	-	-	3	*2*	*1*	MN	Hotspot delineation	
18	46.700695	-92.20543	3	Hotspot Delineation	4	4	*2*	*2*	4	*2*	*2*	4	*2*	*2*	2	*2*	-	4	*2*	*2*	WI	Extent in Wisconsin - Step out from 51	051 Dioxin 174 PPT (surf), 47 PPT (0.15 to 0.5 m), 5.77 PPM PCBs at 052
19	46.6998019	-92.2050958	3	Hotspot Delineation	4	4	*2*	*2*	4	*2*	*2*	4	*2*	*2*	2	*2*	-	4	*2*	*2*	WI	Extent in Wisconsin	036 dioxin 15 PPT (0.15 to 0.42m), no surface sample
20	46.7022881	-92.2050967	4	Wisconsin Extent - Shallows	3	3	*2*	*1*	3	*2*	*1*	-	-	-	-	-	-	3	*2*	*1*	WI	Extent in Wisconsin - Step out	
21	46.7015415	-92.2051481	4	Wisconsin Extent - Shallows	3	3	*2*	*1*	3	*2*	*1*	2	*2*	-	2	*2*	-	3	*2*	*1*	WI	Extent in Wisconsin - Step out	
22	46.7006604	-92.2048787	4	Wisconsin Extent - Shallows	3	3	*2*	*1*	3	*2*	*1*	3	*2*	*1*	2	*2*	-	3	*2*	*1*	WI	Extent in Wisconsin - Step out	
23	46.6985479	-92.2044861	4	Wisconsin Extent - Shallows	3	3	*2*	*1*	3	*2*	*1*	-	-	-	-	-	-	3	*2*	*1*	WI	Extent in Wisconsin - Step out	037 PCB 1.57 ppm, no dioxin, ML4 higest PEC-Q in RI (metals, PAHs, ESB)
24	46.698175	-92.204775	5	US Footprint Confirmation	4	4	*2*	*2*	4	*2*	*2*	-	-	-	-	-	-	4	*2*	*2*	WI	Extent in Wisconsin	
25	46.698865	-92.2055435	5	US Footprint Confirmation	3	3	*2*	*1*	3	*2*	*1*	-	-	-	-	-	-	3	*2*	*1*	MN	Extent in Wisconsin	
26	46.698551	-92.205084	5	US Footprint Confirmation	4	4	*2*	*2*	4	*2*	*2*	-	-	-	-	-	-	4	*2*	*2*	WI	Extent in Wisconsin	
27	46.696742	-92.2061051	5	US Footprint Confirmation	1	1	*1*	-	1	*1*	-	-	-	-	-	-	-	1	*1*	-	MN	Limited spatial resolution - large area	
28	46.6966678	-92.2051767	5	US Footprint Confirmation	1	1	*1*	-	1	*1*	-	-	-	-	-	-	-	1	*1*	-	MN	Limited spatial resolution - large area	
29	46.7002128	-92.1947423	6	Clough Island	1	-	-	-	1	*1*	-	-	-	-	-	-	-	1	*1*	-	WI	ponar	Surface - dioxin only
30	46.6988164	-92.1944312	6	Clough Island	1	-	-	-	1	*1*	-	-	-	-	-	-	-	1	*1*	-	WI	ponar	Surface - dioxin only
31	46.6980294	-92.194609	6	Clough Island	1	-	-	-	1	*1*	-	-	-	-	-	-	-	1	*1*	-	WI	ponar	Surface - dioxin only
32	46.697877	-92.1936759	6	Clough Island	1	-	-	-	1	*1*	-	-	-	-	-	-	-	1	*1*	-	WI	ponar	Surface - dioxin only
				Stewart Creek	2	2	*2*	-	2	*2*	-	2	*2*	-	-	-	-	2	*2*	-	MN		
				Stewart Creek	2	2	*2*	-	2	*2*	-	2	*2*	-	-	-	-	2	*2*	-	MN		
				Stewart Creek	2	2	*2*	-	2	*2*	-	2	*2*	-	-	-	-	2	*2*	-	MN		
				Stewart Creek	2	2	*2*	-	2	*2*	-	2	*2*	-	-	-	-	2	*2*	-	MN		
				Snively Creek	2	2	*2*	-	2	*2*	-	2	*2*	-	-	-	-	2	*2*	-	MN		
				Snively Creek	2	2	*2*	-	2	*2*	-	2	*2*	-	-	-	-	2	*2*	-	MN		
				Snively Creek	2	2	*2*	-	2	*2*	-	2	*2*	-	-	-	-	2	*2*	-	MN		
				Snively Creek	2	2	*2*	-	2	*2*	-	2	*2*	-	-	-	-	2	*2*	-	MN		

	Locations	PCB	Analyze	Hold	Dioxin	Analyze	Hold	HG	Analyze	Hold	MeHG	Analyze	Hold	TOC	Analyze	Hold
Total	40	94	62	32	114	74	40	65	44	21	20	20	0	114	74	40
Wisconsin	20															
Minnesota	20															