NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION

Division of Environmental Remediation, Remedial Bureau D
625 Broadway, 12th Floor, Albany, NY 12233-7013
P: (518) 402-9676 I F: (518) 402-9773
www.dec.ny.gov

September 12, 2023

Shane Blauvelt, P.E.
Honeywell International, Inc.
301 Plainfield Road
Suite 330
Syracuse, NY 13212

Re: Quality Assurance Project Plan Onondaga Lake, Geddes Brook, Ninemile Creek & LCP OU-1 Media Monitoring - 2022 And 2023

Dear Shane:

The New York State Department of Environmental Conservation (NYSDEC) has received and reviewed the above-referenced subject document, that was submitted via email by Anne Burnham of Parsons on September 8, 2023. Based on our review, the *Quality Assurance Project Plan Onondaga Lake, Geddes Brook, Ninemile Creek & LCP OU-1 Media Monitoring - 2022 And 2023* is approved. If you have any questions, please contact me at 518-402-9796.

Sincerely,

Tracy A. Smith
Project Manager

ecc:
J. Pelton, NYSDEC
J. Becker, NYSDEC
M. Spera, AECOM
E. Glaza, Parsons
J. Carr, Parsons
K. Granzen, NYSDEC
R. Quail, NYSDEC
V. Rubino, USEPA
M. Arrigo, Parsons
M. Kosciewicz, Parsons

NEW YORK STATE | Department of Environmental Conservation

QUALITY ASSURANCE PROJECT PLAN
ONONDAGA LAKE, GEDDES BROOK, NINEMILE CREEK & LCP OU-1 MEDIA MONITORING - 2022 AND 2023

Prepared For:

Honeywell

301 Plainfield Road, Suite 330
Syracuse, NY 13212

Prepared By:

PARSONS

301 Plainfield Road, Suite 350
Syracuse, New York 13212

REVISED SEPTEMBER 2023

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WORKSHEETS #1 AND #2: TITLE AND APPROVAL PAGE

Document Title:	Quality Assurance Project Plan for Onondaga Lake, Geddes Brook (GB), Ninemile Creek (NMC) and LCP OU-1 Media Monitoring
Project Name and Site Location:	Onondaga Lake, Geddes Brook, Ninemile Creek and LCP OU-1
Prepared for:	Honeywell
Prepared by:	Parsons
Document Version	0
Revision Number:	2
Revision Date:	September 8, 2023

This QAPP addresses ongoing monitoring for Onondaga Lake, Geddes Brook, Ninemile Creek, and LCP OU-1 with the exception of cap monitoring for Onondaga Lake which is presented in a separate QAPP (Parsons, Revision 2, November 2022). This QAPP is an update of the November 2022 QAPP approved by NYSDEC.

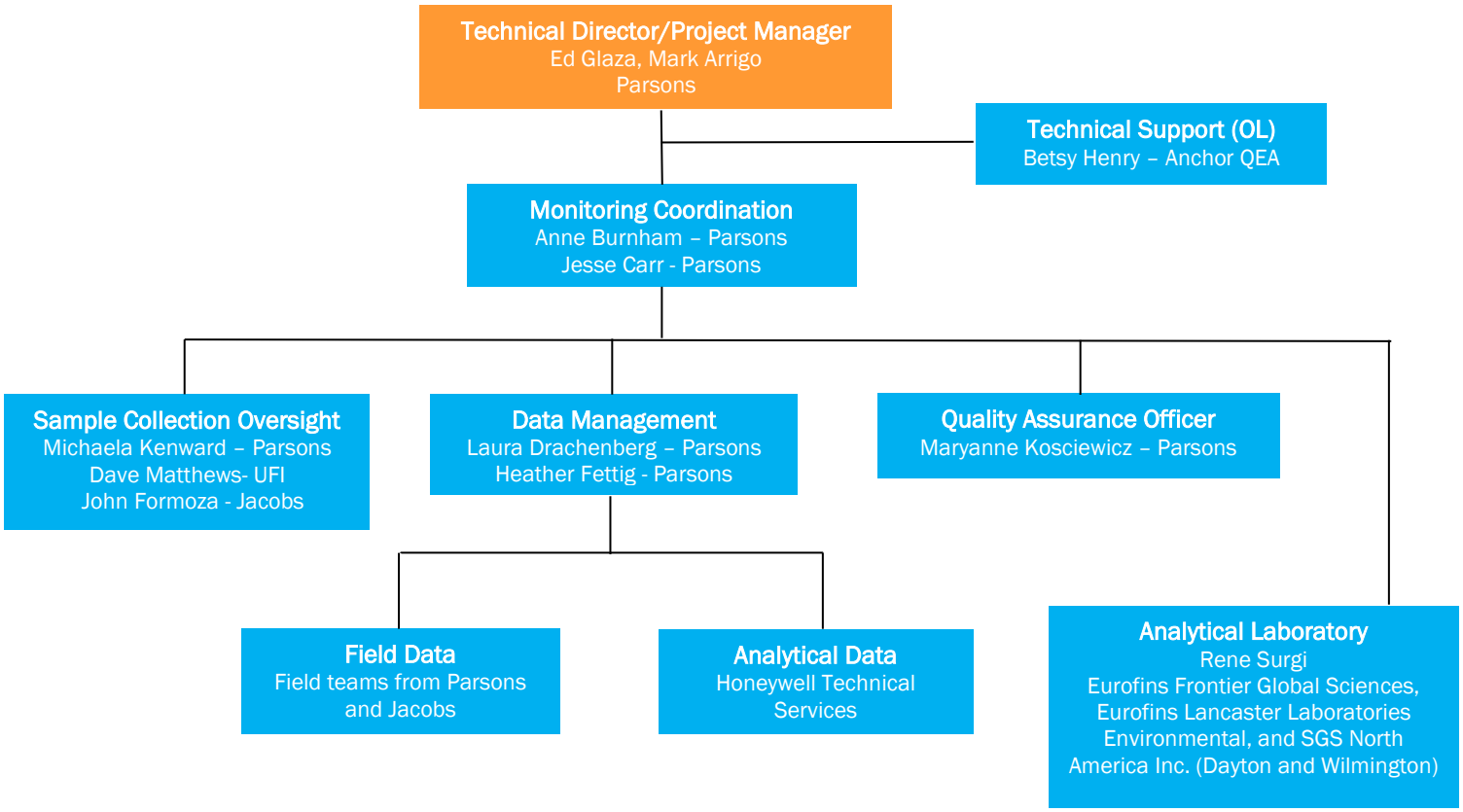
Relevant plans and reports from previous investigations are described in Worksheets #10 and #13.

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

Mark Arrigo, Parsons, Project Manager		9/8/2023
Maryanne Kosciewicz, Parsons, Project QA Officer		Date 9/8/2023
Tracy Smith, NYSDEC Senior Project Manager	Concurrence provided via email	Date
		Date

WORKSHEETS #3 AND 5: PROJECT ORGANIZATION AND QAPP DISTRIBUTION

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



WORKSHEET #4, #7 AND #8: KEY PROJECT PERSONNEL, SPECIAL PERSONNEL TRAINING REQUIREMENTS

Project Tile/Role	Name/Organization	Contact Information (phone, fax, email)	Experience
Remediation Manager	Shane Blauvelt, Honeywell	shane.blauvelt@honeywell.com	B.S. Engineering
Technical Director	Ed Glaza, Parsons	315-552-9691, 315-451-9570, edward.glaza@parsons.com	B.S. Engineering
Project Manager (OL/NMC/GB/LCP	Mark Arrigo, Parsons	315-552-9648, 315-451-9570, mark.arrigo@parsons.com	*M.S. Fisheries Biology/Aquatic Ecology 20 years' experience*
Technical Support (OL)	Betsy Henry, Anchor QEA	518-886-0636, 518-321-6188 bhenry@anchorqea.com	B.S. Agronomy, PhD Environmental Engineering, 30 years' experience
Project Manager	Dave Matthews, UFI	315-431-4962, NA, damatthews@upstatefreshwater.org	*PhD in Water Resources Engineering, 20+ years' experience*
Monitoring Coordinator (OL/NMC/GB/LCP)	Anne Burnham, Parsons	315-552-9775, 315-451-9570, Anne.Burnham@parsons.com	*M.S. Ecology 7 years' experience*
Monitoring Coordinator (OL/NMC/GB/LCP)	Jesse Carr, Parsons	315-552-9756, 315-451-9570, Jesse.carr@parsons.com	*B.S. Environmental Systems Science 8 years' experience*
Sample Collection Oversight	Michaela Kenward, Parsons	315-552-4821 Michaela.Kenward@parsons.com	*M.S. Environmental and Forest Biology 2 years' experience*
QA Officer	Maryanne Kosciewicz, Parsons	315-552-9703, 315-451-9570, maryanne.kosciewicz@parsons.com	*B.S. Mathematics B.S. Chemistry 28 years' experience*
Data Management	Laura Drachenberg, Parsons	315-552-9687 Laura.Drachenberg@parsons.com	M.S. Environmental Pollution Control 20 years' experience
Data Management	Heather Fettig, Parsons	315-552-9678 Heather.Fettig@parsons.com	*B.S. Environmental Science 20 years' experience*
Project Manager (OL/GB/NMC)	Tracy Smith, NYSDEC	518-402-9796, 518-402-9773, Tracy.Smith@dec.ny.gov	
Project Manager (LCP)	Kristin Granzen, NYSDEC	518-402-9772, 518-402-9772 Kristin.granzen@dec.ny.gov	

Project Tile/Role	Name/Organization	Contact Information (phone, fax, email)	Experience
Project Manager (OL/GB/NMC)	Victoria Rubino, U.S. EPA Region 2	212-637-4252 rubino.victoria@epa.gov	
Project Manager (LCP)	Mark Granger, U.S. EPA Region 2	212-637-3351, 212-637-3966, Granger.Mark@epa.gov	
Project Manager	Natalie Luciano, Eurofins Lancaster Laboratories	717-556-7258 Natalie.luciano@eurofinset.com	*BA Biology* *14 years' Experience*
Project Manager	Patrick Garcia Strickland, Eurofins Frontier Global Sciences	206-351-9522 Patrick.Garcia-Strickland@eurofinset.com	*BS Chemistry* *22 years' experience*
Lab Technical Director	Richard Karam, Eurofins Lancaster Laboratories	716-656-2300, 717-656-6766, Richard.Karam@eurofinset.com	*BS Environmental Studies* *17 years' experience*
Project Manager	John Formoza, Jacobs	315-468-1663, 315-468-1644, John.Formoza@jacobs.com	*BS Civil Engineering* *20 years' experience*
Project Manager	Kristin DeGraw, SGS North America Inc.	609-240-8928, NA, Kristin.degraw@sgs.com	M.S. Marine Biology 11 years' experience
Account Manager	Stephen Grant, SGS North America Inc.	732-355-4557 Stephen.grant@sgs.com	BS Chemistry 32 years' experience
Senior Project Manager	Tamara Burkamper, SGS North America Inc.	910-794-2527 tamara.burkamper@sgs.com	BS Chemistry; BS Marine Biology 21 years' experience
Technical Consultant	Rene Surgi, AESI	847-835-0983, NA, ReneSurgi@aesi.us	*Ph.D. Analytical Chemistry* *32 years' experience*

Project Function	Specialized Training Title or Description of Course	Training Provider	Training Date[1]	Personnel/ Groups Receiving Training	Personnel Titles/Organizational Affiliation	Location of Training Records/Certificates
Surface water sampling for low-level mercury analysis	Clean hands – dirty hands sampling protocol	Honeywell/Parsons	Annually	Parsons, UFI	Field Staff	Project Folder
Fish tissue processing and homogenization	DC_379.2 (Fish Prep HRMS)	SGS North America Inc.	On the job training; SOP Attestation forms	SGS Chemists	Laboratory staff	Filed with SGS N.A. Inc Quality Assurance

[1] Training will be carried out annually prior to conducting relevant field activities.

WORKSHEET #6: COMMUNICATION PATHWAYS

Communication Driver	Organization	Name	Procedure (timing, pathway, documentation, etc.)
Point of contact with data users	Lead Organization and Project Manager	Mark Arrigo-OL/GB/NMC/LCP	All materials and information about the project will be forwarded to the data users by Mark Arrigo or his designee.
Manage all project phases	Lead Organization and Project Manager	Mark Arrigo – OL/GB/NMC/LCP	Mark Arrigo will be the liaison with data users.
Coordinate field collection at Onondaga Lake, Geddes Brook, Ninemile Creek and LCP monitoring activities. Manage field collection for Onondaga Lake	Monitoring Coordinator/Sample Collection oversight	Anne Burnham	Notify Mark Arrigo of problems by phone or email by COB the next business day.
Manage field collection at NMC/GB/LCP	Sample Collection Oversight at NMC/GB/LCP	Jesse Carr	Notify Anne Burnham of field-related problems by phone or email by COB the next business day.
QAPP changes in the field	Monitoring Coordinator/QA Officer	Anne Burnham/Maryanne Kosciewicz	Notify Anne Burnham/Maryanne Kosciewicz by phone or email of changes to QAPP made in the field and the reasons within one business day. Any major changes to the QAPP must be approved by Anne Burnham/Maryanne Kosciewicz.
Field progress reports	Field Team Leaders	Jesse Carr	Notify Anne Burnham of any problems or issues.
Field corrective actions	Monitoring Coordinator/Quality Assurance Officer	Anne Burnham/Maryanne Kosciewicz	The need for corrective action for field issues will be determined.
Reporting lab data quality issues to Parsons	Laboratory Project Manager – Eurofins Lancaster Laboratories, Eurofins Frontier Global Sciences, and SGS North America Inc.	Natalie Luciano/Patrick Garcia Strickland/Kristin DeGraw	Notify when problems occur, report data and supporting quality assurance information as specified in this QAPP.
QAPP amendments	Project Manager	Mark Arrigo	Notify Mark Arrigo by phone or email of changes to the QAPP. Any major changes to the QAPP must be approved by Mark Arrigo. Any major changes to the QAPP must be approved by NYSDEC.

WORKSHEET #9: PROJECT PLANNING SESSION SUMMARY

Date of planning session: Several (see comments below)
Location: Virtual
Purpose: To discuss monitoring, progress updates
Participants:

Name	Organization	Project Role	Email/Phone
Mark Arrigo	Parsons	Project Management	mark.arrigo@parsons.com 315-552-9684
Anne Burnham	Parsons	Coordinate Monitoring Activities, QAPP preparation	anne.burnham@parsons.com 315-552-9775
Maryanne Kosciewicz	Parsons	Quality Assurance	Maryanne.kosciewicz@parsons.com 315-552-9703
Jesse Carr	Parsons	Sampling Oversight	jesse.carr@parsons.com 315-552-9756
Dave Matthews	UFI	Sampling Oversight	damatthews@upstatefreshwater.org 315-431-4962 x107
Natalie Luciano	Eurofins-Lancaster	OL, GB, NMC and LCP Laboratory contact	Natalie.Luciano@eurofinset.com 717-556-7258
Patrick Garcia-Strickland	Eurofins-Frontier	OL, GB, NMC, and LCP Laboratory contact	Patrick.Garcia-Strickland@eurofinset.com 206-351-9522
Kristin DeGraw	SGS North America Inc.	OL, GB, and NMC Fish Laboratory contact	Kristin.degraw@sgs.com 609-240-8928
Tamara Burkamper	SGS North America Inc.	OL, GB, and NMC Fish Laboratory contact	Tamara.burkamper@sgs.com 910-794-2527

Dates and title of QAPP documents written for previous site work, if applicable:

Title	Date
LCP Bridge Street QAPP	September 2009
QAPP for Onondaga Lake Construction Media Monitoring	March 2015
QAPP for Performance Evaluation Media Monitoring at LCP (OU-1), Geddes Brook and Ninemile Creek (Surface Water, Sediment, & Biota)	September 2016

Notes/Comments: This QAPP supersedes the above QAPPs and is an update to the approved 2021 QAPP. This QAPP encompasses the following monitoring plans: Onondaga Lake Maintenance and Monitoring Plan (June 2018), Geddes Brook Operation, Maintenance and Monitoring Plan (February 2011), Ninemile Creek Maintenance and Monitoring Plan (August 2018), and the Operation, Maintenance and Monitoring Plan for the LCP Bridge Street Site (September 2009) and the Nitrate Addition Operation and Maintenance Plan (August 2014). Annual Scope Memos are prepared as needed to document annual activities, including any recommendations. Annual kickoff meetings are held with field monitoring teams and NYSDEC to discuss the scope and goals of the various sampling programs. In 2022, scoping sessions were held to discuss surface water and nitrate addition on April 7th and to discuss MNR and fish on May 4th. In 2023, scoping sessions were held to discuss MNR on April 13 and to discuss surface water and nitrate addition on April 18th.

Consensus decisions made:

Action Items:

Action	Responsible Party	Due Date

WORKSHEET #10A: PROJECT DESCRIPTION – GEDDES BROOK, NINEMILE CREEK, AND LCP OU-1

Problem Definition and Background

Linden Chemicals and Plastics (LCP) Operable Unit No. 1 (OU-1) is a former chemical production area that was closed in 1988 and now contains a containment area where remediation was completed in 2008. The LCP OU-1 containment area is surrounded by a barrier wall, with capping completed in 2015 following the remediation of Ninemile Creek, which was completed in 2014. Runoff from LCP OU-1 primarily drains to a series of wetlands and then to the West Flume that drains to Geddes Brook and then to Ninemile Creek. Remediation of the West Flume was completed as part of the LCP OU-1 remedy. Remediation in Geddes Brook and Ninemile Creek was completed in 2012 and 2014, respectively. This monitoring will permit evaluation of changes that result from remedial action and verification of remedy effectiveness in achieving the remedial action objectives and preliminary remediation goals for fish, sediment and surface water.

Project Description

The primary tasks associated with monitoring these sites are discussed in their respective approved monitoring and maintenance plans and includes collection and analysis of surface water, groundwater, sediment, and biota samples and to assess wetland and upland habitat establishment in restored areas. Biota monitoring (depending upon the area being sampled) has previously included fish, benthic macroinvertebrate, small mammal and earthworm sampling as outlined in the respective approved OMM plans for each area. Future monitoring may include a subset of these media, as negotiated in discussions with NYSDEC. Wetland and upland habitat monitoring parameters include vegetation type, percent cover and frequency; hydrology (wetlands only); invasive species abundance, and wildlife usage. Approved changes to these programs are documented in the sections of the annual report devoted the respective areas. This QAPP will be modified in future years to include future year monitoring work scopes.

WORKSHEET #10B: PROJECT DESCRIPTION – ONONDAGA LAKE

Problem Definition and Background

The purpose and background for the remediation of the Onondaga Lake Bottom Subsite are summarized in the ROD (NYSDEC and USEPA 2005) and presented in detail in the Feasibility Study Report (Parsons 2004) and the Final Design for Sediment Capping, Dredging, Habitat and SMU 8 (Parsons and Anchor QEA 2012). This monitoring will permit evaluation of changes that result from remedial action and verification of remedy effectiveness in achieving the remedial action objectives and preliminary remediation goals for fish, sediment and surface water.

Project Description

The primary tasks are to collect and analyze surface water, biota tissues (typically zooplankton and fish), sediment, and sediment trap from various locations around the lake. The below bullet points summarize tasks that have occurred previously, which may also be needed in the future. Specific monitoring needs are detailed in the OLMMP and in annual scope memorandums.

- Surface water from the littoral and the profundal zone was sampled and analyzed to evaluate the effects of remedy implementation on lake water quality in 2017 and 2018, with additional sampling in the lake and tributaries in 2021. Surface water is also sampled from the profundal zone as part of the Nitrate Addition program.
- Fish are collected from around the littoral zone of the lake to be analyzed to evaluate for achievement of fish tissue goals and target concentrations. Zooplankton and benthic macroinvertebrate (2017 only) sampling to help to evaluate the effects on fish mercury concentrations and increase understanding of the effectiveness of the remedy in achieving fish tissue target concentrations.
- Analyses of surface sediment samples has been conducted every three years from the profundal zone (SMU 8) to continue to assess ongoing natural recovery. 2022 represents the second of two years of an expanded sampling event to assess compliance. Sediment trap slurries are also collected from the profundal zone annually as part of the ongoing assessment of natural recovery.
- Note, a separate QAPP was developed for the cap monitoring component of the OLMMP.

Specifics on the scopes of work for each given component are described in the Onondaga Lake Monitoring and Maintenance Plan (Parsons et al. 2018) and the OM Plan for Nitrate Addition to the hypolimnion of Onondaga Lake. This QAPP will be modified as needed in future years to include future year monitoring work scopes.

WORKSHEET #11A: PROJECT/DATA QUALITY OBJECTIVES – GEDDES BROOK, NINEMILE CREEK, AND LCP OU-1

Who will use the data?

Data collected will be used by Honeywell and its consultants/contractors, NYSDEC and its consultants, and USEPA. These data will also be included in the approved annual report that is made available to the public.

What will the data be used for?

- Monitor short-term effectiveness of the remediation efforts
- Long- term monitoring will evaluate the long-term effectiveness of remediation efforts
- To measure achievement of the applicable remedial goals (RGs) for soil, sediment, groundwater, surface water, and fish tissue established in the Record of Decisions for the respective sites

What type of data are needed?

It should be noted that the below summarizes data collected previously. Additional data collection may be needed and will be determined in consultation with NYSDEC.

LCP OU-1: Groundwater, surface water, and sediment have been monitored since 2008. Biota tissue monitoring (forage fish) were conducted from 2008-2012 and again in 2015, 2017, 2018, and 2021. Future monitoring is dependent on discussions with NYSDEC. Target analytes for laboratory analyses are as follows:

- Total mercury and methylmercury in surface water, sediment; and total mercury in forage fish
- Total mercury in surface water and groundwater (USEPA Method 1631 (surface water) and 7470A (groundwater))
- Methylmercury analyses using (USEPA Method 1630)

Surface water and/or groundwater temperature, conductivity and pH will also be recorded.

Geddes Brook: Sediment and surface water were monitored annually for five years following completion of the Geddes Brook IRM in 2012. Surface water and biota (forage fish) were also monitored in 2019. Biota tissue monitoring at the Site has included forage fish, benthic macroinvertebrates, small mammals and earthworms. Forage fish collection is planned for 2022. Target analytes for laboratory analyses are as follows:

- Total mercury and methylmercury in sediment, benthic macroinvertebrates, small mammals and earthworms (USEPA Method 7471 [Total mercury] USEPA Method 1630 [Methylmercury])
- Dissolved mercury, total mercury in surface water and total mercury in fish (USEPA Method 1631 in surface water and 7471A in biota)
- Methylmercury in surface water using USEPA Method 1630

Surface water measurements are also collected for temperature, conductivity and pH when sampling occurs

Ninemile Creek: Surface water was monitored annually from 2015-2017, at which point it was determined that monitoring could end as remedial goals were met. Biota tissue monitoring included sport fish and forage fish from 2015-2017 and in 2019. Floodplain and channel sediment were collected in 2016 and 2018. Benthic

macroinvertebrate, earthworms, and small mammals were collected in 2016. Sport and forage fish will be collected in 2022. Target analytes for laboratory analyses are as follows:

- Total mercury in surface water, fish, sediment and floodplain soil, and biota other than fish (USEPA Method 1631 in water and 7471A in biota and sediment). Methylmercury in sediment and floodplain soil, and biota other than fish (USEPA Method 1630), and dissolved mercury analyses in surface water (USEPA Method 1631)
- Percent moisture, PCB aroclors, lipid content and dioxins-furans in a sub-set of fish (various USEPA methods)

Surface water is also monitored in-situ for temperature, dissolved oxygen, conductivity and pH when sampling occurs. The channel may be surveyed, as has been done in the past, for elevation and composition of surface material as dictated in the Ninemile Creek MM Plan.

SYW-10: SYW-10 is located at the mouth of Ninemile Creek, where it meets Onondaga Lake (See NMC MM Plan for detailed figures). Soil/sediment were monitored for three years following completion of the remedy. Biota tissue monitoring included small mammals and earthworms. Samples will be collected in both the remediated and unremediated areas in the years sampling is conducted. Target analytes for laboratory analyses are as follows:

- Total mercury in sediment and earthworms (USEPA Method 7471A in sediment and biota)
- Total mercury in small mammals (USEPA Method 7471A in sediment and biota)
- Methylmercury analyses in sediment and earthworms (USEPA Method 1630)

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

The data must support comparison to remedial goals for chemical concentrations in groundwater, surface water, sediment and biota. The key analytes in terms of decision-making are total mercury and methylmercury. Analytes will be subject to data validation in accordance with prescribed guidelines as described in Worksheet #36.

How much data are needed? (number of samples for each analytical group, matrix, and concentration)

See Worksheet #18

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

Samples for chemical analyses will generally be collected from May through November (with the exception of groundwater at LCP OU-1, which is quarterly) using field sampling techniques summarized in Worksheet #21 and provided in Appendix A.

Who will collect and generate the data?

At LCP OU-1 Jacobs will collect groundwater samples; Parsons will collect surface water, sediment and biota samples. Parsons will collect surface water, sediment samples, biota samples, and conduct physical monitoring at Geddes Brook, Ninemile Creek and in SYW-10. Laboratory analyses of mercury, PCBs, dioxins-furans, and lipid content will be performed by commercial laboratories procured through Honeywell.

How will the data be reported?

Chemical data will be presented in one or more annual Data Usability Summary Reports and summarized along with physical monitoring and survey data in annual reports. All laboratory data will also be reported in EDD format for Geddes Brook, Ninemile Creek and LCP OU-1.

How will the data be archived?

Field and laboratory data and chain-of-custody information will be stored in a data management system maintained on behalf of Honeywell.

Additionally, field databases, if used during sample collection, will be archived. Electronic data management systems will be implemented to process the information effectively without loss or alteration.

The laboratory will store laboratory data and related records in a secure fashion. Records will be stored in archived storage, and electronic records consist of hard copies, write-protected backup copies, or an electronic audit trail controlling access. Electronic records will be backed up on the laboratory's archive server on a local area network. Records will not be removed from the archive, unless otherwise specified.

WORKSHEET #11B: PROJECT/DATA QUALITY OBJECTIVES – ONONDAGA LAKE

Who will use the data?

Data collected will be used by Honeywell and its consultants/contractors, NYSDEC and its consultants, NYSDOH, and USEPA. These data will also be made available to the public once validated.

What will the data be used for?

The primary data uses are presented in Worksheet #10.

What type of data are needed?

It should be noted that the below summarizes data collected previously. Additional data collection may be needed and will be determined in consultation with NYSDEC.

Target analytes for laboratory analyses are as follows:

- Total mercury and total dissolved mercury in surface water (USEPA Method 1631)
- Total mercury in zooplankton, benthic macroinvertebrates, and fish (USEPA Method 1631 in zooplankton/invertebrates and 7471A in fish)
- Total mercury and Total Fixed/Dissolved Solids in sediment trap slurry samples (USEPA Method 1631 for mercury)
- Methylmercury in surface water, zooplankton and benthic macroinvertebrates (USEPA Method 1630)
- PCBs in surface water (Method 1668A)
- PCB aroclors, DDT and metabolites, hexachlorobenzene, lipid content, percent moisture and dioxins-furans in fish as needed (various USEPA methods)
- Volatile organic compounds, semivolatile organic compounds (surface water compliance sampling only) (Methods SW8260C/8270D). Note: analyzed in 2017 and 2018; not part of current monitoring program.
- Various wet chemistry parameters such as multiple forms of nitrogen, phosphorus, and total suspended solids from profundal zone surface water samples
- Total mercury in profundal and littoral zone lake sediment for assessments of monitored natural recovery (SW7471).
- Physical parameters to be measured for fish include:
    - Weight (in grams) and total length (in mm)
    - Age and sex for adult sport fish
- On-site measurements for water quality will also be made for:
    - Temperature
    - Dissolved oxygen
    - Nitrate –nitrogen at numerous locations associated with nitrate addition and measured using an *in situ* ultraviolet spectrophotometer (ISUS) or a submersible ultraviolet nitrogen analyzer (SUNA).
    - Conductivity, turbidity and pH. Note: Turbidity data was collected as a part of the nitrate program as well as related to the Wastebeds 1-8 Shoreline Stabilization area (conducted in 2017).

Concentration levels (i.e., project action and quantitation limits, analytical and achievable laboratory method detection and quantitation limits) for the laboratory analytes are documented in Worksheet #15, field sampling techniques are referenced in Worksheet #21, and laboratory analytical techniques are referenced in Worksheet #23.

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

The data must support remedial goals for chemical concentrations in surface water, sediment and fish. All analytes will be subject to Level III validation as described in Worksheet #36. In addition, 10 percent of the analytical data will be validated based on Level IV protocols as described in Worksheet #36.

How much data is needed? (number of samples for each analytical group, matrix, and concentration)

See Worksheet #18.

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

Samples for chemical analyses will generally be collected in Onondaga Lake from May through November using field sampling techniques summarized in Worksheet #21 and provided in Appendix A.

Who will collect and generate the data?

Samples are collected by Upstate Freshwater Institute and Parsons field teams for media except fish tissue. Fish samples have been and will generally be collected by the State University of New York College of Environmental Science and Forestry (SUNY-ESF) and processed by Parsons. Ages of adult sport fish will be quantified by SUNY ESF based on evaluation of fish otoliths from Smallmouth Bass, Common Carp and Walleye, and scales from Pumpkinseed.

Laboratory analyses for mercury, PCBs, PCDDs/Fs, etc. will be performed as dictated by the scopes of work by one or more commercial laboratories to be procured for 3 years as possible. UFI will analyze water samples for more conventional "wet chemistry" parameters.

How will the data be reported?

Data will be presented in one or more annual Data Summary Reports and/or accompanying Data Usability Summary Reports. Data will also be provided in EDD and flat file (excel) formats.

How will the data be archived?

Field and laboratory data and chain-of-custody information will be stored in a data management system maintained on behalf of Honeywell. Additionally, field databases used during sample collection will be archived. Electronic data management systems will be implemented to process the information effectively without loss or alteration.

The laboratory will store laboratory data and related records in a secure fashion. Records will be stored in archived storage, and electronic records consist of hard copies, write-protected backup copies, or an electronic audit trail controlling access. Electronic records will be backed up on the laboratory's archive server on a local area network. Records will not be removed from the archive, unless otherwise specified.

WORKSHEET #12: MEASUREMENT PERFORMANCE CRITERIA

Matrix: Biota Tissue
Analytical Group or Method: Total Mercury
Concentration Level: Moderate
Lab: SGS Dayton

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
Appendix A S-2, S-15 through S-17	EPA Method 7471B, L-3E	Precision	RPD 20%	Matrix spike, matrix spike duplicate, laboratory duplicate	A
		Accuracy/Bias	Control limit recovery 80-120%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 80-120%	Laboratory control samples	A
			80-120% of certified value	CRM (DORM-5)[3]	A
		Lab Contamination	Less than reporting limit	Method Preparation Blank	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	0.033 µg/g wet	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] Reference number from QAPP Worksheet #21
[2] Reference number from QAPP Worksheet #23
[3] Per attachment 1, DORM-4 was previously used as the certified reference material for mercury in fish tissue. DORM-4 is no longer commercially available. Therefore, DORM-5 will be used.

Matrix: Sediment
Analytical Group[1] or Method: Total Mercury
Concentration Level: Moderate
Lab: Eurofins Lancaster

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
Appendix A S-3, S-13	USEPA 7471B, L-2A	Accuracy/Bias	Control limit recovery 80-120%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 80-120%	Laboratory control samples	A
		Precision - Lab	RPD 20%	Lab duplicate samples	S&A
		Precision – Field	RPD 50%	Field duplicate samples	S&A
		Contamination	No analytes detected > 1/2 RL or >1/10 the amount measured in any sample	Method blank	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	0.1 mg/kg	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] TNI/NELAC and ELAP certified method.
[2] Reference number from QAPP Worksheet #21.
[3] Reference number from QAPP Worksheet #23

Matrix: Groundwater
Analytical Group[1] or Method: Total Mercury
Concentration Level: Moderate
Lab: SGS Dayton

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
Appendix A S-21	USEPA 7470, L-3G	Accuracy/Bias	Control limit recovery 75-125%	Matrix spike and matrix spike duplicates	S&A
		Precision – Field	RPD 30%	Field duplicate samples	S&A
		Precision – Lab	RPD 20%	Laboratory duplicate samples/Matrix Spike Duplicate	S&A
		Contamination	<1/2 RL	Method Blank	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory results	S&A
		Sensitivity	0.2 ug/L (groundwater)	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

Note: Groundwater analyzed by SGS North America Inc.
[1] TNI/NELAC and ELAP certified method
[2] Reference number from QAPP Worksheet #21
[3] Reference number from QAPP Worksheet #23

Matrix: Surface water, sediment slurry, and biota
Analytical Group[1] or Method: Total Mercury (including dissolved mercury)
Concentration Level: Low
Lab: Eurofins Frontier

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
Appendix A S-7, S-14; S-11; S-4, S-8	EPA Method 1631 series, L-2C, L-2G, L-2D, L-2F	Accuracy/Bias	Control limit recovery 71-125%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 80-120%	Laboratory control samples	A
		Precision – Field	RPD 30%	Field duplicate samples (with the exception of biota samples)	S&A
		Precision – Lab	RPD 24%	Laboratory duplicate samples	A
			77-123%	Ongoing precision and recovery samples	A
		Contamination	Less than reporting limit 0.5 ng/L (water) 0.4 ng/g wet (biota)	Field, method, and instrument blanks	A
		Representativeness	Use of standardized collection and analytical methods	Field and laboratory audits	S&A
		Sensitivity	0.5 ng/L for water 0.4 ng/g wet biota	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] Reference number from QAPP Worksheet #21
[2] Reference number from QAPP Worksheet #23.

Matrix: Surface water and biota
Analytical Group or Method: Methylmercury
Concentration Level: Low
Lab: Eurofins Frontier

Sampling Procedure[1]	Analytical Method/SOP[2]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
Appendix A S-7, S-14, S-4, S-8	USEPA 1630 series methods, L-2B, L-2H, L-2E	Precision	RPD 35% (lab duplicate) RPD 30% (water field duplicate)	Laboratory and field duplicate samples	S&A
		Accuracy/Bias	Control limit recovery 65-130%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 70-130%	Laboratory control samples	A
		Precision – Lab Contamination	Less than reporting limit 0.05 ng/L (water) 2.0 ng/g wet (biota)	Method preparation blank	A
		Representativeness	Use of standardized collection and analytical method	Field audits and laboratory audits	S&A
		Sensitivity	0.05 ng/L (water) 2.0 ng/g wet (biota)	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] Reference number from QAPP Worksheet #21
[2] Reference number form QAPP Worksheet #23

Matrix: Sediment
Analytical Group[1] or Method: Methylmercury
Concentration Level: Moderate
Lab: Eurofins Frontier

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
Appendix A S-13	USEPA 1630, L-2B	Accuracy/Bias	Control limit recovery 65-130%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 70-130%	Laboratory control samples	A
		Precision - Lab	RPD 35%	Lab duplicate samples	A
		Precision – Field	RPD 50%	Field duplicate samples	S&A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	0.05 ng/g	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] TNI/ELAC and ELAP certified method
[2] Reference number from QAPP Worksheet #21
[3] Reference number from QAPP Worksheet #23

Matrix: Profundal zone[1] surface water
Analytical Group[2] or Method: Nitrate plus nitrite and also nitrite
Concentration Level: Low
Lab: Upstate Freshwater Institute

Sampling Procedure[3]	Analytical Method/SOP[4]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-7	SM 22nd ed. 4500-NO3-F, L-1A	Precision – Field	RPD 30%	Field duplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate	A
			RPD 10% for warning limits and 15% for control limits, and 90-110% recovery for warning limits and 85-115% recovery for control limits	Matrix spike duplicate samples	
		Accuracy/Bias	90-110% recovery for warning limits and 85-115% recovery for control limits	Matrix spike	A
				Laboratory control samples	A
				Reference samples	A
		Contamination	Less than or equal to achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than or equal to half of the achievable Laboratory Method Quantitation Limit	Method blanks	A
			Less than or equal to achievable Laboratory Method Detection Limit	Field blanks	S&A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	NOX: 30 µg/L NO2: 6 µg/L	Reporting Limit	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] Profundal zone is generally defined as areas of the lake where total water depths exceed 30 feet (9 meters)
[2] TNI/NELAC and ELAP certified method
[3] Reference number from QAPP Worksheet #21
[4] Reference number from QAPP Worksheet #23

Matrix: Profundal zone[1] surface water
Analytical Group[2] or Method: Ammonia
Concentration Level: Low
Lab: Upstate Freshwater Institute

Sampling Procedure[3]	Analytical Method/SOP[4]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-7	SM 22ND ed. 4500-NH3-H, L-1B	Precision – Field	RPD 30%	Field duplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate	A
			RPD 10% for warning limits and 15% for control limits, and 90-110% recovery for warning limits and 85-115% recovery for control limits	Matrix spike duplicate samples	
		Accuracy/Bias	90-110% recovery for warning limits and 85-115% recovery for control limits	Matrix spike	A
				Laboratory control samples	A
				Reference sample	A
		Contamination	Less than or equal to the achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than equal to or half of the achievable Laboratory Method Quantitation Limit	Method blanks	A
			Less than or equal to the achievable Laboratory Method Detection Limit	Field blanks	S&A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	48 µg/L	Reporting Limit	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] Profundal zone is generally defined as areas of the lake where total water depths exceed 30 feet (9 meters)
[2] ELAP only certified method
[3] Reference number from QAPP Worksheet #21
[4] Reference number from QAPP Worksheet #23

Matrix: Profundal zone[1] surface water
Analytical Group[2] or Method: Soluble Reactive Phosphorus
Concentration Level: Low
Lab: Upstate Freshwater Institute

Sampling Procedure[3]	Analytical Method/SOP[4]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-7	SM 4500-P E-99, -11, L-1C	Precision – Field	RPD 30%	Field duplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
			Percent Recovery 90-110% for warning limits 85-115% for control limits	Matrix spike duplicate samples	
		Accuracy/Bias	Percent Recovery 90-110% for warning limits 85-115% for control limits	Matrix spikes	A
				Laboratory control samples	A
				Reference samples	A
		Contamination	Less than or equal to achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than or equal to half of the achievable Laboratory Method Quantitation Limit	Method blanks	A
			Less than or equal to half of the achievable Laboratory Method Quantitation Limit	Field blanks	S&A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	2.9 µg/L	Reporting Limit	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] Profundal zone is generally defined as areas of the lake where total water depths exceed 30 feet (9 meters)
[2] TNI/NELAC and ELAP certified method
[3] Reference number from QAPP Worksheet #21
[4] Reference number from QAPP Worksheet #23

Matrix: Profundal zone[1] sediment trap slurry (performed by UFI)
Analytical Group[2] or Method: Total, fixed and volatile suspended solids
Concentration Level: Low
Lab: Upstate Freshwater Institute

Sampling Procedure[3]	Analytical Method/SOP[4]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-11	SM 2540 D-97, -11, L-1E, L-1G	Precision – Field	RPD CV 50% (flux measurements)	Field duplicate samples	S&A
		Precision – Lab	RPD 5% for warning limits and 5% for control limits	Laboratory duplicate	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Not applicable	A
				Not applicable	A
				Not applicable	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Not applicable	A
			Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Not applicable	S&A
		Representativeness	Use of standardized collection and analytical methods	Field and laboratory audits	S&A
		Sensitivity	2.5 mg	Reporting Limit	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] Profundal zone is generally defined as areas of the lake where total water depths exceed 30 feet (9 meters)
[2] There is no NELAC/ELAP certification available for DOC. UFI is TNI/NELAC and ELAP certified for TOC. DOC samples are filtered and run as a TOC.
[3] Reference number from QAPP Worksheet #21
[4] Reference number from QAPP Worksheet #23

Matrix: Fish Tissue
Analytical Group[1] or Method: Pesticide compounds
Concentration Level: Low
Lab: SGS Dayton

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-2	USEPA 8081B, L-3D	Precision	RPD 50% when <5x the MDL, 30% when >5x the MDL	Laboratory duplicate[4] samples	S&A
			+/- 30%	Matrix spike duplicate samples	A
		Accuracy/Bias	+/- 30%	Matrix spike	A
				Laboratory control samples	A
			70-130% of certified value	CRM (NIST 1947)	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Blanks	S&A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	0.0031-0.0037 µg/g wet	Reporting Limit	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs	S&A

[1] TNI/NELAC and ELAP certified method.
[2] Reference number from QAPP Worksheet #21.
[3] Reference number from QAPP Worksheet #23.
[4] A laboratory duplicate will be analyzed for this method based upon sample volume available.

Matrix: Water
Analytical Group[1] or Method: Temperature
Concentration Level: Average

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicator (DQI)	Measurement Performance Criteria[4]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-10, S-12, S-14	NA	Precision – Field	± 0.0003°C	Field calibration	A
		Representativeness	Use of standardized collection methods	Field audits	S
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] No NELAC/ELAP certification for this test is available.
[2] Reference number from QAPP Worksheet #21.
[3] Reference number from QAPP Worksheet #23.
[4] Sensors are factory calibrated annually and maintained according to manufacturers' instructions.

Matrix: Water
Analytical Group[1] or Method: pH
Concentration Level: Average

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicator (DQI)	Measurement Performance Criteria[4]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-10, S-12, S-14	NA	Precision – Field	± 0.2 pH unit	Field calibration	A
		Representativeness	Use of standardized collection methods	Field audits	S
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] No NELAC/ELAP certification for this test is available.
[2] Reference number from QAPP Worksheet #21.
[3] Reference number from QAPP Worksheet #23.
[4] Sensors are factory calibrated annually and maintained according to manufacturers' instructions.

Matrix: Water
Analytical Group[1] or Method: Specific conductance
Concentration Level: Average

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicator (DQI)	Measurement Performance Criteria[4]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-10, S-12, S-14	NA	Precision – Field	± 0.5% of reading in µS/cm	Field calibration	A
		Representativeness	Use of standardized collection methods	Field audits	S
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical methods	S&A

[1] No NELAC/ELAP certification for this test is available.
[2] Reference number from QAPP Worksheet #21.
[3] Reference number from QAPP Worksheet #23.
[4] Sensors are factory calibrated annually and maintained according to manufacturers' instructions.

Matrix: Water
Analytical Group[1] or Method: Dissolved oxygen
Concentration Level: Average

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicator (DQI)	Measurement Performance Criteria[4]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-10, S-12, S-14	NA	Precision – Field	± 0.2% of reading in mg/L	Field calibration	A
		Representativeness	Use of standardized collection methods	Field audits	S
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical methods	S&A

[1] No NELAC/ELAP certification for this test is available.
[2] Reference number from QAPP Worksheet #21.
[3] Reference number from QAPP Worksheet #23.
[4] Sensors are factory calibrated annually and maintained according to manufacturers' instructions.

Matrix: Water
Analytical Group[1] or Method: Nitrate
Concentration Level: Low to high

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicator (DQI)	Measurement Performance Criteria[4]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-9	NA	Precision – Field	± 2 µM	Control sample	A
		Accuracy/Bias	± 2 µM	Control sample	A
		Representativeness	Use of standardized collection methods	Field audits	S
		Completeness	95% for all measurements	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs in field and comparison to laboratory results	S&A

[1] No NELAC/ELAP certification for this test is available.
[2] Reference number from QAPP Worksheet #21B.
[3] Reference number from QAPP Worksheet #23.
[4] Sensors are factory calibrated annually and maintained according to manufacturers' instructions.

Matrix: Water
Analytical Group[1] or Method: Turbidity
Concentration Level: Low to high

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicator (DQI)	Measurement Performance Criteria[4]	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-9	NA	Precision – Field	± 0.25 NTU	Control sample	A
		Accuracy/Bias	± 0.25 NTU	Control sample	A
		Representativeness	Use of standardized collection methods	Field audits	S
		Completeness	95% for all measurements	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs in field and comparison to laboratory results	S&A

[1] No NELAC/ELAP certification for this test is available.
[2] Reference number from QAPP Worksheet #21B.
[3] Reference number from QAPP Worksheet #23.
[4] Sensors are factory calibrated annually and maintained according to manufacturers' instructions.

Matrix: Fish Tissue
Analytical Group or Method: Percent Lipids by method 3550C
Concentration Level: Low to High
Lab: SGS Wilmington

Sampling Procedure	Analytical Method/SOP	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
Appendix A S-2, S-17	Method 3550C/L-3A	Precision	30% RPD	Laboratory duplicate sample [1]	A
		Accuracy/Bias	70-130% of certified value	CARP-2	A
		Sensitivity	0.05%	Reporting limits	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Completeness	95%	Comparison of number of confident quantifications to total quantifications	A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] A laboratory duplicate will be analyzed for this method based upon sample volume available.

Matrix: Fish Tissue
Analytical Group or Method: PCBs (Aroclor)
Concentration Level: Low
Lab: SGS Dayton

Sampling Procedure	Analytical Method/SOP	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
Appendix A S-2, S-17	SW 8082A, L-3C	Precision	RPD ≤ 50% when < 5x the MDL, 30% when >5x the MDL	Matrix spike, matrix spike duplicate, lab duplicate[1]	A
		Accuracy/Bias	<MDL	Laboratory blank	A
			+/- 30%	Matrix spike and matrix spike duplicates	A
			+/- 30%	Laboratory control samples	A
			Lab statistical surrogate control recovery	All samples and associated quality controls	A
			70-130 % of certified value	CRM (NIST 1947)	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	34 µg/kg wet	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] A laboratory duplicate will be analyzed for this method based upon sample volume available.

Matrix: Fish Tissue
Analytical Group or Method: Dioxins-Furans
Concentration Level: Low
Lab: SGS Wilmington

Sampling Procedure	Analytical Method/SOP	Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
Appendix A S-2, S-17	SW-8290, L-3F	Precision	Method defined QC windows for LCS, OPR, and internal standard recoveries	Laboratory Control Sample/On-going Precision Recovery (OPR) Sample and laboratory duplicate[1]	A
		Accuracy/Bias	Less than the lower limit of quantitation (LLOQ)	Laboratory blank	A
			Method defined QC windows for LCS and OPR	Laboratory Control Sample/On-going Precision Recovery (OPR) Sample	A
			70-130% of certified value	CARP 2	A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Sensitivity	0.5-5 pg/g	Reporting limits	A
		Completeness	95% for all analyses	Data completeness check	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1] A laboratory duplicate will be analyzed for this method based upon sample volume available.

WORKSHEET #13: SECONDARY DATA USES AND LIMITATIONS

Secondary Data	Data Source (Originating Organization, Report Title, Date)	Data Generator(s) (Originating Organization, Data Types, Data Generation/Collection Dates)	How Data Will Be Used	Limitations on Data Use
Robotic measurements from multiple depths at South Deep	UFI robotic buoy data are available at www.upstatefreshwater.org	UFI; data include dissolved oxygen, temperature, specific conductance, pH, fluorometric chlorophyll, and turbidity monitored at multiple water depths.	Seasonality of thermal stratification, oxygen depletion, density of water layers, general water quality conditions.	No limitations.
OCDWEP surface water and fish data	Onondaga Lake Ambient Monitoring Plan Annual Reports, Onondaga County Department of Water and Environment Protection.	OCDWEP data include various surface water parameters as well as fish count, length, weight and unit effort for fish.	The fish data will be used to continue to assess trends in abundance and community composition.	No limitations.
NYSDEC fish data	NYSDEC database	Data include mercury concentration and percent moisture from fillet samples in largemouth and smallmouth bass. PCBs, DDT and metabolites, hexachlorobenzene analyzed in select years.	The data will be used for comparison of current mercury levels to historical data.	No limitations.
Baseline Monitoring Program	Honeywell/Parsons	Includes data as part of the baseline monitoring program collected beginning in 2008 pertaining to surface water, sediment, and biota sampling for a full scope of analytes (i.e., mercury, methylmercury, dioxin/furans, etc.).	The data will be used for comparison of current levels to historical data.	No limitations.
Construction Completion Reports	Honeywell/Parsons	Includes as-built survey data (one per site i.e., Onondaga Lake, Geddes Brook; Ninemile Creek Reach CD; Ninemile Creek AB/BC, LCP; etc.).	The data will be used for comparison of current conditions to as-built.	No limitations.
Annual Monitoring and Maintenance Reports	Honeywell/Parsons	Presents comprehensive results from lake monitoring program, including data related to SMU 8 monitored natural recovery, biota tissue, surface water, cap maintenance and monitoring, habitat reestablishment and biological response, Wastebeds 1-8 shoreline stabilization turbidity monitoring, institutional controls, and nitrate addition.	Data will be used to track progress and ultimately verify remedy effectiveness in achieving the preliminary remedial goals (PRGs) and remedial action objectives (RAOs) specified in the Record of Decision (ROD)	Due to a potential misinterpretation of the lipids analysis SOP by the laboratory in 2017 and 2018, lipid results for many of the 2017 and 2018 fish were potentially biased high. Archived samples with sufficient mass remaining have been reanalyzed and is included in the 2019 Annual Report. 2019 fish tissue data not considered usable due to processing/ homogenization challenges
		Presents comprehensive results for Geddes Brook, Ninemile Creek, and LCP OU-1 monitoring program, including data related to soil, sediment, groundwater, surface water, and biota tissue.		2019 fish tissue data not considered usable due to processing/homogenization challenges

WORKSHEET #14A AND #16A: PROJECT TASKS & SCHEDULE – GEDDES BROOK, NINEMILE CREEK, AND LCP OU-1

Sampling Tasks:

Note: The scope for annual sampling is discussed in the years' respective Monitoring Scope Memos (beginning with 2019, as approved by NYSDEC and any supplemental work plans. The below is a general summary of sampling tasks that have occurred in the past and may occur in the monitoring year covered in this QAPP or in the future.

1. Groundwater will be collected from piezometers and monitoring wells associated with LCP OU-1.
2. Surface water will be collected as surface grabs at multiple locations as per the approved Monitoring Scope Memos as applicable.
3. Sediment and floodplain soil will be collected as grab samples at multiple locations as per the approved Monitoring Scope Memos and/or supplemental work plans. Samples are collected per the approved SOP at the given intervals in the respective Plan(s).
4. Adult sport fish and prey (forage) fish will be collected as per the approved Monitoring Scope Memos using seine netting, angling, minnow traps, and/or electrofishing. Fillets will be processed from adult sport fish collected in Ninemile Creek consistent with the NYSDEC SOP PrepLab4 (May 2014) and SOP L-3I (SGS Wilmington's processing SOP) while whole body composites for prey fish will be collected and composited at the laboratory. Total length and weight measurements of individual adult sport fish and all prey fish individuals used in composites will be measured in the field (see Worksheet #21, main text).
5. For adult sport fish individuals, the downstream location in Ninemile Creek has been sampled to collect up to 8 individuals from up to three species in years that sampling occurs. The upstream reference location in Ninemile Creek has been sampled for up to 6 individuals from one species in years that sampling occurs. The individuals sampled at the upstream location will be from one of the three species sampled at the downstream locations, unless otherwise approved by NYSDEC. Future monitoring will be discussed with NYSDEC.
6. A maximum of five composite prey fish samples were collected from each of three locations in Geddes Brook in years where sampling occurred. Composite samples consisted of the same species and similar sized individuals as much as possible. In addition, up to three locations within the Ninemile Creek restoration area and one upstream reference location were sampled for up to 20 samples (up to 5 samples per location) in years when sampling occurred. Composites generally consisted of 10 to 15 individuals or a sufficient number to obtain biomass needed for chemical analyses. Future monitoring will be discussed with NYSDEC.
7. Benthic macroinvertebrates were collected in Geddes Brook from the three forage fish sample locations; a grab sampler, polypropylene sieve and aquatic nets will be used. Benthic samples were also collected from the NMC channel in 2016. Up to five small mammals were collected from terrestrial habitats adjacent to the Geddes Brook floodplain using traps. One composite sample of earthworms were collected from up to three locations adjacent to open water areas. Small mammals were also be collected. Small mammals and earthworms were collected in SYW-10 in 2015, 2016 and 2018. Small mammals and earthworms were also collected from the NMC floodplain in 2016. Future sampling of these media in NMC will be completed, as needed in consultation with NYSDEC.
8. Vegetation monitoring was completed for five years following successful installation and evaluated annually.

9. Channel elevation and wetland connection monitoring was completed annually for five years (with a gap year in 2016 as per the OMM Plan) in Geddes Brook. Formal wetland delineations were conducted in Year 5 in both Geddes Brook and Ninemile Creek to quantify wetland acreages as described in the Geddes Brook OMM Plan and the Ninemile Creek MM Plan.
10. Channel elevation monitoring in Ninemile Creek was completed from 2014 through 2018. In the event of a 50-year or greater flow event (greater than 3,400 cubic feet per second [cfs] based on Onondaga Creek flows), all ten previously monitored stations will be surveyed. Should a 100-year or greater flow event (greater than 4,000 cfs based on Onondaga Creek flows) occur first, then no additional surveys will be necessary if the post 100-year survey results are within tolerance. In the event of other types of disturbances such as ice scour or slope instability, the need for additional surveys in the impacted area will be discussed with and ultimately approved by NYSDEC.

Analysis Tasks:

The commercial laboratory will analyze groundwater, surface water, sediment, and biota samples for total mercury, and also analyze most sample types for methylmercury (see Worksheet #11). In addition, a sub-set of adult fish samples collected historically from Ninemile Creek were analyzed for PCB aroclors, dioxins-furans and lipid content in select years. Future analyses will be discussed with NYSDEC.

Quality Control Tasks:

1. Implement SOPs for sample collection, packaging, transport, and storage prior to analysis. QC sample handling protocols are described on Worksheet #26 of the main text.
2. Collect field quality control samples including MS/MSDs, field duplicates and field blanks as warranted (see Worksheet #20).

Secondary Data:

See Worksheet #13

Data Management Tasks:

Records generated during sample collection and analyses document the validity and authenticity of the project data. The project team will maintain a field database a temporary repository for all sampling records generated in the field. Field and analytical data from the laboratory will later be transferred to the data management system maintained on behalf of Honeywell International.

Documentation and Records:

1. This QAPP will be distributed to each contractor responsible for the collection, generation, and interpretation of field and analytical data. The QA Program Manager will be responsible for ensuring that necessary changes occur so that the QAPP is up to date with actual practices.
2. Appropriate records will be maintained to provide adequate documentation of the entire data generation process, including field sampling and laboratory analysis.
3. Field sampling records may include
    a. Field logs and field notebooks to records daily activities and conditions
    b. An electronic field data management system (database)

   c. Sample Chain-of-Custody documentation
4. Lab documentation will include
   a. Operational calibration records
   b. Equipment maintenance records
   c. Nonconformance memos as applicable
   d. Corrective action memos as warranted
   e. Analytical data reports.

Assessment/Audit Tasks:

1. Project oversight (field and laboratory) will include periodic inspection and audits of sampling and analytical techniques. No additional field or laboratory audits are planned. Testing and calibration activities will also be reviewed. All audit and review findings and any corrective actions that arise from them will be documented. The laboratory director will ensure that corrective actions are carried out promptly. Where the audit findings cast doubt on the correctness or validity of the laboratory's calibrations or test results, immediate corrective action will be taken and any client whose work is affected will be notified immediately in writing.
2. The following reports may be completed if a deviation from the field sample matrix or QAPP is encountered, or to document an audit:
   a. Corrective action reports documenting any problems encountered during field activities and corrective actions taken.
   b. System and performance audit reports completed during the investigation and a summary of any changes made to document procedures, and the rationale for the changes
3. Data management includes working with the laboratories to provide deliverables that meet Honeywell data requirements and DEC deliverable requirements pertaining to EQUIS.
4. See Worksheets #31 and #32 for explanation of project assessments, assessment findings, and corrective action responses.
5. Lab SOPs will be assessed annually. Any changes to lab SOPs will be provided to NYSDEC.
6. The annual monitoring report where fish tissue results are presented will include confirmation that processing of tissue samples were completed in accordance with standard protocols specified in this QAPP.
7. NYSDEC split fish tissue sample results, if collected, will be compared with results from the laboratory analyses conducted in accordance with this QAPP.

Data Review Tasks:

1. The laboratory will perform data reduction as described in each test method for this project and will submit sample results and QA/QC results.
2. The laboratory quality assurance officer and/or laboratory director are responsible for reviewing the laboratory data and QA/QC reports and checking data reduction prior to submittal to Honeywell. The laboratory will correct any transcription or computational errors identified during this review.
3. Test results will be certified to meet all requirements of the NELAC standards, or reasons are provided if they do not.
4. Complete laboratory data packages will be provided to NYSDEC upon request.

Activity	Organization	Dates		Deliverable(s)	Deliverable due date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Mobilization	Parsons (GB, NMC and SYW-10) and Jacobs (LCP OU-1 Groundwater[1])	January for Groundwater May, June and August for surface water, sediment, and biota	December for groundwater October/November for surface water, sediment and biota.	NA	NA
Field Sampling	Parsons	May	Late November	NA	NA
	Jacobs	January	December	NA	NA
Sample analysis	Eurofins-Frontier, Eurofins-Lancaster, and SGS North America Inc.	January (LCP OU-1) July (GB/NMC)	December	Unvalidated data	Due from laboratory to Parsons 21 days following submission of the last set of samples
Electronic data deliverables	Parsons	December	February (of year following sampling)	Files	Due as soon as possible following data validation
Data Usability Summary Report (DUSR) LCP OU-1/NMC/GB	Parsons	January of following year	April (of year following sampling)	DUSR	Due to NYSDEC first or second quarter of year following sample collection.

[1] Groundwater sampling at LCP OU-1 occurs quarterly.

WORKSHEET #14B AND #16B: PROJECT TASKS & SCHEDULE – ONONDAGA LAKE

Sampling Tasks:

Note: The scope for annual sampling is discussed in the years' respective Monitoring Scope Memos (beginning with 2019, as approved by NYSDEC and any supplemental work plans. The below is a general summary of sampling tasks that have occurred in the past and may occur in the monitoring year covered in this QAPP or in the future.

1. Adult sport fish and prey fish will be collected using various methods as appropriate: electroshocking, trap nets, gill nets, and seine netting. Fillets of adult sport fish will be prepared by the laboratory from adult sport fish consistent with NYSDEC SOP PrepLab4 (May 28, 2014) and SOP L-3I (SGS Wilmington's processing SOP). Individual whole-body individuals for large prey fish will be collected and processed as a whole-body sample at the laboratory. Whole body composites for small prey fish will be collected in the field, grouping fish by size so that the smallest individual is no less than 75% of the lengths of the largest individual. Total length and weight measurements of individual fish will be measured in the field and sex will be determined by the laboratory. Otoliths or scales will be sampled from adult sport fish for age to be quantified by SUNY ESF. (see Worksheet #21).
2. For adult sport fish individuals, eight locations will be sampled to collect 25 individuals lakewide from each of up to four species (Smallmouth Bass, Walleye, Pumpkinseed and Common Carp). As practical, adult sport fish will be evenly distributed among the sampling locations.
3. A maximum of three composite small prey fish samples will be collected from each of eight locations for small prey fish. Composite samples will consist of 10 to 15 individual fish (or enough individuals to reach the necessary mass to complete the analyses) of the same species and approximate same size, as possible.
4. A total of twenty-four large prey fish (typically White Suckers or similar) will be collected from eight locations (3 individuals per location).
5. Zooplankton and benthic macroinvertebrate (2017 only) samples will be collected for mercury and methylmercury analysis.
6. Sediment traps will be deployed/collected for mercury and total dissolved/fixed solids as dictated by the work plan.
7. Surface water samples will be collected using a Kemmerer at the appropriate depth as dictated in the OM plan for Nitrate Addition. Surface water sampling for PCBs will be collected in the lake using a submersible pump, while tributary samples will be collected using grab sampling as specified in the 2021 Onondaga Lake and Tributary Surface Water Monitoring for PCBs Memo.
8. *In Situ* surface water nitrate-nitrogen measurements will be conducted by UFI using an in-situ ultraviolet spectrophotometer.
9. Sediment will be sampled as warranted in the middle of the lake (SMU 8) for mercury analyses.

Analysis Tasks:

1. The commercial laboratory will analyze fish and sediment samples for total mercury. Surface water will be analyzed for total mercury, dissolved mercury, and methylmercury. Zooplankton from the profundal zone and benthic macroinvertebrates (2017 only)) will be analyzed for total mercury and methylmercury. Sediment trap slurries will be analyzed for total mercury. In addition, a fish sample sub-set will be analyzed as needed for

organic compounds of interest and percent lipids, and surface water samples from the littoral zone will be analyzed for organic compounds of interest.

2. UFI's laboratory will analyze surface water samples for nitrate+nitrite, nitrite, ammonia, and phosphorus.

Quality Control Tasks:

1. The Parsons field team leader will evaluate fish and sediment samples and applicable field quality control samples for acceptability for transport/ submission to the laboratory.
2. The UFI field team leader will evaluate littoral and profundal zone surface water samples and applicable field quality control samples for acceptability for transport/submission to the laboratory.
3. Implement SOPs for sample collection, packaging, transport, and storage prior to analysis. QC sample handling protocols are described on Worksheet #26 in the main text of this QAPP.
4. Collect field quality control samples including MS/MSDs, field duplicates and field blanks as warranted (see Worksheet #20).

Secondary Data:

See Worksheet #13

Data Management Tasks:

Records generated during sample collection and analyses document the validity and authenticity of the project data. The project team will maintain a field database as a temporary repository for all sampling records generated in the field. Field and analytical data from the laboratory will later be transferred to the data management system maintained on behalf of Honeywell International.

Documentation and Records:

1. This QAPP will be distributed to each contractor responsible for the collection, generation, and interpretation of field and analytical data. The QA Program Manager will be responsible for ensuring that necessary changes occur so that the QAPP is up to date with actual practices.
2. Appropriate records will be maintained to provide adequate documentation of the entire data generation process, including field sampling and laboratory analysis.
3. Field sampling records will include:
    a. Electronic field logs and field notebooks to records daily activities and conditions
    b. An electronic field data management system (database)
    c. Sample Chain-of-Custody documentation
4. Lab documentation will include:
    a. Operational calibration records
    b. Equipment maintenance records
    c. Nonconformance memos as applicable
    d. Corrective action memos as warranted
    e. Analytical data reports

5. UFI routinely reports environmental test results using a "simplified" format (NELAC, 2003). Additional detailed information and records related to sampling, testing, and QC results, as required by NELAC, are maintained by the laboratory and are considered a separate laboratory work request.

Assessment/Audit Tasks:

1. Project oversight (field and laboratory) will include periodic inspection and audits of sampling and analytical techniques. No additional field or laboratory audits are planned. Testing and calibration activities will also be reviewed. All audit and review findings and any corrective actions that arise from them will be documented. The laboratory director will ensure that corrective actions are carried out promptly. Where the audit findings cast doubt on the correctness or validity of the laboratory's calibrations or test results, immediate corrective action will be taken, and any client whose work is affected will be notified immediately in writing.
2. The following reports may be completed if a deviation from the field sample matrix or QAPP is encountered, or to document an audit:
    a. Corrective action reports documenting any problems encountered during field activities and corrective actions taken
    b. System and performance audit reports completed during the investigation and a summary of any changes made to document procedures, and the rationale for the changes
3. Data management includes working with the laboratories to provide deliverables that meet Honeywell data requirements and DEC deliverable requirements pertaining to EQUIS.
4. See Worksheets #31 and #32 for explanation of project assessments, assessment findings, and corrective action responses.
5. Lab SOPs will be assessed annually. Any changes to lab SOPs will be provided to NYSDEC.
6. The annual monitoring report where fish tissue results are presented will include confirmation that processing of tissue samples were completed in accordance with standard protocols specified in this QAPP.
7. NYSDEC split fish tissue sample results, if collected, will be compared with results from the laboratory analyses conducted in accordance with this QAPP.

Data Review Tasks:

1. The laboratory will perform data reduction as described in each test method for this project and will submit sample results and QA/QC results.
2. The laboratory quality assurance officer and/or laboratory director are responsible for reviewing the laboratory data and QA/QC reports and checking data reduction prior to submittal to Honeywell. The laboratory will correct any transcription or computational errors identified during this review.
3. Test results will be certified to meet all requirements of the NELAC standards, or reasons are provided if they do not.
4. Complete laboratory data packages will be provided to NYSDEC upon request.

Activity	Organization	Dates		Deliverable(s)	Deliverable due date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Mobilization	SUNY ESF/UFI/Parsons	May	Late June for fish tissue, November for surface water, zooplankton, and sediment trap sampling	NA	NA
Field Sampling	SUNY ESF/UFI/Parsons	May	Late November	NA	NA
Sample Analysis	Eurofins Lancaster Laboratories and Eurofins Frontier Global Sciences, UFI, SGS North America Inc.	May	Late December	Unvalidated data	Due from laboratory to Parsons 21 days following submission of last set of samples for analysis for given sampling effort
Electronic data deliverables	Parsons	December	February (of year following sampling)	Files	Due as soon as possible following data validation
Data Usability and Summary Report (DUSR)	Parsons	January (of year following sampling)	April (of year following sampling)	DUSRs	Generally due to NYSDEC by June 15 of the year following sampling

WORKSHEET #15: PROJECT ACTION LIMITS AND LABORATORY SPECIFIC DETECTION/QUANTITATION LIMITS

Matrix: Groundwater
Analytical Group: Mercury (7470A)
Concentration Level: Moderate

Analyte	CAS Number	Project Goal[1]	Project Quantitation Limit	Analytical Method[2]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	0.7 ug/L	0.2 ug/L	0.0952 ug/L	0.2 ug/L	0.0952 ug/L	0.2 ug/L

[1] September 2000 Record of Decision for LCP Bridge Street
[2] Analytical MDLs and QLs are those documented by SGS North America Inc (Dayton). MDLs and QLs will be evaluated on an annual basis.

Matrix: Surface Water, Sediment slurry
Analytical Group: Mercury (E1630/1631), including dissolved
Concentration Level: Low

Analyte	CAS Number	Project Goal[1]	Project Quantitation Limit	Analytical Method[2]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	0.7 ng/L (dissolved), 2.6 ng/L (dissolved)	0.5 ng/L	0.08 ng/L	0.5 ng/L	0.08 ng/L	0.5 ng/L
Methyl mercury	22967-92-6	None	0.05 ng/L	0.026 ng/L	0.05 ng/L	0.026 ng/L	0.05 ng/L

[1] Criteria for protection of human health: 0.7 ng/L; criteria for protection of wildlife: 2.6 ng/L. respective long term monitoring plans for information on project goals.
[2] Analytical MDLs and QLs are those documented by Eurofins Frontier Global Sciences. MDLs and QLs will be evaluated on an annual basis.

Matrix: Water
Analytical Group: Ammonia ($T\text{-}NH_3$)
Concentration Level: Low

Analyte	CAS Number	Project Goal	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
$T\text{-}NH_3$	7664-41-7	NA	48 µg/L	16 µg/L	48 µg/L	16 µg/L	48 µg/L

[1] Achievable laboratory MDLs and QLs are those documented in validated methods and obtained from UFI. MDLs and QLs will be evaluated on an annual basis

Matrix: Water
Analytical Group: Nitrate+Nitrite (NO_X)
Concentration Level: Low

Analyte	CAS Number	Project Goal	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
NO_X	1104-93-1	NA	30 µg/L	10 µg/L	30 µg/L	10 µg/L	30 µg/L

[1] Achievable laboratory MDLs and QLs are those documented in validated methods and obtained from UFI. MDLs and QLs will be evaluated on an annual basis

Matrix: Water
Analytical Group: Nitrite (NO_2)
Concentration Level: Low

Analyte	CAS Number	Project Goal	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
NO_2	10102-44-0	NA	6 µg/L	2 µg/L	6 µg/L	2 µg/L	6 µg/L

[1] Achievable laboratory MDLs and QLs are those documented in validated methods and obtained from UFI. MDLs and QLs will be evaluated on an annual basis

Matrix: Water (Sediment Traps, analyzed by Upstate Freshwater Institute)
Analytical Group: Total/Volatile Suspended Solids (TSS/VSS)
Concentration Level: Low

Analyte	CAS Number	Project Goal	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
TSS/VSS	7732-18-5	NA	2.5 mg	1.0 mg	2.5 mg	1.0 mg	2.5 mg

[1] Achievable laboratory MDLs and QLs are those documented in validated methods and obtained from UFI. MDLs and QLs will be evaluated on an annual basis

Matrix: Water
Analytical Group: Soluble Reactive Phosphorus (SRP)
Concentration Level: Low

Analyte	CAS Number	Project Goal	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
SRP	7723-14-0	NA	2.7 µg/L	0.9 µg/L	2.7 µg/L	0.9 µg/L	2.7 µg/L

[1] Achievable laboratory MDLs and QLs are those documented in validated methods and obtained from UFI. MDLs and QLs will be evaluated on an annual basis

Matrix: Sediment
Analytical Group: Mercury (7471B)
Concentration Level: Moderate

Analyte	CAS Number	Project Goal[1]	Project Quantitation Limit	Analytical Method[2]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
Total Mercury	7439-97-6	--	0.1 mg/Kg	0.02 mg/Kg	0.06 mg/Kg	0.02 mg/Kg	0.06 mg/Kg

[1] See respective long term monitoring plans for information on project goals
[2] Analytical MDLs and QLs are those documented by Eurofins Lancaster Laboratories. MDLs and QLs will be evaluated on an annual basis.

Matrix: Sediment
Analytical Group: Methyl Mercury (1630)
Concentration Level: Low

Analyte	CAS Number	Project Goal	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs
Methyl mercury	22967-92-6	NA	0.058 ng/g	0.017 ng/g	0.058 ng/g	0.017 ng/g wet	0.058 ng/g wet

[1] Analytical MDLs and QLs are those documented by Eurofins Frontier Global Sciences. MDLs and QLs will be evaluated on an annual basis.

Matrix: Biota
Analytical Group: Mercury (7471B)
Concentration Level: Moderate

Analyte	CAS Number	Project Goal[1]	Project Quantitation Limit[2]	Analytical Method[3]		Achievable Laboratory Limits[4]	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7438-97-6	0.1 to 0.3 mg/kg wet weight	0.05 mg/Kg	0.015 mg/Kg	0.06 mg/Kg	0.0145 mg/Kg	0.033 mg/Kg

[1] See respective long term monitoring plans for information on project goals
[2] The laboratory will provide expected necessary sample weight to achieve the Project Quantitation Limit.
[3] Analytical MDLs and QLs are those documented by SGS North America Inc (Dayton). MDLs and QLs will be evaluated on an annual basis.
[4] The MDL and QL concentrations are dependent on the amount of tissue collected / available at the lab for analysis.

Matrix: Biota
Analytical Group: Mercury (1631)/Methylmercury (1630)
Concentration Level: Low

Analyte	CAS Number	Project Goal[1]	Project Quantitation Limit[2]	Analytical Method[3]		Achievable Laboratory Limits[4]	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	NA	0.8 ng/g wet	0.09 ng/g wet	0.8 ng/g wet	0.09 ng/g wet	0.8 ng/g wet
Methyl mercury	22967-92-6	NA	2 ng/g wet	0.5 ng/g wet	2 ng/g wet	0.5 ng/g wet	2 ng/g wet

[1] These methods to be utilized for analysis of benthic invertebrates and zooplankton, for which there are no remedial goals. The quantitation limits are sufficient for assessing the contaminant reduction trends.
[2] The laboratory will provide expected sample weight to achieve the Project Quantitation Limit.
[3] Analytical MDLs and QLs are those documented by Eurofins Frontier Global Sciences. MDLs and QLs will be evaluated on an annual basis.
[4] The MDL and QL concentrations are dependent on amount of biota collected.

Matrix: Fish Tissue
Analytical Group: Lipids
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Limit[1]	Achievable Laboratory Limits
Percent Lipids	LP001	NA	0.05%	0.05%

[1] The laboratory (SGS North America Inc [Wilmington]) will provide expected necessary sample weight to achieve the Project Limit.

Matrix: Fish Tissue
Analytical Group: PCBs (Aroclors, 8082A)[1]
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[2]	Project Quantitation Limit[3]	Analytical Method[4]		Achievable Laboratory Limits[5]	
				MDLs	Method QLs	MDLs	QLs
Aroclor 1016		--	13 µg/kg wet	13 µg/kg wet	34 µg/kg wet	13 µg/kg wet	34 µg/kg wet
Aroclor 1221		--	13 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet
Aroclor 1232		--	13 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet
Aroclor 1242		--	13 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet
Aroclor 1248		--	13 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet
Aroclor 1254		--	13 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet
Aroclor 1260		--	13 µg/kg wet	8.9 µg/kg wet	34 µg/kg wet	8.9 µg/kg wet	34 µg/kg wet
Aroclor 1262		--	13 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet
Aroclor 1268		--	13 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet	6.6 µg/kg wet	34 µg/kg wet

[1] Total PCBs are reported as a summation of detected Aroclors.
[2] The target fish tissue concentrations for Total PCBs vary by site and receptor; values are presented in the associated RODs. MDLs shown will be sufficient for evaluating the data.
[3] The laboratory will provide expected necessary sample weight to achieve the Project Quantitation Limit.
[4] Analytical MDLs and QLs are those documented by SGS North America Inc (Dayton). MDLs and QLs will be evaluated on an annual basis.
[5] Achievable MDLs and QLs are limits that the laboratory can achieve when performing a specific analytical method.

Matrix: Fish Tissue
Analytical Group: Pesticides
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit	Analytical Method[2]		Achievable Laboratory Limits[3]	
				MDLs	Method QLs	MDLs	QLs
DDT and metabolites		--	0.005 µg/g wet	0.00021 to 0.00025 µg/g wet	0.002 µg/g wet	0.00042 to 0.0016 µg/g wet	0.0034 to 0.0037 µg/g wet
Hexachlorobenzene		--	0.005 µg/g wet	0.00025 µg/g wet	0.002 µg/g wet	0.0012 µg/g wet	0.0031 µg/g wet

[1] For DDT and metabolites, the target fish tissue concentrations vary by site and receptor; values are presented in the associated RODs. MDLs shown will be sufficient for evaluating the data. There are no fish tissue targets in the RODs for hexachlorobenzene.

[2] Analytical MDLs and QLs are those documented in validated methods. MDLs and QLs will be evaluated on an annual basis.

[3] Achievable MDLs and QLs are limits in *u*g/g on a wet-weight basis that the laboratory (SGS North America Inc [Dayton]) can achieve when performing the specific analytical method.

Matrix: Fish Tissue
Analytical Group: Dioxins-Furans
Concentration Level: Low

Analyte	CAS Number	Project Action Limit[1]	Project Quantitation Limit[2]	Analytical Method[3]		Achievable Laboratory Limits[4]	
				MDLs	Method QLs	MDLs[5]	QLs
2,3,7,8-TCDD	1746-01-6	--	1.0 ng/kg	NA	1.0 ng/kg	0.373 ng/kg	0.5 ng/kg
1,2,3,7,8-PeCDD	40321-76-4	--	5.0 ng/kg	NA	5.0 ng/kg	1.12 ng/kg	2.5 ng/kg
1,2,3,4,7,8-HxCDD	39227-28-6	--	5.0 ng/kg	NA	5.0 ng/kg	1.04 ng/kg	2.5 ng/kg
1,2,3,6,7,8-HxCDD	57653-85-7	--	5.0 ng/kg	NA	5.0 ng/kg	1.62 ng/kg	2.5 ng/kg
1,2,3,7,8,9-HxCDD	19408-74-3	--	5.0 ng/kg	NA	5.0 ng/kg	1.21 ng/kg	2.5 ng/kg
1,2,3,4,6,7,8-HPCDD	35822-46-9	--	5.0 ng/kg	NA	5.0 ng/kg	1.18 ng/kg	2.5 ng/kg
OCDD	3268-87-9	--	10 ng/kg	NA	10 ng/kg	4.08 ng/kg	5.0 ng/kg
2,3,7,8-TCDF	51207-31-9	--	1.0 ng/kg	NA	1.0 ng/kg	0.239 ng/kg	0.5 ng/kg
1,2,3,7,8-PECDF	57117-41-6	--	5.0 ng/kg	NA	5.0 ng/kg	1.12 ng/kg	2.5 ng/kg
2,3,4,7,8-PECDF	57117-31-4	--	5.0 ng/kg	NA	5.0 ng/kg	1.30 ng/kg	2.5 ng/kg
1,2,3,4,7,8-HXCDF	70648-26-9	--	5.0 ng/kg	NA	5.0 ng/kg	0.979 ng/kg	2.5 ng/kg
1,2,3,6,7,8-HXCDF	57117-44-9	--	5.0 ng/kg	NA	5.0 ng/kg	1.16 ng/kg	2.5 ng/kg
2,3,4,6,7,8-HXCDF	60851-34-5	--	5.0 ng/kg	NA	5.0 ng/kg	0.968 ng/kg	2.5 ng/kg
1,2,3,7,8,9-HXCDF	72918-21-9	--	5.0 ng/kg	NA	5.0 ng/kg	0.872 ng/kg	2.5 ng/kg
1,2,3,4,6,7,8-HPCDF	67562-39-4	--	5.0 ng/kg	NA	5.0 ng/kg	0.862 ng/kg	2.5 ng/kg
1,2,3,4,7,8,9-HPCDF	5673-89-7	--	5.0 ng/kg	NA	5.0 ng/kg	1.08 ng/kg	2.5 ng/kg
OCDF	39001-02-0	--	10 ng/kg	NA	10 ng/kg	2.16 ng/kg	5.0 ng/kg

[1] The target fish tissue concentrations vary by site and receptor; values are presented in the associated RODs. MDLs shown will be sufficient for evaluating the data.
[2] The laboratory (SGS North America Inc [Wilmington]) will provide expected necessary sample weight to achieve the Project Quantitation Limit.
[3] Analytical MDLs and QLs are those documented in validated methods.
[4] Achievable MDLs and QLs are limits that the laboratory can achieve when performing a specific analytical method. MDLs and QLs will be evaluated on an annual basis.
[5] Laboratory will report sample specific estimated detection limits (EDLs), based on achieved signal-to-noise during sample analysis.

WORKSHEET #17A: SAMPLING DESIGN AND RATIONALE – GEDDES BROOK, NINEMILE CREEK, AND LCP OU-1

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach):

Geddes Brook

Sample locations were chosen, with NYSDEC approval, in a stratified random fashion to ensure that the west basin, east basin, Geddes Brook channel, and Outfall-19 were each represented.

Ninemile Creek and SYW-10

Sample locations were chosen, with NYSDEC approval, to be consistent with locations of baseline sampling, to the extent practicable.

LCP OU-1

Sample locations were chosen, with NYSDEC approval, in a stratified random fashion to ensure that key areas such as wetlands and the West Flume were represented.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations):

See Operation Maintenance and Monitoring Plans, Annual Scoping Memos, and/or Supplemental Workplans for each sub site for sampling locations and sampling schedules. See Worksheet #18 for matrices, analytical groups, concentration levels, and number of samples.

Activity	Number of Locations	Total Number of samples annually per location	Number of species / types	Sample Preparation	Sample Collection Timeframe
Adult sport fish tissue	2 in Ninemile Creek (1 upstream station, 1 downstream station)	6 samples per species at upstream location; 8 samples per species at downstream station	1 species at upstream station; 3 species at downstream station	Fillets	Spring, summer or fall months
Forage fish tissue	10 based on 3 each at LCP OU-1 and Geddes Brook (GB) and 4 at Ninemile Creek	5	Variable (samples are composites of a prey species)	Whole body composites	Summer or fall months.
Groundwater at LCP OU-1	15[1]	4	N/A	N/A	One round of samples each quarter
Surface water[2]	9 at LCP OU-1, 6 in GB and 5 in Ninemile Creek	1 at LCP OU-1, 1 in GB and 2 in Ninemile Creek	N/A	N/A	Summer or fall at Geddes Brook and LCP OU-1. Low flow and high flow in Ninemile Creek.
Soil/Sediment[2, 3]	9 at LCP OU-1, 6 in GB and 10 in SYW-10, 7 in NMC[4]	1	N/A	Each sample is a composite of 5 grab samples	Summer or fall months
Benthic macroinvertebrates	3 in GB and 3 in NMC[5]	3 per location in GB, 1 per location in NMC	To be determined based on availability.	Each sample is a composite of 3 grab or net samples	Summer or fall months
Small mammals	Up to 5 at GB; and up to 10 total samples from two zones in SYW-10, 5 in NMC floodplain[5]	1	To be determined based on availability.	Individuals to be composited based on lab needs	Summer or fall months
Earthworms[3]	Up to 3 at GB, 10 at SYW-10, 3 in NMC[5]	1	N/A	Individuals to be composited	Summer or fall months

[1] 15 locations include 3 depths (shallow, intermediate, deep) at 4 locations (PZ-1B, PZ-2B, PZ-3B, PZ-4B) and at deep wells only at 3 other locations (MW-34, MW-35, MW-36)

[2] Surface water and sediment samples co-located in Geddes Brook and LCP OU-1.

[3] Sediment and earthworms co-located in SYW-10. Additional sampling in Wetland A at LCP conducted per supplemental work plans; sample scheme is detailed in the approved plan and has varied.

[4] Three floodplain soil/sediment locations, four channel sediment locations

[5] Conducted in 2016

WORKSHEET #17B: SAMPLING DESIGN AND RATIONALE – ONONDAGA LAKE

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach):

Locations for fish sampling are dispersed around the lake coinciding with previous sampling locations from the Remedial Investigation, baseline monitoring and Onondaga County's Ambient Monitoring Program. Some locations were adjusted for sampling conducted beginning in 2017 to focus on remediation areas.

Surface water samples will be collected at compliance monitoring locations at one water depth for multiple water quality parameters. Surface water samples will be collected at South Deep at multiple water depths from May to November as part of the nitrate addition effort.

ISUS/SUNA gridding will be conducted in the profundal zone to evaluate the horizontal and vertical distribution of nitrate in the water column based on measurements at approximately 34 pre-determined locations. For the ongoing nitrate addition work, an understanding of nitrate concentrations is needed on a small geographic scale laterally and at multiple water depths. Locations for turbidity monitoring related to the WB 1-8 Shoreline Stabilization area were chosen to be consistent with baseline monitoring and are representative locations.

Zooplankton samples will be collected at South Deep.

Benthic macroinvertebrate samples will be collected at three locations in SMU 8.

Sediment samples for continuing the assessment of natural recovery will be collected at representative locations throughout SMU 8. Sediment samples in the littoral zone will also be needed to assess compliance with the BSQV as per the MNR work plan.

Additional information regarding the sampling design and rationale is provided in the relevant work plans included in the OLMMP.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations):

See Operation Maintenance and Monitoring Plan, Annual Scoping Memos, and/or Supplemental Workplans for sampling locations and sampling schedules.
See Worksheet #18 for matrices, analytical groups, concentration levels, and number of samples.

Activity	Number of Locations	Total Number of samples annually per location	Number of species / types	Sample Preparation	Sample Collection Timeframe
Adult Sport Fish Tissue	8	3-4 per species per location[1]	4 species	Fillets	Spring, summer months
Large Prey Fish	8	3	Variable [2]	Whole body	Spring, summer months
Small Prey Fish	8	3	Variable [3]	Composite whole body	August
Benthic Macroinvertebrates (2017 only)	3	1	Variable	Composited into a single sample at each location	June
Sediment	22 (SMU 8, Routine Monitoring Locations) 49 (SMU 8, Compliance Monitoring Locations) 14 (Littoral Zone, Compliance Monitoring Locations)	1	2 depths per location in SMU 8 locations; 1 depth per location at littoral zone locations	N/A	Spring
Sediment (Slurry)	1 (South Deep)	Variable [4]	N/A	N/A	Approximately 18 sampling events (dependent on fall turnover)
Zooplankton	1 (South Deep)	17-18 (once each in May and June, twice per month in July and August, weekly from September through fall turnover, twice per month in November)	Variable	Entire sample	May-November

Activity	Number of Locations	Total Number of samples annually per location	Number of species / types	Sample Preparation	Sample Collection Timeframe
Surface Water (Compliance Verification)	12	2	N/A	N/A	Variable (1 pre-turnover event, 1 post-turnover event)
Surface Water (Nitrate Addition Monitoring)	1 (South Deep)	Variable (May-November	N/A	N/A	Variable

[1] Target for collecting individual sport fish is 25 Common Carp, 25 Pumpkinseed, 25 Smallmouth Bass, and 25 Walleye evenly distributed amongst each of the sampling locations, as practical.

[2] Target for collecting 24 individual large prey fish evenly distributed among the sampling locations, as practical. Target species include White Sucker and Shorthead Redhorse

[3] Target for collecting 24 composites of small prey fish. Each small prey fish composite will consist of a single species. Banded Killifish is the primary target species, with Round Goby as the secondary target if tissue mass cannot be achieved.

[4] Sediment traps are deployed at South Deep weekly for TSS measurements. Mercury analysis is conducted every 2 weeks from mid-May through August, weekly from September until fall turnover, then every two weeks until mid-November, for a total of approximately 18 sediment trap sampling events (dependent upon fall turnover).

WORKSHEET #18A: SAMPLING LOCATIONS AND METHODS – GEDDES BROOK, NINEMILE CREEK, AND LCP OU-1 MEDIA MONITORING

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations):

See the respective Geddes Brook OM&M Plan, Ninemile Creek M&M Plan, and respective LCP OM&M Plan, and annual reports for sampling locations. See worksheets #14, 16, and 17 for number of locations, samples per location, and sampling duration within each month. The matrices, analytical groups, concentration levels, and number of samples is presented in the table below.

Sampling Location/ID Number	Matrix	Depth units	Analytical Group	Concentration Level	Number of Samples (field duplicates)	Sampling Procedure Reference	Rationale for Sampling Location
LCP OU-1, Geddes Brook and Ninemile Creek	Surface Water	One water depth	Mercury (total and dissolved), USEPA Method 1631	Low	9 (1) from LCP OU-1, 6 (1) from GB, and 10 (1) from NMC	S-14	OMM Plan(s) approved by NYSDEC
			Methylmercury, USEPA Method 1630	Low	Same as for mercury (Hg)		
LCP OU-1	Groundwater	Three depths[1]	Total Mercury, USEPA Method 7470	Low	60 (4) annually	S-21	
LCP OU-1, Geddes Brook, SYW-10, and NMC	Soil/Sediment[2]	NA	Total mercury (Hg), USEPA Method 7471	Moderate	9 (1) from LCP OU-1, 6 (1) from GB, 10 (1) from SYW-10, and 7 (1) from NMC	S-13	
			Methylmercury, USEPA Method 1630	Low	Same as for Hg		
Ninemile Creek	Adult sport fish (3 species)[3]	NA	Total mercury (Hg) and percent moisture, USEPA Method 7471	Moderate	30	S-17	
			PCB aroclors, dioxins-furans and lipid content, various USEPA methods	Low	10	S-17	
LCP OU-1, Geddes Brook and Ninemile Creek	Prey fish (composite samples)	NA	Total Mercury (Hg), USEPA Method 7471; and percent moisture (NMC only)	Moderate	15 each from both LCP OU-1 and GB and 20 from NMC	S-17	OMM Plan(s) approved by NYSDEC

Sampling Location/ID Number	Matrix	Depth units	Analytical Group	Concentration Level	Number of Samples (field duplicates)	Sampling Procedure Reference	Rationale for Sampling Location
			PCB aroclors; dioxins-furans and lipid content; various USEPA methods	Low	10 from NMC only		
Geddes Brook and NMC[4]	Benthic macroinvertebrates	NA	Total Mercury (Hg), USEPA Method 7471	Moderate	9 from GB, 3 in NMC	S-16	
			Methylmercury, USEPA Method 1630	Low	Same as for Hg		
Geddes Brook, NMC[4], and SYW-10	Small mammals	NA	Total Mercury (Hg), USEPA Method 7471	Moderate	5 from GB, 5 from NMC, 10 from SYW-10	S-18	
			Methylmercury, USEPA Method 1630	Low	5 from GB		
Geddes Brook, NMC[4], and SYW-10	Earthworms	NA	Total Mercury (Hg), USEPA Method 7471	Moderate	3 from GB, 3 from NMC, 10 from SYW-10	S-15	
			Methylmercury, USEPA Method 1630	Low	Same as for Hg		

[1] Three depths of wells are sampled (deep, middle, and shallow); individual depths to the screen vary by well. Specific information on the depths of the wells can be found in the LCP OU-1 OM&M Plan (Parsons, 2009).

[2] Sampling depths as discussed in the applicable approved Plan

[3] Standard sport fish sampling in Ninemile Creek includes 6 samples at the upstream station (1 species) and 24 samples at the downstream location (3 species). Per approved Scope Memos, sampling conducted in 2019 and 2022 consisted of sampling for 8 Rock Bass from the downstream location only.

[4] Conducted in 2016.

WORKSHEET #18B: SAMPLING LOCATIONS AND METHODS – ONONDAGA LAKE

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations):

See the respective Appendices to the OLMMP and the Nitrate Addition OM Plan for sampling locations. See worksheets #14, 16, and 17 for number of locations, samples per location, and sampling duration within each month. The matrices, analytical groups, concentration levels, and number of samples is presented in the table below.

Sampling Location/ID Number	Matrix	Depth units	Analytical Group	Concentration Level	Number of Samples (field duplicates)[1]	Sampling Procedure Reference[2]	Rationale for Sampling Location
Lakewide	Adult sport fish (4 species)	Littoral zone	Total mercury	Low	100	S-2	OMM Plan(s) approved by NYSDEC OMM Plan(s) approved by NYSDEC
			PCBs	Low	100		
			Hexachlorobenzene	Low	100		
			Dioxins/Furans	Low	12/species		
			% lipids	Low	100		
			% moisture	Low	100		
Lakewide	Prey fish (whole body composites small prey fish, individual whole body large prey fish)	Littoral zone	Total mercury	Low	48	S-2	
			PCBs	Low	48		
			Hexachlorobenzene	Low	48		
			DDT and metabolites	Low	48		
			% lipids	Low	48		
			% moisture	Low	48		
Lakewide (SMU 8)	Benthic Macroinvertebrates	Profundal zone	Total mercury	Low	3	S-4	
			Methylmercury				
Lakewide (SMU 8)	Sediment	0-4 and 4-10 cm	Mercury	Moderate	44 (2) (Routine Locations) 98 (5) (Compliance Locations)	S-3	
Lakewide (Littoral Zone)		0-6 inches			14 (1)		

Sampling Location/ID Number	Matrix	Depth units	Analytical Group	Concentration Level	Number of Samples (field duplicates)[1]	Sampling Procedure Reference[2]	Rationale for Sampling Location
South Deep (SMU 8)	Sediment (Slurry)	10 m water depth	Mercury	Low	18	S-11	
			Total/Volatile Suspended Solids (TSS/VSS)	Low			
South Deep	Zooplankton	13 m water depth	Total mercury	Low	17-18[3]	S-8	
			Methylmercury				
Nitrate addition monitoring	Surface water	Multiple water depths at South Deep	Total mercury, methylmercury, nitrate+nitrite, nitrate, ammonia	Low	83 (22)	S-7	
			Total dissolved mercury	Low	15 (2)		
			Soluble reactive phosphorous (lower depths)	Low	30 (11)		
		Multiple	Robotic buoy and ISUS[4] parameters	Moderate	Varying	S-9, S-10	
Lakewide	Surface water	Mid-point of water column	Total mercury	Low	24 (2)	S-7/S-20	OMM Plan(s) approved by NYSDEC, 2021 Onondaga Lake and Tributary Surface Water Monitoring for PCBs
			Dissolved mercury	Low			
			Methylmercury	Low			

[1] Field duplicates not collected for tissue.

[2] Standard Operating Procedures presented in Appendix A.

[3] Number of zooplankton samples can vary annually. Samples are collected once each in May and June, twice per month in July and August, weekly from September through fall turnover, twice per month in November.

[4] ISUS (*in situ* ultraviolet spectrophotometer) parameters include NO_3^- and HS^-.

WORKSHEET #19 & 30: SAMPLE CONTAINERS, PRESERVATION, AND HOLD TIMES

Laboratory: Eurofins-Frontier, 11770 North Creek Parkway, North, Suite 400, Bothell, WA 98011
Back-up Laboratory: N/A
Sample Delivery Method: FedEx or similar

Analytical Group	Matrix	Concentration Level	Number of Locations	Analytical SOP	Sample Mass or Volume	Container(s) (number, size, &type per sample)	Preservation	Maximum Holding Time (preparation/ analysis)[2]	Data Package Turnaround
Methylmercury	Surface Water	Low	See Worksheet #17 and #18	USEPA, Method 1630, L-2B, L-2H	500 mL	Glass or Teflon (500 mL or 1 L)	HCl or sulfuric acid to pH<2, cool to 4ºC	48 hours to preserve 180 days to analysis	21 days
	Sediment			USEPA Method 1630, L-2B	4 ounces	Glass	Cool to 4ºC	6 months	21 days
	Zooplankton			USEPA Method 1630, L-2B, L-2E	1-5 g (preferably 2-10 g)	Glass or Teflon bottle (250-500 mL)	Cool to 4°C, freeze upon receipt, or freeze dry	90 days	21 days
	Benthic macroinvertebrates (OL)			USEPA, Method 1630, L-2B, L-2E	1-5 g (preferably 2-10 g)	Glass or Teflon bottle (250-500 mL)	Cool to 4°C, freeze upon receipt, or freeze dry	6 months (frozen)	21 days
	Benthic macroinvertebrates (GB/NMC)			USEPA, Method 1630, L-2B, L-2E	10 g minimum	Resealable bags and glass	Weigh (wet-weight) and freeze dry to <-10ºC	6 months (frozen)	21 days
	Small mammals and earthworms			USEPA 1630, L-2B, L-2E	10 g minimum	Resealable bags and glass	Cool to 4ºC until analysis	28 days	21 days

Laboratory: Eurofins Lancaster, 2425 New Holland Pike, Lancaster, PA 17605 and Eurofins-Frontier, 11770 North Creek Parkway, North, Suite 40, Bothell WA 98011
Back-up Laboratory: N/A
Sample Delivery Method: FedEx or similar

Analytical Group	Matrix	Concentration Level	Number of Locations	Analytical SOP	Sample Mass or Volume	Container(s) (number, size, &type per sample)	Preservation[1]	Maximum Holding Time (preparation/ analysis)[2]	Data Package Turnaround
Total Mercury[3]	Surface Water	Low	See Worksheet #17 and #18	USEPA, Method 1631, L-2C, L-2G, L-2F	500 mL	Glass or Teflon (500 mL or 1 L)	HCl or BrCl to pH < 2, cool to 4°C	14 days to preserve 90 days to analysis	21 days
	Sediment Traps	Low		USEPA, Method 1631, L-2C, L-2D, L-2F	500 mL	Glass or Teflon (500 mL or 1 L)	HCl or BrCl to pH <2, cool to 4 °C	14 days to preserve 90 days to analysis	21 days
	Sediment	Moderate		USEPA, Method 7471B, L-2A	4 ounces	125 mL wide mouth glass	Cool to 4ºC	28 days	21 days
	Zooplankton	Low		USEPA, Method 1631, L-2C, L-2G	1-5 g (preferably 2-10 g)	Glass or Teflon bottle (250 – 500 mL)	Cool to 4ºC, freeze upon receipt, or freeze dry	90 days	21 days
	Benthic Macroinvertebrates (OL)	Low		USEPA, Method 1631, L-2C, L-2G				6 months (frozen)	21 days
	Benthic Macroinvertebrates (GB/NMC)	Moderate		USEPA, Method 7471A, L-2A	10 grams minimum	Resealable bags and glass	Weigh (wet-weight) and freeze dry to <-10°C	28 days	21 days
	Small mammals and earthworms	Moderate		USEPA 7471A, L-2A	10 gram minimum	Resealable bags and glass	Cool to 4ºC until analysis	28 days	21 days

[1] Freezing allows extended hold time on tissue samples. Samples should be frozen if not being processed immediately.
[2] From date of sample collection.
[3] The above requirements are also applicable to Dissolved Mercury using Method 1631.

Laboratory: SGS North America Inc., 2235 US-130, Dayton, NJ 08810
Back-up Laboratory: N/A
Sample Delivery Method: courier then FedEx or similar

Analytical Group	Matrix	Concentration Level	Number of Locations	Analytical SOP	Sample Mass or Volume	Container(s) (number, size, &type per sample)	Preservation[1]	Maximum Holding Time (preparation/ analysis)[2]	Data Package Turnaround
Total Mercury	Groundwater	Moderate	See Worksheet #17 and #18	USEPA Method 7470, L-3G	250 mL	250 mL, oblong plastic	HNO_3 to pH <2, cool to 4°C	28 days	21 days
Total Mercury	Fish Tissue	Low		USEPA, Method 7471A, L-3E	2-10 grams	Resealable bags and glass	Cool to <4° ± 2°C until homogenized and sub-sampled and then freeze to <-10°C, or freeze dry	28 days once defrosted	21 days
Total PCB aroclors		Low		EPA 8082A, L-3C	40 grams	Resealable bags and glass	Cool to <4° ± 2°C until homogenized and sub-sampled and then, freeze to <-10°C, or freeze dry	1 year to extraction, 40 days to analysis	21 days
DDT Metabolites, Hexachloroben zene		Low		SW-846 8081B, L-3D	10 grams	Resealable bags and glass	Cool, 4°±2°C until homogenized and sub-sampled and then freeze to <-10°C	14 days to extraction, 40 days to analysis	21 days

[1] Freezing allows extended hold time on tissue samples. Samples should be frozen if not being processed immediately.
[2] From date of sample collection. Note: hold times for fish typically begin when the fish is thawed for processing at the laboratory.

Laboratory: SGS North America Inc., 5500 Business Drive, Wilmington, NC 28405
List any required accreditations/certifications:
Back-up Laboratory: N/A
Sample Delivery Method

Analytical Group	Matrix	Concentration Level	Number of Locations	Analytical SOP	Sample Mass or Volume	Container(s) (number, size, &type per sample)	Preservation[1]	Maximum Holding Time (preparation/ analysis)[2]	Data Package Turnaround
PCDD/PCDFs	Fish Tissue	Low	See Worksheet #17 and #18	EPA 8290, L-3F	50 grams	Resealable bags and glass	Store at ≤ 10 °C in the dark until homogenized and sub-sampled and then, freeze to <-10°C	1 year to extraction, 40 days to analysis	21 days
Lipid Content		Low		Method 3540C/L-3A	10 grams	Resealable bags and glass	Store at ≤ 10 °C in the dark until homogenized and sub-sampled and then, freeze to <-10°C	1 year to extraction, 40 days to analysis	21 days

[1] Freezing allows extended hold time on tissue samples. Samples should be frozen if not being processed immediately.

[2] From date of sample collection. Note: hold times for fish typically begin when the fish is thawed for processing at the laboratory.

Laboratory: UFI, 224 Midler Park Drive, Syracuse, NY 13206, Gina Kehoe 315-431-4962 ext. 115
List any required accreditations/certifications:
Back-up Laboratory: N/A
Sample Delivery Method:

Analytical Group	Matrix	Concentration Level	Sample Locations	Analytical SOP	Sample Mass or Volume	Container(s) (number, size, &type per sample)	Preservation	Maximum Holding Time (preparation/analysis)[1]	Data Package Turnaround
Nitrate/Nitrite as N (NO_x)	Water	Low	South Deep	UFI SOP 239, SM 22nd ed. 4500-NO_3-F, L-1A	10 mL	Opaque plastic bottle (60 mL)	H_2SO_4 to pH <2, Cool to 4°C	28 days	21 days
Nitrite	Water	Low	South Deep	UFI SOP 239, SM 22nd ed. 4500-NO_3-F, L-1A	10 mL	Opaque plastic bottle (60 mL)	Cool to 4°C	48 hours	21 days
Ammonia	Water	Low	South Deep	UFI SOP 238, SM 22nd ed. 4500-NH_3-H, L-1B	10 mL	Opaque plastic bottle (60 mL)	H_2SO_4 to pH <2, Cool to 6°C	28 days	21 days
Soluble Reactive Phosphorus	Water	Low	South Deep	UFI SOP 107, SM 4500-P E-99, -11, L-1C	50 mL	Clear borosilicate glass bottle (250 mL)	Cool to 6°C	48 hours	21 days
Total/Volatile Suspended Solids	Slurry	Low	South Deep	UFI SOP 101/202 SM 20 2540D, L-1E	100 mL	1 L Plastic	Cool to 6°C	7 days	21 days

[1] From date of sample collection.

WORKSHEET #20A: FIELD QUALITY CONTROL SAMPLE TABLE – GEDDES BROOK, NINEMILE CREEK, AND LCP OU-1

Matrix	Analyte/Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	Total Number of Samples[2]	No. of Field Duplicates	No. of MS and MSDs[3]	No. of Field Blanks	No. of Equip. Blanks	No. of CRM Samples[6]	Total No. of Samples to Laboratories[4]
Surface Water	Total mercury (Hg)	Low	USEPA, Method 1631	25 (1 location/2 events, 2 locations/ 1 event)	4	4	4	4	0	41
	Dissolved Hg	Low	USEPA, Method 1631	25 (1 location/2 events, 2 locations/ 1 event)	4	4	4	4	0	41
	Methylmercury (MeHg)	Low	USEPA, Method 1630	25 (1 location/2 events, 2 locations/ 1 event)	4	4	4	4	0	41
Groundwater	Total Hg	Low	USEPA Method 7470	15 X 4 quarters = 60	4	8	4	4	0	80
Soil/Sediment	Total Hg	Moderate	USEPA 7471A	Variable	Variable[5]	Variable[5]	0	Variable[5]	0	Variable
	MeHg	Low	1630	Variable	Variable[5]	Variable[5]	0	Variable[5]	0	Variable
Fish Tissue	Mercury	Moderate	7471A	80 total (3 locations, 1 event per location); consisting of 50 from NMC (30 sport, 20 prey), 15 from both GB and LCP OU-1	0	10	0	0	5	90
	PCB aroclors	Low	USEPA 8082	20 (1 location/ 1 event)	0	2	0	0	1	22
	Dioxins/Furans	Low	USEPA 8290	20 (1 location/ 1 event)	0	2	0	0	1	22
	Lipid content	Low	Lab SOP	20 (1 location/ 1 event)	0	2	0	0	1	22
	Percent moisture	Low	Lab SOP	50 (NMC fish samples only)	0	3	0	0	3	53

Matrix	Analyte/Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	Total Number of Samples[2]	No. of Field Duplicates	No. of MS and MSDs[3]	No. of Field Blanks	No. of Equip. Blanks	No. of CRM Samples[6]	Total No. of Samples to Laboratories[4]
Macroinvertebrates	Total Hg	Moderate	7471A	12 (2 locations/ 1 event)	0	4	0	0	0	16
	MeHg	Low	1630	12 (2 locations/ 1 event)	0	4	0	0	0	16
Small mammals	Total Hg	Moderate	7471A	20 (3 locations/ 1 event per location)	0	6	0	0	0	26
	MeHg	Low	1630	5 (1 location/1 event per location)	0	1	0	0	0	6
Earthworms	Total Hg	Moderate	7471A	16 (3 locations/ 1 event per location)	0	6	0	0	0	22
	MeHg	Low	1630	16 (2 locations/ 1 event per location)	0	6	0	0	0	22

[1] See analytical SOP References Table (worksheet #23)

[2] Text in parenthesis indicates number of sampling locations and number of events per location where QC samples will be collected.

[3] MS – matrix spike and MSD – matrix spike duplicate.

[4] Note that the numbers in these columns represent number of combined samples sent from GB/NMC and LCP OU-1.

[5] Field duplicates, MS/MSDs, and equipment blanks will be collected at a frequency of 1 in every 20 samples for soil/sediment samples at Geddes Brook, Ninemile Creek, and LCP OU-1.

[6] For CRM samples to be analyzed using NIST 1947 as the reference material, a reduced frequency may be analyzed in consultation with NYSDEC due to material shortages.

WORKSHEET #20B: FIELD QUALITY CONTROL SAMPLE TABLE – ONONDAGA LAKE

Matrix	Analyte/Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	Total Number of Samples[2]	No. of Field Duplicates	No. of MS and MSDs[3]	No. of Field Blanks[4]	No. of Equip. Blanks	No. of CRM Samples[8]	Total No. of Samples to Laboratories
Surface Water	Total Mercury, unfiltered	Low	USEPA, Method 1631	83 for Nitrate addition, 24 for compliance monitoring	22 for nitrate addition, 2 for compliance monitoring	2 MS, 2 MSD for compliance monitoring	22 for nitrate addition, 2 for compliance monitoring	11 for nitrate addition, 2 for compliance monitoring	0	138 for nitrate addition, 32 for compliance monitoring
	Total mercury, filtered (dissolved)[5]	Low	USEPA, Method 1631	15 for nitrate addition, 24 for compliance sampling	2 for nitrate addition[7], 2 for compliance monitoring	2 MS, 2 MSD for compliance monitoring	2 for nitrate addition, 2 for compliance monitoring	2 for nitrate addition, 2 for compliance monitoring	0	21 for nitrate addition, 32 for compliance monitoring
	Methylmercury	Low	USEPA, Method 1630	83 for nitrate addition, 24 for compliance sampling	22 for nitrate addition, 2 for compliance monitoring	2 MS, 2 MSD for compliance monitoring	22 for nitrate addition, 2 for compliance monitoring	11 for nitrate addition	0	138 for nitrate addition, 32 for compliance monitoring
	Nitrate/ Nitrite as N (NO_x)	Low	SM 22nd ed. 4500-NO_3-F	83	22		22	0	0	127
	Nitrite as N (NO_2)	Low	SM 22nd ed. 4500-NO_3-F	83	22		22	0	0	127
	Ammonia as N (T-NH_3)	Low	SM 22nd ed. 4500-NH_3-H	83	22		22	0	0	127
	Soluble reactive phosphorus (SRP)	Low	SM 18-20 4500-P E	30	10		10	0	0	50
Zooplankton	Total mercury	Low	USEPA Method 1631	18	0	4	0	0	0	22
	Methylmercury	Low	USEPA Method 1630	18	0	4	0	0	0	22

Matrix	Analyte/Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	Total Number of Samples[2]	No. of Field Duplicates	No. of MS and MSDs[3]	No. of Field Blanks[4]	No. of Equip. Blanks	No. of CRM Samples[8]	Total No. of Samples to Laboratories
Fish Tissue[6]	Total mercury	Low	SW 7471	148	0	16	0	0	8	172
	Pesticides; DDT and metabolites or hexachlorobenzene	Low	SW 8081B	148	0	16	0	0	8	172
	PCDD/PCDFs	Low	SW 8290	48	0	6	0	0	3	57
	PCBs (aroclors)	Low	SW 8082	148	0	16	0	0	8	172
	Percent lipids	Low	Lab SOP	148	0	16	0	0	8	172
	Percent moisture	Low	Lab SOP	148	0	16	0	0	8	172
Sediment (slurry)	Total mercury	Low	EPA 1631	18	0	4	0	0	0	22
Sediment	Total mercury	Low	SW 7471	44	3	6	3	0	0	56

[1] See analytical SOP References Table (worksheet #23).
[2] Where surface water samples will be collected at different depths at one location, each discrete sampling depth will be counted as a separate sample.
[3] Matrix spike and matrix spike duplicate samples will be prepared by the laboratory at a frequency of at least one per 20 samples, unless otherwise noted.
[4] A field blank for total mercury and methylmercury will consist of mercury-free water (i.e., water containing mercury at concentrations below the minimum detection limit) placed in a clean sample bottle in the laboratory, transported to the fields, poured into a second, clean sample bottle, and returned to the laboratory.
[5] Surface water samples for dissolved mercury will be filtered by the lab prior to analysis.
[6] For adult sport fish: 8 locations, 4 species, 25 fish per species for a total of 100 fillet samples. For prey fish, 8 locations, 3 composites of small prey fish and three large prey fish per location, for a total of 48 samples.
[7] Although the OM Plan only calls for two duplicates for dissolved mercury to be collected, an additional 6 duplicate samples to be collected for dissolved Hg analysis to assess field methods.
[8] For CRM samples to be analyzed using NIST 1947 as the reference material, a reduced frequency may be analyzed in consultation with NYSDEC due to material shortages.

WORKSHEET #21A: PROJECT SAMPLING SOP REFERENCE TABLES – GEDDES BROOK, NINEMILE CREEK, AND LCP OU-1

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	Equipment Type	Modified for Project? Y/N	Comments
S-1	Decontamination Procedures	Parsons	Bristle brushes, wash/rinse tubs, low phosphate detergent, nitric acid rinse, distilled or de-ionized water, HPLC quality grade acetone, containers for collection and storage	N	Includes information for both small and large sampling equipment decontamination
S-6	Wetland Monitoring	Parsons	Waders, measuring tape, 6-foot stakes, pin flags, throw rake	N	Describes quantitative and qualitative vegetation monitoring for Geddes Brook, Ninemile Creek, and LCP OU-1
S-14	Surface Water Sampling	Parsons	Sample containers, gloves, water quality meter	N	Includes information on decon procedures and sample handling, including clean hands technique for low-level mercury analyses.
S-13	Sediment Sample Collection	Parsons	Grab sampler, sample containers, gloves,	Y for sediment processing	Includes information on sample handling
S-17	Fish Collection and Processing	Parsons	Seine, gill net, trap net, backpack electroshocking unit, balance for weighing fish, measuring board, aluminum foil, re-sealable plastic bags, cooler(s), and knives	N	Includes information on sample handling
L-3I	Fish filleting procedure for adult fish	SGS North America - Wilmington	Lab specific SOP, includes NYSDEC SOP updated in 2014	Y	Includes information on state approved fish processing procedures
S-16	Benthic macroinvertebrate sampling	Parsons	Grab sampler, nalgene sieve, dip net, balance for weighing samples, aluminum foil, re-sealable plastic bags, and cooler(s).	N	Includes information on sample handling
S-18	Small mammal sampling	Parsons	Traps, balance for weighing samples, aluminum foil, re-sealable plastic bags, and cooler(s).	N	Includes information on sample handling

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	Equipment Type	Modified for Project? Y/N	Comments
S-19	Transect Survey	Parsons	Boat, oars, trolling motor, rope, GPS unit	N	Includes information for survey the Ninemile Channel and Geddes Brook Channel ad wetland connections
S-15	Earthworm sampling	Parsons	Shovel, balance for weighing samples, aluminum foil, re-sealable plastic bags, and cooler(s).	N	Includes information on sample handling
S-21	Groundwater sampling	Jacobs	Water level meter, water quality meter, water level indicator, pump, polyethylene tubing, plastic sheeting, field book, coolers, ice, shipping supplies.	N	None

WORKSHEET #21B: PROJECT SAMPLING SOP REFERENCE TABLES – ONONDAGA LAKE

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	Equipment Type	Modified for Project? Y/N	Comments
S-1	Decontamination Procedures	Parsons	Bristle brushes, wash/rinse tubs, low phosphate detergent, nitric acid rinse, distilled or de-ionized water, HPLC quality grade acetone, containers for collection and storage	N	Includes information for both small and large sampling equipment decontamination
S-2	Fish Collection, Processing, and Community Assessments	Parsons/SUNY ESF	Seine, gill net, trap net, electroshocking boat, balance for weighing fish, measuring board, aluminum foil, re-sealable plastic bags, knives	N	Includes information on sample processing/handling
S-3	OL MNR Sediment Core Collection and Processing	Parsons	Core sampler, sample containers, boat	Y for sediment processing	Includes information on decon procedures and sample handling
S-4	OL Benthic Macroinvertebrate Collection	Parsons	Ponar, sieve bucket, forceps, sample containers	N	Include information on sample handling and processing
S-5	OL Macrophyte Survey	Parsons	Macrophyte rake, GPS system, Secchi disk	N	Includes descriptions for both quantitative and qualitative macrophyte surveys
S-6	Wetland Monitoring	Parsons	Waders, measuring tape, 6-foot stakes, pin flags, throw rake	N	Includes descriptions for both quantitative and qualitative vegetation monitoring for Onondaga Lake

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	Equipment Type	Modified for Project? Y/N	Comments
S-7	Water Sample Collection with a submersible pump (compliance sampling) or a Kemmerer (nitrate addition) (UFI SOP 303/304); Reduced species (H_2S, CH_4) sample collection (UFI SOP 306); Mercury Sampling (UFI SOP 336), Collection of Equipment Blanks for Mercury (UFI SOP 401); Cleaning sampler (UFI SOP 413)	UFI	Sample containers, boat, marine battery, gloves, water quality meter, submersible pump with conduit, Kemmerer or Van Dorn, reduced species collection bottles, reagent cooler with bottles of zinc acetate solution and 6 N NaOH solution.	N	Includes information on sampling handling, including clean hands technique for low level mercury analysis, procedures for sampling and preservation of reduced species samples, as well as descriptions/ procedures for sampling with a submersible pump
S-8	Zooplankton Collection and Processing	UFI	A sampling net (diameter of 30 cm, length with cup 1 m, mesh size of 64 microns) slowly lowered to given depth.	N	Includes descriptions and procedures for sampling with a mesh net
S-9	ISUS Equipment Calibration and Operation (UFI SOP 330)	UFI	ISUS – *in situ* ultraviolet spectrophotometer uses ultraviolet absorption spectroscopy to measure *in situ* dissolved chemical species. The sensor is a chemical-free, solid-state instrument with accurate, real-time, continuous nitrate and bisulfide concentration measurements. Additional parameters are also integrated into the instrument package. SUNA-submersible ultraviolet nitrogen analyzer that is functionally equivalent to ISUS.	N	Includes description and procedures for sampling with integrated instrument package.
S-10	YSI Sonde & Buoy Calibration and Maintenance (UFI SOPs 315, 331)	UFI	YSI multiprobe sonde, DI water, reagents, and standards	N	Includes information for calibrating YSI sondes before installation on monitoring platform and routine maintenance activities at monitoring buoy
S-11	Sediment Trap Deployment and Collection (UFI SOP 312)	UFI	Sediment trap assemblage, deployment rope, cleaning brush, funnel	N	Includes information for deployment and retrieval of sediment trap assemblages

SOP # or reference	Title, Revision, Date, and URL (if available)	Originating Organization	Equipment Type	Modified for Project? Y/N	Comments
S-12	Wastebeds 1-8 Turbidity Monitoring (UFI SOPs 315, 318, 319)	UFI	YSI multiprobe sonde, DI water, reagents, and standards,	N	Includes information for calibrating YSI sondes, in situ deployment of YSI sondes, and YSI Sonde profiling using the YSI 650 datalogger
S-20	Tributary Surface Water and Rainwater Sampling	Parsons	Teflon dipper, amber glass bottles with fluorocarbon-lined caps, stainless steel funnels, HPLC grade acetone, DI water	N	Includes information for collecting surface water samples from Onondaga Lake, tributaries, and rainwater
L-3I	Prep Lab Standard Operating Procedure; fish filleting procedure	SGS North America – Wilmington	Lab specific SOP, includes NYSDEC SOP updated in 2014	Y	Includes information on state approved fish processing procedures

WORKSHEET #22A: FIELD EQUIPMENT CALIBRATION, MAINTENANCE, TESTING, AND INSPECTION – GEDDES BROOK, NINEMILE CREEK, AND LCP OU-1

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Water quality meter (in conjunction with surface water sample collection and groundwater sampling)	Calibrate prior to each day's activity according to manufactures recommendations	Rinse all sensors with DI water, gently wipe all sensors using optical lens paper	Deionized water checks	Charging batteries, check for damage, surface dirt or debris	Daily	Refer to applicable instrument manual	Repair as soon as possible (in field or at lab)	Parsons Field team leader	S-14, S-21
Submersible pump and tubing for groundwater sampling	Check flow rate at beginning of field season	Rinse with tap water, flush with 10% HCl solution and then DI water. Drain and store in sealed container.	NA	Check for physical damage and/or leaks	Before each sampling event	Visual inspection	Repair as soon as possible (in field if possible or in laboratory)	Field team leader (Jacobs)	S-21
Electronic water level meter for groundwater sampling	Calibrate prior to each day's activity according to manufacturer's recommendations	Leave unit turned off when not in use.	Verify unit is operating correctly by testing probe in distilled or deionized water	Charging batteries	Before each use	Refer to applicable instrument manual	Repair as soon as possible (in field if possible or in laboratory)	Field team leader (Jacobs)	S-21
GPS for wetland delineations	Verify accuracy by checking against established control points around respective sites	Perform software updates as needed	Refer to calibration	Charging batteries, inspect GPS unit for damages prior to use	Before each use	Refer to applicable instrument manual	Repair as soon as possible (in field if possible or at certified manufacture dealer)	Parsons Field team leader	S-6

WORKSHEET #22B: FIELD EQUIPMENT CALIBRATION, MAINTENANCE, TESTING, AND INSPECTION – ONONDAGA LAKE

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
GPS for wetland delineations	Verify accuracy by checking against established control points around respective sites	Perform software updates as needed	Refer to calibration	Charging batteries, inspect GPS unit for damages prior to use	Before each use	Refer to applicable instrument manual	Repair as soon as possible (in field if possible or at certified manufacture dealer)	Parsons Field team leader	S-6
Submersible pump and tubing for surface water sampling	Check flow rate at beginning of field season	Rinse with tap water, flush with 10% HCl solution and then DI water. Drain and store in sealed container.	NA	Check for physical damage and/or leaks	Weekly	Visual inspection	Repair as soon as possible (in field if possible or back at lab)	Field Team Leader	S-7
ISUS/SUNA profiler	Calibrated at factory, perform routine DI water check before and after each use, DI water check done weekly at UFI lab	Rinse all sensors with DI water, gently wipe all sensors dry using optical lens paper	Deionized water checks	Check for physical damage, verify data looks correct and instrument is performing as per manufacturers' instructions	DI water check with each use	Compare with laboratory ground-truth data, verify DI water checks are within ±2 μM	Repair as soon as possible (in field if possible or back at the lab)	UFI field team leader	S-9
Turbidity sondes	Calibrate turbidity and specific conductance according to manufacturer's recommendations	Sonde, including all probes, is cleaned and equipped with fresh batteries	Turbidity and specific conductance readings are checked with standard references	Sonde is inspected for physical damage	Bi-weekly upon recovery. Weekly for WB 1-8 Turbidity Monitoring (when conducted)	Sondes are equipped with internal acceptance criteria	Recalibrate or replace faulty probe	UFI field team leader	S-10

WORKSHEET #23: ANALYTICAL STANDARD OPERATING PROCEDURES

The applicable SOPs to be used for analysis of samples collected during monitoring are listed below in the table. Detailed standard operating procedures are provided in Appendix A.

SOP #	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix/Analytical Group	Instrument	Organization Performing Analysis	Modified for Project? Y/N
L-1A	Determination of Nitrogen, Nitrate + Nitrite, Nitrite (as N; NO_x, NO2) by Standard Methods 4500-NO3 F-2011	Definitive	NO_X and NO_2	FIA-Lachat Quikchem 8500	Upstate Freshwater Institute	N
L-1B	Determination of Nitrogen, Total Ammonia (as N; TNH3) by Standard Methods 4500-NH3 H-2011	Definitive	T-NH_3	FIA-Lachat Quikchem 8500	Upstate Freshwater Institute	N
L-1C	Determination of Phosphorus, Orthophosphate (Soluble Reactive Phosphorus as P; SRP) by Standard Methods 4500-P G-2011	Definitive	Phosphorus	FIA-Lachat Quikchem 8500	Upstate Freshwater Institute	N
L-1E	Determination of Solids, Total Suspended (AH filters; TSS_AH) by Standard Methods 2540 D-2011	Definitive	Total/Volatile, Suspended Solids	Filtration, drying Oven, Furnace, Analytical balance	Upstate Freshwater Institute	N
L-1F	Determination of Turbidity (Tn_L) by Standard Methods 2130 B-2011 Note: This SOP was used for monitoring conducted in 2017 only.	Definitive	Turbidity	HACH 2100AN Turbidimeter	Upstate Freshwater Institute	N
L-1G	Determination of Solids, Fixed Suspended, Volatile Suspended (AH filters; FSS_AH, VSS_AH) by Standard Methods 2540 E-2011	Definitive	Suspended Solids	Drying Oven, Furnace, Analytical balance	Upstate Freshwater Institute	N
L-2A	Mercury in Aqueous, Solid and Tissue Samples by Cold Vapor AA and Preparation of Solids by EPA 7471A or B for Mercury Analysis	Definitive	Total mercury (sediment, benthic macroinvertebrates, small mammals and earthworms)	Mercury Auto-Analyzer; Leeman Labs PS 200 and Leeman Labs Hydra AA with autosampler or equivalent	Eurofins-Lancaster Laboratories	N

SOP #	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix/Analytical Group	Instrument	Organization Performing Analysis	Modified for Project? Y/N
L-2B	Determination of Methyl Mercury in Various Matrices by CV-GC-AFS	Definitive	Methylmercury (surface water, sediment, benthic macroinvertebrates, small mammals and earthworms)	CVAFS	Eurofins-Frontier	N
L-2C	Determination of Total Mercury in Various Matrices by FI-AFS	Definitive	Total mercury	Atomic Fluorescence Spectrophotometer	Eurofins-Frontier	N
L-2D	Preparation of Solids for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion	Definitive	Total mercury	NA	Eurofins-Frontier	N
L-2E	KOH/Methanol Digestion of Tissues for Methyl Mercury Analysis	Definitive	Methyl mercury	NA	Eurofins-Frontier	N
L-2F	Mercury in Water by Oxidation, Purge & Trap and CV-AFS	Definitive	Total mercury	CVAFS	Eurofins-Frontier	N
L-2G	Digestion of Tissues for Total Mercury Analysis using Nitric Acid and Sulfuric Acids	Definitive	Total mercury	NA	Eurofins-Frontier	N
L-2H	Distillation of Aqueous Samples for Methyl Mercury Analysis	Definitive	Methyl mercury	NA	Eurofins-Frontier	N
L-3A	Determination of Lipids in Fish Tissue	Definitive	% Lipids (fish tissue)	Sonicator	SGS Wilmington	N
L-3B	%Moisture Calculation and %Solids Calculation (Gravimetric) by SM 2540 G 1997 and SM G-2011	Definitive	% Moisture (fish tissue)	Drying oven	SGS Wilmington	N

SOP #	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix/Analytical Group	Instrument	Organization Performing Analysis	Modified for Project? Y/N
L-3C	Determination of Polychlorinated Biphenyls (PCBs) by Gas Chromatography and Sulfuric Acid/Permanganate Cleanup	Definitive	PCB Aroclors (fish tissue)	Gas Chromatograph	SGS Dayton	N
L-3D	Determination of Organochlorine Pesticides Using GC System by SW846 8081B and Florisil Column Cleanup	Definitive	Pesticides (fish tissue)	Gas Chromatograph	SGS Dayton	N
L-3E	Cold Water Vapor Analysis of Mercury for Soil Samples by SW846 7471B	Definitive	Total mercury (fish tissue)	Mercury Auto-Analyzer; Leeman Labs PS 200 and Leeman Labs Hydra AA with autosampler or equivalent	SGS Dayton	N
L-3F	Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans (PCDD/Fs)	Definitive	PCDD/Fs (fish tissue)	High Resolution Gas Chromatograph / High Resolution Mass Spectrophotometer	SGS Wilmington	N
L-3G	Cold Vapor Analysis of Mercury for Water Samples	Definitive	Total mercury (water)	Leeman Hydra II	SGS-Accutest	N
L-3H	Standard Operating Procedure for Extraction of Various Matrices and Fractionation (Cleanup Procedure)	Definitive	Cleanup for organic extracts (fish tissue)	NA	SGS Dayton and Wilmington	N
L-3I	Homogenization of Biota/Tissue	Definitive	All analytes (fish tissue)	NA	SGS Wilmington	N
ALL	Determination of Limits of Detection, Limits of Quantification, and Reporting Limits	Definitive	All analytes	NA	Eurofins-Lancaster Laboratories, SGS North America Inc.	N

SOP #	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix/Analytical Group	Instrument	Organization Performing Analysis	Modified for Project? Y/N
S-9	UFI SOP UFI-ISUS/Optical Frame	Definitive	Nitrate	Satlantic Inc., ISUS0095	UFI	N
		Definitive	Bisulfide	Satlantic Inc., ISUS0095	UFI	N
		Definitive	Temperature	SeaBird Elec, Inc., SBE 37-SI MicroCAT	UFI	N
		Definitive	Specific conductance	SeaBird Elec, Inc., SBE 37-SI MicroCAT	UFI	N
		Definitive	Transmissivity	WET Labs, C-Star	UFI	N
		Definitive	Turbidity	WET Labs, Eco Triplet-BB2 FL	UFI	N
		Definitive	Chlorophyll	WET Labs, Eco Triplet-BB2 FL	UFI	N
		Definitive	Light penetration	Biospherical Instruments, QSP-2150	UFI	N

WORKSHEET #24: ANALYTICAL INSTRUMENT CALIBRATION

The Analytical Instrument Calibration Table and the specific analytical method SOP references are provided in in Appendix A of this QAPP.

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
CVAFS, USEPA, Method 1631 USEPA, Method 1630	Refer to SOP	Initial Calibration - Daily prior to sample analysis	5 standards with the RSD ≤15%, or R2 ≥ 0.995 for Method 1631 5 standards with the RSD ≤20%, or R2 ≥ 0.990 for Method 1630	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes	Laboratory Staff	L-2B, L-2F
		Initial Calibration Verification - Immediately after initial calibration	79-121% of expected value for Method 1631 69-131 of expected value for Method 1630-	1. Reanalyze 2. If criteria are still not met, repeat initial calibration		
		Continuing Calibration Verification - After every ten samples and at the end of the run	67-123% of expected value for Method 1630 77-123% of expected value for Method 1631	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCV must be reanalyzed		

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
High Resolution Gas Chromatograph / High Resolution Mass Spectrophotometer	Refer to SOP	Instrument Tune: Tune with DFS before initial calibration	Mass resolution >10,000 (10% valley); mass deviation less than 5 ppm	Retune and recalibrate	Laboratory Staff	L-3F
		Initial Calibration with a minimum of 6 standards: After ICV or CCV fails.	1. S/N ratio ≥10 2. Ion abundance ratios within theoretical ion abundance ratios specified in the EPA method. 3. %RSD for the response factors is <20% for the native compounds. 4. Native compounds that have an isotopically labeled analog are quantitated using the analog as the retention time and quantitation reference. 5. Native congeners that do not have an isotopically labeled analog use the closest eluting labeled congener, with the same LOC, as the retention time reference.	Recalibrate, perform instrument maintenance. If calibration does not meet method criteria, recalibrate.		
		ICV: Once with every ICAL	Target compounds ≤20% drift	Reanalyze the ICV. If ICV fails again do system maintenance and recalibrate.		

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
High Resolution Gas Chromatograph / High Resolution Mass Spectrophotometer	Refer to SOP	CCV: At the beginning of each 12-hour period and at the end of each analytical sequence	Target compounds ≤20% drift	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 CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	Laboratory Staff	L-3F
		Performance Verification (PF): Prior to ICAL and at the beginning of every 12 hours	Peak separation resolved with valley of ≤ 25% TCDD and <40% TCDF Identification of all first and last eluters of the eight homologue retention time windows and documentation by labeling (F/L) on the chromatogram	Reanalyze the PV. If PV fails again do system maintenance or recalibrate.		

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
CVAA	Refer to SOP	Calibration with minimum 5 standards - Daily	Linearity>0.995	Prepare fresh standards, re-analyze, re-calibrate	Laboratory Staff	L-2A, L-3E, L-3G
		ICV - Daily	Within 10% of true value	Re-prepare, re-analyze, re-calibrate		
		CCV - After initial calibration. After every 10 samples and at the end of the run				
Gravimetric determination (% lipids)	Refer to SOP	Daily balance calibration	1g (0.995-1.005) 10g (9.980-10.020) 20g (19.980-20.020)	1. Inspect system 2. Correct problem 3. Rerun calibration	Laboratory Staff	L-3A, L-3B

Instrument	Calibration Procedure	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/position responsible for Corrective Action	SOP Reference
GC/ECD	Refer to SOP	Initial calibration after instrument set up, after major instrument changes, and when continuing calibration criteria are not met.	Initial Calibration % RSD ≤20%. CCV ≤20% drift.	1. Inspect system 2. Correct problem Rerun calibration and affected samples	Laboratory Staff	L-3C, L-3D
FIA – Lachat Quikchem 8500	Refer to SOP	Each new run	ICAL: Correlation coefficient (r) >0.995; ±30% CCV: ±10% of true value	ICAL: Recalibrate, perform instrument maintenance if calibration cannot conform to criteria, recalibrate CCV: Reanalyze	Laboratory Staff	L-1A, L-1B, L-1C
HACH 2100AN Turbidimeter	Refer to SOP	Daily prior to sample analysis	Acceptable calibration and CCV	ICAL: Recalibrate, perform instrument maintenance if calibration cannot conform to criteria, recalibrate CCV: Reanalyze	Laboratory Staff	L-1F
Atomic Fluorescence Spectrometer	Refer to SOP	ICAL: Daily prior to sample analysis ICV: Immediately after ICAL CCV: After every 10 samples and at the end of the run	5 standards with the RSD ≤15%, or R2 ≥ 0.995; ICV 79-121%R; CCV 77-123%R	ICAL: Recalibrate, perform instrument maintenance if calibration cannot conform to criteria, recalibrate CCV: Reanalyze	Laboratory Staff	L-2C
Balance	Refer to SOP	Daily balance calibration	1g (0.995-1.005) 10g (9.980-10.020) 20g (19.980-20.020)	1. Inspect system 2. Correct problem 3. Rerun calibration	Laboratory Staff	L-1E, L-1G

WORKSHEET #25: ANALYTICAL INSTRUMENT AND EQUIPMENT MAINTENANCE, TESTING, AND INSPECTION

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

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
CVAFS	Check ethylation agent and analytical system	Analyze primer and blank	Visually check shape of peak and response	At start of an analysis run	Calibration curve should have a <15%, or R2 > 0.995	Re-calibrate, compare against 2nd source, and OPR	Analyst	L-2B, L-2F
CVAFS	Routine inspections, check intensity of Hg lamp, inspect liquid/gas separator and Nafion Dryer	Change liquid/gas separator and Nafion Dryer	Check argon flow, pump tubing, drain, and soda lime drying tube	Daily except check intensity of Hg lamp semiannually and inspect/change liquid/gas separator and Nafion Dryer as needed	-	Change Hg lamp and/or liquid/gas separator and Nafion Dryer	Analyst	L-2B, L-2F
Leeman Labs Hydra AF gold plus, CVAFS	Routine inspections, check intensity of Hg lamp, inspect liquid/gas separator and Nafion Dryer	Change liquid/gas separator and Nafion Dryer	Check argon flow, pump tubing, drain, and soda lime drying tube	Daily except check intensity of Hg lamp semiannually and inspect/change liquid/gas separator and Nafion Dryer as needed	-	Change Hg lamp and/or liquid/gas separator and Nafion Dryer	Analyst	L-2A, L-3G, L-3E
Gravimetric Determination-Balance	Quarterly check and annual calibration	As specified in Worksheet #24	Check that balance is level, clean, and free of draft and vibration	As specified in SOP	As specified in Worksheet #24	As specified in Worksheet #24	Analyst	L-3A, L-3B

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
GC/ECD	Perform column maintenance, replace injection port liner, clean/bake-out detector	As specified in Worksheet #24	Visual inspection of components	As specified in SOP	As specified in Worksheet #24	As specified in Worksheet #24	Analyst	L-3C, L-3D
HRGC/HRMS	Injection port, column, ion source, others as needed	As specified in Worksheet #24	Visual inspection of components	As specified in SOP	As specified in Worksheet #24	As specified in Worksheet #24	Analyst	L-3F

[1] See the Analytical SOP References table (Worksheet #23)

WORKSHEET #26 & 27: SAMPLE HANDLING, CUSTODY, AND DISPOSAL

Samples should be named in accordance with the SOPs D-1 and H-1 (Appendix A).

Sampling Collection, Packaging, and Shipment

Sample Collection (Personnel/Organization):

- Jacobs for groundwater at LCP.
- Parsons for surface water and sediment and biota at Geddes Brook, Ninemile Creek, SYW-10 and LCP, and sediment and invertebrates in Onondaga Lake. Tributary surface water for Onondaga Lake.
- UFI for in lake surface water, zooplankton, and sediment traps in Onondaga.
- SUNY ESF and Parsons for fish tissues.

Sample Packaging (Personnel/Organization): Same as for sample collection.

Coordination of Shipment (Personnel/Organization): Same as for sample collection.

Type of Shipment/Carrier: Samples for analyses to be shipped on ice by overnight shipment to commercial laboratory or picked up by a courier provided by the laboratory.

Sampling Receipt and Analysis

Sample Receipt (Personnel/Organization): Sample receiving department at laboratories.

Sample Custody and Storage (Personnel/Organization): Laboratory representative.

Sample Preparation (Personnel/Organization): Laboratory representative. For adult sport fish, fillets will be prepared by SGS Wilmington in accordance with NYSDEC's SOP PrepLab4 (May 28, 2014) and in accordance with the SGS Wilmington processing SOP (L-3I).

Sample Determinative Analysis (Personnel/Organization): Laboratory representative.

Sampling Archiving

Field Sample Storage (Number of days from sample collection): See Worksheet #19.

Sample Extract/Digestate Storage (Number of days from extraction/digestion): See Worksheet #19.

Biological Sample Storage (Number of days from sample collection): See Worksheet #19.

Sampling Disposal

Personnel/Organization: Laboratory project manager

Number of Days from Analysis: 60 days (surface water and zooplankton); 6 months (fish tissue, sediment and soil). The lab must contact Parsons (OL/GB/NMC) or Jacobs (LCP) prior to disposing any samples.

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory)

Standard procedures for sample collection and shipping will be followed such that samples are preserved and stored as required (Worksheet #19). All field measurements and sample collection activities will follow approved standard operating procedures. The general procedure is as follows:

- Tissue, sediment, groundwater, and surface water samples will be collected according to the sampling SOPs.
- Appropriate field notes will be taken throughout the sampling process and sample locations, depths, and types will be checked/verified against the field sampling matrix in the project work plan.
- Samples will be kept on ice while in the field.
- Any sample-handling difficulties that are encountered in the field will be described in the field database.
- Samples will be sent on the day that sample collection is completed or the next shipment day at the latest via overnight courier (if possible) to the appropriate laboratory with a fully documented chain-of-custody form. If sampling duration is longer than a day, samples will be frozen and shipped when sampling is complete. Field teams will carefully coordinate sampling activities with the laboratory to assure field holding time requirements are met. When shipping samples, the field personnel will confirm with the laboratory that personnel will be available for receiving.
- Field personnel are responsible for making sure all documentation has been completed and turned over to the laboratory and/or other support personnel.
- Field logs will be reviewed and sample integrity verified as part of the data validation procedures.

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal)

On receipt, laboratory personnel will check samples, and the cooler temperature will be determined. The temperature and condition of the samples will be recorded at the laboratory, and any problems will be described in the narrative for the data report. The field log and narrative will be reviewed during the quality assurance review, and data will be flagged if the sample integrity was compromised. Data may be rejected as unusable if severe handling problems are encountered.

Sample Identification Procedures

On receipt, laboratory personnel will check samples, and the cooler temperature will be determined. The temperature and condition of the samples will be recorded at the laboratory, and any problems will be described in the narrative for the data report. The field log and narrative will be reviewed during the quality assurance review, and data will be flagged if the sample integrity was compromised. Data may be rejected as unusable if severe handling problems are encountered.

Chain-of-Custody Procedures

A continuous record of the possession and proper handling of samples will be documented, so that sample custody and handling are traceable from the time of sample collection until the analytical data have been validated and accepted for use.

WORKSHEET #28: ANALYTICAL QUALITY CONTROL AND CORRECTIVE ACTION

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

Matrix: Fish Tissue
Analytical Group: Total Mercury
Concentration Level: Moderate
Analytical Method/SOP: USEPA, Method 7471/L-3E, S-2, S-15, S-16, S-17
Sampler's Name: Staff
Field Sampling Organization: Parsons
Analytical Organization: SGS Dayton
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/ Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	1 in 20 samples	<RL	• Reanalyze for verification • If criteria are still not met, prepare and reanalyze batch.	Commercial laboratory analyst	Contamination	<RL
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	90-110% for ICV; 80-120% for CCV	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Commercial laboratory analyst	Accuracy	90-110% for ICV; 80-120% for CCV

QC Sample	Frequency/ Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)[1]	1 with every batch of samples	80-120%	• Reanalyze • If criteria are still not met, re-prep LCS and all associated samples. • If recovery is high and the analyte is not detected, document excursion only	Commercial laboratory analyst	Accuracy	80-120%
Certified Reference Material (DORM 5) [2]	1 in 20 samples	80-120%	• Reanalyze	Commercial laboratory analyst	Accuracy	80-120%
Matrix spike and matrix spike duplicate samples (MS/MSD) and laboratory duplicate (fish only)	1 in every batch of 20 samples	80-120% RPD ≤20%	• If recovery and/or RPD is not within QC limits, evaluate LCS. If LCS is within limits, flag data.	Commercial laboratory analyst	Accuracy/Precision	80-120%

[1] Certified reference material (DORM-5 or comparable) will be used as LCS/QC material for fish tissue analysis.

[2] Further details on the use of CRM can be found in Attachment 1 of this QAPP.

Matrix: Sediment, and other (non-fish) biota
Analytical Group: Total Mercury
Concentration Level: Moderate
Analytical Method/SOP: USEPA, Method 7471/L-2A, S-3, S-11, S-13, S-15, S-16, S-18
Sampler's Name: Staff
Field Sampling Organization: Parsons
Analytical Organization: Eurofins-Lancaster
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	1 in 20 samples	<1/2 RL	• Reanalyze for verification • If criteria are still not met, prepare and reanalyze batch.	Commercial laboratory group leader	Contamination	<1/2 RL
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	80-120% for ICV; 80-120% for CCV	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Commercial laboratory group leader	Accuracy	80-120% for ICV; 80-120% for CCV
Laboratory control samples (LCS)	1 with every batch of 20 samples	80-120%	• Reanalyze • If criteria are still not met, re-prep LCS and all associated samples. • If recovery is high and the analyte is not detected, document excursion only	Commercial laboratory group leader	Accuracy	80-120%

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 20 samples	80-120% RPD ≤20%	• If recovery and/or RPD is not within QC limits, evaluate LCS. If LCS is within limits, flag data.	Commercial laboratory group leader	Accuracy/Precision	80-120%

Matrix: Groundwater
Analytical Group: Total Mercury
Concentration Level: Moderate
Analytical Method/SOP: USEPA, Method 7471/, L-3G, S-21
Sampler's Name: Staff
Field Sampling Organization: Jacobs and Parsons
Analytical Organization: SGS-Accutest (groundwater)
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	1 per sampling event	RPD 30%	• If <5x MRL or is non-detect, the FD will be used for precision • If FD does not meet precision criteria requirements, sample will be reanalyzed	Commercial laboratory group leader and QA officer/Project Manager	Precision – Field	RPD 30%
Method blank	1 per every batch of samples	<1/2 RL	• Reanalyze for verification • If criteria are still not met, prepare and reanalyze batch.	Commercial laboratory group leader	Contamination	<1/2 RL
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	80-120% for ICV; 90-110% for CCV	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Commercial laboratory group leader	Accuracy	80-120% for ICV; 80-120% for CCV

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 with every batch of samples	80-120%	• Reanalyze • If criteria are still not met, re-prep LCS and all associated samples. • If recovery is high and the analyte is not detected, document excursion only	Commercial laboratory group leader	Accuracy	80-120%
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 20 samples	80-120% (waters) RPD 20%	• If recovery and/or RPD is not within QC limits, evaluate LCS. If LCS is within limits, flag data.	Commercial laboratory group leader	Accuracy	80-120% RPD 20%

Matrix: Surface water, sediment trap slurry
Analytical Group: Total Mercury
Concentration Level: Low
Analytical Method/SOP: SW 1631/L-2C, L-2G, L-2D, L-2F, S-7, S-11, S-14
Sampler's Name: Staff
Field Sampling Organization: Parsons
Analytical Organization: Eurofins-Frontier
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	1 per sampling event	RPD 30%	• If <5x MRL or is non-detect, the FD will be used for precision • If FD does not meet precision criteria requirements, sample will be reanalyzed	Analytical Laboratory (hereafter called "lab") and QA officer/Project Manager	Precision – Field	RPD 30%
Field and Equipment rinsate blank (Sampling equipment)	1 per sampling event (field) 4 per sampling season (equipment rinsate)	< MRL	• Reanalyze for verification • Notify client	Lab and Field	Contamination	< MRL
Laboratory duplicate	One per batch	RPD 24%	• Reanalyze for verification • Notify client	Lab	Precision - Lab	RPD 24%
Initial Calibration Verification (ICV/QCS)	Beginning of every analytical sequence	79-121%	• If initial is out, terminate analysis; correct the problem; recalibrate or reprep with calibration curve.	Lab	Precision - Lab	79-121% of expected value for ICV.

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	One per sample preparation batch of up to 20 samples. Note: additional prep blanks(s) required if additional BrCl needed in some sample(s).	< RL	• Redigest and reanalyze samples • Sample results greater than 20x the blank concentration are acceptable.	Lab	Contamination	<RL
Initial Calibration Blank (ICB)	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL (0.5 ng/L for aqueous, 1.25 ng/L for solid)	• Terminate analysis; correct the problem; recalibrate or reprep with calibration curve.	Lab	Contamination	The result must be within +/- the RL
Initial calibration	Daily prior to sample analysis/as per method .	Five standards with the RSD ≤15% and low standard recovery 75-125%	• Correct the problem and reanalyze standards • Remake and reanalyze standards	Lab	Accuracy/Bias	5 standards with the RSD ≤15%
Continuing calibration verification samples (CCV/OPR)	After every 10 samples and at the end of each run.	77-123% of expected value for CCV samples	• Terminate analysis, correct the problem • Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve.	Lab	Accuracy/Bias	77-123% of expected value for CCV samples

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	One per sample preparation batch of up to 20 samples.	80-120%	• Terminate analysis, correct the problem • If recovery is high and the analyte is not detected, document excursion only • Redigest and reanalyze all samples associated with the LCS.	Lab	Accuracy/Bias	80-120%
Matrix spike and matrix spike duplicate samples (MS/MSD)	2 sets per sample preparation batch of up to 20 samples. If insufficient volume has been provided, a Duplicate Laboratory Control Sample may be prepared and analyzed.	Recovery (71–125%) and RPD (<24%)	• If recovery is not within QC limits, the LCS must be in control. • If the RPD is >24 %, document the excursion.	Lab	Accuracy/Bias	Recovery 71-125%

Matrix: Surface water, sediment and biota except fish
Analytical Group: Methylmercury
Concentration Level: Low
Analytical Method/SOP: 1630/L-2B, L-2H, L-2E, S-4, S-8, S-13, S-14, S-15, S-16, S-18
Sampler's Name: Staff
Field Sampling Organization: Parsons
Analytical Organization: Eurofins-Frontier
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	1 per sampling event	RPD 30%	• If < 5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Eurofins Frontier (hereafter called "lab") and QA officer/Project Manager	Precision – Field	RPD 30%
Field and Equipment rinsate blank (Sampling equipment)	1 per sampling event (field) 4 per sampling season (equipment rinsate)	< MRL	• Reanalyze for verification • Notify client	Lab	Contamination	< MRL
Laboratory duplicate	1 every 10 samples	RPD 35%	• If < 5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Lab	Precision – Lab	RPD 35%
Initial precision and recovery (IPR)	Set of four analyses	IPR within s (31%) and X (69–131%)	• Reanalyze	Lab	Initial method implementation and Precision – Lab	IPR within s (31%) and X (69–131%)

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Ethylation Blank	Immediately after initial calibration	Less than reporting limit	• Reanalyze • If criteria are still not met, repeat initial calibration • Change air bubble tubing	Lab		
Method blank	3 with every batch of samples	Less than reporting limit	• Reanalyze for verification • If criteria are still not met, calculate batch specific MDL using standard deviation of the method blanks • If samples are non-detects using elevated detection limits, then redistill the affected samples and reanalyze at client's request	Lab	Contamination	Less than reporting limit
Instrument blank	Immediately after initial calibration and after every CCV	Less than reporting limit	• Reanalyze until passes • If criteria are still not met, repeat initial calibration • All samples analyzed on affected equipment must be reanalyzed	Lab	Contamination	Less than reporting limit

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial calibration	Calibrate prior to sample analysis/as per method	5 standards with the RSD ≤15%, Low Std. Recovery 65-135%	• Reanalyze standards • Remake and reanalyze standards • Change all peristaltic pump tubes	Lab	Accuracy/Bias	5 standards with the RSD ≤15%, Low Std. Recovery 65–135%
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	69-131% of expected value for ICV; 67-133% of expected value for CCV samples	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Lab	Accuracy/Bias	69-131% of expected value for ICV; 67-133% of expected value for CCV samples
Laboratory control samples (LCS)	1 with every batch of samples	Recovery within appropriate control limits (70-130%) or as specified in QAPP.	• Reanalyze • If criteria are still not met, reprep LCS and all associated sample. • If recovery is high and the analyte is not detected, document excursion only	Lab	Accuracy/Bias	Recovery within appropriate control limits (70–130%)

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 MS/MSD with every batch of 20 samples	Recovery (65-130%) and RPD (35%) or as specified in QAPP	• If Recovery is not within QC limits, and an RPD criterion is met document excursion. • If recovery is within QC limit, and RPD criterion is not met, reanalyze.	Lab	Accuracy/Bias	Recovery 65–135%
Method Detection Limit (MDL) Minimum reportable Limit (MRL)	Daily prior to sample analysis	0.02 ng/L 0.05 ng/L	• Reanalyze • If criteria are still not met, reprep blank and all associated samples • If concentration is high and the analyte is not detected, document excursion	Lab	Accuracy/Bias	0.02 ng/L 0.05 ng/L

Matrix: Fish Tissue
Analytical Group: Lipids
Concentration Level: Low
Analytical Method/SOP: Method 3550C/L-3A, S-2, S-17
Sampler's Name: Staff
Field Sampling Organization: Parsons
Analytical Organization: SGS Wilmington
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 in 20 samples	No analytes detected > project MDL	Clean the instrument and re-analyze samples	Analyst	Accuracy/Laboratory Contamination	No analytes detected > project MDL
LCS[1]	1 in 20 samples	Laboratory statistical limits (see WS 12)	Re-analyze samples	Analyst	Accuracy/Bias	Results within acceptance limits
Laboratory Duplicate	1 in 20 samples	Laboratory statistical limits (See WS 12)	Flag data	Analyst	Precision	Results within acceptance limits
Certified Reference Materials (CARP 2)[2]	1 in 20 samples	70-130% R	Re-analyze	Analyst	Accuracy	Results within acceptance limits

[1] Sodium sulfate used as LCS during laboratory blanks for fish tissue analysis.
[2] Further details on the use of CRM can be found in Attachment 1 of this QAPP.

Matrix: Fish Tissue
Analytical Group: PCBs
Concentration Level: Low
Analytical Method/SOP: 8082A/L-3C, S-2, S-17
Sampler's Name: Staff
Field Sampling Organization: Parsons
Analytical Organization: SGS Dayton
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Surrogate Spike (organics)	Per sample (including MS/MSD, LCS, and blanks)	Laboratory statistical limits	Reanalyze if outside limits; if confirmed, report.	Analyst	Precision	% recovery within acceptance limits
Method blanks	1 in 20 samples	<MDL	Reanalyze to confirm detections. If detects confirm reextract samples that are not ND or <MDL	Analyst	Representativeness	<MDL
MS/MSD	1 in 20 samples	Laboratory specified recovery limits (see WS 12) and RPD ≤ 30	Evaluation in conjunction with LCS results	Analyst	Accuracy/Bias	RPD <30
Laboratory Duplicate[1]	1 in 20 samples	RPD ≤ 30	Evaluation in conjunction with LCS results	Analyst	Precision	RPD<30
LCS[2]	1 in 20 samples	Laboratory specified recovery limits (see WS 12) and RPD ≤ 30 (if LCSD run)	Reanalyze LCS and associated samples. Analytes in the LCS that fail high and as Non-detect in the samples can be reported.	Analyst	Accuracy/Bias	RPD<30

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Certified Reference Material (NIST 1947) [3]	1 in 20 samples	70-130% R of true value for Total PCBs (Sloan et al)	Reanalyze	ELLE Analyst	Accuracy	Results within acceptance windows

[1] A laboratory duplicate will be analyzed for this method based upon sample volume available.
[2] Ottawa sand used as LCS material for fish tissue analysis.
[3] Further details on the use of CRM can be found in Attachment 1 of this QAPP.

Matrix: Fish Tissue
Analytical Group: Dioxins/Furans
Concentration Level: Low
Analytical Method/SOP: SW-846 8290A/L-3F, S-2, S-17
Sampler's Name: Staff
Field Sampling Organization: Parsons
Analytical Organization: SGS Wilmington
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Labeled Spike	Per sample (including OPR and Blank)	Method Defined	Reextract sample. If the labeled compound fails high and the associated native is ND, the sample can be reported.	Analyst	Accuracy	Results within acceptance limits
Method blanks	1 in 20 samples	No analytes detected ≥ the reporting limit or >1/10 the amount measured in any sample	Reanalyze to confirm detections. If detects confirm reextract samples that are not ND or not >10x the blank value	Analyst	Accuracy/Laboratory Contamination	No analytes detected ≥ the reporting limit or >1/10 the amount measured in any sample
LCS[1]/LCSD	1 in 20 samples	Laboratory statistical limits (see WS 12); RPD ≤30%	Flag outliers	Analyst	Accuracy/Bias/Precision	Results within acceptance limits
MS/MSD	1 in 20 samples	Laboratory statistical limits (see WS 12); RPD ≤20%	Flag outliers	Analyst	Accuracy/Bias/Precision	Results within acceptance limits

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory Duplicate[2]	1 in 20 samples	RPD ≤50% for target <5x RL, <30% for targets >5x the RL	Flag outliers	Analyst	Precision	Results within acceptance limits
Certified Reference Material (CARP-2)[3]	1 in 20 samples	70-130% R of true value for PCDD/F for targets	Reanalyze	Analyst	Accuracy	Results within acceptance limits
OPR (Ongoing Precision and Recovery)	1 in 20 samples	Method Defined	Analytes in the OPR that fail high and are ND in the samples can be reported. All others are re-extracted.	Analyst	Accuracy/ Bias/ Precision	Results within acceptance limits
Internal Standards	Per sample (including OPR and Blank)	Method Defined	Reanalyze, document if confirmed.	Analyst	Precision	Results within acceptance limits

[1] Sodium sulfate used for LCS for fish tissue analysis.
[2] A laboratory duplicate will be analyzed for this method based upon sample volume available.
[3] Further details on the use of CRM can be found in Attachment 1 of this QAPP.

Matrix: Fish Tissue
Analytical Group: OC Pesticides[1]
Concentration Level: Low
Analytical Method/SOP: 8081B/L-3D, S-2
Sampler's Name: Staff
Field Sampling Organization: Parsons
Analytical Organization: SGS Dayton
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Surrogate Spike (organics)	Per sample (including MS/MSD, LCS, and Blanks)	Laboratory statistical limits	Reanalyze if outside limits, if confirmed, report	Analyst	Precision	% recovery within acceptance limits
Method blanks	1 in 20 samples	No analytes detected ≥ the reporting limit or >1/10 the amount measured in any sample	Reanalyze to confirm detections. If detects confirm reextract samples that are not ND or not >10x the blank value	Analyst	Representativeness	No analytes detected ≥ the reporting limit or >1/10 the amount measured in any sample
MS/MSD	1 in 20 samples	Laboratory specified recovery limits (see WS 12) and RPD ≤ 30	Evaluation in conjunction with LCS results	Analyst	Accuracy/Bias	RPD <30
Laboratory Duplicate[2]	1 in 20 samples	RPD 50% when <5x the MDL, 30% when >5x the MDL	Evaluation in conjunction with LCS results	Analyst	Precision	RPD 50% when <5x the MDL, 30% when >5x the MDL
LCS[3]	1 in 20 samples	Laboratory specified recovery limits (see WS 12) and RPD ≤ 30 (if LCSD is run)	Reanalyze LCS and associated samples. Analytes in the LCS that fail high and are Non-detect in the samples can be reported.	Analyst	Accuracy/Bias	RPD <30

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Certified Reference Material (NIST 1947) [4]	1 in 20 samples	70-130 % R of true value	Reanalyze	Analyst	Accuracy	Results within acceptance windows

[1] DDT and metabolites; hexachlorobenzene
[2] A laboratory duplicate will be analyzed for this method based upon sample volume available.
[3] Ottawa sand used for LCS for fish tissue analysis
[4] Further details on the use of CRM can be found in Attachment 1 of this QAPP.

Matrix: Water
Analytical Group: Nitrite
Concentration Level: Low
Analytical Method/SOP: L-1A/S-7
Sampler's Name: Staff
Field Sampling Organization: UFI
Analytical Organization: UFI
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	Every sample batch	RPD 30%	Reanalyze and/or report a failed duplicate sample.	UFI laboratory staff and QA officer/Project Manager	Precision - Field	RPD 30%
Laboratory duplicate	1 every 10 samples or one per sample run, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	UFI laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Reference	1 per sample run	% recovery within 10% for warning limits, 15% for control limits	Report data as associated with failed REF, repeat calibration and analysis if necessary	UFI laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than or equal to the limit of detection	Report data as associated with failed ICB, repeat calibration and analysis if necessary	UFI Laboratory staff	Contamination	Less than or equal to the limit of detection
Method Blank (MB)	1 per sample run	Less than or equal to 1/2 the limit of quantification or less than 1/10 the sample concentration	Reanalyze and/or report MB as failed	UFI Laboratory staff	Contamination	Less than or equal to ½ the limit of quantification or method reporting limit or less than 1/10 the sample concentration

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10 samples afterwards, and the last sample of any run.	% recovery within 5% for warning limits, 10% for control limits	ICV: Remake and reanalyze standards and ICV until it passes CCV: Report data as associated with failed CCV, repeat calibration and analysis if necessary	UFI Laboratory staff	Accuracy/Bias	% recovery within 5% for warning limits, 10% for control limits
Laboratory control samples (LCS)	1 per sample run	% recovery within 10% for warning limits, 15% for control limits	Report LCS as failed or stop the run and begin the corrective action process.	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	% recovery within 10% for warning limits, 15% for control limits	Reanalyze and/or report MS as failed	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Matrix spike duplicate sample (MSD)	1 per run	• RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed MSD.	UFI Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

Matrix: Water
Analytical Group: Nitrate+Nitrite
Concentration Level: Low
Analytical Method/SOP: L-1A/S-7
Sampler's Name: Staff
Field Sampling Organization: UFI
Analytical Organization: UFI
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	Every sample batch	RPD 30%	Reanalyze and/or report a failed duplicate sample	UFI Laboratory staff and QA officer/Project Manager	Precision – Field	RPD 30%
Laboratory duplicate	1 every 10 samples or one per sample run, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate	UFI Laboratory staff	Precision – Lab	RPD within 10% for warning limits, 15% for control limits
Reference	1 per sample run	% recovery within 10% for warning limits, 15% for control limits	Report data as associated with failed REF, repeat calibration and analysis if necessary	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than or equal to the limit of detection	Report data as associated with failed ICB, repeat calibration and analysis if necessary	UFI Laboratory staff	Contamination	Less than or equal to the limit of detection
Method Blank (MB)	1 per sample run	Less than or equal to 1/2 the limit of quantification or less than 1/10 the sample concentration	Reanalyze and/or report MB as failed	UFI Laboratory staff	Contamination	Less than or equal to ½ the limit of quantification or method reporting limit or less than 1/10 the sample concentration

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10 samples afterwards, and the last sample of any run.	% recovery within 5% for warning limits, 10% for control limits	ICV: Remake and reanalyze standards and ICV until it passes CCV: Report data as associated with failed CCV, repeat calibration and analysis if necessary	UFI Laboratory staff	Accuracy/Bias	% recovery within 5% for warning limits, 10% for control limits
Laboratory control samples (LCS)	1 per sample run	% recovery within 10% for warning limits, 15% for control limits	Report LCS as failed or stop the run and begin the corrective action process.	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	% recovery within 10% for warning limits, 15% for control limits	Reanalyze and/or report MS as failed	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Matrix spike duplicate sample (MSD)	1 per run	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed MSD.	UFI Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

Matrix: Water
Analytical Group: Ammonia
Concentration Level: Low
Analytical Method/SOP: L-1B/S-7
Sampler's Name: Staff
Field Sampling Organization: UFI
Analytical Organization: UFI
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	Every sample batch	RPD 30%	Reanalyze and/or report a failed duplicate sample	UFI Laboratory staff and QA officer/Project Manager	Precision – Field	RPD 30%
Laboratory duplicate	1 every 10 samples or one per sample run, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or repot a failed duplicate	UFI Laboratory staff	Precision – Lab	RPD within 10% for warning limits, 15% for control limits
Reference	1 per sample run	% recovery within 10% for warning limits, 15% for control limits	Report data as associated with failed REF, repeat calibration and analysis if necessary	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than or equal to the limit of detection	Report data as associated with failed ICB, repeat calibration and analysis if necessary.	UFI Laboratory staff	Contamination	Less than or equal to the limit of detection
Method Blank (MB)	1 per sample run	Less than or equal to 1/2 the limit of quantification or less than 1/10 the sample concentration	Reanalyze and/or report MB as failed	UFI Laboratory staff	Contamination	Less than or equal to ½ the limit of quantification or method reporting limit or less than 1/10 the sample concentration

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10 samples afterwards, and the last sample of any run.	% recovery within 5% for warning limits, 10% for control limits	ICV: Remake and reanalyze standards and ICV until it passes CCV: Report data as associated with failed CCV, repeat calibration and analysis if necessary	UFI Laboratory staff	Accuracy/Bias	% recovery within 5% for warning limits, 10% for control limits
Laboratory control samples (LCS)	1 per sample run	% recovery within 10% for warning limits, 15% for control limits	Report LCS as failed or stop the run and begin the corrective action process.	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	% recovery within 10% for warning limits, 15% for control limits	Reanalyze and/or report MS as failed	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Matrix spike duplicate sample (MSD)	1 per run	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed MSD.	UFI Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

Matrix: Water
Analytical Group: Soluble Reactive Phosphorus
Concentration Level: Low
Analytical Method/SOP: L-1C/S-7
Sampler's Name: Staff
Field Sampling Organization: UFI
Analytical Organization: UFI
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	Every sample batch	RPD 30%	Reanalyze and/or report a failed duplicate sample	UFI Laboratory staff and QA officer/Project Manager	Precision – Field	RPD 30%
Laboratory duplicate	1 every 10 samples or one per sample run, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or repot a failed duplicate	UFI Laboratory staff	Precision – Lab	RPD within 10% for warning limits, 15% for control limits
Reference	1 per sample run	% recovery within 10% for warning limits, 15% for control limits	Report data as associated with failed REF, repeat calibration and analysis if necessary	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than or equal to the limit of detection	Report data as associated with failed ICB, repeat calibration and analysis if necessary.	UFI Laboratory staff	Contamination	Less than or equal to the limit of detection
Method Blank (MB)	1 per sample run	Less than or equal to ½ the limit of quantification or less than 1/10 the sample concentration	Reanalyze and/or report MB as failed	UFI Laboratory staff	Contamination	Less than or equal to ½ the limit of quantification or method reporting limit or less than 1/10 the sample concentration

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10 samples afterwards, and the last sample of any run.	% recovery within 5% for warning limits, 10% for control limits	ICV: Remake and reanalyze standards and ICV until it passes CCV: Report data as associated with failed CCV, repeat calibration and analysis if necessary	UFI Laboratory staff	Accuracy/Bias	% recovery within 5% for warning limits, 10% for control limits
Laboratory control samples (LCS)	1 per sample run	% recovery within 10% for warning limits, 15% for control limits	Report LCS as failed or stop the run and begin the corrective action process.	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	% recovery within 10% for warning limits, 15% for control limits	Reanalyze and/or report MS as failed	UFI Laboratory staff	Accuracy/Bias	% recovery within 10% for warning limits, 15% for control limits

Matrix: Water
Analytical Group: Total/Volatile Suspended Solids
Concentration Level: Low
Analytical Method/SOP: See Worksheet #23/S-7
Sampler's Name: Staff
Field Sampling Organization: UFI
Analytical Organization: UFI
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	Every sample batch	RPD CV 50% (flux measurements)	Reanalyze and/or report a failed duplicate sample	UFI Laboratory staff and QA officer/Project Manager	Precision – Field	RPD CV 50% (flux measurements)
Method Blank (MB)	1 per sample run	Less than or equal to the limit of quantification or less than 1/10 the sample concentration	Reanalyze and/or report MB as failed	UFI Laboratory staff	Contamination	Less than or equal to the limit of quantification or method reporting limit or less than 1/10 the sample concentration

Matrix: Water
Analytical Group: ISUS rapid profiling sensors (nitrate, bisulfide, temperature, specific conductance, transmissivity, chlorophyll, and light penetration
Concentration Level: Low
Analytical Method/SOP: S-9
Sampler's Name: Staff
Field Sampling Organization: UFI
Analytical Organization: UFI
No. of Sample Locations: See Worksheet #18

QC Sample	Frequency/Number	Method/SOP Acceptance Criteria	Corrective Action	Title/position of person responsible for corrective action	Data Quality Indicator (DQI)	Measurement Performance Criteria
NO_3 instrument validation	~ 25 samples	N/A	DI water checks; DI water recalibration if regular DI check exceeds ± 0.007 mg/L	UFI field team leader	N/A	Acceptable DI water checks (± 0.007 mg/L)
HS^- instrument validation	~ 25 samples	N/A	DI water checks; DI water recalibration if regular DI check exceeds ± 0.016 mg/L	UFI field team leader	N/A	Acceptable DI water checks (± 0.016 mg/L)

WORKSHEET #29: PROJECT DOCUMENTS AND RECORDS

Sample Collection Documents and Records	On-site Analysis Documents and Records	Off-site Analysis Documents and Records	Data Assessment Documents and Records
Field notes	Collection notes (times, any field parameters, etc.) Field forms Calibration records	Sample receipt, custody, and tracking records	Field sampling audit checklists
Chain-of-custody records	Copies of signed COCs	Standard traceability logs	Field analysis audit checklists
Corrective action forms		Equipment calibration logs	Fixed laboratory audit checklists
		Sample preparation logs	Data Usability Summary Report
		Run logs	Corrective action forms
		Equipment maintenance, testing, and inspection logs	
		Corrective action forms	
		Reported field sample results	
		Reported results for standards, QC checks, and QC samples	
		Instrument printouts (raw data) for field samples, standards, QC checks, and QC samples	
		Sample disposal records	
		Telephone logs	
		Raw data (stored on CD or DVD)	

WORKSHEET #31, 32 & 33: ASSESSMENTS AND CORRECTIVE ACTION

Project oversight (field and laboratory) will consist of periodic inspection and audits of sampling and analytical techniques, as required by NELAC/ELAP (annual internal laboratory and field audit; external audit by NELAC/ELAP certified inspectors every two years). No additional field or laboratory audits are planned. Testing and calibration activities will also be reviewed. All audit and review findings and any corrective actions that arise from them will be documented. The laboratory director will ensure that corrective actions are carried out promptly. Where the audit findings cast doubt on the correctness or validity of the laboratory's calibrations or test results, immediate corrective action will be taken, and any client whose work is affected will be notified immediately in writing.

Assessments:

Assessment Type	Responsible Party & Organization	Number/Frequency	Estimated Dates	Assessment Deliverable	Deliverable due date
Field sampling technical systems audit	John Formoza (Jacobs), Mark Arrigo (Parsons)	Yearly	During field/sampling season	Verbal communication or written audit report	Deficiencies reported within 48 hours of audit
Data usability assessment report	Parsons	Yearly	Variable	Data validation report	June following field season

Assessment Response and Corrective Action:

Assessment Type	Responsibility for responding to assessment findings	Assessment Response Documentation	Time Frame for Response	Responsibility for Implementing Corrective Action	Responsible for monitoring Corrective Action implementation
Field sampling technical systems audit	Field staffs	Written document (electronic or hardcopy)	Corrective Action Response within 48 hours of audit report receipt	Field Staff	Project Manager/QA Officer
Data usability assessment report	Chemist/QA Officer	Written document (electronic or hard copy)	June following field season	Project Manager/QA Officer	Project Team

WORKSHEET #34: SAMPLING AND ANALYSIS VERIFICATION (STEP I) PROCESS TABLE

Verification Input	Description	Internal/External	Responsible for Verification (Name, Organization)
Chain-of-custody forms	Chain-of-custody forms will be reviewed internally upon their completion and verified against the packed sample coolers they represent. A copy of the chain-of-custody forms will be attached to the data report.	Internal	Laboratory representative
Field notes	Field notes will be reviewed internally and placed in the site file. A copy of the field notes will be attached to the final report. Laboratory project manager will review notes as provided by Parsons with chain-of-custody documentation.	Internal	Laboratory representative
Laboratory data	Laboratory data packages will be verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal. Received data packages will be verified externally according to the data validation procedures specified in Worksheet #36	Internal or External	Laboratory representative

The laboratory's QA officer or designee will perform a verification of chemical data. The laboratory will be responsible for the review and verification of all work sheets and data packages, manual entry or transcription of data, and any professional judgments made by an analyst during sample preparation, analysis, and calculation, and reporting of the final concentrations. The laboratory will also be responsible for reviewing quality control results to determine whether data are of usable quality or reanalysis is required. Any nonconformance issues identified during the laboratory's quality assurance checks will be corrected and noted by the laboratory. Close contact will be maintained between the Laboratory Director, the QA Officer, and the Scientific/Technical Manager, so that any quality issues can be resolved in a timely manner. Any data quality deviations will be discussed in the laboratory data narrative, including the direction or magnitude of any bias to the data, if possible.

Responsibilities for verification of data and sampling activities

Project Personnel	Verification Activity
Compliance	
Field Team Leader Parsons QA Officer	Assign appropriate staff to perform the work and ensure that all field personnel are familiar with the field SOPs
	Verify that the proper sampling protocols, including sample preservation, handling, and storage are performed during field work
	Conduct field data collection audit to ensure that the proper field procedures are followed
Laboratory Sample Manager	Track the samples sent to the laboratories; verify that the chain-of-custody forms are filled out correctly and that samples were received in good condition at the appropriate laboratory
	Verify that the appropriate number of field blanks and sample duplicates/triplicates are collected
Parsons QA Officer/Laboratory QA Officer or designee	Verify that the laboratory instruments are calibrated, and quality control samples are analyzed (e.g., blanks, duplicates, MS/MSD, LCS)
	Verify that the laboratory conducted proper calibration and quality control sample procedures (i.e., the laboratory followed the contract scope of work)
Laboratory Project Manager	Confirm that the analytical data meet specified detection limits in analytical SOPs
Correctness	
Field Team Leader	Inspect and ensure that the field and analytical equipment are calibrated and properly functioning in accordance with field instrument user manuals and laboratory QA manuals
Parsons QA Officer/Laboratory QA Officer or designee	Review data reduction process, examine the raw data to verify that the correct calculations of sample results were reported by the laboratory or transferred from field logs, examine the raw data for any anomalies, and verify that there are no transcription or reduction errors
Consistency (Comparability)	
Parsons QA Officer	Ensure that proper data-handling procedures were followed (e.g., the SOPs and contract scope of work are followed consistently throughout the project); recheck any handwritten data in field logs for transcription errors
	Review data transfer procedures and make all efforts to minimize data problems
Completeness	
Field Team Leader	Verify proper documentation of chain-of-custody and sample handling/transfer procedures, document any problems encountered during sample collection, identify any problems with damaged samples, and confirm with laboratory that all samples have been received
Field Team Leader/Parson QA Officer	Ensure that an accurate record was maintained during sample collection and analysis
Laboratory QA Officer	Document that general quality control measures were conducted (e.g., instrument calibration, routine monitoring of analytical performance, calibration verification)
	Ensure that a unique sample number was assigned to each sample
	Document deviations from scope of work (e.g., analytical procedures), document any corrective actions taken if QC checks identify a problem, ensure that the appropriate analytical method was used.

Note: LCS - laboratory control sample
MS/MSD - matrix spike/matrix spike duplicate
SOP - standard operating procedure
QA/QC – quality assurance and quality control

WORKSHEET #35: SAMPLING AND ANALYSIS VERIFICATION (STEP IIA AND IIB) PROCESS TABLE

Step IIa/IIb	Validation Input	Description	Responsible for Validation (Name, Organization)
IIa	SOPs	Ensure that all sampling and analytical SOPs were followed	Laboratory Primary and Second level reviewers
IIa	Documentation of Method QC Results	Establish that all method required QC samples were run and met required limits	Laboratory representative
IIb	Documentation of QAPP QC Sample Results	Establish that all QAPP required QC samples were run and met required limits	Laboratory representative
IIb	Project Quantitation Limits	Establish that all sample results met the project quantitation limits specified in the QAPP	Laboratory representative
IIa	Raw Data	Review 100% of raw data to confirm manual laboratory calculations and review 10% review of raw data to confirm automated laboratory calculation	Laboratory representative

WORKSHEET #36: SAMPLING AND ANALYSIS VERIFICATION (STEP IIA AND IIB) SUMMARY TABLE

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)
IIa	All matrices	All analyses	Low	QAPP Worksheets #12, #15, and #28	Parsons chemist, Honeywell chemist (as needed), or subject matter expert

Data verification and assessment will be completed manually by Parsons. EPA has not prepared national functional guidelines for the low-level total mercury, methylmercury, total organic carbon, and the conventional parameter analyses. Therefore, chemical data for these analytes will be verified and assessed following the "evaluation procedures" specified in National Functional Guidelines (e.g., assessment of holding times, accuracy, and precision data) and analytical method. For these data, method-specific quality control requirements and laboratory-established control limits (as presented in the QAPP), as they are applicable to the analytical methods being used, will be used to determine whether data require qualification. The method-specific quality control requirements and laboratory-established control limits (as presented in the QAPP) will be relied on for data evaluation and qualification when these limits differ from those presented in the National Functional Guidelines. In addition to the guidance documents cited, a primary source of validation criteria will be applicable USEPA Region 2 data review SOPs. Specifically, SOP HW-2 will be used for total mercury (with slight modification based on differences between the CLP SOW and SW-846). To the extent applicable, the Region 2 SOPs will take precedence over the more generic National Functional Guidelines.

The first phase of the data review process is contract compliance screening (CCS) and involves review of sample data deliverables for completeness. This process is as follows:

> Completeness is evaluated by ensuring that all required data deliverables are received in a legible format with all required information. The CCS process also includes a review of the chain-of-custody forms, case narratives, and reporting limits. Sample resubmission requests, documentation of nonconformances with respect to data deliverable completeness, and corrective actions often are initiated during the CCS review. The results of the CCS process are incorporated into the data validation process.

The second phase of data review is data validation. All analytical parameters to the extent possible will be validated according to USEPA Stage 2B protocol. The QAPP describes USEPA Stage 2B validation as follows:

> The USEPA Stage 2B validation protocol includes a review of summary information to determine adherence to analytical holding times; results from analysis of field duplicates, method blanks, field blanks, surrogate spikes, MS/MSDs, LCSs, internal standards, instrument calibrations, and sample temperatures during shipping and storage. Data qualifiers are applied to analytical results during the data validation process based on adherence to method protocols and laboratory-specific QA/QC limits.

For USEPA Stage 2B validation, verification of calculations and transcriptions will not be checked because the laboratories will be responsible for 100 percent verification of these results and procedures. Ten percent of the sample data will undergo a USEPA Stage 4 validation, which incorporates the USEPA Stage 2B validation protocol and adds calculation and verification checks from the instrument raw data to that reported by the laboratory on the sample and QC forms. Data qualifiers resulting from data validation will be applied to the results according to procedures described in the USEPA National Functional Guidelines for organic and inorganic data review (USEPA 2020), USEPA Region 2 SOPs, analytical methodologies, and QAPP as applicable.

Algorithms to Assess Quality Control Results

Data verification includes checking that quality control procedures were included at the required frequencies and that the quality control results meet control limits defined in the method descriptions. The equations provided below will be used to determine whether measurement targets for project requirements were met for each quality control procedure.

Duplicate and Triplicate Analyses — Precision for duplicate chemical analyses will be calculated as the relative percent difference (RPD), expressed as an absolute value, between the duplicate samples. Replicate precision will only be assessed for sample results greater than 5 times the method detection limit due to increased variability at low concentrations. When replicate results are less than 5 times the method detection limit, the absolute difference of the results will be evaluated. The formula that will be used to assess precision for both laboratory and field duplicate samples is as follows:

$$RPD = \left| \frac{D_1 - D_2}{(D_1 + D_2)/2} \right| \square\ 100$$

where:

D1 = sample value, and
D2 = duplicate sample value.

The percent relative standard deviation of triplicate sample data points will be calculated to evaluate replicate precision. The formula for relative standard deviation is as follows:

$$\%RSD = \frac{100 \times s}{\bar{x}}$$

where:

s = standard deviation, and
$\bar{x}$ = mean sample value.

Matrix Spike Recoveries — Spiked samples provide an indication of the bias of the analytical system. The recovery of MSs will be calculated as the ratio of the recovered spike concentration to the known spiked quantity:

$$\%R = \frac{A - B}{C} \times 100$$

where:

A = the analyte concentration determined experimentally from the spiked sample,
B = the background level determined by a separate analysis of the unspiked sample, and
C = the amount of the spike added.

Completeness — Completeness will be calculated for each sample type by dividing the number of valid measurements (all measurements except rejected data) actually obtained by the number of valid measurements that were planned:

$$\%\text{Completeness} = \frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} \times 100$$

To be considered complete, the data sets must also contain all quality control check analyses that verify the precision and accuracy of the results.

Sensitivity — The detection limit of the sample preparation and analysis process is defined as "The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results" (40 CFR 136, August 2017); it is the concentration at which qualitative, not quantitative, identification can be made.

Best professional judgment is used to adjust the limit of detection upward in cases where high instrument precision (i.e., low variability) results in a calculated limit of detection and equivalent instrument response that are less than the absolute sensitivity of the analytical instrument. The actual reporting limit for environmental samples is generally higher than the instrument detection limit, because the sample matrix tends to contribute to fluctuations in the instrument's background signal. Although reporting limits have been established (Worksheet #15 series), achievement of these reporting limits is based on the analysis of samples without matrix interferences. In the event that matrix interferences are encountered (on a sample-specific basis), laboratory personnel will determine whether elevated *reporting limits* are required. Whether to report elevated reporting limits will be determined based on the experience of the laboratory with samples of matrix similar to those collected for this study and on the response of each instrument to samples for this study. The MRLs will be verified during data validation.

Blanks Actions – The data will be assessed in accordance with the general guidance specified by the National Functional Guidelines for Inorganic Superfund Methods Data Review (USEPA 2020) since the quality control associated with these analyses are similar to the inorganic methods. With the exception of mercury, there are no published data validation procedures for these analytical methods. For this study, the data validator will try to limit the negation of results due to blank action levels (U qualified) based on the judgment that imprecise low concentration results are more useful in the analysis for this study then negated results. Sample results will be compared to the associated instrument, method, and field blank results to assess the potential for contamination.

Lipid Determinations – Lipid determinations are essentially calculated by measuring the weight lost from a prepared sample after desiccation. Therefore, a non-detect is an appropriate result only if an inadequate or faulty balance was used or if weight lost after desiccation was not measurable. Rules for assigning data qualifiers developed for reporting chemical results are not entirely applicable for reporting lipid determinations.

WORKSHEET #37: DATA USABILITY ASSESSMENT

Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used:

See Worksheet #36 and associated text.

Describe the evaluative procedures used to assess overall measurement error associated with the project:

Algorithms to Assess Quality Control Results

See Worksheet #36 and associated text.

Identify the personnel responsible for performing the usability assessment:

See Worksheet #36 and associated text.

Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations), and anomalies:

The data quality and usability report will be prepared by Parsons on behalf of Honeywell. The report will meet the requirements for a NYSDEC data usability summary report (DUSR) as described in document DER-10, Appendix 2B (NYSDEC Division of Environmental Remediation, Albany, NY). The report will summarize the results of the data validation and data quality review and will describe any significant quality assurance problems that were encountered. The report will include the following items:

- Project Objectives and Background
- Description of sample collection methods (including a description of deviations from planned sampling activities that may have occurred and the impact, if any, on the project and quality objectives) and shipping, including chain-of-custody and holding-time documentation
- Description of analytical methods (including a description of deviations in laboratory procedures that may have occurred and the impact, if any, on the project and quality objectives) and detection limits
- Summary of Data Verification performed by the laboratory and a description of any deviations from the work plan and quality assurance project plan
- Summary of Data Validation performed by Parsons with appendix tables detailing the validation findings
- General overview and test-specific summaries of data usability
- Tables detailing 1) target analyte list, methods, and method detection and reporting limits; 2) listing of study analytes and projected and actual analyses, 3) verification activities and responsible project personnel, 4) analytical components and associated appendix tables, 5) sample analysis summary count by event date, and 6) data usability summary by parameter.
- Appendices containing the data validation summary tables, analytical result summary tables, analytical result graphs, analytical quality control results, chain-of-custody documents, and results of the biological components of the work (i.e., field observations).

References:

Parsons, 2009. LCP OU-1 Quality Assurance Project Plan, Syracuse, New York. Prepared for Honeywell, Morristown, NJ. Parsons, Liverpool, NY.

Parsons, 2011. *100% Design Report for Geddes Brook Interim Remedial Measure. Appendix E: Operation, Maintenance and Monitoring Plan for the Geddes Brook Site.* Prepared for Honeywell. Syracuse, New York. February 2011.

Parsons, 2015. *Ninemile Creek OM&M 2015 Surface Water, Soil, and Biota Sampling Work Plan*. Prepared for Honeywell. Syracuse, New York, September 2015.

Parsons, 2018. *Maintenance and Monitoring Plan for Ninemile Creek.* Prepared For Honeywell, Syracuse, New York.

Parsons, 2018. *Onondaga Lake Maintenance and Monitoring Plan*. Prepared for Honeywell, Syracuse, New York.

USEPA, 2017. National Functional Guidelines for Organic Superfund Methods Data Review. EPA-540-R-2017-002. U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation, Washington, DC.

USEPA, 2017. National Functional Guidelines for Inorganic Superfund Methods Data Review. EPA-540-R-2017-001. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

APPENDIX A: STANDARD OPERATING PROCEDURES (ONONDAGA LAKE, GEDDES BROOK, NINEMILE CREEK AND LCP OU-1)

APPENDIX A
STANDARD OPERATING PROCEDURES (SOPs)

Reference Number	Title of Standard Operating Procedure (SOP)	Originating Organization	Revision Date	Worksheets Referenced In
S-1	Decontamination Procedures	Parsons	Effective Date: 8/4/2021	21A, 21B
S-2	Onondaga Lake Fish Collection, Processing, and Community Assessments	Parsons	Effective Date: 8/4/2023	12, 18B, 21B, 28
S-3	Monitored Natural Recovery SMU-8 Sediment Core Collection and Processing	Parsons	Effective Date: 8/4/2021	12, 18B, 21B, 28
S-4	Benthic Macroinvertebrate Collection and Processing for Tissue or Community Analysis	Parsons	Effective Date: 8/4/2021	12, 18B, 21B, 28
S-5	Onondaga Lake Macrophyte Survey	Parsons	Effective Date: 8/4/2021	21B
S-6	Geddes Brook, Ninemile Creek, LCP OU-1 and Onondaga Lake Wetland Monitoring	Parsons	Effective Date: 9/27/2022	21A, 21B, 22A, 22B
S-7	Water Sample Collection with a Submersible Pump for Compliance and Nitrate Program Sampling[1] (includes SOP Nos.: 303,304, 336, 306, 401)	UFI	Effective Date: 4/1/2021	12, 18B, 21B, 22B, 28
S-8	Zooplankton Collection and Processing[1] (includes SOP Nos.: 310 and 336)	UFI	Effective Date: 4/1/2021	12, 18B, 21B, 28
S-9	ISUS Equipment Calibration and Operation	UFI	Effective Date: 4/1/2021	18B, 21B, 22B, 23, 28
S-10	YSI Sonde & Buoy Calibration and Maintenance (includes SOP Nos.: 315, 331)	UFI	Effective Date: 4/1/2021	12, 18B, 21B, 22B
S-11	Sediment Trap Deployment and Collection	UFI	Effective Date: 4/1/2021	12, 18B, 21B, 28
S-12	Wastebeds 1-8 Turbidity Monitoring (Includes SOP Nos., 315, 318, 319) (Not used in 2019/2020/2021)	UFI	N/A	12, 21B
S-13	Geddes Brook, Ninemile Creek, and LCP Floodplain Sediment Sampling and Processing	Parsons	Effective Date: 8/4/2021	12, 18A, 21A, 28
S-14	Geddes Brook, Ninemile Creek, and LCP Surface Water Sampling and Processing[1]	Parsons	Effective Date: 8/4/2021	12, 18A, 21A, 22A, 28
S-15	Earthworm Collection and Processing	Parsons	Effective Date: 8/4/2021	12, 18A, 21A, 28
S-16	Benthic Macroinvertebrate Collection and Processing	Parsons	Effective Date: 8/4/2021	12, 18A, 21A, 28
S-17	Geddes Brook, Ninemile Creek and LCP Fish Collection and Processing	Parsons	Effective Date: 8/4/2021	12, 18A, 21A, 28
S-18	Small Mammal Collection and Processing	Parsons	Effective Date: 8/4/2021	18A, 21A, 28

Reference Number	Title of Standard Operating Procedure (SOP)	Originating Organization	Revision Date	Worksheets Referenced In
S-19	Ninemile Creek Transect Survey	Parsons	Effective Date: 8/4/2021	21A
S-20	Tributary Surface Water and Rainwater Sampling and Processing	Parsons	Effective Date: 8/4/2021	18B, 21B
S-21	Groundwater Sampling	Jacobs	Effective Date:	12, 18A, 21A, 22A, 28
L-1A	SOP 239 Nitrogen, Nitrate + Nitrite, Nitrite (as N; NOx, NO_2)	UFI	Effective Date: 4/1/2021	12, 19&30, 23, 28
L-1B	SOP 105.1 Nitrogen, Total Ammonia (as N; tNH_3)		Effective Date: 4/1/2021	12, 19&30, 23, 28
L-1C	SOP 107 Phosphorus, Orthophosphate (Soluble Reactive Phosphorus as P; SRP)		Effective Date: 4/1/2021	12, 19&30, 23, 28
L-1E	SOP 101 Solids, Total Suspended (AH filters; TSS_AH)		Effective Date: 4/1/2020	12, 19&30, 23
L-1F	Turbidity (Tn_L)		Effective Date: 4/1/2020	23
L-1G	SOP 202 Solids, Fixed Suspended, Volatile Suspended (AH filters; FSS_AH, VSS_AH)		Effective Date:4/1/2020	12, 23
L-2A	Mercury in Aqueous, Solid and Tissue Samples by EPA 7471A, 7471B, 7470A and 245.1 Rev 3 by Cold Vapor AA Preparation of Solids by EPA 7471A or B for Mercury Analysis	Eurofins Lancaster Laboratories and Eurofins Frontier Global Sciences	Effective Date: 4/27/2022	12, 19&30, 23, 24, 25, 28
L-2B	Determination of Methyl Mercury in Various Matrices by CV-GC-AFS	Eurofins Frontier Global Sciences	Effective Date: 11/6/2020	12, 19&30, 23, 24, 25
L-2C	Determination of Total Mercury in Various Matrices by FI-AFS	Eurofins Frontier Global Sciences	Effective Date: 5/12/2023	12, 19&30, 23, 24, 28
L-2D	Preparation of Solids Samples for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion	Eurofins Frontier Global Sciences	Effective Date: 4/11/2020	12, 19&30, 23, 24, 28
L-2E	KOH/Methanol Digestion of Tissues for Methyl Mercury Analysis	Eurofins Frontier Global Sciences	Effective Date: 6/26/2020	12, 19&30, 23, 28
L-2F	Mercury in Water by Oxidation, Purge & Trap and CV-AFS (EPA Method 1631, Rev E)	Eurofins Frontier Global Sciences	Effective Date: 11/6/2020	12, 19&30, 23, 24, 25, 28
L-2G	Digestion of Tissues for Total Mercury Analysis Using Nitric Acid and Sulfuric Acids (70:30)	Eurofins Frontier Global Sciences	Effective Date: 11/11/2019	12, 19&30, 23, 24, 25, 28
L-2H	Distillation of Aqueous Samples for Methyl Mercury Analysis	Eurofins Frontier Global Sciences	Effective Date: 11/6/2020	12, 19&30, 23, 25, 28

Reference Number	Title of Standard Operating Procedure (SOP)	Originating Organization	Revision Date	Worksheets Referenced In
L-3A	Determination of Lipids in Tissue	SGS North America Inc. – Wilmington	Issue Date: 6/14/2023	12, 19&30, 23, 24, 25, 28
L-3B	% Moisture Calculation and % Solids Calculation (Gravimetric) by SM 2540 G 1997 and SM G-2011	SGS North America Inc. - Wilmington	Issue Date: 10/12/2017	23, 25
L-3C	SW846 8082A: Determination of Polychlorinated Biphenyls (PCBs) by Gas Chromatography Sulfuric Acid/Permanganate Cleanup	SGS North America Inc. - Dayton	Effective Date: 3/12/2021	12, 19&30, 23, 24, 25. 28
L-3D	Determination of Organochlorine Pesticides Using GC System by SW846 8081B Florisil Column Cleanup	SGS North America Inc. - Dayton	Effective Date: 4/16/2020	12, 19&30, 23, 24, 25, 28
L-3E	Cold Vapor Analysis of Mercury for Soil Samples by SW846 7471B	SGS North America Inc. – Dayton	Effective Date: 2/14/2022	12, 19&30, 23, ,25, 28
L-3F	Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans (PCDD/Fs)	SGS North America Inc. – Wilmington	Issue Date: 2/11/2022	12, 19&30, 23, 24, 25, 28
L-3G	Cold Vapor Analysis of Mercury for Water Samples	SGS North America Inc. - Dayton	Effective Date: 2/14/2022	12, 19&30, 23, 25, 28
L-3H	Standard Operating Procedure for Extraction of Various Matrices Fractionation (Cleanup Procedure)	SGS North America Inc. – Wilmington	Issue Date: 2/11/2022	23
L-3I	Homogenization of Biota/Tissue (Includes Prep Lab Standard Operating Procedure: NYS Department of Environmental Conservation)	SGS North America Inc. – Wilmington	Issue Date: 9/22/2022	14A &16A, 14B & 16B, 21A, 21B, 23, 26 & 27
H-1	Containers, Preservation, Handling and Tracking of Samples for Laboratory Analysis	Parsons	Effective Date: 6/23/2022	26&27
D-1	Data Management	Parsons	Effective Date: 6/23/2022	26&27

[1] Clean hands/dirty hands sampling for low-level mercury analyses are incorporated into these SOPs.

These procedures are to be followed as specified; any substantive modifications to the procedures shall be approved by the appropriate Field Team Leader in consultation with the Project Manager or Task Manager.

S-1 DECONTAMINATION

SECTION 1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for decontamination of equipment, instruments and other materials. Decontamination is the process of neutralization, washing, and rinsing exposed outer equipment surfaces and any equipment surfaces that may contact the sampled media to minimize the potential for contaminant migration and/or cross-contamination. This SOP does not apply to personnel decontamination which is described in the Project Safety Health and Environmental Plan (PSHEP).

The overall objective of the sampling program is to obtain samples that accurately depict the chemical and physical conditions at the sampling site. Extraneous contaminant materials can be brought to a sampling location and/or introduced into the medium of interest during the sampling program (e.g., by coring sediments) with equipment previously used at another sampling site or location. Trace quantities of these materials may introduce concentrations into other samples and lead to false positive analytical results and, ultimately, to an incorrect assessment of site conditions. Decontamination of sampling equipment (e.g., core tubes, water bottles, and other sampling equipment) and field support equipment (e.g., coring barge) is required so that sampling cross-contamination is prevented and on-site contaminants are not carried off the site.

The decontamination procedures described herein are to be followed. Substantive modifications to the procedure shall be approved in advance by the Field Sampling Manager.

SECTION 2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks per this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 3.0 DECONTAMINATION PROCEDURES

3.1 Equipment List

The following equipment list contains materials that may be needed in carrying out the procedures contained in this SOP. Since multiple procedures may be contained in the SOP, not all of which are necessarily conducted when using the SOP, not all materials on the equipment list may be required for a specific activity.

- Bristle brushes
- Wash/rinse tubs

- Low phosphate detergent
- Nitric acid rinse (10 percent)
- Distilled or de-ionized water
- HPLC quality grade acetone
- Aluminum foil
- Polyethylene sheeting
- Tap water (from any treated municipal water supply)
- Containers for collection and storage of decontamination fluids
- Appropriate health and safety equipment
- Sample container(s) for rinsate blank
- Field logbook and pen

3.2 Sampling Equipment Decontamination

Sampling equipment will be decontaminated prior to use in the field to minimize cross-contamination. While performing the decontamination procedure, "phthalate-free gloves", such as nitrile or butyl rubber, must be used to prevent phthalate contamination of the sampling equipment or the samples. The equipment will be decontaminated in a designated area for decontamination.

Decontamination procedures will be implemented prior to each sampling event for all non-dedicated sampling equipment that will come in contact with the media to be sampled as summarized in the following sections.

Not all sampling equipment will require the full decontamination procedures listed above. For instance, gross decontamination of boat decks and large equipment that will not directly contact samples may be conducted using lake water. Decontamination fluids from non-dedicated sampling equipment will be held in buckets or other containers, and transferred to drums in the waste handling area for proper disposal. New disposable equipment (sampling spoons, liners, tubes, catchers, etc.) that was delivered pre-cleaned and in sealed containers will not be decontaminated at the site before use. Specific decontamination will be performed based on the usage of the sampling equipment as defined below.

3.2.1 Small Sampling Equipment Decontamination

The following steps will be used to decontaminate small sampling equipment that will come in contact with media designated for potential chemical analysis (e.g., re-used sampling equipment) and materials which have come in contact with media and that may be destined for disposal at a municipal waste facility (e.g., used or damaged stainless steel or aluminum core tubes, or used and returned sample containers):

- Personnel will dress in suitable safety equipment to reduce personal exposure (see PSHEP).
- Equipment that will not be damaged by water will be placed in a wash tub or bucket containing Alconox (or other low-phosphate detergent) along with tap water, and scrubbed with a bristle brush or similar utensil. Solvent rinses are not needed, as the rinse procedures described above are sufficient for removal of organics prior to sampling.
- This rinse shall utilize sufficient amounts of water to flush rather than just wet the surface.
- Next the equipment will be rinsed with tap water then DI water in a second wash tub
- Next the equipment will be rinsed with 10 percent nitric acid (when samples are being analyzed for metals).
- Next the equipment will be rinsed with DI water.
- The various rinse fluids will be collected in a bucket for subsequent disposal.

- Following decontamination, equipment will be placed in a clean area and allowed to air dry to the extent practicable. If it is not planned to be used in the near future, the equipment that will be used for sampling will be wrapped in aluminum foil following air drying.
- Rinsate waste and detergent water will be replaced with new solutions daily, when visibly impacted by residuals, or between sampling areas or changes in operations. Used decontamination water will be collected and handled in accordance with residuals management protocols.

3.2.2 Vessels and Large Sample Equipment Decontamination

The following steps will be used to decontaminate vessels, boat equipment such as boat anchors, lines, ropes, buoy marker weights, and large sampling equipment such as submersible pump and hose, Vibracoring head, and stainless steel outer tubes:

- Personnel will dress in suitable safety equipment to reduce personal exposure (see PSP).
- Decontamination of the decks of the vessels will consist of lake water washing of all sediment, residues, and associated water. Decontamination will be conducted daily, or between sampling locations, whichever is more frequent.
- Large sampling equipment and boat equipment that has directly contacted sediments or wastes shall be decontaminated between sampling locations, and prior to leaving the site. The sampling equipment will be scrubbed with a bristle brush and detergent, and rinsed with lake water. General boat equipment will be rinsed with lake water.
- Rinse water will be allowed to return to the lake.

3.3 Field Instruments and Equipment

Instrumentation should be cleaned as per manufacturer's instructions. Probes such as those used in pH, ORP and specific conductivity meters will be carefully wiped clean using a sponge and detergent water and rinsed with deionized water. Care will be taken to prevent damage to equipment. When necessary, instruments which are difficult to decontaminate, such as cameras and logging instruments, may be protectively wrapped to reduce or eliminate the need for decontamination.

3.4 Equipment Leaving the SITE

All sampling equipment leaving the site will be decontaminated according to this SOP.

4.0 DOCUMENTATION

The field personnel are responsible for documenting decontamination activities related to their on-site activities. Observations and data will be recorded with ink in a field logbook with consecutively numbered pages. The information in the field logbook will include the following as a minimum:

- Project name, locations, date of activity
- Responsible person's name
- Date and time of activity
- Information concerning items decontaminated and the procedure(s) utilized
- Information related to the collection of blank samples

SECTION 5.0 REVISIONS/REVIEWS

Doc Number: Rev No.: 0 Date: August 4, 2021

Reviewer: Parsons

What was changed: N/A

S-2 ONONDAGA LAKE FISH COLLECTION, PROCESSING, AND COMMUNITY ASSESSMENTS

SECTION 1.0 SCOPE

These procedures are to be followed; any substantive modifications to the procedures shall be approved by the Field Team Leader.

Several methods may be used to collect fish for tissue analysis for the program. This SOP includes procedures to collect fish by gillnetting, seining, trap netting, and electrofishing in Onondaga Lake. Use of each method will be dependent on species and life stages being targeted; a combination of methods likely will be necessary to obtain the required species.

This SOP also describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct fish community assessments and Northern pike monitoring in WBB/HB Outboard. Fish community sampling will occur from May to October during several sampling events. The sampling techniques to be used will include electrofishing, trap nets, gillnets, and seining, as implemented for tissue collection. Angling may be used to supplement collection of tissue collection, as needed. Sampling for Northern Pike targeting spawning adults will occur in early spring when water temperatures are between 41°F and 55°F, when spawning by Northern Pike normally occurs. Sampling techniques will include trap nets and visual site walks. Additional sampling will occur in the summer months to capture young—of-the-year Northern Pike and/or other wetland spawning species that may be present. A variety of sampling techniques will be used, including visual surveys, trap nets, and minnow traps. These procedures are to be followed, and any substantive modifications to the procedures need to be approved by the Field Team Leader.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and lake sampling include: caution deploying and retrieving heavy equipment, stepping in the sight of lines or cables, slips, trips, falls, and the proper use of personal flotation devices (PFDs) and personal protective equipment (PPE). Do not overload any vessel and load vessels evenly so they are not prone to capsizing. These safety considerations apply to the vessel and sampling crews whenever working on the water.

The use of electrofishing equipment involves potential hazards related to the high voltage output. Because water is an excellent conductor of electricity, the operator of the electrofishing equipment must observe certain precautions to avoid injury. For example, the acceptable voltage range for electroshocking is 300 to 400 volts, and the acceptable current range is 19 to 23 amps based on experience from previous investigations.

SECTION 3.0 FISH SAMPLE COLLECTION EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Since multiple procedures or alternate methods may be employed to achieve the objectives, not all materials and equipment included on the list may be necessary to complete the task.

- Seine net
- Gill net
- Anchors with approximately one meter of rope attached for gill net (2 per net)
- Buoys with rope attached for gill net (2 per net)
- Trap net
- Sampling vessel
- Electroshocking boat
- Utility boat
- High voltage gloves
- PFDs, gloves, and safety glasses
- Waders
- Measuring board
- Weight scale
- Small and large baskets for weighing fish
- Fish holding tubs (live wells)
- Minnow nets
- Large dip nets
- Long handled nets
- Angling equipment
- Water quality meter
- Digital camera
- Field notebook
- GPS unit
- Cellular phone

SECTION 4.0 FISH SAMPLING PROCEDURES

4.1 Fish Community Characterization

Sampling for community studies will be conducted following protocols for fish collection sampling and fish samples analyzed according to the procedures below. Sampling with trap and gill nets will be conducted once a month for five days (Monday through Friday) at a total of 10 locations around the lake. Trap nets will be set up early during a day so fish can collect overnight. Gill nets will be used for approximately one to two hours to reduce stress to recaptured fish. Beach seining will be conducted in August to assess juvenile and prey fish communities.

- Place fish in a live well for processing following collection.
- Identify to species, determine life history stage and count all fish collected during a sampling event. The first 30 individuals of each species will be checked for total length and weight and recorded in the field log. Remaining individuals of a given species will be counted.

4.2 Sampling with a Seine

For near shore shallow study areas with minimal to no macrophyte coverage, a bag seine (30 m [98.4 ft.] length; 0.635 [0.25 in.] cm mesh) will be used to collect juvenile and prey fish for abundance estimates and prey fish tissue samples. The bag seine is typically used in shallow water where the net wall can extend from the surface of the water to the bottom. It is useful in the capture of near-shore species or for species that use the near-shore area seasonally or daily. In addition, the substrate needs to be relatively smooth so that the lead line of the seine drags along the bottom of the river preventing fish escapement. The fish are herded into the net as it is swept through the water. Seining will be conducted by a minimum of three people. The following outlines the procedures for seine netting (based on NYSDEC, 1989):

4.2.1 Sampling

1. Proceed to the appropriate station and record in a field log.
2. Record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface where the net will be located.
3. Prior to entering the water stretch the bag seine out on shore and remove any material lodged in the mesh. Inspect the net for holes and make repairs, if necessary.
4. One person begins extending the seine perpendicular to the shoreline until the net is straightened out or the water becomes too deep. Be sure bag is fully deployed and not tangled.
5. One person holds the on-shore brail stationary while the off shore person sweeps the brail towards shore. A third persons walks behind the bag to dislodge any snags if the seine becomes stuck. Reject the sample if the lead line is lifted or if the seine is stopped to dislodge a snag.
6. As the person holding the offshore brail approaches shore, the two ends are worked together to beach the seine while maintaining the integrity of the bag section and keeping the lead line on the bottom.
7. Fish are removed from the net and placed into holding buckets for identification. Be sure to pick through any debris captured in the net to retrieve all fish.
8. Stretch out the seine on shore and remove any material lodged in the net.
9. Process fish for assessment of abundance estimates according to 4.1 above. If fish are being retained for tissue assessment, record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface location where the net was placed. Fish not required for other analyses will be released.

4.3 Gill Net Sampling

Fish collection for tissue analysis and community assessment may be conducted with gill net sets. Fish are captured when they swim into the gill net and become entangled in the mesh of the net. A gill net consists of a net vertically suspended between a float line on top and a weighted lead line at the bottom. The mesh size of the net can consist of different sized panels or one single size for the entire length of net. For this sampling, two gill nets will be used, one size mesh (15.24 cm [6.0 in.] stretch), 38.1 m [125 ft.] long and 2.44 m [8.0 ft.] high, and a larger variable mesh net (8 panels [37.5 ft.] of mesh sizes of 15.24, 20.32, 25.4, and 30.48 cm [6, 8, 10, and 12 inch] stretch mesh oriented in sequence for two series, 91.44 meters [300 ft.] long, and 2.44 m [8.0 ft.] high). To keep the net in a vertical orientation, anchors are attached to either end of the lead line and buoys are attached to either end of the float line. The lengths of the anchor and buoy lines are adjusted so that the net is suspended at the target water depth. The following describes the procedure for sampling with gill nets:

4.3.1 Setting the gill net perpendicular to shore:

1. Proceed to the appropriate station and record in the field log.
2. Attach anchors to both ends of the lead line and attach buoys to both ends of the float line
3. Stack the gillnet in a large storage bucket by placing the end with the larger mesh size in the tub first (if the net has variable mesh sizes), and coiling the rest of the net into the tub. This procedure facilitates setting the net.
4. Beginning close to shore, or in water approximately 2 m deep (no less than 2.5 m for variable mesh net), remove the outer end of the net from the storage bucket and drop the anchor (attached to the lead line) and buoy (attached to the float line) over the bow of the boat. Adjust the buoy line so that the buoy is floating and the line is relatively taut.
5. Begin slowly backing the boat away from the shore.
6. Carefully, play out the remainder of the net as the boat is moving backwards, shaking out any tangles.
7. Once the inner end of the net is reached, stop the boat and pull on the net until it is taut.
8. Drop the anchor (attached to the lead line) overboard.
9. Pull on the float line to make sure the net is taut.
10. Drop the buoy that is attached to the float line into the water. Adjust the buoy line so that the buoy is floating and the line is relatively taut.
11. Allow the gill net to be in place for the prescribed sampling period (e.g., 1-4 hours).

4.3.2 Retrieving the gill net:

1. Arrive at the end of the net in deeper water and retrieve the buoy and anchor.
2. Begin pulling the net on board the boat and stacking it in coils in the storage bucket.
3. Remove fish from the net as it is brought aboard the boat and place in holding bucket. All fish will be placed in the holding bucket until the entire net is retrieved. If fish are being retained for tissue assessment, record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface location where the net was placed.
4. Process fish according to procedures detailed below. Fish not required for other analyses will be released.

4.4 Trap Net Sampling

A trap net is used as a passive sampling device to capture fish as they swim along the shoreline. Samples will be collected in the trap net for tissue analysis and population studies. A trap net consists of a leader line (23 m [75.4 ft.] length), two wings (11.5 m [37.7 ft.] each), and a series of hoops; the entire net consists of 0.635 cm [0.25 in.] stretch mesh. The net is set perpendicular to and facing the shoreline. When fish encounter the leader line, they are directed offshore into the mouth of the net, through the hoops, and into the end of the net. As fish move through the series of hoops, escape becomes increasingly difficult. Fish may be attracted to the net by other fish that are already captured in it.

4.4.1 Station selection:

1. Proceed to the appropriate station and record in field log.
2. Record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface where net will be located.

4.4.2 Setting the net:

1. Anchor the shoreward end of the leader line near the shoreline or attach it to the shoreline by tying it to a fixed object on shore (e.g., tree).
2. Extend the leader line out into the water and perpendicular to shore, until it is taut.
3. Extend each wing at a 45 to 90 degree angle to the leader line. This can be done either by boat or by wading, depending on the water depth and substrate characteristics.
4. Anchor the lower ends of both wings with anchors and attach buoys to the upper ends of the wings. Adjust the buoy lines so that the buoys are floating and the lines are relatively taut.
5. Extend the hoops of the trap away from shore in line with the leader line and pull on the end of the net until all of the hoops are upright.
6. Close the end of the net with a piece of line.
7. Attach an anchor to the end of the net to keep it submerged and attach a buoy to the anchor to mark the location of the end of the net. Record the depth below the water surface of the far end of the net.
8. Allow the net to soak (i.e., fish) for the prescribed sampling period (e.g., 24 to 48 hours).

4.4.3 Sample Collection

1. Arrive at the buoy at the end of the net and pull the buoy and its anchor into the boat.
2. Retrieve the hoops in sequence, while moving toward shore.
3. Starting at the mouth of the net, shake the captured fish into the closed end of the net.
4. Once all captured fish are in the end of the net, remove the piece of line from the end of the net and empty fish into the collection buckets.
5. If sampling will continue at the collection site, reset the trap according to steps 3 through 8 above for setting a trap net.
6. Process fish according to procedures in 4.1 (above). If fish are being retained for tissue assessment, record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface location where the net was placed. Fish not required for other analyses will be released.

4.5 Boat Electrofishing

Electrofishing uses electrical currents to immobilize fish for capture. Electrofishing is less effective in deeper waters, where fish can swim and avoid the current, therefore this method will be limited to areas that are less than 4 meters [13.2 ft.] deep. The following outlines the procedures for electrofishing:

1. Personnel performing the electroshocking will wear appropriate health and safety gear (work boots, high-voltage gloves, PFD).
2. Position the electrofishing boat in the water.
3. Optional use of a “fish finder” may increase efficiency and aid in targeting locations for sampling.
4. Measure the water conductivity and temperature to determine the appropriate operating voltage and amperage.
5. Adjust the output voltage and amperage dials until the desired output setting is obtained without harming fish. Use pulsed output to reduce stress on fish.
6. Maintain the output for a predetermined amount of time or sampling area.
7. Collect the fish with dip nets and place in bucket of water or livewell for processing.
8. Release all unselected fish following processing.

9. Process fish retained for analysis according to the procedures in 4.1. If fish are being retained for tissue assessment, record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface location where the net was placed.

4.6 Angling

Angling efforts will follow all rules and regulations set forth by the NYSDEC. Each sampler must have a valid NYS fishing license. All undesired fish will be released immediately. Fish will be processed for analysis according to Section 4.1.

4.7 Spawning Northern Pike Sampling

Sampling for spawning Northern Pike in the WBB/HB Outboard Area will focus on the early spring, when water temperatures are between 41ºF and 55ºF, when spawning by Northern Pike typically occurs. Sampling will consist of visual site walks along the shoreline, as well as a minimum of two trap nets set from shore each week, periodically rotating between three locations within the WBB/HB Outboard Area or other locations within the WBB/HB Outboard Area, as site conditions allow.

4.7.1 Station Selection

1. Proceed to the appropriate station or area within WBB/HB Outboard and record in field log.
2. Record water temperature.

4.7.2 Setting the Net

1. Anchor the shoreward end of the leader line near the shoreline or attach it to the shoreline by tying it to a fixed object on shore (e.g., tree, stake)
2. With at least one person on each side of the hoops, wade into the water, pulling the leader line out into the water and perpendicular to shore, until it is taut.
3. Extend the hoops of the trap away from the shore in line with the leader line and pull on the end of the net until all of the hoops are upright.
4. Close the end of the net with a piece of line.
5. Attach an anchor to the end of the net to keep it submerged and attach a buoy to the anchor to mark the location of the end of the net.
6. Extend each wing to a 45 to 90 degree angle to the leader line.
7. If substrate allows secure anchors by attaching to a stake driven into the sediment. If substrate is too rocky for a stake, anchor the lower ends of both wings with anchors and attach buoys to the upper ends of the wings. Adjust the buoy lines so that the buoys are floating and the lines are relatively taut.
8. Allow the net to soak (i.e., fish) for the prescribed sampling period (e.g., 24 to 48 hours).

4.7.3 Sample Collection

1. Arrive at the net site and detach wings from stakes or weights.
2. Wade to the deep end of the net. With one person on each side of the hoop closest to shore and a third person holding up anchor at the back, slowly move net towards shore.
3. Once on shore, starting at the mouth of the net, shake the captured into the closed end of the net.

4. Once all captured fish are in the end of the net, remove the piece of line from the end of the net and empty fish into the collection buckets.
5. If sampling will continue at the collection site, reset the trap net according to steps 3 through 8 above for setting a trap net.
6. Process fish above according to procedures in 4.1 (above). If fish are being retained for tissue assessment, record water quality (temperature, pH, dissolved oxygen, conductivity) at the near surface location where the net was placed. Fish not required for other analyses will be released.

4.8 Juvenile Northern Pike Sampling

Sampling for juvenile Northern Pike in the WBB/HB Outboard Area will focus occur during July and August, when young of year Northern Pike are most likely to be captured. Monitoring will include visual inspection and minnow traps, in order to minimize disturbance of establishing vegetation. A minnow trap is used as a passive sampling device to capture juvenile fish as well as the adult individuals of small fish species. Fish are captured when they swim into the trap through a funnel-shaped opening that makes escape difficult. Minnow traps are available in a variety of shapes and sizes, such as cylindrical, umbrella, or folding/accordion style. The trap is generally set in shallow nearshore areas. The trap can be deployed with bait inside (bread) to attract fish or without bait. Fish may be attracted to the trap by other fish that are already captured in it.

4.8.1 Station Selection

1. Proceed to the appropriate station or area within the WBB/HB Outboard and record in field log. Record type/style of minnow trap being used.

4.8.2 Setting and Retrieving Nets

1. Assemble the net. If bait will be used, the trap can be baited at this time.
2. Wade into the water and lower the minnow trap into the water. Tie a long piece of rope onto the trap, and attach securely to a stake driven into the ground, or, if present, to a habitat structure such as a downed tree limb.
3. Allow the trap to soak for the prescribed sampling period (e.g., 24–48 hours).
4. After 24-48 hours, retrieve the net by wading into the water. Bring trap to shore to process fish.
5. Open the trap, and transfer the captured fish to the collection buckets.
6. Process fish according to procedures in 4.1. (above).

SECTION 5.0 SAMPLING PERSONNEL

The Project Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Project Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Project Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 6.0 FISH SAMPLE PROCESSING PRIOR TO LABORATORY RECEIPT

6.1 Equipment List

- Measuring board (1 meter in length)
- Balance for weighing samples (35 pound capacity)
- Small and large baskets for weighing fish
- Scale envelopes
- Knife
- Forceps
- Cut proof gloves
- Safety glasses
- Sample vials
- Paper towels
- Foil
- Sample labels
- Resealable plastic bags
- Wet ice
- Coolers
- Cellular phone
- Digital camera
- Field notebook

6.2 Fish Sample Processing Procedure

1. For each individual, record the species, total length and weight in the field log. For Pumpkinseed, remove several scales from behind the pectoral fin of the fish and place at least 10 scales in a labeled scale envelope. Adult sport fish and large prey fish will be collected as individual samples; while small prey fish will include a composite of 10 to 15 individuals of the same species, or enough individuals to achieve the necessary sample mass (grouping fish by size so that the smallest individual is no less than 75% of the lengths of the largest individual).
2. For Smallmouth Bass, Walleye, and Common Carp, remove the otoliths from the head and clean to remove any remaining tissue (see Secor et al. 1991 for cleaning procedures), and place into a small vial. Label the vial with species, fish tag number, and date.
3. Wrap fish in clean foil (shiny side out) and attach an identification label that includes the fish tag number, date, sample type, and location sampled.
4. Place the entire sample into a resealable plastic bag, place a secondary label on the bag, and place in a cooler on wet ice.
5. Prior to shipping the samples, print the chain of custody form and include with the shipment. Print the field collection log and retain a hard copy of the log.

6.3 Sample Transport to Laboratory

If shipping to the laboratory the same day as collection, ship immediately on wet ice. If not being shipped to the laboratory the day of collection, store fish at a temperature below 0 degrees Celsius. Once ready to ship to the analytical laboratory, immediately place on wet ice. Provide Chain of Custody and Analysis Request documents with the fish shipment.

6.4 Tissue Preparation at the Laboratory

Fillets will be prepared at the laboratory for adult Smallmouth Bass, Walleye, Pumpkinseed and Common Carp samples. The adult fish fillets will be prepared in accordance with the NYSDEC filleting procedure (NYSDEC 2014). Small prey fish (as whole body composites) and large prey fish (as whole body individuals) will be processed following analytical laboratory protocols.

SECTION 7.0 METHODS FOR AGE DETERMINATION USING OTOLITHS AND SCALES

Otoliths are aged by using a low-speed, Buehler Isomet saw to cut a 0.3-mm thin section through the focus and perpendicular to the sulcus of a sagittal otolith from each fish or through the spine's articulating process perpendicular to the long axis of the spine. The thin section is then mounted on a microscope slide with epoxy and polished with sanding disks ranging from 320-1200 grit. For scales, several scales from a single fish are pressed onto acetate for viewing under a compound microscope. Mounted sections of pressed scales are viewed under a compound microscope at 40 to 100x. Annuli are counted from the focus to edge of the section.

Each scale or mounted otolith cross-section is aged by two people independently. If the two readers do not agree on the age of a particular fish, the sample is read a third time by both readers together to resolve the discrepancy in age interpretation and arrive at a consensus of the age.

The age of a fish is recorded as the number of distinct annuli observed on the scale or mounted cross-section of the otolith or spine. If the last annuls is observed at the edge of the section and no growth is visible beyond the annulus, the age is recorded as the number of annuli counted. If some growth is observed beyond the last annulus (i.e., between the last annulus and the edge of the section), the age is recorded as the number of annuli counted followed by a plus (+) symbol to indicate that growth had occurred since the last annulus had formed

SECTION 8.0 REFERENCES

New York State Department of Environmental Conservation. 1989. Guidelines for the Collection, Analysis, and Interpretation of Fisheries Data by Units of the NYSDEC Division of Fish and Wildlife.

Secor, D.H., J.M. Dean, and E.H. Laban. 1991. Otolith Removal and Preparation for Microstructural Examination: A User's Manual. Electrical Power Research Institute and the Belle W. Baruch Institute for Marine Biology and Coastal Research.

SECTION 9.0 REVISIONS/REVIEWS

Doc Number: Rev No.: 1 Date: August 4, 2023

Reviewer: Parsons

What was changed: Section 6.2, Fish Sample Processing Procedure

S-3 MONITORED NATURAL RECOVERY SMU-8 SEDIMENT CORE COLLECTION AND PROCESSING

SECTION 1.0 SCOPE

Based on assessing numerous types of sediment cores for SMU 8-related sampling work, a particular gravity corer was selected and used beginning in 2009 to collect sediment samples from the upper few inches of SMU 8 sediment for microbead placement analyses. The selected gravity corer is manufactured by Eijkelkamp, The Netherlands, and was pre-tested extensively in SMU 8 during 2009 before being used effectively in Onondaga Lake during 2010-2012 and 2014-2015. The gravity corer consists of a frame with strengthening ribs, falling weight, and sampler. This corer was selected due to its ability to collect samples while not disturbing the surface sediment.

Sediment samples approximately 2 to 4 inches in diameter that are relatively undisturbed are collected with the gravity corer. Weights can be placed over the gravity corer as needed to improve penetration into the sediment. Using a hoisting unit on board of a boat, the sampler can be lowered in free fall. By its own weight and velocity, the apparatus penetrates the submerged sediment. The depth of penetration is in part determined by the composition of the submerged sediment. Two different cores may need to be collected from each location to provide sufficient quantity of sample for the specified laboratory analyses.

These procedures are to be followed; any substantive modifications to the procedures shall be approved by the Field Team Leader.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and lake sampling include: caution deploying and retrieving heavy equipment; stepping in the sight of lines or cables; slips, trips, falls; and the proper use of PFDs and PPE. Do not overload any vessel and load vessels evenly so they are not prone to capsizing. Suitable gloves are to be used while handling the corer to minimize any potential cuts or scrapes. These safety considerations apply to the vessel and sampling crews whenever working on the water.

SECTION 3.0 SEDIMENT SAMPLING EQUIPMENT

3.1 Gravity Core Apparatus

- Core tube (3-5/8-inch diameter) and caps
- Rubber ‘Fernco’ coupling (attaches core tube to core apparatus)
- Hose clamps (secures rubber coupling)

- Weight carabineer (secures gravity core apparatus and rope)
- Rope (approximately 50 ft. long)
- 4 lengths of chain (20-30 links each)
- 8 threaded chain links
- Round flange weights

3.2 Tools

- Measuring tape
- Hacksaw (for cutting lengths of core tube)
- Reciprocating saw (for sample cross sectioning)
- Crescent wrench (for threaded chain links)
- Nut driver or flathead screwdriver (for hose clamps)
- Large putty knife
- Heat gun
- Dry wall tapping knife

3.3 Additional Items

- Duct tape (sample labels) and permanent marker
- 5gal/2gal buckets with lids
- Digital camera
- Permanent marker
- Gloves
- Coolers
- Cradle (for holding cores during cross-sectioning)
- Pedestal (for core extrusion)
- PVC plug
- Pre-cut tube measured to the appropriate sample thickness (for core sub-sectioning)
- Paper towels

SECTION 4.0 SEDIMENT SAMPLING PROCEDURE

4.1 Sample Collection

1. Check corer condition prior to each use.
2. Measure water depth.
3. Securely attach the corer to a winch with cable or line of sufficient strength to accommodate the weight of the sampler, any additional weights, and sediment to be sampled.
4. Slowly lower the corer using a winch and A-frame or boom arm through a moon pool or over the side of the vessel. Maintain tension on the corer to keep it vertical.
5. After the corer contacts the sediments on the bottom, relax the tension as needed to allow the corer to penetrate into the sediment.
6. Place tension on the cable/line and slowly retrieve the corer and sediment sample.

7. When corer and sediment sample reach the surface, place a cap on the bottom of the core prior to removing the core from the water, or as it is breaking the surface of the water (as is possible depending on height of deck from water's surface) to avoid losing any sample. Once safely on deck, secure the cap with duct tape.
8. Discard the sample if less than 9 inches of sediment are collected or if there is any sign of sample washout.
9. Set the corer into a bracket on the boat deck to hold the corer in a stable vertical position.
10. Record observations about the suitability of the core including penetration depth, sample depth, presence of any debris, bubbles, coloring, or evidence of agitation due to sample collection. Also, record any evidence that the surface sediment is undisturbed and intact (e.g., any different color or texture and corresponding depth). If the sample is being collected near capped areas, examine for evidence of cap material (i.e., presence of sand/gravel). If cap material is noted, the sample would be rejected and resampled. If the core is collected within a microbead plot, note any visual band of microbeads or spread down the edges, measure any definite band or layer. Take two to three digital photographs of the core.
11. Unthread the core from the corer apparatus.
12. Set the corer into a bracket on the boat deck to hold the corer in a stable vertical position.
13. Drain excess water off the top of the core without disturbing the surface of the sediment. Cap the top of each tube while minimizing head space.
14. Wipe the outside of each tube.
15. While maintaining tubes in a vertical position, record any visual variations in sediment characteristics with depth.
16. Seal the top end with cap.
17. Using a permanent marker, label the outside of each core tube with the sample identification (ID) and core orientation with an up arrow. Also label the top cap with the sample ID.
18. Maintain core in a vertical position while transporting to a processing facility on shore.
19. Decontaminate the corer as needed and discard any excess sample as non-hazardous waste.

5.0 SMU 8 SEDIMENT SAMPLE PROCESSING

This procedure describes how sediment samples will be segmented from each collected sediment core. Samples for chemical analysis to further assess natural recovery in SMU 8 are to be discrete depth sections with no transferring of sediment between subsections. This segmenting is essential to obtain accurate depth profiles and it was tested and used successfully during multiple sampling events. Additionally, visual observations of frozen cores have been tested and used successfully to document the presence of microbead markers at various SMU 8 locations. Contact between sampler gloves and sample must be avoided. During transport, every effort should be made to ensure that each core is not disturbed. Place the core vertically into a cooler for transport. For each sample location, the procedure for processing the tubes of sediment is as follows:

5.1 Procedure for transporting and slicing frozen cores (visual observations)

1. Place the core in a freezer so it can be cut without disturbing the sediment cross section.
2. Once the core has been completely frozen (generally after 24 hours), lay flat into a cradle to prevent the cores from moving. The cores should be frozen to a point where it is difficult to scrape excess ice off the surface of the exposed cross-section following cutting.
3. Using a reciprocating saw, cut the core lengthwise into two cross sections.

4. A heat source may be applied sparingly to melt the ice slightly along the cut surface to allow excess ice to be scraped from the cores using a standard dry wall tapping knife. Following heating and additional scraping, the exposed cross-surfaces of the frozen cores can be visually inspected for varves/layers (annually laminated sediments).
5. The presence and thickness of light brown sediments at the top of the core should be noted and documented (to assess the minimum depth of mixing).
6. Document the starting depth and thicknesses of varves/layers.
7. If core is collected from a microbead plot, document the depth and thickness of microbeads, if present.
8. The depth of any burrowing benthic organisms should be noted, if present.

5.2 Preparation of sediment cores for sub-sampling

Cores should be stored in a cooler (not frozen) until processing for analytical analysis. Prior to subsampling the collected sediment cores, it is necessary to remove the overlying water (as described in the next section, "Sub-sampling: Sample processing"). Additionally, each sediment core is to be photographed and described, with particular detail being paid to the following:

- Evidence of microbeads (if the core is from a microbead plot), including details of whether present as a band or as a smear on the core tube, and depth microbeads are observed.
- Evidence of disturbance to sediment core, particularly due to gas escaping from the sediment during or after collection.
- Physical features, such as presence of varves and light brown sediments in top layers, as practicable.

After the core is photographed and described, record total sediment depth (or top of sediment position) within each tube. Note any settling which may have occurred between the top of sediment in the core tube recorded on the boat and the top of sediment in the core tube recorded prior to beginning sample extrusion.

5.3 Sub-sampling: Sample processing

1. Carefully and slowly siphon any overlying water from each core using a clean, plastic syringe (or equivalent). Note that the siphoning speed can be adjusted by raising or lowering the discharge hose with the slowest speeds experienced when the discharge is just below the water level inside the core tube. Do not elevate the discharge hose above the level of water in the core tube because this may cause the siphon to reverse direction and cause a jet of water to be directed onto the sediment surface. Slight disturbance of the sediment at or near the outside rim of each core is acceptable when siphoning water; however it is essential that the surface sediment in the center of the core remains undisturbed.
2. Remove the bottom cap of the core and insert a PVC plug into the base of the tube to allow the tube and its contents to be placed on a pedestal. Slowly push down the tube on the pedestal forcing the sediment to be pushed up to extract the necessary intervals.
3. While on the pedestal, use a pre-cut piece of tube measured to the appropriate sample thickness (i.e., 4 cm for the 0 to 4 cm and 6 cm for the 4 to 10 cm depth interval). Place the pre-cut tube on top of the core tube, and then pull down to extract the sediment into the pre-cut piece. Next, insert a putty knife at the bottom of the pre-cut piece. After inserting the putty knife, the pre-cut piece should be easily removed with little or no loss of sediment. This method of extraction ensures that the proper sample interval is collected and analyzed.

4. For volatile analysis if needed: place a small amount of sediment from each of the intervals into the appropriate jar (40 mL vial or other appropriate container) with as little headspace as possible. Be cautious not to collect any sediment that was touching the sides of the sample core tube.
5. Place the remaining sample and putty knife into a clean aluminum pan.
6. Remove the center portion of the sample by inserting a clean, small-diameter plastic tube into the sediment. Remove the outer pre-cut tube and wipe clean from the inner portion of the tube the sediment on the perimeter.
7. Transfer the sediment sample to a clean aluminum pan to homogenize the sediment within a particular sampling interval from a single sampling location. Designate one pan for each vertical interval.
8. Homogenize the sediment using plastic dedicated/disposable spoons or nitrile-gloved hands.
9. Place individual subsamples into appropriate jars provided by the laboratory conducting the chemical analyses and label each jar and chain-of-custody. Decontaminate instruments as necessary between samples.
10. Send the jarred samples to the laboratory that day or refrigerate and send to the lab as soon as practical.
11. Waste sediment will be accumulated in containers that will be used to ship the waste to a disposal facility. As a result, these containers must meet both Department of Transportation (DOT) and United States Environmental Protection Agency (USEPA) requirements. Waste containers to be used will be authorized by DOT and meet United Nations (UN) performance-oriented packaging standards for the waste that will be shipped. Only personnel with the required DOT training and who are certified by their employer may select containers for accumulation and shipping of waste from the Honeywell Syracuse sites. Waste storage, transport and disposal efforts will be managed in accordance with USEPA and NYSDEC requirements. Waste containers will be in good condition and stored and labeled properly.

SECTION 6.0 PERSONNEL

The Project Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Project Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Project Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 7.0 REVISIONS/REVIEWS

Doc Number: Rev No.: 0 Date: August 4, 2021

Reviewer: Parsons

What was changed: N/A

S-4 BENTHIC MACROINVERTEBRATE COLLECTION AND PROCESSING FOR TISSUE OR COMMUNITY ANALYSIS

SECTION 1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for benthic macroinvertebrate collection in Onondaga Lake. Benthic invertebrate sampling will be conducted to collect organisms for assessing community composition. Community composition will be assessed using two methods; ponar and multiplates. Sampling with ponars will be conducted in accordance with 2018 NYSDEC standard procedures (Duffy and Garry 2018). Multiplate sampler design will be consistent with NYSDEC; multiplates will be deployed in a modified fashion that is consistent with recent work conducted by NYSDEC detailed in the above referenced SOP, and others across New York State. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the benthic macroinvertebrate sampling. The scope of work including quantities and locations is defined in the Work Plan.

SECTION 2.0 EQUIPMENT LIST

2.1 Sampling with a ponar

- Petite ponar with rope
- US Standard No. 30 mesh (600 µm opening) Nalgene sieve
- Benthic sieve bucket (500 µm mesh)
- 5 gal buckets
- Wash bottle and garden sprayer
- Water quality meter
- Sampling vessel
- Personal flotation device (PFD) to be worn by each person on water and on land within 6 ft. of the lakeshore
- Sample containers (as provided by laboratory)
- Rose bengal dye (as needed)
- Sample labels
- Digital global positioning system (DGPS)
- Resealable plastic bags
- Sample containers
- Tray (for sorting)
- 95 percent ethyl alcohol
- Forceps
- Petri dish
- Nitrile gloves
- Spatula
- Vials

- Alcohol proof marker
- Deionized water
- Wide width tape
- Balance for weighing samples
- Cellular phone
- Digital camera
- Field notebook

2.2 Sampling with multiplates

- Multiplates (shown below in 4.0, in accordance with NYSDEC 2018) 1 ft x 1 ft concrete block (one per location)
- 12 gage electrical wire (or similar thickness plastic coated wiring)
- Labeled buoys (or 2-liter bottles filled with Styrofoam chips)
- 3-inch wide paint scraper
- US Standard No. 30 mesh (600 µm opening) Nalgene sieve
- Benthic sieve bucket
- 95 percent ethyl alcohol

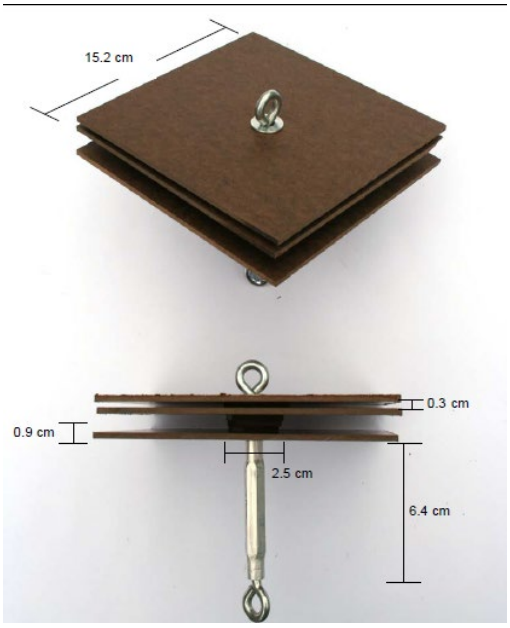


Photo: NYSDEC 2018

SECTION 3.0 PROCEDURES (PONAR)

3.1 Sample Collection

1. Upon arrival at a sampling station, position the boat at desired water depth. Record water depth and location coordinates.
2. Collect and record water quality data at one meter intervals through the water column, and within 0.5 ft. of the bottom (pH, DO, temperature, conductivity) in the field notebook.
3. If collecting for analytical (mercury) analysis, decon the ponar sampler prior to collection of the first sample in accordance with previously-implemented decontamination procedures outlined in S-1.
4. Tie one end of a rope to the ponar and the other to the boat. Before lowering the ponar into the water, with the line taut, remove the safety pin and replace with the pinch pin. As long as the line is taut the pinch pin will stay in place. The petite ponar is now set, and will be lowered into the water, and allowed to free-fall for the last 0.5 m [1.6 ft.] to the bottom with a slack line. The impact with the bottom activates the closing mechanism, and the dredge is then slowly brought to the surface.
5. Retrieve the ponar sampler. Once at the surface, place the petite ponar over a 500 µm mesh sieve pail, check the surface of the sample prior to opening the jaws allowing the contents to drop into the pail. Gently wash the sample with lake water to remove small particles (clays and silts). Transfer the contents remaining in the sieve to a labeled bucket for transfer to the tissue processing team. As practical, record abundances/taxonomic identification. If collecting more than one ponar at the same sample location, be sure to sample from different points on the boat so as not to sample the exact same location twice.
6. Repeat procedure to obtain the necessary replicates (for community analysis[1]) or sample mass (for tissue analysis). If samples are being collected for analytical (tissue) analysis, follow the procedure outline below under Tissue Sample Processing. If samples are being collected for community composition, proceed to the steps below for Community Composition Collection.

3.2 Tissue Sample Processing (if conducted; not planned under current scope)

1. The processing team will pick through each sample and remove macroinvertebrates. Transfer a portion of the sample to a labeled clean tray for picking. Once all macroinvertebrates have been picked, weigh to evaluate is adequate sample mass has been obtained or if additional mass needs to be collected.
2. Place each taxon in a labeled decontaminated Petri dish for enumeration and continue picking until enough biomass is obtained.
3. After enumeration by taxon, place the invertebrates in a resealable plastic bag. If there are sufficient quantities, taxon will be analyzed separately. Place the bag in a jar (if required by the laboratory) and place in a cooler on sufficient quantities of wet ice to fill the cooler for shipment or into a freezer if not shipping immediately.
4. Repeat the procedure as necessary for additional samples/locations as dictated by the work plan.

[1] Two replicates will be processed and sent to a laboratory for identification, while one additional replicate will be collected and stored as archive samples for future use, if necessary.

3.3 Community Composition Collection

1. Place the contents of the sample into a U.S. Standard No. 30 mesh (600 µm) sieve inside a washtub overhanging on the side of the boat. Gently wash the sample with lake water using a small impeller pump to remove small particles (clays and silts). Transfer the contents remaining in the sieve to a labeled wide mouth plastic sample jar (size can vary depending on the amount of material). Jars should not be filled more than half way. Multiple jars should be used as necessary and labeled appropriately (i.e., Jar 1 of 3, 2 of 3). Add 95 percent ethyl alcohol to the shoulder of the jar to preserve. If requested by the identifying laboratory, add rose Bengal dye (wear Nitrile gloves during this operation). Cap tightly and gently invert the sample several times to distribute the solution. Double check the label(s) to make sure that all the required information is recorded. Tape around the lid of the jar.
2. Repeat the procedures at the necessary locations. When sampling is completed, prepare a Chain of Custody for the samples and turn over to the identifying laboratory.
3. Sorting and identification procedures will be carried out by a specialized laboratory in accordance with NYSDEC procedures as detailed in Duffy et. al. 2018.

SECTION 4.0 PROCEDURES (MULTIPLATE)

4.1 Deployment

1. Arrive at location. Record water depth and location coordinates.
2. Collect and record water quality data at one meter intervals through the water column, and within 0.5 ft. of the bottom (pH, DO, temperature, conductivity) in the field notebook.
3. Attach multiplate structures to patio either end of patio block (2 multiplate units per patio block). Connect tops of multiplates with piece of wire. Attach spool of wire to center of connecting wire (to serve as line from unit to buoy).
4. Lower unit slowly through the water column until unit is resting on the lake bottom. Ensure that unit is resting on a flat area (as practical) and not on a significant slope/slant.
5. Allowing for some extra slack in the line, clip wire and attach labeled buoy to line. Leave in water for five (5) weeks to allow for colonization.

4.2 Collection

1. Carefully raise sampler to surface of water. Remove units from patio block and place in bucket of water. Disassemble sampler using pliers and/or screwdrivers as needed.
2. Scrape all organisms and accumulated material from the plates using a 3-inch wide paint scraper into the water in the bucket. The resultant slurry is poured into a U.S. no. 30 standard sieve, the residue rinsed with lake water, and placed in a 4 -ounce glass jar. Jars should not be filled more than half way. Multiple jars should be used as necessary and labeled appropriately (i.e., Jar 1 of 3, 2 of 3). Add 95 percent ethyl alcohol to the shoulder of the jar to preserve. If requested by the identifying laboratory, add rose Bengal dye (wear Nitrile gloves during this operation).
3. Repeat procedure with second multiplate unit, to be archived for later use as necessary.
4. Repeat procedure as necessary for all locations being sampled with multiplates. When sampling is completed, prepare Chain of Custody for the samples and turn over to the identifying laboratory.

5. Sorting and identification will be carried out by a specialized laboratory in accordance with the procedures detailed in Duffy et. al. 2018.

SECTION 5.0 PERSONNEL

Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training. An aquatic biologist with invertebrate experience will oversee these activities.

SECTION 6.0 REFERENCES

Duffy, B. And Garry, R.A. 2018. *Standard Operating Procedure: Biological Monitoring of Surface Waters in New York State*. NYSDEC, Division of Water. March 2019.

SECTION 7.0 REVISIONS/REVIEWS

Doc Number: Rev No.: 0 Date: August 4, 2021

Reviewer: Parsons

What was changed: N/A

S-5 ONONDAGA LAKE MACROPHYTE SURVEY

SECTION 1.0 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for aquatic macrophyte sampling in Onondaga Lake. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct the macrophyte sampling. A crew of three people are needed for the surveys: a boat driver, a record keeper, and an observer who identifies the macrophyte species. These procedures are to be followed, and any substantive modifications to the procedures shall be approved by the Field Sampling Manager.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and marine sampling include: caution deploying and retrieving heavy equipment; stepping in the sight of lines or cables; slips, trips, and falls; and the proper use of PFDs and PPE. Do not overload any vessel and load vessels evenly so they are not prone to capsizing. These safety considerations apply to the vessel and sampling crews whenever working on the water.

SECTION 3.0 EQUIPMENT LIST

- Macrophyte rake
- 5-gal bucket
- Sampling vessel
- PFDs
- GPS system
- 100 m tape measure with weight tied to the end (for measuring water depth)
- Digital camera
- Depth finder
- Secchi disk
- Maps of remediation areas
- Field notebook
- Boat anchor with 10 m of line

SECTION 4.0 PROCEDURES

4.1 Quantitative Macrophyte Survey Methods

1. Upload coordinates for the point transects, as dictated by the work plan into the GPS system.
2. Position the boat on the first point to be sampled using the GPS.

3. When on point, the observer will identify macrophyte species collected on a rake tossed to the bottom. The record keeper will record the species present in the log book. The observer will measure the water depth using a tape measure with a weight at the end.
4. Repeat steps 2 and 3 for each point.

4.2 Qualitative Macrophyte Survey Methods

1. On a mostly sunny day with low wind speeds, proceed to the starting point for the respective remediation area..
2. Slowly drive transects perpendicular to shore between the 20-ft. water depth interval and shore. Spacing between transects and total depth the survey is conducted out to will be dictated by water clarity with the intent that any plants present between transects in the area will be visible. If the field crew deems that water clarity may be impeding the visibility of plants at a certain depth, a secchi disk will be used to assess the water clarity. Based on this assessment, observations may be limited to less than 20 feet in depth. If limited to water depths that do not permit perpendicular transects (i.e., if visibility is less than 3 meters), transects will be driven parallel with the shoreline at 1 meter intervals.
3. Document on the appropriate map for the transect the extent of macrophyte beds observed in the transect (approximate size/extent of the bed, water depth, density of plants). If possible, document dominant species of the bed. Photographs of the beds should be taken as practical.

SECTION 4.0 PERSONNEL

The Field Sampling Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Field Sampling Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks per this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Field Sampling Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 5.0 REVISIONS/REVIEWS

Doc Number: Rev No.: 0 Date: August 4, 2021

Reviewer: Parsons

What was changed: N/A

S-6 GEDDES BROOK, NINEMILE CREEK, LCP OU-1, AND ONONDAGA LAKE WETLAND MONITORING

SECTION 1.0 SCOPE

This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to conduct Wetland Monitoring tasks (quantitative and qualitative vegetation, large trees, wildlife, and erosion monitoring). This SOP will be utilized at Geddes Brook, Ninemile Creek, LCP OU-1, as well as the following areas of Onondaga Lake: Wastebed B/ Harbor Brook Outboard Area, Ninemile Creek Spits, and the In-lake planted areas. The methods for monitoring of the Wastebeds 1-8 Connected Wetlands are addressed in the *Integrated IRM, Mitigation Wetlands, and Remediated Area Hydraulic Control System 100% Design Report Wastebeds 1-8* (O'Brien and Gere Rev. Ed. 2013).

These procedures are to be followed; any substantive modifications to the procedures shall be approved by the Field Team Leader.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each field visit. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water survey include: caution for slips, trips, falls, the proper use of personal flotation devices (PFDs) when monitoring in water and personal protective equipment (PPE). AHAs associated with each task will be reviewed and signed-off on prior to conducting any monitoring activities.

SECTION 3.0 GENERAL EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out any of the monitoring tasks included in this SOP. Equipment needed for a specific monitoring task will be included in each specific monitoring section.

- PFDs
- Waders
- Hard hat (as needed) and safety glasses
- Gloves
- Safety Glasses
- Digital camera
- Field notebook/iPad
- Photographs from pervious sampling events
- Species lists from previous years
- Cellular phone

- Measuring tape
- 6 ft. stakes
- Pin flags
- Throw rake
- Jon Boat (for lake work)
- GPS unit

SECTION 4.0 QUANTITATIVE VEGETATION MONITORING

This section describes procedures for quantitative vegetation monitoring in Geddes Brook, Ninemile Creek, LCP OU-1, and Onondaga Lake.

4.1 Geddes Brook/Ninemile Creek / LCP OU-1

Sampling locations have been previously established and agreed upon by NYSDEC. A GPS unit may be used to aid in locating plots in remote areas.

1. At each vegetation plot stake, use the measuring tape and flags to mark two circular plots – one of 100 sq. ft. and another of 400 sq. ft. The smaller plot is the area where herbaceous vegetation will be identified, and the larger is where all woody vegetation is counted.
2. Before surveying the plot, photographs will be taken of the stake (with the plot number mark visible in the photograph), and of the plot with the flags as visible as possible. Refer to the photographs of the same plot from previous years to verify the orientation which the photographs should be taken.
3. Identify and record vegetation cover type within the plot.
4. If plot is located in water, record estimated water depth within the plot.
5. Identify and record each plant species within the 100-sq. ft. plot, photograph and visually estimate its relative cover within that plot (photographs of each plant species will be taken at different zoom intervals to obtain enough detail to verify the identity of the species after the sampling has been completed, if needed).
6. Once all species have been identified record the estimated overall aerial cover of vegetation within the plot.
7. When the 100-sq. ft. circle has been finished move on to the 400-sq. ft. plot.
8. Identify, count, and record all woody species in the 400-sq. ft. plot.
9. Record if woody species are alive or dead.
10. General site conditions and observations (i.e., wildlife, erosion, etc.) should also be recorded.
11. Once field data is collected, identify the wetland indicator statuses for each species by utilizing https://plants.usda.gov/java/.

4.2 Onondaga Lake

Sampling locations have been previously established and agreed upon by NYSDEC. Each sampling plot will be located with a GPS unit at the time of sampling.

4.2.1 Herbaceous Vegetation Monitoring (50 sq. ft.)

1. At each vegetation plot, use the measuring tape and flags to mark a 50-sq. ft. circle.
2. Before surveying the plot, photographs will be taken of the plot with the flags as visible as possible. Refer to the photographs of the same plot from previous years to verify the orientation which the photographs should be taken.
3. Identify and record vegetation cover type within the plot.
4. If the plot is located in water, record estimated water depth within the plot.
5. Identify and record each plant species within the 50 sq. ft. plot, photograph and visually estimate its relative cover within plot (photographs of each plant species will be taken at different zoom intervals to obtain enough detail to verify the identity of the species after the sampling has been completed, if needed).
6. Once all species have been identified record the estimated overall aerial cover of vegetation within the plot.
7. General site conditions and observations (i.e., wildlife, erosion, etc.) should also be recorded.
8. Note: A throw rake may be used at plots located in deep water (i.e., Deep Floating Aquatic Zone of 4A) and where vegetation is not visible. The rake will be thrown into the plot boundary a minimum of two throws per plot. More throws may be utilized at the discretion of the field team. Density of the vegetation retrieved by the rake will be determined using a 0 to 3 scale. Zero indicates no vegetation was observed and three indicates that the rake was full of vegetation.
9. Once field data is collected, identify the wetland indicator statuses for each species by utilizing https://plants.usda.gov/java/

4.2.2 Woody Vegetation Monitoring (200 sq. ft.)

Plots located in zones zone 6A3 (Restoration Area – A) and zones 8A, 9B1, 9B2 and 30 ft. Planting zone on berms (Outboard and Harbor Brook) will be evaluated for woody species within a 200-sq. ft. circular plot in addition to the 50-sq. ft. herbaceous monitoring plot.

1. At each plot, use the measuring tape and flags to mark a 200-sq. ft. circle.
2. Take photographs of plot and of the plot with the flags as visible as possible (refer to the photographs of the same plot from previous years to verify the orientation which the photographs should be taken).
3. Record the number of each woody plant species within the 200-sq. ft. circle.
4. Once a species is identified, take several photographs at different zoom intervals to obtain enough detail to verify the identity of the species after the sampling has been completed.
5. Record if woody is dead or alive.
6. General site conditions and observations (i.e., wildlife, erosion, etc.) should also be recorded.
7. Note: If woody species are identified in plots outside of the designated zones outlined above, those plots are to follow the same procedures as above.

SECTION 5.0 QUALITATIVE RECONNAISSANCE SURVEYS

Two qualitative reconnaissance surveys will be conducted per year in Geddes Brook, Ninemile Creek, and LCP OU-1 and a minimum of two surveys will be conducted in Onondaga Lake. These surveys include observations of overall vegetation establishment, erosion, and wildlife usage.

5.1 Surveying

1. Each site is walked in its entirety to the extent practical.
2. Wildlife usage will be assessed by recording evidence of reptiles, amphibians, birds and mammals within the restoration area, and the vicinity through standard field observation methods (e.g., visual and audio observation, tracks, scat, etc.). Refer to section H. for further details.
3. Identify and record all plant species that are encountered.
4. Record any invasive plant species encountered (mark approximant locations of site maps when possible).
5. Walk and inspect the banks of Ninemile Creek and the Geddes Brook channel looking for any signs of erosion.
6. Take photographs and record on a site map approximant location of any issues/concerns, erosion, and/or bare areas.

SECTION 6.0 LARGE TREE CONDITION SURVEYS

Large trees will be for surveyed for diameter at the breast height (DBH), estimated total height, and overall condition.

6.1 Surveying

1. Take at least four photos of each tree (the first will be of the numbered tag on the tree, second will be of the entire tree, and the third and fourth photo will be of the leaves/bark of the tree).
2. Record the diameter at DBH. (Geddes Brook and Ninemile Creek only)
3. Record the estimated height (ft.). (Geddes Brook and Ninemile Creek only)
4. Record the overall condition of the tree.
5. Record any other additional comments (i.e., root sprouts, dead, and fruit).
6. Record (field notebook/iPad and/or with the digital camera) any general observations (erosion, wildlife, plants, etc.).
7. Mark up on a site map approximate location of any issues/concerns, erosion, and/or bare areas.

SECTION 7.0 WILDLIFE MONITORING

Wildlife monitoring will take place during routine site visits (i.e., bi-weekly inspections, qualitative and quantitative events, large tree surveys, analytical sampling). In addition to these times, specialized site visits will be conducted during important seasonal wildlife activity peaks, such as during the spring mating season for amphibians and/or during the fall for migratory birds.

1. Record in a field notebook/iPad and take photographs, when possible, of any sightings of wildlife encountered during site visits.
2. Record number of individuals.
3. Record life stage.
4. Record location of observation.
5. Record any evidence of wildlife (i.e., scat, tracks, dens etc.).
6. Trail cameras may be used to document wildlife where appropriate.

7. Use binoculars or spotting scope to identify wildlife from a distance to avoid scaring them.
8. Check under logs, rocks, or any other structures where wildlife may not be visible on the surface.
9. Some visits should be conducted at first or last light to provide the best chance to record the widest range of species.

SECTION 8.0 WETLAND DELINEATIONS

A formal delineation will be completed in Year 5 of monitoring to quantify wetland acreage. Boundaries will be delineated by a qualified wetland scientist using the state and federal criteria for delineating wetlands (NYSDEC 1995, Environmental Laboratory 1987, USACE 2012, USACE 2018, and USDA NRCS 2017). In addition to the procedures outlined in the state and Federal criteria, the following site specific procedures will be followed:

1. Place surveyor ribbons along the wetland/waters boundaries based on observations of vegetation, soils, and hydrologic conditions. Label each wetland flag with a letter identifier of the wetland and number consecutively.
2. Collect plot data on vegetation, soils, and hydrology in plots located along the wetland boundaries. Record plot data on wetland determination forms designed to follow requirements in USACE (2012).
3. Take representative photographs of each plot.
4. Record the coordinates of each numbered flag along the wetland boundary using a GPS unit with sub 2-inch accuracy.

SECTION 9.0 SAMPLING PERSONNEL

The Project Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Project Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Project Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 10.0 REFERENCES

NYSDEC. 1995. *Freshwater Wetlands Delineation Manual.* New York State Department of Environmental Conservation, Albany, NY. Environmental Laboratory, 1987. *Corps of Engineers Wetlands Delineation Manual*. Technical Report Y-87-1, U.S. Army Engineers Waterways Experiment Station, Vicksburg, MS.

O'Brien & Gere, 2012. *Integrated IRM, Mitigation Wetlands, and Remediation Area Hydraulic Control System 100% Design Report Wastebeds 1-8.* Prepared for Honeywell, Morristown, NJ. October 2012. Revised, January 2013.

USACE. 2012. *Regional Supplement to the Corps of Engineers Wetland Delineation Manual: Northcentral and Northeast Region (Version 2.0),* ed. J.S. Wakeley, R.W. Lichvar, C.V. Noble, and J.F. Berkowitz. ERDC/EL TR-12-1. U.S. Army Engineer Research and Development Center, Vicksburg, MS.

USACE. 2018. National Wetland Plant List, version 3.4 http://wetland-plants.usace.army.mil/. U. S. Army Corps of Engineers, Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH.

USDA NRCS. 2017. *Field Indicators of Hydric Soils in the United States,* Version 8.1. L. M. Vasilas, G.W. Hurt, and J. F. Berkowitz (eds.). United States Department of Agriculture, Natural Resources Conservation Service, in cooperation with the National Technical Committee for Hydric Soils.

SECTION 11.0 REVISIONS/REVIEWS

Doc Number: Rev No.: 1 Date: September 27, 2022

Reviewer: Parsons

What was changed: Updated General Equipment List (Section 3.0) to include GPS unit. Added Wetland Delineation (Section 8.0) was added. References (Section 10.0) updated to include NYSDEC 1995, USACE 2012, USACE 2018, and USDA NRCS 2017.

SOP No. 303: Water Sample Collection with Kemmerers/Van Dorns

1. Test method: Water Sample Collection with Kemmerers and/or Van Dorns
2. Applicable matrix or matrices: Water.
3. Detection limit: NA.
4. Scope and application: Drinking, surface and saline waters.
5. Summary of test method:
   Kemmerers and Van Dorns are both used to collect water chemistry samples from discrete depths in lakes, reservoirs, or rivers of sufficient depth. Both devices are similar so they are both included in this single SOP document. The primary difference between the two devices is orientation. A Kemmerer has a vertical orientation and the Van Dorn has a horizontal orientation. Operation of the two devices is essentially identical. The device is opened by attaching the covers to a release mechanism. Then the device is lowered to the depth of interest with an attached rope or cable. At the depth of interest, a weighted messenger is sent down rope or cable to the release mechanism which triggers device closure. The device is then raised to the surface and the sample collected.
6. Definitions: None.
7. Interferences:
   Surface particulates, disturbed bottom.
8. Safety:
   Always use proper boating safety techniques when sampling from boats (see the most current New York State Boater's Safety Guide). Standard field procedures involving moderate lifting should be applied. Keep hands away from the device opening as it may close prematurely and injury could result.
9. Equipment and supplies:
   Collection bottles, appropriate clothing, latex (or nitrile) gloves, cooler, ice, chains of custody, Kemmerer (1-6L) or Van Dorn (6L), filtering equipment (if applicable, field SOP 344).
10. Reagents and standards:
    None. See collection of Winkler Dissolved Oxygen (field SOP 305),Reduced Species (field SOP 306), and/or Mercury Sampling (field SOP 336) if applicable.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage:
    All samples will be stored on ice after collection, kept out of direct sunlight, transported to UFI laboratories in coolers, and be accompanied by the necessary documentation (chains of custody) unless specifically noted.
13. Quality Control:
    Verify bottle labels match sampling location, verify chains of custody are correct, do not allow contact with sediment. Avoid skin contact with water sample during collection. Rinse bottles prior three times to filling, record all information, complete chains of custody, store on ice in a cooler (4°C). Device cleaned before each use with 5% HCl metals grade wash acid.
14. Calibration and standardization: NA.
15. Procedure:
    I. Kemmerers and Van Dorns
        i. attach the covers to the release mechanism via the cover cables or pull on covers until "locked" in place
        ii. rinse the device with water from the surface three times and ensure the sampling port is closed prior to sample collection

iii. lower the device to the depth of interest using the depth increments on the line, verify depth with the boat's depth finder
iv. when at the depth of interest, send the messenger down the line to the release mechanism which triggers device closure [Note: you will feel the line jerk when the device closes]
v. raise to the surface
vi. secure the tubing to the sampling port on the device.
1. For general sample collection
a. verify bottle label matches sampling location (date, station, depth, etc.)
b. rinse bottles and caps three times
c. fill bottles
2. For sample collection that includes mercury analyses, follow field SOP 336
3. For sample collection without introducing outside air, such as the Winkler Dissolved Oxygen and Reduced Species, follow field SOPs 305 and 306 respectively
ii. place samples in a cooler with ice (4°C), keep out of direct sunlight
iii. record information on chains of custody

II. Field Filtering
i. if field filtering is required as specified on the chain of custody, see field SOP 344

III. Churning
i. if the sample requires churning, see field SOP 342

16. Calculations: NA.
17. Method performance: This is an accepted UFI procedure.
18. Pollution prevention: NA.
19. Data assessment and acceptance criteria for quality control measures: NA.
20. Corrective actions for out-of-control or unacceptable data: NA.
21. Contingencies for handling out of control or unacceptable data: NA.
22. Waste management: This procedure generates no hazardous waste.
23. References:

- field SOPs 305, 306, 336, 342, 344

SOP No. 304: Water Sample Collection with a Submersible Pump

1. Test method: Water Sample Collection with a Submersible Pump
2. Applicable matrix or matrices: Water.
3. Detection limit: NA.
4. Scope and application: Drinking, surface and saline waters.
5. Summary of test method:
   The submersible pump is used when a large number of samples need to be collected from discrete depths in a lake or reservoir. The pump with attached conduit (tubing, hose, or MasterFlex) can be used to collect water chemistry samples from discrete depths in a lake, reservoir, or river of sufficient depth. A 12 V marine battery powers the pump.
6. Definitions: None.
7. Interferences:
   Surface particulates, disturbed bottom, disturbed streambed material, cavitation of conduit.
8. Safety:
   Always use proper boating safety techniques when sampling from boats (see the most current New York State Boater's Safety Guide). Electrical connections at the marine battery should be treated with caution. Make sure to properly connect leads (red to positive and black to negative). Only connect pump leads to battery after the pump has been placed in the water. After connection, cover battery and keep out of direct sunlight.
9. Equipment and supplies:
   Collection bottles, appropriate clothing, latex (or nitrile) gloves, cooler, ice, chains of custody, submersible pump with conduit, marine battery, filtering equipment (if applicable, field SOP 344).
10. Reagents and standards:
    None. See collection of Winkler Dissolved Oxygen (field SOP 305) and/or Reduced Species (field SOP 306) if applicable.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage:
    All samples will be stored on ice after collection, kept out of direct sunlight, transported to UFI laboratories in coolers, and be accompanied by the necessary documentation (chains of custody) unless specifically noted.
13. Quality Control:
    Verify bottle labels match sampling location, verify chains of custody are correct, and do not allow contact with sediment. Allow the pump to flush for at least 90 seconds prior to sample collection, rinse all bottles prior to filling, complete chains of custody. If bottom is contacted, raise pump a minimum of 5m off the bottom (if possible) and flush for a minimum of 3 minutes and longer if needed to completely flush particles out of pump and hose. Avoid skin contact with water sample during collection. Rinse bottles three times prior to filling, record all information, complete chains of custody, store on ice in a cooler (4°C). Hosing is cleaned prior to sampling.
14. Calibration and standardization: NA.
15. Procedure:
    I. Submersible Pumps
        i. do not power the pump on in the air as this will cause cavitation and result in sampling problems

ii. place pump at the depth of interest using conduit markings and verify with the boat's depth finder
iii. attach the electrical hookups to the proper terminals on the marine battery
iv. flush the pump for 90 seconds prior to sample collection at each depth before beginning to fill bottles to flush out any old water
    1. For general sample collection
        a. verify bottle label matches sampling location (date, station, depth, etc.)
        b. rinse bottles and caps three times
        c. fill bottles
    2. For sample collection that includes mercury analyses, follow field SOP 336
    3. For sample collection without introducing outside air, such as Winkler Dissolved Oxygen and Reduced Species, follow field SOPs 305 and 306 respectively
    4. For composite samples, follow field SOP 302
v. place samples in a cooler with ice (4°C), keep out of direct sunlight
vi. record information on chains of custody

II. Field Filtering
    i. if field filtering is required as specified on the chain of custody, see field SOP 344

III. Churning
    i. if the sample requires churning, see field SOP 342

16. Calculations: NA.
17. Method performance: This is an accepted standard UFI procedure.
18. Pollution prevention: NA.
19. Data assessment and acceptance criteria for quality control measures: NA.
20. Corrective actions for out-of-control or unacceptable data: NA.
21. Contingencies for handling out of control or unacceptable data: NA.
22. Waste management: This procedure generates no hazardous waste.
23. References:
    - field SOPs 302, 305, 306, 336, 342, 344

SOP No. 306: Reduced Species (tH_2S, CH_4 and Fe^{2+}) Sample Collection

1. Test method: Reduced Species (tH_2S, CH_4 and Fe^{2+}) Sample Collection
2. Applicable matrix or matrices: Water.
3. Detection limit: NA.
4. Scope and application:
   This method is applicable for use with most waters (drinking, surface and saline waters) and waste waters if samples are anoxic (without dissolved oxygen).
5. Summary of test method:
   The UFI reduced species sampled are total hydrogen sulfide (tH_2S), methane (CH_4), and reduced or ferrous iron (Fe^{2+}). Methane and ferrous iron are collected in accordance with the standard protocol for collecting anoxic samples (field SOPs 303, 304) with no preservatives. Two total hydrogen sulfides samples are collected in the field. These are the total hydrogen sulfide to be analyzed in the lab by the titration method (tH_2S_ti) and by the electrode (tH_2S_el). Both are collected as anoxic samples, but the tH_2S_ti requires the addition of reagents zinc acetate and 6N sodium hydroxide (NaOH). 2 ml of zinc acetate is placed into the bottom of a 300 ml tH_2S_ti BOD bottle. The sample is added via small tubing by filling the BOD underneath the zinc acetate. The BOD is filled to the base of the neck (not overflow). 2 ml of 6N sodium hydroxide is then added. tH_2S_el is collected as described for general anoxic samples.
6. Definitions: None.
7. Interferences:
   Allowing air to enter the collection BOD bottle will introduce error to the results. Addition of the reagents in the incorrect order will result in invalid results.
8. Safety:
   Zinc acetate may cause skin irritation. Sodium hydroxide is very dangerous. It will cause severe burns and irritation. If allowed prolonged contact with the eyes, blindness can occur. Handle with care. Avoid contact with skin and eyes. Wear latex gloves and eye protection when using reagents.
9. Equipment and supplies:
   BOD collection bottles, glass stoppers, caps, appropriate clothing, latex (or nitrile) gloves, cooler, ice, chains of custody, collection device, reagent cooler with bottles of zinc acetate solution and 6 N NaOH solution.
10. Reagents and standards: Zinc acetate solution, and 6 N sodium hydroxide for tH_2S_{ti} only
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage:
    Samples should be collected in 300 ml BOD bottles being careful to exclude air bubbles. Stopper carefully to exclude air and cap. All samples will be stored on ice after collection, transported to UFI laboratories in coolers, and be accompanied by the necessary documentation (chains of custody) unless specifically noted.
    a. Methane and Ferrous Iron
       Samples should be collected in 300 ml BOD bottles from the bottom-up, flushing the bottle at least 3 times its volume, and being careful to exclude air bubbles. Stopper carefully to exclude air and cap. **No preservatives are added.**
    b. Total Hydrogen Sulfide-Titration (tH_2S_ti)
       2 ml of zinc acetate are added to the bottom of a 300 ml BOD bottle. Sample is filled under (tubing is slowly raised as bottle fills, but remains under the sample water surface to prevent aeration) the zinc acetate to the base of the neck of the BOD. 2 ml of 6 N

NaOH is added to the bottle neck. Invert to mix. Stopper carefully to exclude air bubbles and mix by inverting bottles several times and then cap.

c. Total Hydrogen Sulfide-Electrode (tH_2S_el)
Samples should be collected in 300 ml BOD bottles from the bottom-up, flushing the bottle at least 3 times its volume, and being careful to exclude air bubbles. Stopper carefully to exclude air and cap. **No preservatives are added.**

13. Quality Control:
Verify bottle labels match sampling location, verify chains of custody are correct, do not allow contact with sediment. Avoid skin contact with water sample during collection. Rinse bottles prior to filling, record all information, complete chains of custody, store on ice in a cooler (4°C). Do not allow air to be introduced to the sample during any part of collection and add reagents in the correct order (if applicable). Check after collection, if bubbles are present in the sample the sample should be discarded and recollected.
14. Calibration and standardization: NA.
15. Procedure:

I. Methane and Ferrous Iron
   i. verify bottle label matches sampling location (date, station, depth, etc…)
   ii. attach small diameter sample tubing to the nozzle and turn the nozzle on so that water flows out at a slow rate.
   iii. insert tubing into bottle
   iv. rinse bottles and caps three times
   v. slowing open sampling port
   vi. fill bottles slowly so that there is minimal turbulence (i.e. no splashing, no swirling, no stray bubbles). This will help ensure the sample remains anoxic.
   vii. allow bottles to flush for three volumes, then cap
   viii. place samples in a cooler with ice (4°C), keep out of direct sunlight
   ix. record information on chains of custody

II. Total Hydrogen Sulfide
   i. Titration
      1. verify bottle label matches sampling location (date, station, depth, etc…)
      2. attach small diameter sample tubing to the nozzle
      3. add 2 ml of zinc acetate to the bottom of the H_2S BOD bottle
      4. insert tubing onto the bottom of the bottle
      5. slowing open sampling port
      6. fill bottles slowly so that there is minimal turbulence (i.e. no splashing, no swirling, no stray bubbles). This will help ensure the sample remains anoxic.
      7. fill to base of bottle neck
      8. add 2ml of azide 6 N NaOH, the bottle should be filled with no headspace
      9. stopper the bottle with care to be sure no air is introduced. Mix the sample by inverting several times. Check for air bubbles; discard the sample and start over if any are seen.
      10. stopper the bottle with care to be sure no air is introduced. Mix the sample by inverting several times. Check for air bubbles; discard the sample and start over if any are seen. A white cloud of precipitate will appear. When this floc has settled to the bottom, mix the sample by turning it upside down several times.
      11. rinse the bottle to remove reagents on the outside of the bottle
      12. add a small amount of water onto the stopper (water seal)

13. place the plastic cap on the BOD
14. place samples in a cooler with ice (4°C), keep out of direct sunlight record information on chains of custody.

III. Total Hydrogen Sulfide

i. Electrode

1. See I. (Methane and Ferrous Iron), i-ix.

16. Calculations: NA.
17. Method performance: This is the standard method of reduced species collection.
18. Pollution prevention: NA.
19. Data assessment and acceptance criteria for quality control measures: NA.
20. Corrective actions for out-of-control or unacceptable data: NA.
21. Contingencies for handling out of control or unacceptable data: NA.
22. Waste management:
    Wastes from this procedure should be collected in an appropriate container and washed down the sink with the tap running upon return to UFI.
23. References:

- 1992. Standard Methods for the Examination of Water and Wastewater 18th Edition. American Public Health Association. American Water Works Association. Water Environment Federation

SOP No. 336: Mercury Sampling

1. Test Method: Mercury Sampling
2. Applicable matrix or matrices: Water.
3. Detection limit: NA.
4. Scope and application: Drinking, surface and saline waters.
5. Summary of test method:
   Mercury (Hg) is a trace metal and during the collection process, the samples are prone to contamination. There are specific procedures for the sampling of mercury. Upon arrival at the sampling station, one person of the two person crew is designated the 'dirty hands' sampler and the other is designated the 'clean hands' sampler. 'Dirty hands' is responsible for: (1) removal of double bagged sample containers from cooler, (2) holding and opening of outer bag, (3) filling out of chains of custody, (3) operation of sampling apparatus (pump, grab sampler, or dipper). 'Clean hands' is responsible for: (1) opening and closing the inner bag, (2) direct handling of the sample container, and (3) the transfer of the sample to the sampling container. Steps should be taken to avoid contamination. Such steps include: (1) avoid contact with precipitation, dust, gasoline or oil (including vapors), or skin, (2) collect samples facing upstream or upwind, and (3) limit exposure to the air.
6. Definitions: None.
7. Interferences:
   Contact with precipitation, dust, gasoline or oil (including vapors), or skin can contaminate samples.
8. Safety:
   Use caution and best judgment if working in streams especially during high flow periods. Use caution if using grab sample techniques from a boat. Always use proper boating safety techniques when sampling from boats (see the most current New York State Boater's Safety Guide).
9. Equipment and supplies:
   Teflon, MasterFlex (6424-82) tubing, or Kemmerer (if collecting from a lake/reservoir), Teflon dipper, double-bagged collection bottles, latex (or nitrile) gloves, appropriate clothing, cooler, ice, chains of custody.
10. Reagents and standards: Mercury-free clean water for blanks, individually portioned 1 ml HCl.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage:
    Samples for methyl-mercury must be field preserved with 1 ml HCl, samples should be labelled and marked on chains of custody. Mercury samples are initially double bagged to prevent contamination. All samples will be stored on ice after collection, transported to UFI laboratories in coolers, and be accompanied by the necessary documentation (field sheets and chains of custody) unless specifically noted. The samples are then placed in another bag and re-iced to be sent priority overnight shipment to contract labs for analysis. (see field SOP 400)
13. Quality Control:
    Verify bottle labels match sampling location, verify chains of custody are correct, rinse bottles prior to filling (unless preserved), always use clean hands-dirty hands sampling techniques at all times, avoid interferences, limit exposure to the air, always double bag (at minimum), record all information, complete chains of custody, store on ice in a cooler (4°C). All equipment must be cleaned prior to use.
14. Calibration and standardization: NA.

15. Procedure:

I. Sampling from submersible pumps

i. 'Dirty hands'

1. put on latex gloves
2. remove double bagged sample from cooler
3. properly label outer bag (or verify label is correct for system, sampling station, date, etc.)
4. open outer bag
5. if preservation is necessary (i.e. methyl-mercury), open bags containing field preservative (HCl) and pour into sample once filled while avoiding contact with bottle
6. reseal outer bag when sample container is filled and back in inner bag

ii. 'Clean hands'

1. put on latex gloves
2. open inner bag
3. verify that label is correct
4. remove and open sample container
5. rinse container 3 times (unless contains preservative)
6. fill container with sample, avoiding contact with hose
7. prevent hose from contacting bottle
8. if preservation is necessary (i.e. methyl-mercury), allow field preservative to be poured into sample, seal and gently invert to mix
9. place back in inner bag and seal
10. reseal outer bag

II. Stream sampling – grab sampling

i. 'Dirty hands'

1. put on latex gloves
2. remove double bagged sample from cooler
3. properly label outer bag (or verify label is correct for system, sampling station, date, etc.)
4. open outer bag
5. if preservation is necessary (i.e. methyl-mercury), open bags containing field preservative (HCl) and pour into sample once filled while avoiding contact with bottle
6. reseal outer bag when sample container is filled and back in inner bag

ii. 'Clean hands'

1. put on latex gloves
2. open inner bag
3. verify that label is correct
4. remove and open sample container
5. rinse container 3 times (unless contains preservative)
6. wade to center of channel (if possible) from downstream and walk upstream to sampling location
7. fill container with sample by dipping the container into the creek, completely submerge container when filling
8. if preservation is necessary (i.e. methyl-mercury), allow field preservative to be poured into sample, seal and gently invert to mix
9. place back in inner bag and seal
10. reseal outer bag

III. Stream sampling – dipper
   i. 'Dirty hands'
      1. put on latex gloves
      2. remove double bagged sample from cooler
      3. properly label outer bag (or verify label is correct for system, sampling station, date, etc.)
      4. open outer bag
      5. allow 'clean hands' to take container
      6. have 'clean hands' tuck inner bag into outer bag
      7. store outer bag
      8. rinse dipper in creek
      9. fill dipper from center of flow
      10. pour sample into container
      11. if preservation is necessary (i.e. methyl-mercury), open bags containing field preservative (HCl) and pour into sample once filled while avoiding contact with bottle
      12. reseal outer bag when sample container is filled and back in inner bag
   ii. 'Clean hands'
      1. put on latex gloves
      2. open inner bag
      3. verify that label is correct
      4. remove and open sample container
      5. rinse container 3 times (unless contains preservative)
      6. fill container with sample from dipper
      7. if preservation is necessary (i.e. methyl-mercury), allow field preservative to be poured into sample, seal and gently invert to mix
      8. place back in inner bag and seal
      9. reseal outer bag

IV. Sampling from Kemmerer
   i. 'Dirty hands'
      1. Put on latex gloves
      2. Remove double bagged sample from cooler
      3. Properly label outer bag (or verify label is correct for system, sampling station, date, etc.)
      4. Open outer bag
      5. Hold Kemmerer and transfer water into sample container.
      6. if preservation is necessary (i.e. methyl-mercury), open bags containing field preservative (HCl) and pour into sample once filled while avoiding contact with bottle
      7. Reseal outer bag when sample container is filled and back in inner bag
   ii. 'Clean hands'
      1. Put on latex gloves
      2. Open inner bag
      3. Verify that label is correct
      4. Remove and open sample container
      5. Rinse container 3 times (unless contains preservative)
      6. Allow container to be filled from Kemmerer
      7. if preservation is necessary (i.e. methyl-mercury), allow field preservative to be poured into sample, seal and gently invert to mix

8. Place back in inner bag and seal
9. Reseal outer bag

V. Zooplankton Sampling

i. 'Dirty hands'

1. Put on latex gloves
2. Remove double bagged sample from cooler
3. Properly label outer bag (or verify label is correct for system, sampling station, date, etc.)
4. Open outer bag and let other person take out sampling container
5. Follow field SOP 310 to complete tow
6. Transfer contents of cup to the bottle
7. Repeat tow at least 3 times
8. Reseal outer bag when sample container is filled and placed back into bags

ii. 'Clean hands'

1. Put on latex gloves
2. Open inner bag and hold onto sample container until other person has completed the tow
3. Open container and let container be filled from cup (a funnel may be used to aid in this process as long as it has been rinsed with mercury-free water and does not contact the mouth of the sample container)
4. Replace the lid between tows
5. After final tow and collection, seal container and place into inner bag. **No preservatives are necessary.** Seal this bag and place in outer bag

16. Calculations: None.
17. Method performance: Accepted method for mercury sampling.
18. Pollution prevention: This procedure has no discernible negative impact on the environment.
19. Data assessment and acceptance criteria for quality control measures:
    Assessment of results is done at UFI facilities (post collection). Acceptance criteria for quality control include consideration of field notation concerning interferences and presence of data points outside parameter detection range values.
20. Corrective actions for out-of-control or unacceptable data: See of contract labs' specifications.
21. Contingencies for handling out of control or unacceptable data:
    See of contract labs' specifications.
22. Waste management: None.
23. References:

- 1992. Standard Methods for the Examination of Water and Wastewater 18th Edition. American Public Health Association. American Water Works Association. Water Environment Federation
- EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (July, 1996), EPA Method 1669 – www.brooksrand.com/FileLib/1669.pdf
- Brooks Rand Laboratories, attn: Misty Kennard-Mayer, 3958 6th Avenue NW, Seattle, WA 98107, www.brooksrand.com
- Field SOPs 303, 304, 310, 400

SOP No. 401: Collection of Equipment Blanks for Mercury

1. Test method: Collection of Equipment Blanks for Mercury
2. Applicable matrix or matrices: Blank water.
3. Detection limit: NA.
4. Scope and application:
   Blank water chemistry samples collected by UFI sent to contract laboratories to confirm validity of measurements.
5. Summary of test method:
   Mercury free clean water is passed through the sampling equipment to determine the effect the sampling equipment has on mercury content of the clean water. This procedure is used to determine if the sampling equipment is contaminating samples collected in the field.
6. Definitions: None.
7. Interferences:
   Contamination of samples during collection, not adhering to clean hands/dirty hands procedures.
8. Safety:
   Standard field procedures involving moderate lifting should be applied. Use care when rinsing the equipment with the metals grade 5% HCl, and always wear nitrile gloves and splash goggles. Take care if water is spilled on the floor when rinsing (slippery surface).
9. Equipment and supplies:
   Nitrile gloves, 5 gallon wash bucket, sample collection equipment (e.g. Masterflex mercury sampling tubing and pump or Kemmerer), 20L UFI DI water, 25-30 L mercury free water (from contract lab), 10L of 5% HCl metals grade wash acid, battery to power pump if used Masterflex, mercury sample bottles, cooler, packing materials, labels, and chain of custody.
10. Reagents and standards: None.
11. Reference Solution: None
12. Sample collection, preservation, shipment and storage:
    All samples will be stored on ice after collection, and be accompanied by the necessary documentation (chain of custody) unless specifically noted.
13. Quality Control:
    Verify bottle labels match sample types, use clean hands/dirty hands sampling procedure for mercury (field SOP 336), verify chain of custody is correct, record all information, complete chains of custody, and store on ice in a cooler (4°C).
14. Calibration and standardization: NA.
15. Procedure:
    I. Equipment Blank Collection: Collecting the Field Blank
       a. arrange sample bottles on counter
       b. arrange all containers of clean water for easy access
       c. collect a field blank (FB) from a container of clean water as normal (field SOP 336).
       d. label the FB and place in the cooler
       e. the label should contain:
          i. the date and time
          ii. analyses required: total mercury (1631E LL Hg), dissolved mercury (1631E LL Diss Hg), and methyl mercury (1630 meHg).
          iii. ID number
    II. Collecting Equipment Blank with Masterflex

a. Collecting the Bucket Blank (EB)
    i. place pump bin near sink with wash bucket next to the bin
    ii. rinse the bucket 3 times with a generous amount of wash acid
    iii. discard each rinse to the sink with running tap water
    iv. fill the bucket with ~ 3-4 gallons of wash acid
    v. place the pump and tube ends in the wash acid
    vi. power the pump and cycle wash acid through the pump and tubing for 5 minutes **[make sure tube ends are secure in bucket to prevent acid spills]**
    vii. power off pump
    viii. place ends into sink and discard acid to sink by powering the pump [do not pump the bucket dry]
    ix. when only 2-3 inches of acid are remaining, power off pump
    x. discard acid into sink
    xi. rinse bucket with UFI DIW
    xii. fill bucket with UFI DIW
    xiii. power the pump on and pump DIW out of bucket [do not pump the bucket dry]
    xiv. repeat xii. to xii, then xiv.
    xv. power off pump and remove from bucket, you will need a third person to hold the pump so that it does not contact anything and become contaminated
    xvi. rinse bucket 3 times (1 L each rinse) with mercury free water and discard the rinse
    xvii. add 4 L of mercury free water to the bucket
    xviii. collect a sample from the bucket (EB) using normal clean hands/dirty hands procedures
    xix. label the bucket blank (as previously described) and place in cooler
b. Collecting the Equipment Blank (EB2)
    i. rinse pump with mercury free water by pouring 1 L of mercury free water over the pump over the sink
    ii. add mercury free water fill bucket
    iii. place pump in bucket
    iv. secure tube end in the sink so that do not contact the sink surface
    v. power on pump
    vi. pump ~ 3-4 gallons (16-20 L) of mercury free water through the pump to simulate 3 flushes (add more mercury free water to bucket if running low)
    vii. fill the equipment blank (EB2) with water coming out of the pump tubing
    viii. label the equipment blank (as previously described) and place in cooler

III. Collecting Equipment Blank with Kemmerer (EB)
a. ensure Kemmerer has been cleaned after use and prior to equipment blank
b. three people are necessary to complete equipment blank, and all should wear gloves
    i. Person 1
        1) Hold Kemmerer line taut above bucket throughout process
    ii. Person 2 ‘Dirty Hands’
        1) Open top of Kemmerer (without opening the bottom cover) and pour 1 L of mercury-free water into Kemmerer, make sure the spigot is closed.
        2) Open the spigot and let the water run through the Kemmerer into the bucket
        3) Close the spigot and as before, pour 1 L of mercury-free water into the Kemmerer
        4) Open the outer bag for ‘clean hands’ person
        5) Open the spigot slowly in order to rinse the sample container 3 times

6) Open the spigot fully to fill the container
7) If preservative is necessary (i.e. methyl-mercury), pour the field preservative (1 ml HCl aliquot) into the container without touching the container
8) Seal outer bag once the container has been sealed, bagged, and placed in the outer bag.

iii. Person 3 'Clean Hands'

1) Take out the container from the inner bag, and place the inner bag into the outer bag
2) Without touching anything (i.e. Kemmerer, bucket, self, etc.), allow the container to fill slightly and rinse three times
3) After rinsed, allow container to be filled
4) If preservative is necessary, allow HCl to be poured into the sample. Cap the sample, and gently invert to mix
5) Place sealed container in inner bag. Seal inner bag and place inside outer bag

IV. Sample Preparation and Shipment

a. follow field SOP 400

16. Calculations: NA.
17. Method performance: This is an accepted UFI procedure.
18. Pollution prevention: NA.
19. Data assessment and acceptance criteria for quality control measures: NA.
20. Corrective actions for out-of-control or unacceptable data: NA.
21. Contingencies for handling out of control or unacceptable data: NA.
22. Waste management: This procedure generates no hazardous waste.
23. References:

- UFI field SOPs 300-304 and 336, 400

SOP No. 413: Cleaning Water Collection Equipment

1. Test Method: Cleaning water collection equipment for trace metal sampling programs
2. Applicable matrix or matrices: Salt and fresh surface waters
3. Detection limit: None.
4. Scope and application: Provide proper maintenance for Kemmerer and/or submersible pump used for quantifying trace metals.
5. Summary of test method:
   Trace metals, such as mercury (Hg), can be found in small concentrations nearly everywhere, including in the air and water supplies. While cleaning sample collection equipment is essential for any water sampling program, it is especially critical when testing for trace metals as relevant concentrations can be on the scale of ng/L or parts per trillion. Proper cleaning techniques and methods reduce the risk of contaminating samples.
6. Definitions: None.
7. Interferences: None.
8. Safety:
   Keep work area clean and clutter free. Wear eye protection, long sleeves, pants, and an apron when handling acid and acid wash. Wear nitrile gloves.
9. Equipment and supplies:
   Water collection equipment (Kemmerer or submersible pump), 5% HCl metal-grade acid wash, mercury free water, tubing
10. Reagents and standards: Mercury free water, 5% HCl metal-grade acid wash
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage: None.
13. Quality Control: Equipment blanks are periodically completed to evaluate level of contamination present (typically prior to Onondaga Nitrate Addition project in May, mid-season in August, and final sampling event in November).
14. Calibration and standardization: None.
15. Procedure:
    I. Equipment used to collect water samples for trace metal analysis should be washed upon return to UFI, or as soon as possible, to ensure the equipment is clean and dry prior to the next sampling event.
    II. Personnel should initial, date, and time (24-hour format) the cleaning log located next to the utility sink upon completion.
    III. Kemmerer
        i. Hang Kemmerer above utility sink
        ii. Open Kemmerer so all water remaining from sample collection drains
        iii. If a tube is attached to the drain valve, remove it
        iv. Close the Kemmerer and add approximately 0.6 L (approximately 4 inches) of 5% HCl metal-grade acid wash. Take down to gently invert and swish wash through entire bottle.
        v. Hang Kemmerer back above sink and turn on tap water. Open Kemmerer so acid was travels through drain valve.
        vi. Let acid wash drain completely then lift top of Kemmerer so any remaining acid wash escapes.
        vii. Close the drain valve and turn off tap water.
        viii. Using mercury free water, rinse the outside of the Kemmerer and fill it.

ix. Open the drain valve and let drain completely, repeat the previous step 4 additional times.
x. Upon completion of 5 total rinses, place Kemmerer into a new, clean plastic bag with the drain valve open and top/bottom caps slightly ajar. Close the bag as much as possible with only a small portion of the rod poking out. Put the bagged Kemmerer into the carrying case.
xi. Wash the tubing that was removed from the drain valve by submerging it in a small basin of acid wash.
xii. Rinse the tubing using mercury free water 5 times, ensuring both the inside and outside have been rinsed.
xiii. Discard acid wash bath down drain with running tap water.
xiv. Put washed tubing in a plastic bag, seal. Place inside open compartment inside carrying case.
xv. Bring case, clean Kemmerer, and clean hose inside office and leave slightly ajar so the case lining dries. Close once dry.

IV. Submersible Pump
i. Place pump housing and outflow nozzles in a clean 5-gallon bucket.
ii. Add approximately 6 inches of 5% metal-grade HCl acid wash to the bucket.
iii. Turn on the pump and allow the rinse to circulate through the MasterFlex tubing for 5 minutes. Ensure nozzles are secure and there are no leaks.
iv. Turn on tap water in utility sink and discard the acid wash.
v. Turn off the pump and tap water.
vi. Rinse the bucket with mercury free water 3 times then fill with 4.5-5 gallons of mercury free water.
vii. Place outflows in utility sink and pump water to the sink until 6 inches of rinse water remains in bucket, do not pump dry.

16. Calculations: None.
17. Method performance: This procedure is in accordance with the accepted manufacturer methods.
18. Pollution prevention: This procedure has no discernible negative impact on the environment. All acid can be discarded down the drain with running tap water.
19. Data assessment and acceptance criteria for quality control measures: None.
20. Corrective actions for out-of-control or unacceptable data: None.
21. Contingencies for handling out of control or unacceptable data: None.
22. Waste management: All acid can be discarded down the drain with running tap water.
23. References:
    - Field SOPs 303, 304, 336

SOP No. 310: Zooplankton Sample Collection

1. Test method: Zooplankton Sample Collection.
2. Applicable matrix or matrices: Water.
3. Detection limit: NA.
4. Scope and application: Collection and preservation of zooplankton samples.
5. Summary of test method:
   A sampling net (diameter of 30 cm, length with cup 1 m, and a mesh size of 64 µm) is slowly lowered to a depth (below thermocline or full water column), then raised at a rate of 1.0 m/s to the surface. Zooplankton are trapped in the collection cup during the upwards profile of the net. The contents of the collection cup are retrieved in a sample bottle then preserved in 70 % ethyl alcohol for later identification at UFI.
6. Definitions: None.
7. Interferences:
   Improper lowering technique causing the net to invert or become tangled. High concentrations of filamentous algae (i.e. during large blooms) can clog the net and make zooplankton sample retrieval difficult. Improper rinsing of the net during collection. Failure to add Alka Seltzer after collection and failure to preserve with ethyl alcohol (95 % diluted to ~ 70 % upon addition to sample) upon return to UFI will cause problems during sample processing. High flows in a river system can sweep the net downstream (horizontally) instead of the desired vertical haul, this causes processing/analysis problems.
8. Safety:
   Always use proper boating safety techniques when sampling from boats (see the most current New York State Boater's Safety Guide). Standard field procedures involving light to moderate lifting should be applied. Wear gloves during retrieval and deployment.
9. Equipment and supplies:
   Zooplankton net (Teflon net if Hg sample collection, field SOP 336), collection cup, rope, squeeze bottle(s) for rinse, DI water, appropriate clothing, field sheets Alka Seltzer tablets, and 95% ethanol.
10. Reagents and standards: 95% ethanol for preservation.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage:
    No preservatives for samples being tested for mercury (field SOP 336). Place 1/4 of an Alka-Seltzer tablet in sample bottle after collection and preserve with 95 % ethanol (to ~ 70 % final concentration). Store samples on ice after collection and transfer to UFI biology lab staff.
13. Quality Control:
    Prior to sampling check the net and collection screen are in good condition (clean and free of tears). Slowly lower the net to avoid tangling or net inversion. Rinse the residual accumulation on the net to retrieve all zooplankton. Add Alka Seltzer to relax zooplankton which aides in identification. Upon return to UFI preserve samples properly. Document field sheets properly. Net rinsed prior to collection.
14. Calibration and standardization: NA.
15. Procedure:
    I. Net maintenance
        i. Remove net and rinse with lake/reservoir water two or three times
        ii. assemble zooplankton net by attaching net and sample collection cup.

iii. record the initial counter value on net's flow meter (if available) on the zooplankton field sheets (along with other requested information on sheets).

II. Tow

a. For a full water column tow:
   i. slowly lower zooplankton net to within 1 meter of the bottom, track the drop using the depth finder.
   ii. pull the net back up to the surface using a steady and consistent speed (0.5 m/s)
   iii. once net has broken the water surface, record the final counter value (if applicable) from the net's flow meter on the zooplankton field sheet
   iv. the net should be immersed in the water up to the level of the black non-mesh panel. Make sure that no water enters the net from the top. Lift the net up to wash any zooplankton clinging to the sides of the net down to the cup. Repeat two times
   v. once the net is rinsed, the collection bucket can be tapped and swirled to further reduce the water volume to approximately ¼ of the bucket volume
   vi. unscrew the collection bucket and pour the contents into a 250 ml sample bottle – rinse down bucket with spray bottle and drain into sample bottle
   vii. If sample volume is greater than 125 mL, the sample is returned to the collection bucket and reduced in volume to less than 125 mL

b. For a thermocline tow:
   i. follow instruction steps as above, but lower the net to one meter below the thermocline not one meter off the bottom

c. rinse the collection bucket with DI water and store with net.

III. Preservation

a. General
   i. For samples equal to or less than 125 mL, fill remainder of bottle (to the top) with 95 % ethanol taking care to not overflow the bottle
   ii. add 1/4 Alka Seltzer tablet to the sample bottle to narcotize the zooplankton [Note: the Alka Seltzer addition is very important as it relaxes the zooplankton prior to euthanizing them. The relaxation of the zooplankton aides in the processing and identification of the zooplankton later on].
   iii. preserve samples upon return to UFI by filling the sample bottle with 95 % ethanol

b. Mercury
   i. No field preservation is necessary.

16. Calculations: NA.
17. Method performance: This is the standard method for zooplankton collection.
18. Pollution prevention: NA.
19. Data assessment and acceptance criteria for quality control measures: NA.
20. Corrective actions for out-of-control or unacceptable data: NA.
21. Contingencies for handling out of control or unacceptable data: NA.
22. Waste management: This procedure generates no hazardous waste.
23. References:

- 1957. Edmondson, W.T. Freshwater Biology. 2nd Ed. Wiley InterScience
- 1992. Standard Methods for the Examination of Water and Wastewater 18th Edition. American Public Health Association. American Water Works Association. Water Environment Federation.
- 1995. Hebert, P.D.N. The Daphnia of North America: An illustrated fauna, version 1.CD-ROM AuthorWare.

- field SOP 336

SOP No. 336: Mercury Sampling

1. Test Method: Mercury Sampling
2. Applicable matrix or matrices: Water.
3. Detection limit: NA.
4. Scope and application: Drinking, surface and saline waters.
5. Summary of test method:
   Mercury (Hg) is a trace metal and during the collection process, the samples are prone to contamination. There are specific procedures for the sampling of mercury. Upon arrival at the sampling station, one person of the two person crew is designated the 'dirty hands' sampler and the other is designated the 'clean hands' sampler. 'Dirty hands' is responsible for: (1) removal of double bagged sample containers from cooler, (2) holding and opening of outer bag, (3) filling out of chains of custody, (3) operation of sampling apparatus (pump, grab sampler, or dipper). 'Clean hands' is responsible for: (1) opening and closing the inner bag, (2) direct handling of the sample container, and (3) the transfer of the sample to the sampling container. Steps should be taken to avoid contamination. Such steps include: (1) avoid contact with precipitation, dust, gasoline or oil (including vapors), or skin, (2) collect samples facing upstream or upwind, and (3) limit exposure to the air.
6. Definitions: None.
7. Interferences:
   Contact with precipitation, dust, gasoline or oil (including vapors), or skin can contaminate samples.
8. Safety:
   Use caution and best judgment if working in streams especially during high flow periods. Use caution if using grab sample techniques from a boat. Always use proper boating safety techniques when sampling from boats (see the most current New York State Boater's Safety Guide).
9. Equipment and supplies:
   Teflon, MasterFlex (6424-82) tubing, or Kemmerer (if collecting from a lake/reservoir), Teflon dipper, double-bagged collection bottles, latex (or nitrile) gloves, appropriate clothing, cooler, ice, chains of custody.
10. Reagents and standards: Mercury-free clean water for blanks, individually portioned 1 ml HCl.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage:
    Samples for methyl-mercury must be field preserved with 1 ml HCl, samples should be labelled and marked on chains of custody. Mercury samples are initially double bagged to prevent contamination. All samples will be stored on ice after collection, transported to UFI laboratories in coolers, and be accompanied by the necessary documentation (field sheets and chains of custody) unless specifically noted. The samples are then placed in another bag and re-iced to be sent priority overnight shipment to contract labs for analysis. (see field SOP 400)
13. Quality Control:
    Verify bottle labels match sampling location, verify chains of custody are correct, rinse bottles prior to filling (unless preserved), always use clean hands-dirty hands sampling techniques at all times, avoid interferences, limit exposure to the air, always double bag (at minimum), record all information, complete chains of custody, store on ice in a cooler (4°C). All equipment must be cleaned prior to use.
14. Calibration and standardization: NA.

15. Procedure:

I. Sampling from submersible pumps

i. 'Dirty hands'

1. put on latex gloves
2. remove double bagged sample from cooler
3. properly label outer bag (or verify label is correct for system, sampling station, date, etc.)
4. open outer bag
5. if preservation is necessary (i.e. methyl-mercury), open bags containing field preservative (HCl) and pour into sample once filled while avoiding contact with bottle
6. reseal outer bag when sample container is filled and back in inner bag

ii. 'Clean hands'

1. put on latex gloves
2. open inner bag
3. verify that label is correct
4. remove and open sample container
5. rinse container 3 times (unless contains preservative)
6. fill container with sample, avoiding contact with hose
7. prevent hose from contacting bottle
8. if preservation is necessary (i.e. methyl-mercury), allow field preservative to be poured into sample, seal and gently invert to mix
9. place back in inner bag and seal
10. reseal outer bag

II. Stream sampling – grab sampling

i. 'Dirty hands'

1. put on latex gloves
2. remove double bagged sample from cooler
3. properly label outer bag (or verify label is correct for system, sampling station, date, etc.)
4. open outer bag
5. if preservation is necessary (i.e. methyl-mercury), open bags containing field preservative (HCl) and pour into sample once filled while avoiding contact with bottle
6. reseal outer bag when sample container is filled and back in inner bag

ii. 'Clean hands'

1. put on latex gloves
2. open inner bag
3. verify that label is correct
4. remove and open sample container
5. rinse container 3 times (unless contains preservative)
6. wade to center of channel (if possible) from downstream and walk upstream to sampling location
7. fill container with sample by dipping the container into the creek, completely submerge container when filling
8. if preservation is necessary (i.e. methyl-mercury), allow field preservative to be poured into sample, seal and gently invert to mix
9. place back in inner bag and seal
10. reseal outer bag

III. Stream sampling – dipper
   i. 'Dirty hands'
      1. put on latex gloves
      2. remove double bagged sample from cooler
      3. properly label outer bag (or verify label is correct for system, sampling station, date, etc.)
      4. open outer bag
      5. allow 'clean hands' to take container
      6. have 'clean hands' tuck inner bag into outer bag
      7. store outer bag
      8. rinse dipper in creek
      9. fill dipper from center of flow
      10. pour sample into container
      11. if preservation is necessary (i.e. methyl-mercury), open bags containing field preservative (HCl) and pour into sample once filled while avoiding contact with bottle
      12. reseal outer bag when sample container is filled and back in inner bag
   ii. 'Clean hands'
      1. put on latex gloves
      2. open inner bag
      3. verify that label is correct
      4. remove and open sample container
      5. rinse container 3 times (unless contains preservative)
      6. fill container with sample from dipper
      7. if preservation is necessary (i.e. methyl-mercury), allow field preservative to be poured into sample, seal and gently invert to mix
      8. place back in inner bag and seal
      9. reseal outer bag

IV. Sampling from Kemmerer
   i. 'Dirty hands'
      1. Put on latex gloves
      2. Remove double bagged sample from cooler
      3. Properly label outer bag (or verify label is correct for system, sampling station, date, etc.)
      4. Open outer bag
      5. Hold Kemmerer and transfer water into sample container.
      6. if preservation is necessary (i.e. methyl-mercury), open bags containing field preservative (HCl) and pour into sample once filled while avoiding contact with bottle
      7. Reseal outer bag when sample container is filled and back in inner bag
   ii. 'Clean hands'
      1. Put on latex gloves
      2. Open inner bag
      3. Verify that label is correct
      4. Remove and open sample container
      5. Rinse container 3 times (unless contains preservative)
      6. Allow container to be filled from Kemmerer
      7. if preservation is necessary (i.e. methyl-mercury), allow field preservative to be poured into sample, seal and gently invert to mix

8. Place back in inner bag and seal
9. Reseal outer bag

V. Zooplankton Sampling

i. 'Dirty hands'

1. Put on latex gloves
2. Remove double bagged sample from cooler
3. Properly label outer bag (or verify label is correct for system, sampling station, date, etc.)
4. Open outer bag and let other person take out sampling container
5. Follow field SOP 310 to complete tow
6. Transfer contents of cup to the bottle
7. Repeat tow at least 3 times
8. Reseal outer bag when sample container is filled and placed back into bags

ii. 'Clean hands'

1. Put on latex gloves
2. Open inner bag and hold onto sample container until other person has completed the tow
3. Open container and let container be filled from cup (a funnel may be used to aid in this process as long as it has been rinsed with mercury-free water and does not contact the mouth of the sample container)
4. Replace the lid between tows
5. After final tow and collection, seal container and place into inner bag. **No preservatives are necessary.** Seal this bag and place in outer bag

16. Calculations: None.
17. Method performance: Accepted method for mercury sampling.
18. Pollution prevention: This procedure has no discernible negative impact on the environment.
19. Data assessment and acceptance criteria for quality control measures:
    Assessment of results is done at UFI facilities (post collection). Acceptance criteria for quality control include consideration of field notation concerning interferences and presence of data points outside parameter detection range values.
20. Corrective actions for out-of-control or unacceptable data: See of contract labs' specifications.
21. Contingencies for handling out of control or unacceptable data:
    See of contract labs' specifications.
22. Waste management: None.
23. References:

- 1992. Standard Methods for the Examination of Water and Wastewater 18th Edition. American Public Health Association. American Water Works Association. Water Environment Federation
- EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (July, 1996), EPA Method 1669 – www.brooksrand.com/FileLib/1669.pdf
- Brooks Rand Laboratories, attn: Misty Kennard-Mayer, 3958 6th Avenue NW, Seattle, WA 98107, www.brooksrand.com
- Field SOPs 303, 304, 310, 400

***SOP No. 330:* In-Situ Nitrate/Optical Frame**

1. Test Method: In-Situ Nitrate/Optical Frame
2. Applicable matrix or matrices: Salt and fresh surface waters
3. Detection limit: see Table below
   Table 1. Detection limits for Nitrate/Optical Frame Parameters

Parameter	Manufacturer	Model	Range of Detection	Resolution
Nitrate, NO_3^- (µMol)*	Satlantic Inc.	ISUS0095 or SUNA	0.5 - 200 µM[1]	**+/- 2 µM**
Bisulfide, HS^- (µMol)	Satlantic Inc.	ISUS0095 or SUNA	na[2]	**+/- 2 µM**
Temperature, T (°C)	SeaBird Elec, Inc.	SBE 37-SI MicroCAT	-5 – 35 °C	**0.0001 °C**
Specific Conductance, SC (mS/cm)	SeaBird Elec, Inc.	SBE 37-SI MicroCAT	0 – 70 mS/cm	**0.0001 mS/cm**
Pressure (depth) (m)	SeaBird Elec, Inc.	SBE 37-SI MicroCAT	0 - 100m	**0.002 % of range**
Altitude, ALT (m)	Teledyne Benthos	PSA-916	1000 m	**1 - 2.5 cm**
Transmissometery, c_{660} (m^{-1})	WET Labs	C-Star	~ 0.003 to 138.15 1/m	**see WET Labs c_{660} sop # 323**
Optical Backscattering, OBS (NTU)	WET Labs	Eco Triplet-BB2 FL	0 – 25 NTU	**0.004 NTU**
Optical Backscattering, OBS (NTU)	WET Labs	Eco Triplet-BB2 FL	0 – 1000 NTU	**0.25 NTU**
Chlorophyll Fluorescence, FL (µg/L)	WET Labs	Eco Triplet-BB2 FL	0.01 – 50 µg/L	**0.02 µg/L**
Scalar PAR Sensor, PAR ($\mu E/m^2/s$)	**Biospherical Instruments**	**QSP-2150**	**400 – 700 nm (spectral)**	**> +/- 10 % quantum response**

* ISUS or SUNA
1 200 µM is the standard working range, however, the data can be reprocessed for concentrations above this value
2 range of detection unknown as HS- analysis is supplemental and requires data reprocessing, assumed the same as NO_3^-

4. Scope and application:
   In situ spectrophotometric measurement of NO_3^- and HS^- of drinking, surface, and saline waters and associated metrics and drivers of water quality, including: thermal stratification (T), salinity (SC) light attenuation (c660), turbidity (OBS at low and high range), solar radiation (PAR) and chlorophyll content (fluorescence).
5. Summary of test method:
   The In-Situ Nitrate/Optical Frame is a combination of many instruments (see Table 1). The overall purpose of this instrument is to detect NO_3^- and NO_3^- and HS^- patterns in specific study systems. *The Satlantic ISUS or SUNA are the specific instruments used to detect NO_3^- and HS^-.* The SUNA (Submersible ultraviolet nitrate analyzer) is currently the preferred instrument, and the ISUS (In-Situ Ultraviolet Spectroradiometer) is not in use. Inorganic chemical species absorb different wavelengths of Ultra-Violet light (200-400 nm). By illuminating a sample of water with UV light onto a spectrophotometer, the absorption spectra can be measured. The known UV absorption spectra of NO_3^- is known by the instruments processing computer. The

instrument uses the absorptive characteristics of NO_3^- to provide in situ measurements of NO_3^- concentration. HS^- can also be detected with a data reprocessing technique from the archived absorption spectra. The other parameters measured along with NO_3^- and HS^- will help to define the mechanisms for NO_3^- and HS^- distribution in the study system. All supplemental parameters are measured simultaneously and integrated with NO_3^- in the instrument's data logger. In addition, the parameters are paired with depth to resolve vertical patterns. To operate, the integrated instrument package is connected to a laptop computer via an underwater profiling cable through a deck box and USB connection. The unit is powered from an on-board generator through the deck box. Once powered on, the instrument can be placed in the water and profiled from the surface to a distance of at least 1 m from the bottom. When conditions dictate (calm surface conditions, absence of interferences, etc.), the instrument may be lowered to within 0.5 m of the bottom. The profiling rate should be 5cm/s or a 20m profile should take approximately 6 minutes to complete. The data will be reported in average 0.25 m bins, so this profiling rate is needed to obtain a reasonable sample size within each 0.25 m.

6. Definitions: None.
7. Interferences:
   Highly turbid waters resulting in sensor interference and contact with the bottom. Contact with direct sunlight on the boat deck for prolonged periods can cause erroneous readings and permanently damage many of the major components. The boat's shadow can interfere with PAR measurements. Bubbles in the T, SC sensor can cause erroneous measurements.
8. Safety:
   Always use proper boating safety techniques when sampling from boats (see the most current New York State Boater's Safety Guide). Standard field procedures involving moderate lifting should be applied. Wear gloves when using winch and avoid loose fitting clothing. Keep work area clean and clutter free. Keep cables arranged neatly on deck to avoid tripping. Use proper electrical connections and keep battery and invertor out of direct sunlight and/or rain. Use leather gloves when using the electrical winch, avoid pinching/abrasions on cable.
9. Equipment and supplies:
   Appropriate field sheets, In-Situ Nitrate/Optical Frame unit, laptop computer, connection cables (underwater cable and communication cable), deck box, solar reflective cover, Kim wipes, battery, power invertor, and the Honda generator.
10. Reagents and standards: None.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage: No water samples collected.
13. Quality Control:
    When deploying In-Situ Nitrate/Optical Frame lower in water ~ 2-3m and shake cable to expel bubbles from sensors before starting profile. Avoid contact with bottom, interferences, and keep out of direct sunlight to keep instruments from overheating (see # 7).
14. Calibration and standardization:
    No on-site calibration is necessary; follow manufactures recommendation for deployment initialization. The unit is returned to the manufacturer periodically (usually annually) for complete calibration. DI checks for the nitrate sensor are performed periodically in the lab (usually weekly).
15. Procedure:
    I. Warmup
       i. turn on laptop computer
       ii. start Honda generator or plug inverter into battery
       iii. connect underwater cable to the deck box and the In-Situ Nitrate/Optical Frame at the designated terminal.

iv. remove conductivity plugs, OBS sensor cap, and light sensor cap.
v. connect power cable to the deck box and power up (either with generator or battery).
vi. allow the unit to warm up for 15 minutes (this is essential as the readings will not be accurate until the internal UV light source stabilizes).
vii. connect the USB communication cable to the deck box and laptop computer.
viii. access the WLHOST 7.09 icon on the desktop.
ix. in the PORTs window:
x. change the Com Port setting to COM 10.
xi. change the baud rate to 115200.
xii. click on Logger tab
xiii. at toolbar, open Modes tab.
xiv. select 'Advanced User' option.
xv. click "Get Setup" button. This retrieves the setup instructions from the DH4 logger.
xvi. click "Begin Sample" button – this activates the instruments to begin streaming data to the logger on the frame [It does not send or save any data to the laptop].
xvii. access the real-time-data tab. From this tab you can view the data from all the instruments as it streams to the logger. See the list below for a detailed list of the ports and associated data.

Table 2. Date Port Settings

Port	Instrument	Parameter	Format	Column Number
1	ISUS/SUNA	device name[1]	text	1
		year	YYYYJJJ	2
		fraction JD	HH.HHH	3
		NO_3^-	data	4
		spectral data	data	5-250
2	SBE 37-Si	T	data	1
		SC	data	2
		depth	data	3
3	BB2 FL	na	na	numerous
4	QSP 2150	counts	optical counts	1
		T	data	2
		voltage	data	3
5	PSA 916	altitude	data	1
9	C-Star	c_{660}	data	1

1 Note that the ISUS actively writes light frame data (SATNLF0095) which contains real data, and dark frame data (SATNDF0095) which is only used by the instrument internally.

xviii. click "Display Data" on port 1 to verify that the instrument is on and streaming data. If not streaming data, check "Data Status" tab. Port 1 is the ISUS and should be sending data at a rate of ~1000 bytes/s. If not, power down, disconnect and try again. If still no communication, contact UFI for assistance.

II. Profiling
i. place the In-Situ Nitrate/Optical Frame in the water and lower to 2-3 m (or as deep as possible without hitting bottom).
ii. vigorously shake the cable to dislodge bubbles from the T/SC sensor
iii. bring the In-Situ Nitrate/Optical Frame in the water at the surface.

iv. access the Recording tab.
v. click "Record Archive" to begin saving the profile using the following naming scheme: mmddyysystem abbrev_site.000. For example: on May 5, 2012, the profile at site 05 on Onondaga Lake would be named 050512onl_05.000.
vi. after the logging has started, begin profiling at a rate of 5 cm/s or 20 sec per meter.
vii. as the instrument nears the bottom, watch the altimeter (PORT5 column 1) and boat depth finder.
viii. stop profiling when within 1 m from the bottom or closer as conditions dictate.
ix. access the Recording tab.
x. click "Stop Recording" to end the file.
xi. return the instrument to the boat, and continue to the next site [Note: If the instrument will not be deployed for some time between sites, cover it with a rain jacket or other reflective cover.
xii. if the waters are turbid or the bottom is contacted, rinse well with DI water once each profile is complete.
xiii. use the same profiling procedure at each station.

III. Maintenance
i. rinse all sensors with DI water
ii. gently wipe all sensors dry with optical lens paper

16. Calculations: Raw data are converted to units of scientific measure internally by the sensor.
17. Method performance:
This procedure is in accordance with the manufacturer's recommendations.
18. Pollution prevention: This procedure has no discernible negative impact on the environment.
19. Data assessment and acceptance criteria for quality control measures:
Assessment of results is done at UFI facilities (post collection). Acceptance criteria for quality control include consideration of field notation concerning interferences, presence of data points outside parameter detection range values, and comparison to other data sources (i.e. ground truth). Pre and post deployment DI checks are used to ensure probes are functioning properly.
20. Corrective actions for out-of-control or unacceptable data:
If unacceptable data is determined to be a result of instrument malfunction, then instrument will be returned for repair. If unacceptable data is determined to be due to inappropriate use by the field crew, then a review of the procedure will be conducted to ensure the problem will not happen again.
21. Contingencies for handling out of control or unacceptable data:
Identify data that fail QA/QC, record throughout data transfer to client. Analyze cause of unacceptable data (i.e. instrument error or interferences). Return instrument to manufacturer for repair and recalibration if deemed necessary.
22. Waste management: None.
23. References:

- Biospehrical Instruments, Inc., 5340 Riley Street, San Diego, CA 92110-2621 USA, Phone: (619) 686-1888, Fax: (619) 686-1887, support@biospherical.com, www.biospherical.com
- Satlantic Incorporated, Richmond Terminal, Pier 9, 3481 North Marginal Road, Halifax, Nova Scotia, CANADA, Phone: (902) 492-4780, Fax: (902) 492-4781, info@satlantic.com, www.satlantic.com
- Sea-Bird Electronics, Inc., 1808 136th Place NE, Bellevue, Washington 98005 USA, Phone: (425) 643-9866, Fax: (425) 643-9954, www.seabird.com

- Teledyne Benthos, Inc., Inc., 49 Edgerton Drive, North Falmouth, MA 02556, Phone: (508) 563-1000, Fax: (508) 563-6444, sales@benthos.com
- WetLabs, Inc., PO Box 518, Philomath, OR 97370, Phone: (541) 929-5650, Fax: (541) 929-5277, wetlabs@wetlabs.com, www.wetlabs.com

***SOP No. 315:* YSI Sonde Calibration and Maintenance**

1. Test method: YSI Sonde Calibration and Maintenance
2. Applicable matrix or matrices: Water.
3. Detection limit: see Table 1 below.

Table 1. Detection limits for YSI Parameters

Parameter	Manufacturer	Range of Detection	Accuracy	Resolution
Temperature, T (°C)	YSI	-5 to 45 °C	±0.15°C	0.01°C
Specific Conductance, SC (µS/cm)	YSI	0 to 100 mS/cm	±0.5% reading/0.001 mS/cm	0.001 mS/cm to 0.1 mS/cm range dependent
pH, (units)	YSI	0 to 14 units		
Dissolved Oxygen, DO (mg/L) – 6562 Standard	YSI	0 to 50 mg/L		
Dissolved Oxygen, DO (mg/L) – 6150 Optical	YSI	0 to 50 mg/L	0-20 mg/L ± 1% of reading, 20-50mg/L ±15% of reading	0.01 mg/L
Percent Saturation, DO % Sat (%)	YSI	0 to 500 % air sat		
Turbidity, Tn (NTU)	YSI	0 to 1000 NTU	± 2% of reading or 0.3NTU whichever is worse	0.1 NTU
Chlorophyll Fluorescence, CHL (µg/L)	YSI	0 to 400 µg/L	none provided	0.1 µg/L
Oxidation Reduction Potential, ORP (mV)*	YSI	-999 to 999 mV		
Depth (pressure), z (m)	YSI	0 to 200 m	0.12m	0.0003m

*ORP not currently calibrated on YSI sondes

4. Scope and application: Drinking, surface and saline waters.
5. Summary of test method:

YSI sondes need to be fully calibrated before field installation on robotic monitoring platforms, incorporation into an stream automated sampling unit, use with a datalogger and/or standalone deployment. The following parameters need to be calibrated before each deployment: specific conductance, pH, dissolved oxygen, turbidity, chlorophyll, and ORP. Calibration is system dependent (i.e. not all parameters are sampled on all systems). Calibration involves adjusting the values of parameters to that of known standards. Calibration needs to be performed only on clean multiprobes and all calibration information needs to be recorded in the log book. **Calibration must be done in accordance with manufacturer's recommendations.**

6. Definitions:

Specific Conductance – the ability of a solution to conduct an electrical current normalized to 25 °C

Fluorescence – the emission of light radiation by algae and organic matter stimulated by the absorption of incident light

Turbidity – a measure of light scattering by particles at an angle of 90°

Oxidation Reduction Potential – the tendency of a chemical species to acquire electrons and be reduced.

7. Interferences: see YSI User's Manual for probe specific information.
8. Safety:
   Wear protective glasses and latex gloves. Wear covered shoes, and if possible wear long sleeved shirts, and long pants. For specific information on each chemical used in the maintenance or calibration of a sonde, see the Material Safety Data Sheets located in the sonde room.
9. Equipment and supplies:
   YSI multiprobe sonde, communication cable, computer, ring stand, DI water, paper towels, Kim wipes, pH buffers (7 and 10), specific conductivity standard, turbidity reference solutions (low range and high range NTU), rhodamine dye, Zobell solution, appropriate clothing, eye protection, and latex gloves.
10. Reagents and standards:
    1.409 mS/cm specific conductivity standard, 7.00 and 10.00 pH buffer standards, YSI 6072 low range NTU and YSI 6073G high range NTU turbidity standards, Rhodamine dye solution, and Zobell solution.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage: NA.
13. Quality Control:
    Calibration must be done in accordance with manufacturer's recommendations. An annual review will be performed to ensure proper functioning of the temperature probes. The review will include temperature verification with an ASTM thermometer. The sondes all come equipped with internal QC measures (i.e. it will not accept a calibration that deviates from a certain range for each parameter). It is vital that UFI keep accurate records of sonde readings of standards before and after deployment as well as detailed records of sonde deployment locations.
14. Calibration and standardization: This is the topic of this SOP.
15. Procedure:
    I. Maintenance
        i. rinse probes thoroughly several time with tap water
        ii. remove calibration cup
        iii. invert sonde and place securely in ring stand
        iv. gently begin the process of removing dirt and debris from the sonde housing and probes.
        v. use optic wipes or Kim wipes to clean optical windows on the turbidity and chlorophyll probes
        vi. be careful while cleaning the ORP/pH reference bulb. It is fragile.
        vii. intermittently, remove sonde from stand and flush with tap water
        viii. continue this process until the probes and sonde housing are clean
        ix. wipe pH and ORP probes with DI water
        x. rinse with tap water
        xi. fill calibration cup with tap water and secure on sonde.
        xii. store until needed
        xiii. flush pressure sensor
            1. DO Probe Maintenance
                a. Standard 6562 Probe
                    i. remove black O-ring
                    ii. remove and throw away old membrane
                    iii. very gently rub the probe's metal surface with very fine sandpaper if metal looks tarnished
                    iv. rinse inside of probe with DI
                    v. flush inside of probe with YSI DO electrolyte 3 times

vi. Place sonde on ring stand
vii. fill DO probe basin with DO electrolyte so that a meniscus is formed
viii. put a YSI Standard ½ membrane sheet over meniscus
ix. place O-ring over membrane and fit around probe
x. check that the membrane is smooth (no wrinkles)
xi. check for bubbles under the membrane by shaking the YSI gently upside down if there are bubbles repeat procedure from step 7)
xii. fill cup ½ fill with tap water

b. Optical 6150 Probe
i. remove optical probe wiper
ii. inspect for damage and wear
iii. replace wiper if needed
iv. rinse probe with DI
v. fill cup ½ fill with tap water

II. Calibration [The manufacturer has set internal controls on the criteria of calibration acceptance. UFI follows the guidelines of calibration as directed by the manufacturer]
i. turn on computer
ii. connect bench cable labeled YSI to serial port and YSI unit.
iii. plug in power cable labeled YSI
iv. select the YSI Terminal icon located on the desktop
v. at the # sign type menu
vi. select 2 for the Calibration menu
vii. note: calibration should only be performed on cleaned sondes
viii. it is important to calibrate Specific Conductance before calibrating pH. pH buffer solutions are highly saline and therefore can cause Specific Conductance calibration problems.

1. Calibration of Specific Conductance

a. rinse probes with DI water. Repeat.
b. fill cup with DI water and record DI SC value on calibration form (this is just a check, not a calibration). If the DI value is greater than 5 µS/cm, corrective action is required.
c. add a small portion of standard to rinse the sensors. Repeat.
d. add enough standard to cover the probes.
e. choose conductivity calibration from the menu
f. choose spCond
g. press <enter> -- probe data should be showing on the screen.
h. find conductivity value and record on calibration sheet. [If the specific conductivity reading is more than ± 40 µS/cm of standard, do not calibrate. Re-clean probes with DI. Retry. If specific conductivity reading is still more than ± 40 µS/cm of the standard, empty contents from the pour bottle and obtain new specific conductivity standard from the storage container Re-clean the probes and try again. If the problem persists then corrective action is required.
i. type <enter> -- this will update the conductivity calibration
j. type <enter> to continue

k. type <0> -- this will return you to the sensor selection list for calibration
l. reuse standard.
m. record information on calibration sheets

2. pH

a. rinse probes with DI water. Repeat.
b. rinse probes with 7 pH buffer. Repeat.
c. add enough 7 pH buffer to cover the probes.
d. choose pH calibration from the menu
e. choose 2-point calibration
f. type 7.0 at prompt <enter> -- probe data should be showing on the screen.
g. find pH value and record on calibration sheet.
h. <enter> -- this will update the pH calibration for point 1 (7 pH)
i. <enter>
j. reuse buffer.
k. rinse probes with DI water. Repeat.
l. rinse probes with 10 pH buffer. Repeat.
m. add enough 10 pH buffer to cover the probes.
n. type 10.0 at the prompt <enter>
o. find pH value and record on calibration sheet.
p. <enter> -- this will update the pH calibration for point 2 (10)
q. <enter>
r. type <0>
s. reuse buffer
t. record information on calibration sheets

3. Dissolved Oxygen

a. Standard 6562 Probe
   i. calibration of DO should only be done 12-24 hours after DO probe maintenance
   ii. rinse probes with DI water. Repeat.
   iii. fill calibration cup with DI water up to, but below DO probe.
   iv. if water is on membrane surface, gently dab with clean Kimwipe.
   v. loosely place cap on calibration cup, allowing space for air equilibrium.
   vi. choose Dissolved Oxygen calibration from the menu
   vii. choose %DO Sat
   viii. type the atmospheric pressure in mmHg at the prompt
   ix. <enter> -- probe data should be showing on the screen.
   x. find %DO Sat value.
   xi. allow several minutes (at least 5 minutes, 10-15 ideally) for values to stabilize
   xii. <enter> -- this will update the DO calibration (note that DO will not necessarily read 100 % Saturation.)
   xiii. <enter>
   xiv. type <0>
   xv. record information on calibration sheets

b. Optical 6150 Probe (ROX sensor)

i. rinse probes with DI water. Repeat.
ii. fill calibration cup with DI water up to, but below Temperature probe.
iii. if water is on membrane surface, gently dab with clean Kimwipe.
iv. loosely place cap on calibration cup, allowing space for air equilibrium.
v. choose Optical Dissolved Oxygen calibration from the menu
vi. choose %DO Sat
vii. type the atmospheric pressure in mmHg at the prompt
viii. <enter> -- probe data should be showing on the screen.
ix. find %DO Sat value.
x. allow several minutes (at least 5 minutes, 10-15 ideally) for values to stabilize
xi. <enter> -- this will update the DO calibration (note that DO will not necessarily read 100 % Saturation.)
xii. <enter>
xiii. type <0>
xiv. record information on calibration sheets

4. Chlorophyll

a. Two point calibration [Note: 2 point calibrations are only done prior to initial deployment and may be done mid-field season to verify proper functioning]

i. go to the Advanced menu
ii. select Sensors
iii. set CHL Temp Co % to ZERO (0.0)
iv. go back to the calibration menu.
v. rinse probes with DI water. Repeat.
vi. when conducting chlorophyll calibration use dark calibration cup.
vii. fill cup nearly completely full of DDI water and secure cap.
viii. invert unit so that the CHL sensor is completely covered with water.
ix. gently tap YSI unit to free any bubble attached to sensor surface.
x. choose CHL calibration from the menu
xi. choose ug/L
xii. choose or 2 point calibration
xiii. type 0.0 at prompt <enter> -- probe data should be showing on the screen.
xiv. type '3' to cause wiper to clean (remove micro-bubbles from) chlorophyll sensor's surface.
xv. find CHL value and record on calibration sheet.
xvi. <enter> -- this will update the fluorometer calibration for point 1 (0 ug/L)
xvii. after completing 0 ug/L calibration replace, DI water with Dye solution (obtained from lab).

xviii. type dye equivalent ug/L at prompt for point 2.
xix. type '3' to cause wiper to clean (remove micro-bubbles from) chlorophyll sensor's surface.
xx. find CHL value Find CHL value and record on calibration sheet.
xxi. <enter> -- this will update the fluorometer calibration for point 2 (dye ug/L)
xxii. <enter>
xxiii. type <0>
xxiv. discard solution.
xxv. go back to Filters under the advanced menu and turn CHL Temp Co % to previous value.
xxvi. record information on calibration sheets

b. One point calibration [Note: 1 point calibrations are done every time the sonde is calibrated]

i. rinse probes with DDI water. Repeat.
ii. when conducting chlorophyll calibration use dark calibration cup.
iii. fill cup nearly completely full of DDI water and secure cap.
iv. invert unit so that the CHL sensor is completely cover with water.
v. gentle tap YSI unit to free any bubble attached to sensor surface.
vi. choose CHL calibration from the menu
vii. choose ug/L
viii. choose 1 point calibration
ix. type 0.0 at prompt <enter> -- probe data should be showing on the screen.
x. type '3' to cause wiper to clean (remove micro-bubbles from) chlorophyll sensor's surface.
xi. find CHL value and record on calibration sheet.
xii. <enter> -- this will update the fluorometer calibration for point 1 (0 ug/L)

Table 2. T and CHL relationship for Rhodamine dye

T (°C)	CHL (µg/L)	T (°C)	CHL (µg/L)
30.00	100.00	18.50	121.00
29.50	100.75	18.00	122.00
29.00	101.50	17.50	123.00
28.50	102.25	17.00	124.00
28.00	103.00	16.50	125.00
27.50	103.75	16.00	126.00
27.00	104.50	15.50	127.25
26.50	105.25	15.00	128.50
26.00	106.00	14.50	129.75
25.50	107.00	14.00	131.00
25.00	108.00	13.50	132.25
24.50	109.00	13.00	133.50
24.00	110.00	12.50	134.75
23.50	110.75	12.00	136.00
23.00	111.50	11.50	137.00
22.50	112.25	11.00	138.00
22.00	113.00	10.50	139.00
21.50	114.25	10.00	140.00
21.00	115.50	9.50	141.00
20.50	116.75	9.00	142.00
20.00	118.00	8.50	143.00
19.50	119.00	8.00	144.00
19.00	120.00		

Rhodamine dye is reported to be a possible carcinogen, therefore handle appropriately!!!

5. Turbidity

a. dry YSI Multiprobe completely
b. remove Tn and Chl wipers (DO wiper if present)
c. fill calibration cup with DI water
d. place inverted sonde in calibration cup 5 cm above cup bottom
e. chose Turbidity calibration from the menu
f. chose 2-point calibration
g. type 0.0 at prompt <enter> -- probe data should be showing on the screen.
h. find turbidity value and record on calibration sheet.
i. <enter> -- this will update the turbidity calibration for point 1 (0.0 NTU)
j. <enter>
k. invert sonde and place in a calibration cup with high NTU standard obtained from YSI 6073G Tn Standard container
l. gently tap YSI unit to free any bubbles attached to sensor surface.
m. type high NTU value at prompt <enter> -- probe data should be showing on the screen.
n. find turbidity value and record on calibration sheet.
o. 1<enter> -- this will update the turbidity calibration for point 2 (high range NTU)

p. <enter>
q. reuse standard.
r. dry YSI Multiprobe completely
s. invert sonde and place in a calibration cup with low NTU standard obtained from YSI 6072 Tn Standard container
t. observe and record Tn reading in low NTU Standard on calibration sheet
u. re-attach Tn and Chl wipers

6. Oxidation Reduction Potential

a. Please see User's Manual for ORP calibrations (currently UFI does not perform ORP measurements - 06/03/16)

7. Rhodamine probe

a. will be calibrated and checked prior to use as per the manufacturer's instructions - please see User's manual.

8. Blue green algae probe

b. will be calibrated and checked prior to use as per the manufacturer's instructions - please see User's manual.

III. Replacing Wipers

i. using the appropriate Allen wrench, remove the wipers on both the turbidity and chlorophyll probes
ii. remove old wiping foam from wiper
iii. replace with new wiping foam
iv. reattach wipers to probes with appropriate Allen wrench

16. Calculations: Raw data are converted to units of scientific measure internally by the sensor.
17. Method performance: Performed according to manufacturer's recommendations.
18. Pollution prevention:
All calibration solutions are flushed down the drain in the sink with tap water.
19. Data assessment and acceptance criteria for quality control measures:
YSI multiprobe sondes all come equipped with internal QC measures (i.e. it will not accept a calibration that deviates from a certain range for each parameter).
20. Corrective actions for out-of-control or unacceptable data:
If a probe or sonde continually fails calibration then the instrument will be replaced with a new one or returned to the manufacturer for repair.
21. Contingencies for handling out of control or unacceptable data:
Identify data that fail QA/QC, record throughout data transfer to client. Analyze cause of unacceptable data (i.e. instrument error or interferences). Return instrument to manufacturer for repair and recalibration if deemed necessary.
22. Waste management:
All calibration solutions are flushed down the drain in the sink with tap water.
23. References:

- YSI Environmental Operations Manual revision J (3/2012), 1700/1725 Brannum Lane, Yellow Springs, OH 45387, www.ysi.com

SOP No. 331: YSI Buoy Maintenance

1. Test Method: YSI Buoy Maintenance
2. Applicable matrix or matrices: Salt and fresh surface waters.
3. Detection limit: see field SOP 315.
4. Scope and application: Drinking, surface and saline waters.
5. Summary of test method:
   Weekly (or biweekly), deployed data sondes need to be removed for cleaning and calibration. Cleaned and fully calibrated data sondes need to be installed to replace those sondes removed. Data sondes are calibrated in the lab, and then integrated with YSI platforms which are located on various aquatic systems. Calibration is described in detail in the YSI user manual (see References: section 23) and YSI sonde calibration SOP 315. Data sondes are integrated with the YSI datalogger with an underwater profiling cable. Sonde integration is straight forward; however, sonde recognition by the YSI buoys on-board computer must be verified. A laptop computer is wirelessly connected to the YSI datalogger using communication software. Proper functioning of the new data sonde is verified.
6. Definitions: None.
7. Interferences: see field SOP 315.
8. Safety:
   Standard field procedures involving moderate lifting should be applied.
   Use caution and follow standard boating safety procedures. Wear gloves when lowering. Keep work area clean and clutter free.
9. Equipment and supplies: See system specific equipment list.
10. Reagents and standards: None.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage: No water samples collected.
13. Quality Control:
    Verify recognition of sonde by YSI platform. Check that data looks reasonable via the laptop and communication software. Avoid interferences (see # 7).
14. Calibration and standardization:
    The calibration of each component of the integrated profiling unit is done in the lab by UFI technicians according to manufacturer's instructions (see # 23) and field SOP 315.
15. Procedure:
    I. Buoy Deployment
        i. place fully charged battery in compartment but DO NOT connect
        ii. connect anchor line-harness to buoy I-bolts
        iii. hook anchor line-harness to boat and tow to site
        iv. connect buoy-harnesses to anchor lines
        v. install counter weight
        vi. install depth finder
        vii. connect sonde to data cable
        viii. attached field cup
        ix. lower sonde to park depth
        x. connect battery to datalogger
        xi. if the buoy will not respond initially, the battery may not be receiving enough charge from the solar panel (overcast conditions may be limiting) See IV. Toubleshooting v. dead battery)

II. Routine Maintenance
   i. At the buoy
      1. tether boat to buoy
      2. inspect for problems with buoy (listing, broken anchor line, etc…)
      3. unlock solar covers to access datalogger
   ii. Communicating with the buoy
      1. turn on laptop
      2. access wireless internet connection
      3. open Campbell Scientific/Loggernet software
      4. select buoy of interest
      5. click connect (may take several seconds)
      6. open numerical screen and ports and flags screen
   iii. Before sonde exchange
      1. inspect internal connections
         a. inspect battery-datalogger connections
         b. inspect datasonde-datalogger connections
      2. DO NOT attempt to service a buoy that is actively profiling!!! Wait until profile is complete.
      3. verify buoy is not in 'Service' mode (if in 'Service' see IV. Troubleshooting)
      4. set buoy to 'Service' (Flag 2) with software on laptop
      5. verify datasonde at park depth (Sonde/Start Profile, Flag 5) . Send to park if not at park depth (Park Depth, Flag 7)
      6. record parameters from existing datasonde on field sheet
   iv. Sonde exchange
      1. manually pull existing sonde into the boat
      2. disconnect from data cable
      3. check pins for corrosion, moisture, etc…, check cable for damage
      4. record sonde coming out (#) and sonde going in (#)
      5. after connecting the new sonde lower it back to the park depth
      6. clean field cup
      7. lower to park depth
   v. After sonde exchange
      1. click 'Reset' (Flag 1)
      2. click 'Sonde Parameters' (Flag 8): verify if a normal response or error message (if error, check sonde configuration- date, time, depth (m) enabled, else see User's manual)
      3. click 'Synchronize Time' (Flag 6): verify if a normal response/no error message (if error, see IV. Troubleshooting)
      4. verify that the datasonde is at park depth (if not move to park depth ('Park Depth, Flag #)
      5. record parameters ('Sonde/Start Profile', Flag 5) from new datasonde
      6. record battery voltage (should be above 12.3 V): if the battery is less than 12.3 then replace (or schedule replacement) battery (this will verify that the battery is charging)
      7. record datalogger temperature (should be between -30 - + 50°C, if not contact YSI to replace sensor)
      8. record datalogger RH (should be below 40%): schedule a desiccant change for next trip if RH greater than 40%

9. confirm reservoir depth with buoy depth finder (Flag 3)
10. turn off 'Service' (Flag 2)
11. Start profile ('Sonde/Start Profile', Flag 5) and verify buoy is functioning properly (performing a profile, collecting data, spooling properly, etc…)
12. disconnect from Loggernet

vi. Meteorological Station Verification (if applicable)
1. connect to meteorological station (may take several seconds-minute)
2. verify real-time data, log compass, pitch, and roll on left-hand column
3. record parameters from met station, 15min averaged (right hand column)

vii. Physical buoy inspection
1. inspect hulls and decking for integrity
2. inspect winch assembly
3. visually inspect anchor lines and shackles
4. visually inspect solar panels and clean if needed

III. Buoy inspection
i. inspect hulls
ii. inspect decking
iii. inspect winch assembly
iv. visually inspect anchor lines
v. visually inspect shackles
vi. visually inspect solar panels and clean

IV. Buoy Recovery
i. disconnect battery from datalogger
ii. remove sonde from water and disconnect
iii. remove depth finder
iv. disconnect anchor lines from harnesses
v. remove rope and subsurface buoys
vi. attached anchor lines to over winter buoys
vii. hook anchor line-harness to boat and tow to recovery site
viii. remove counterweight
ix. tow to shore and recover on trailer
x. disconnect components including Me.t station if applicable
xi. trailer buoy and secure it with straps/tie-downs

V. Troubleshooting
i. buoy in 'Service'
1. determine the depth of the sonde (park depth, bottom, surface, etc…)
2. determine if sonde is hung up (physically) on an anchor line, bottom debris, or can freely move (you can do this manually by pulling the cable into the boat)
3. if hung-up, attempt to free from obstruction
4. if the sonde can move freely, attempt to start a profile
    a. turn off 'Service'
    b. click 'Sonde/Start Profile', Flag 5
    c. if buoy performs a profile without problems, continue with maintenance
    d. if profile aborts, continue with troubleshooting
5. determine if winch and spool are functioning properly
    a. if functioning properly continue with troubleshooting
    b. if not contact support

6. determine if old sonde is the problem by attempting sonde change
    a. pull existing sonde into boat and replace with new sonde as indicated in II. Routine Maintenance and see if new sonde responds as normal (pay attention to connectors; broken pins, moisture in connection, corrosion, bends/breaks in cable, etc…)
    b. if functioning properly continue with routine maintenance
7. if there are no physical problems with buoy, the problem could be software, contact support
8. leave buoy in 'Service' if unable to repair and wait for support instructions

ii. 'Sonde Parameters' error: check sonde configuration and retry
iii. 'Synchronize Time' error: check sonde date/time setup and retry
iv. desiccant change if RH is greater than 40%.
1. open datalogger housing
2. remove old desiccant
3. add new desiccant pouch
4. seal housing lid gasket and close housing

v. initial setup or low/dead battery
1. connect buoy power leads to battery, verifying that the negative lead (-) is connected to the negative terminal (-) and that the positive lead (+) is connected to the positive terminal (+).
2. with the solar panels connected, verify that the "Charging" LED illuminates (depending on incident light conditions and initial battery charge the light may switch on and off -- this is normal).
3. check that the "Activated" LED is not illuminated. If it is not (off), then after a few minutes proceed to step v). If the "Activated" LED is illuminated (on), then proceed to step iv)
4. Note: The charge controller regulates the solar panels charging of the battery. If the battery is less than fully charged (less than 13V) it will prevent power from being made available to the electronics until the voltage exceeds 13V. This only occurs when the battery is first connected and when the battery voltage is less than 13V. When this occurs the "Activated" LED will be illuminated. To bypass this feature, either supply an external source of power (for example a battery charger) or with the solar panels connect and proving a minimum of 17.5V, the fuse holder can be opened then closed (this effectively temporarily disconnecting the positive terminal). The "Activated" light should go out and power should now be supplied to the electronics. There are a few LEDs that are marginally visible through the clear end of electronics enclosure. You can look to see if these are illuminated to verify that power is being supplied to the electronics.
5. v) re-attempt to communicate with the buoy

16. Calculations: None.
17. Method performance:
This procedure is in accordance with the manufacturer's recommendations.
18. Pollution prevention: This procedure has no discernible negative impact on the environment.
19. Data assessment and acceptance criteria for quality control measures:
Assessment of results is done at UFI facilities (post collection). Acceptance criteria for quality control include consideration of field notation concerning interferences, presence of data points

outside parameter detection range values, and comparison to other data sources (i.e. ground truth).

20. Corrective actions for out-of-control or unacceptable data:
    If unacceptable data is determined to be a result of instrument malfunction, then instrument will be returned for repair. If unacceptable data is determined to be due to inappropriate use by the field crew, then a review of the procedure will be conducted to ensure the problem will not happen again.
21. Contingencies for handling out of control or unacceptable data:
    Identify data that fail QA/QC, record throughout data transfer to client. Analyze cause of unacceptable data (i.e. instrument error or interferences). Return instrument to manufacturer for repair and recalibration if deemed necessary.
22. Waste management: None.
23. References:
    - YSI Environmental Operations Manual revision J (3/2012), 1700/1725 Brannum Lane, Yellow Springs, OH 45387, www.ysi.com
    - see field SOP 315

SOP No. 312: Sediment Trap Deployment and Collection

1. Test method: Sediment Trap Deployment and Collection.
2. Applicable matrix or matrices: Water.
3. Detection limit: NA.
4. Scope and application: Drinking, surface and saline waters.
5. Summary of test method:
   A sediment trap is a cylindrical PVC tube with an aspect ratio (height/diameter) of 6 and a diameter of 8.9 cm closed on the bottom and open at the top to collect particulates as they settle through the water column of a lake or reservoir. These PVC tubes are deployed as assemblages of three. Sediment traps are used to quantify downward flux (DF) of particles in a water body and the settling velocity of particles (SV). Routine chemical analyses can be performed on the sediment trap sample as well. Theses analyses include but are not limited to total suspended solids, volatile suspended solids, and fixed (or non-volatile) suspended solids. A sediment trap assemblage is deployed in the water column at a depth which is site and sampling purpose specific. For example, sediment traps can be deployed just below the thermocline to estimate downward flux of particles from the epilimnion, or sediment traps can be deployed near the bottom of a water body to estimate sediment resuspension.
6. Definitions:
   Downward flux (DF) – The downward movement of particles quantified by mass per unit area per unit time (mass/area/time)
   Settling Velocity (SV) – The settling distance of particles per unit time (length/time) or the ratio of DF to particle concentration (mass/volume).
7. Interferences:
   Improper deployment (not vertical) and improper cleaning can invalidate results, deployment at the incorrect depth (i.e. too close to the bottom), shaking of the traps during collection, improper (too fast) draining of the overlying water in the trap will cause in-trap resuspension and loss.
8. Safety:
   Be careful leaning over the gunwale when retrieving the sediment trap/buoy. Always use proper boating safety techniques when sampling from boats (see the most current New York State Boater's Safety Guide). Standard field procedures involving moderate lifting should be applied. Wear leather gloves during retrieval and deployment.
9. Equipment and supplies:
   Sediment trap assemblage (arrangements of three), deployment rope, sub-surface float, surface float, anchor, black rubber stoppers, cleaning brush, funnel, collection bottles, and chains of custody.
10. Reagents and standards: None.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage:
    All samples will be stored on ice after collection, transported to UFI laboratories in coolers, and be accompanied by the necessary documentation (chains of custody) unless specifically noted.
13. Quality Control:
    While deploying be sure that the black rubber stoppers are securely inserted into PVC trap drain holes. Make sure the traps are sitting vertical in the water column (**and not in the sediment**) and verify trap depths after deployment. Upon retrieval log sediment trap depth, water column depth, trap location with GPS coordinates, date and time of deployment and retrieval, and any other appropriate field notes (runoff events or algae blooms during the deployment period) on the

sediment trap field sheets. During sample collection, drain water from the trap slowly to prevent in-trap resuspension. Secure caps to sediment trap prior to trap shaking. Pour slowly into collection bottle and use a funnel to prevent spillage. Record all information and complete the chain of custody.

14. Calibration and standardization: NA.
15. Procedure:

I. Deployment
   i. traps should be deployed so that a metalimnetic trap is below and should remain below the upper mixed layer during maximum stratification (depth is system dependent). Lines should be readjusted as needed. A hypolimnetic trap is placed approximately 1 to 2 meters above the bottom sediments
   ii. traps should be put over the side of the boat and lowered by hand – try not to disturb bottom sediments when deploying to avoid possibility of false high deposition measurements associated with resuspension
   iii. lower the assembly in the following manner: (1) anchor, (2) bottom trap, (3) top trap, (4) subsurface float, and (5) surface marker float.
   iv. depth of traps should be marked with the depth finder and recorded on the field sheet
   v. slack in the line at the surface is recommended and helps prevent trap re-location after changes in water surface elevation.

II. Collection
   i. pull the boat up next to the sediment trap buoy.
   ii. using the depth finder, check and record the depth of the trap on the field sheet
   iii. pull trap buoy and slack line into the boat (depending on weather conditions, someone may need to keep the boat in position).
   iv. pull the sediment trap up through the water column in a steady and consistent manner
   v. once trap is in the boat, tie off trap anchor line (or pull into boat).
   vi. drain trap by slowing removing plugs from the side of the trap
   vii. once drained, replace plugs, and cap traps
   viii. shake up traps until well mixed and pour off into sediment trap bottles (depending on the system, pour all traps into one sample bottle or pour each cylinder into its own sample bottle)
   ix. clean the traps (inside and outside) by scrubbing them with a brush and rinse 2-3 times with water (**be sure to mark that the traps have been cleaned on the chains of custody**)
   x. cap sample bottles and place in a cooler with ice
   xi. properly fill out chain of custody
   xii. redeploy

III. Contingencies for missing traps and/or when trap collection varies from routine sampling schedule
   i. Sediment traps not collected on the scheduled day of routine collection
      1. Fill out chain of custody header (sampled by and date of collection)
      2. Record NS (Not Sampled) on check boxes for each trap
      3. Provide reason for NS in Comments/Deviations from Sampling Plan box (trap missing, bad weather prevented collection etc.)
   ii. Deployment of new sediment traps
      1. Fill out chain of custody header (sampled by and date of collection)
      2. Record NS (Not Sampled) on check boxes for each trap

3. Provide reason for NS in Comments/Deviations from Sampling Plan box (trap redeployed etc.)

iii. Chains of custody documenting the above inconsistencies will be kept on file with other sediment trap chains to provide and accurate documentation of the sediment trap collection record.

16. Calculations (performed by analysts, not be field crew upon collection):

Downward flux (DF) = $\left(\frac{W}{A \times t}\right)$ where W is the mass of the collected constituents (g), A is the area of the trap opening (m2), and t is the time of deployment (d).

Settling Velocity (SV) = $S_V = \left(\frac{D_F}{particle\,conc.}\right)$ where (DF) is the downward flux ($g/m^2/d$), and particle conc. is the concentration of particles in (g/m^3)

17. Method performance:
This is an accepted UFI procedure, performed as recommended by scientific literature.
18. Pollution prevention: NA.
19. Data assessment and acceptance criteria for quality control measures: NA.
20. Corrective actions for out-of-control or unacceptable data: NA.
21. Contingencies for handling out of control or unacceptable data: NA.
22. Waste management: This procedure generates no hazardous waste.
23. References:

- Bloesch, J., 1996. Towards a New Generation of Sediment Traps and a Better Measurement/Understanding of Settling Particulate Flux in Lakes and Oceans: A Hydrodynamic Protocol. Aquatic Science 58:283-296.

***SOP No. 315:* YSI Sonde Calibration and Maintenance**

1. Test method: YSI Sonde Calibration and Maintenance
2. Applicable matrix or matrices: Water.
3. Detection limit: see Table 1 below.

Table 1. Detection limits for YSI Parameters

Parameter	Manufacturer	Range of Detection	Accuracy	Resolution
Temperature, T (°C)	YSI	-5 to 45 °C	±0.15°C	0.01°C
Specific Conductance, SC (µS/cm)	YSI	0 to 100 mS/cm	±0.5% reading/0.001 mS/cm	0.001 mS/cm to 0.1 mS/cm range dependent
pH, (units)	YSI	0 to 14 units		
Dissolved Oxygen, DO (mg/L) – 6562 Standard	YSI	0 to 50 mg/L		
Dissolved Oxygen, DO (mg/L) – 6150 Optical	YSI	0 to 50 mg/L	0-20 mg/L ± 1% of reading, 20-50mg/L ±15% of reading	0.01 mg/L
Percent Saturation, DO % Sat (%)	YSI	0 to 500 % air sat		
Turbidity, Tn (NTU)	YSI	0 to 1000 NTU	± 2% of reading or 0.3NTU whichever is worse	0.1 NTU
Chlorophyll Fluorescence, CHL (µg/L)	YSI	0 to 400 µg/L	none provided	0.1 µg/L
Oxidation Reduction Potential, ORP (mV)*	YSI	-999 to 999 mV		
Depth (pressure), z (m)	YSI	0 to 200 m	0.12m	0.0003m

*ORP not currently calibrated on YSI sondes

4. Scope and application: Drinking, surface and saline waters.
5. Summary of test method:

YSI sondes need to be fully calibrated before field installation on robotic monitoring platforms, incorporation into an stream automated sampling unit, use with a datalogger and/or standalone deployment. The following parameters need to be calibrated before each deployment: specific conductance, pH, dissolved oxygen, turbidity, chlorophyll, and ORP. Calibration is system dependent (i.e. not all parameters are sampled on all systems). Calibration involves adjusting the values of parameters to that of known standards. Calibration needs to be performed only on clean multiprobes and all calibration information needs to be recorded in the log book. **Calibration must be done in accordance with manufacturer's recommendations.**

6. Definitions:

Specific Conductance – the ability of a solution to conduct an electrical current normalized to 25 °C

Fluorescence – the emission of light radiation by algae and organic matter stimulated by the absorption of incident light

Turbidity – a measure of light scattering by particles at an angle of 90°

Oxidation Reduction Potential – the tendency of a chemical species to acquire electrons and be reduced.

7. Interferences: see YSI User's Manual for probe specific information.
8. Safety:
   Wear protective glasses and latex gloves. Wear covered shoes, and if possible wear long sleeved shirts, and long pants. For specific information on each chemical used in the maintenance or calibration of a sonde, see the Material Safety Data Sheets located in the sonde room.
9. Equipment and supplies:
   YSI multiprobe sonde, communication cable, computer, ring stand, DI water, paper towels, Kim wipes, pH buffers (7 and 10), specific conductivity standard, turbidity reference solutions (low range and high range NTU), rhodamine dye, Zobell solution, appropriate clothing, eye protection, and latex gloves.
10. Reagents and standards:
    1.409 mS/cm specific conductivity standard, 7.00 and 10.00 pH buffer standards, YSI 6072 low range NTU and YSI 6073G high range NTU turbidity standards, Rhodamine dye solution, and Zobell solution.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage: NA.
13. Quality Control:
    Calibration must be done in accordance with manufacturer's recommendations. An annual review will be performed to ensure proper functioning of the temperature probes. The review will include temperature verification with an ASTM thermometer. The sondes all come equipped with internal QC measures (i.e. it will not accept a calibration that deviates from a certain range for each parameter). It is vital that UFI keep accurate records of sonde readings of standards before and after deployment as well as detailed records of sonde deployment locations.
14. Calibration and standardization: This is the topic of this SOP.
15. Procedure:
    I. Maintenance
        i. rinse probes thoroughly several time with tap water
        ii. remove calibration cup
        iii. invert sonde and place securely in ring stand
        iv. gently begin the process of removing dirt and debris from the sonde housing and probes.
        v. use optic wipes or Kim wipes to clean optical windows on the turbidity and chlorophyll probes
        vi. be careful while cleaning the ORP/pH reference bulb. It is fragile.
        vii. intermittently, remove sonde from stand and flush with tap water
        viii. continue this process until the probes and sonde housing are clean
        ix. wipe pH and ORP probes with DI water
        x. rinse with tap water
        xi. fill calibration cup with tap water and secure on sonde.
        xii. store until needed
        xiii. flush pressure sensor
            1. DO Probe Maintenance
                a. Standard 6562 Probe
                    i. remove black O-ring
                    ii. remove and throw away old membrane
                    iii. very gently rub the probe's metal surface with very fine sandpaper if metal looks tarnished
                    iv. rinse inside of probe with DI
                    v. flush inside of probe with YSI DO electrolyte 3 times

vi. Place sonde on ring stand
vii. fill DO probe basin with DO electrolyte so that a meniscus is formed
viii. put a YSI Standard ½ membrane sheet over meniscus
ix. place O-ring over membrane and fit around probe
x. check that the membrane is smooth (no wrinkles)
xi. check for bubbles under the membrane by shaking the YSI gently upside down if there are bubbles repeat procedure from step 7)
xii. fill cup ½ fill with tap water

b. Optical 6150 Probe
i. remove optical probe wiper
ii. inspect for damage and wear
iii. replace wiper if needed
iv. rinse probe with DI
v. fill cup ½ fill with tap water

II. Calibration [The manufacturer has set internal controls on the criteria of calibration acceptance. UFI follows the guidelines of calibration as directed by the manufacturer]
i. turn on computer
ii. connect bench cable labeled YSI to serial port and YSI unit.
iii. plug in power cable labeled YSI
iv. select the YSI Terminal icon located on the desktop
v. at the # sign type menu
vi. select 2 for the Calibration menu
vii. note: calibration should only be performed on cleaned sondes
viii. it is important to calibrate Specific Conductance before calibrating pH. pH buffer solutions are highly saline and therefore can cause Specific Conductance calibration problems.

1. Calibration of Specific Conductance

a. rinse probes with DI water. Repeat.
b. fill cup with DI water and record DI SC value on calibration form (this is just a check, not a calibration). If the DI value is greater than 5 µS/cm, corrective action is required.
c. add a small portion of standard to rinse the sensors. Repeat.
d. add enough standard to cover the probes.
e. choose conductivity calibration from the menu
f. choose spCond
g. press <enter> -- probe data should be showing on the screen.
h. find conductivity value and record on calibration sheet. [If the specific conductivity reading is more than ± 40 µS/cm of standard, do not calibrate. Re-clean probes with DI. Retry. If specific conductivity reading is still more than ± 40 µS/cm of the standard, empty contents from the pour bottle and obtain new specific conductivity standard from the storage container Re-clean the probes and try again. If the problem persists then corrective action is required.
i. type <enter> -- this will update the conductivity calibration
j. type <enter> to continue

k. type <0> -- this will return you to the sensor selection list for calibration
l. reuse standard.
m. record information on calibration sheets

2. pH

a. rinse probes with DI water. Repeat.
b. rinse probes with 7 pH buffer. Repeat.
c. add enough 7 pH buffer to cover the probes.
d. choose pH calibration from the menu
e. choose 2-point calibration
f. type 7.0 at prompt <enter> -- probe data should be showing on the screen.
g. find pH value and record on calibration sheet.
h. <enter> -- this will update the pH calibration for point 1 (7 pH)
i. <enter>
j. reuse buffer.
k. rinse probes with DI water. Repeat.
l. rinse probes with 10 pH buffer. Repeat.
m. add enough 10 pH buffer to cover the probes.
n. type 10.0 at the prompt <enter>
o. find pH value and record on calibration sheet.
p. <enter> -- this will update the pH calibration for point 2 (10)
q. <enter>
r. type <0>
s. reuse buffer
t. record information on calibration sheets

3. Dissolved Oxygen

a. Standard 6562 Probe
   i. calibration of DO should only be done 12-24 hours after DO probe maintenance
   ii. rinse probes with DI water. Repeat.
   iii. fill calibration cup with DI water up to, but below DO probe.
   iv. if water is on membrane surface, gently dab with clean Kimwipe.
   v. loosely place cap on calibration cup, allowing space for air equilibrium.
   vi. choose Dissolved Oxygen calibration from the menu
   vii. choose %DO Sat
   viii. type the atmospheric pressure in mmHg at the prompt
   ix. <enter> -- probe data should be showing on the screen.
   x. find %DO Sat value.
   xi. allow several minutes (at least 5 minutes, 10-15 ideally) for values to stabilize
   xii. <enter> -- this will update the DO calibration (note that DO will not necessarily read 100 % Saturation.)
   xiii. <enter>
   xiv. type <0>
   xv. record information on calibration sheets

b. Optical 6150 Probe (ROX sensor)

i. rinse probes with DI water. Repeat.
ii. fill calibration cup with DI water up to, but below Temperature probe.
iii. if water is on membrane surface, gently dab with clean Kimwipe.
iv. loosely place cap on calibration cup, allowing space for air equilibrium.
v. choose Optical Dissolved Oxygen calibration from the menu
vi. choose %DO Sat
vii. type the atmospheric pressure in mmHg at the prompt
viii. <enter> -- probe data should be showing on the screen.
ix. find %DO Sat value.
x. allow several minutes (at least 5 minutes, 10-15 ideally) for values to stabilize
xi. <enter> -- this will update the DO calibration (note that DO will not necessarily read 100 % Saturation.)
xii. <enter>
xiii. type <0>
xiv. record information on calibration sheets

4. Chlorophyll

a. Two point calibration [Note: 2 point calibrations are only done prior to initial deployment and may be done mid-field season to verify proper functioning]

i. go to the Advanced menu
ii. select Sensors
iii. set CHL Temp Co % to ZERO (0.0)
iv. go back to the calibration menu.
v. rinse probes with DI water. Repeat.
vi. when conducting chlorophyll calibration use dark calibration cup.
vii. fill cup nearly completely full of DDI water and secure cap.
viii. invert unit so that the CHL sensor is completely covered with water.
ix. gently tap YSI unit to free any bubble attached to sensor surface.
x. choose CHL calibration from the menu
xi. choose ug/L
xii. choose or 2 point calibration
xiii. type 0.0 at prompt <enter> -- probe data should be showing on the screen.
xiv. type '3' to cause wiper to clean (remove micro-bubbles from) chlorophyll sensor's surface.
xv. find CHL value and record on calibration sheet.
xvi. <enter> -- this will update the fluorometer calibration for point 1 (0 ug/L)
xvii. after completing 0 ug/L calibration replace, DI water with Dye solution (obtained from lab).

xviii. type dye equivalent ug/L at prompt for point 2.
xix. type '3' to cause wiper to clean (remove micro-bubbles from) chlorophyll sensor's surface.
xx. find CHL value Find CHL value and record on calibration sheet.
xxi. <enter> -- this will update the fluorometer calibration for point 2 (dye ug/L)
xxii. <enter>
xxiii. type <0>
xxiv. discard solution.
xxv. go back to Filters under the advanced menu and turn CHL Temp Co % to previous value.
xxvi. record information on calibration sheets

b. One point calibration [Note: 1 point calibrations are done every time the sonde is calibrated]

i. rinse probes with DDI water. Repeat.
ii. when conducting chlorophyll calibration use dark calibration cup.
iii. fill cup nearly completely full of DDI water and secure cap.
iv. invert unit so that the CHL sensor is completely cover with water.
v. gentle tap YSI unit to free any bubble attached to sensor surface.
vi. choose CHL calibration from the menu
vii. choose ug/L
viii. choose 1 point calibration
ix. type 0.0 at prompt <enter> -- probe data should be showing on the screen.
x. type '3' to cause wiper to clean (remove micro-bubbles from) chlorophyll sensor's surface.
xi. find CHL value and record on calibration sheet.
xii. <enter> -- this will update the fluorometer calibration for point 1 (0 ug/L)

Table 2. T and CHL relationship for Rhodamine dye

T (°C)	CHL (µg/L)	T (°C)	CHL (µg/L)
30.00	100.00	18.50	121.00
29.50	100.75	18.00	122.00
29.00	101.50	17.50	123.00
28.50	102.25	17.00	124.00
28.00	103.00	16.50	125.00
27.50	103.75	16.00	126.00
27.00	104.50	15.50	127.25
26.50	105.25	15.00	128.50
26.00	106.00	14.50	129.75
25.50	107.00	14.00	131.00
25.00	108.00	13.50	132.25
24.50	109.00	13.00	133.50
24.00	110.00	12.50	134.75
23.50	110.75	12.00	136.00
23.00	111.50	11.50	137.00
22.50	112.25	11.00	138.00
22.00	113.00	10.50	139.00
21.50	114.25	10.00	140.00
21.00	115.50	9.50	141.00
20.50	116.75	9.00	142.00
20.00	118.00	8.50	143.00
19.50	119.00	8.00	144.00
19.00	120.00		

Rhodamine dye is reported to be a possible carcinogen, therefore handle appropriately!!!

5. Turbidity

a. dry YSI Multiprobe completely
b. remove Tn and Chl wipers (DO wiper if present)
c. fill calibration cup with DI water
d. place inverted sonde in calibration cup 5 cm above cup bottom
e. chose Turbidity calibration from the menu
f. chose 2-point calibration
g. type 0.0 at prompt <enter> -- probe data should be showing on the screen.
h. find turbidity value and record on calibration sheet.
i. <enter> -- this will update the turbidity calibration for point 1 (0.0 NTU)
j. <enter>
k. invert sonde and place in a calibration cup with high NTU standard obtained from YSI 6073G Tn Standard container
l. gently tap YSI unit to free any bubbles attached to sensor surface.
m. type high NTU value at prompt <enter> -- probe data should be showing on the screen.
n. find turbidity value and record on calibration sheet.
o. 1<enter> -- this will update the turbidity calibration for point 2 (high range NTU)

p. <enter>
q. reuse standard.
r. dry YSI Multiprobe completely
s. invert sonde and place in a calibration cup with low NTU standard obtained from YSI 6072 Tn Standard container
t. observe and record Tn reading in low NTU Standard on calibration sheet
u. re-attach Tn and Chl wipers

6. Oxidation Reduction Potential

a. Please see User's Manual for ORP calibrations (currently UFI does not perform ORP measurements - 06/03/16)

7. Rhodamine probe

a. will be calibrated and checked prior to use as per the manufacturer's instructions - please see User's manual.

8. Blue green algae probe

b. will be calibrated and checked prior to use as per the manufacturer's instructions - please see User's manual.

III. Replacing Wipers

i. using the appropriate Allen wrench, remove the wipers on both the turbidity and chlorophyll probes
ii. remove old wiping foam from wiper
iii. replace with new wiping foam
iv. reattach wipers to probes with appropriate Allen wrench

16. Calculations: Raw data are converted to units of scientific measure internally by the sensor.
17. Method performance: Performed according to manufacturer's recommendations.
18. Pollution prevention:
All calibration solutions are flushed down the drain in the sink with tap water.
19. Data assessment and acceptance criteria for quality control measures:
YSI multiprobe sondes all come equipped with internal QC measures (i.e. it will not accept a calibration that deviates from a certain range for each parameter).
20. Corrective actions for out-of-control or unacceptable data:
If a probe or sonde continually fails calibration then the instrument will be replaced with a new one or returned to the manufacturer for repair.
21. Contingencies for handling out of control or unacceptable data:
Identify data that fail QA/QC, record throughout data transfer to client. Analyze cause of unacceptable data (i.e. instrument error or interferences). Return instrument to manufacturer for repair and recalibration if deemed necessary.
22. Waste management:
All calibration solutions are flushed down the drain in the sink with tap water.
23. References:

- YSI Environmental Operations Manual revision J (3/2012), 1700/1725 Brannum Lane, Yellow Springs, OH 45387, www.ysi.com

SOP No. 318: In situ Deployment of YSI Sondes

1. Test method: In situ Deployment of YSI Sondes
2. Applicable matrix or matrices: Water.
3. Detection limit: see field SOP 315.
4. Scope and application: Drinking, surface and saline waters.
5. Summary of test method:
   All YSI sondes have the option to be deployed for long time periods without the user being present. Initially the YSI is connected to a computer at UFI at which time the sampling regiment is entered to the sonde's internal software. Using 8 C batteries as a power source, the sonde is then taken to the deployment site and left for an extended period to sample according to the pre-described sampling interval. Sampling can be conducted for a given period of time (user defined) or can be left until there is no longer enough power to support sampling. The sonde is then brought back to UFI for data uploading and calibration.
6. Definitions: see field SOP 315.
7. Interferences: see field SOP 315.
8. Safety:
   Use caution if using grab sample techniques from a boat. Always use proper boating safety techniques when sampling from boats (see the most current New York State Boater's Safety Guide). Use caution and best judgment if working from bridges. Be sure to park as far on the shoulder as possible. Use parking cones, wear reflective vests, and use truck emergency warning lights, and affix warning light to top of truck. Standard field procedures involving moderate lifting should be applied.
9. Equipment and supplies:
   Computer with appropriate YSI software, YSI communication cable, YSI multiprobe sonde, and 8 C batteries, field cup, deployment platform, rope (or cable), quick clasps, locks, and log sheet.
10. Reagents and standards: None.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage: NA.
13. Quality Control:
    YSI sonde is calibrated prior to deployment and checked after retrieval to verify successful operation.
14. Calibration and standardization: See YSI sonde calibration SOP 315.
15. Procedure:
    I. Logging Setup
        i. inset 8 C batteries into sonde
        ii. turn on computer
        iii. connect bench cable labeled YSI to serial port and YSI unit.
        iv. plug in power cable labeled YSI
        v. select the YSI Terminal icon located on the desktop
        vi. at the # sign type 1 to enter the RUN menu
        vii. select 2 inside the Run menu
        viii. a 12 option menu will appear. Change menu options according to your sampling needs
        ix. sampling interval in HHMMSS
        x. start Date in MMDDYY
        xi. start Time in HHMMSS

xii. duration is the number of days that the sonde will be deployed
xiii. file – name a file to describe sonde deployment
xiv. site – Enter the system name that the sonde will be deployed on
xv. bat. Volts – the YSI sonde reports the voltage of the 8 C batteries
xvi. bat. Life – the YSI sonde calculates the maximum number of days the sonde can log data based on battery voltage
xvii. free mem – the YSI sonde calculates the maximum number of days the sonde can log data available internal memory
xviii. A. The YSI sonde reports time until sampling begins
xix. B. View parameters that will be included in sampling report
xx. C. Start logging. Press C to begin logging at indicated start date and time. Type 1 to verify start logging
xxi. exit YSI software by pressing ESC until past the main menu
xxii. detach YSI from computer and apply the dummy cover on pins

II. Deployment
i. secure all connections on the datasondes (battery compartment, probes, etc.)
ii. connect appropriate dummy plugs to all exposed connector pins
iii. remove the calibration cup and replace with a field cup
iv. secure cable or chain to platform (rock, bridge, flotation buoy, or etc.) with a quick clip and lock
v. attach datasondes to the other end of the cable or chain with a quick clip and lock. Be sure to lock both the sonde and quick clip to the cable or chain
vi. place the sonde in the water and vigorously shake to dislodge air bubbles and debris from SC sensor (also, try to deploy SC facing up to prevent bubbles from getting trapped in the sensor and creating erroneous readings).
vii. be sure the sonde is placed in such a way that it will be covered with water during the duration of its deployment
viii. record deployment information on the log sheet (sonde type and number, place of deployment, time of deployment, lock number or type, and other field notes)

III. Data Retrieval
i. turn on computer
ii. connect bench cable labeled YSI to serial port and YSI unit.
iii. plug in power cable labeled YSI
iv. select the YSI Terminal icon located on the desktop
v. at the # sign type 1 to enter the RUN menu
vi. select 3 inside the Run menu to Quick Upload the data file
vii. select 3 to convert data to an ACSI Text file [the file will automatically upload to the computer's C: directory
viii. minimize the YSI Terminal software
ix. view the file with WORDPAD to ensure the data transfer was successful
x. in the YSI Terminal window, press esc to back up one level
xi. type 6 to delete the file just uploaded

16. Calculations: Raw data are converted to units of scientific measure internally by the sensor.
17. Method performance:
This procedure is in accordance with the manufacturer's recommendations.
18. Pollution prevention: This procedure has no discernible negative impact on the environment.
19. Data assessment and acceptance criteria for quality control measures:
Assessment of results is done at UFI facilities (post collection). Acceptance criteria for quality control include consideration of field notation concerning interferences, presence of data points

outside parameter detection range values, and comparison to other data sources (i.e. ground truth).

20. Corrective actions for out-of-control or unacceptable data:
If unacceptable data is determined to be a result of instrument malfunction, then instrument will be returned for repair. If unacceptable data is determined to be due to inappropriate use by the field crew, then a review of the procedure will be conducted to ensure the problem will not happen again.
21. Contingencies for handling out of control or unacceptable data:
Identify data that fail QA/QC, record throughout data transfer to client. Analyze cause of unacceptable data (i.e. instrument error or interferences). Return instrument to manufacturer for repair and recalibration if deemed necessary.
22. Waste management: None.
23. References:
    - YSI Environmental Operations Manual revision J (3/2012), 1700/1725 Brannum Lane, Yellow Springs, OH 45387, www.ysi.com
    - YSI Sonde Calibration SOP 315

SOP No. 319: YSI Sonde Profiling using the YSI 650 Datalogger

1. Test method: YSI Sonde Profiling using the YSI 650 Datalogger
2. Applicable matrix or matrices: Water.
3. Detection limit: see field SOP 315.
4. Scope and application: Drinking, surface and saline waters.
5. Summary of test method:
   A calibrated YSI sonde is attached to the YSI 650 datalogger and used to measure water quality parameters at discrete depths in the water column or specific locations in a creek or stream.
6. Definitions: None.
7. Interferences: None.
8. Safety:
   Always use proper boating safety techniques when sampling from boats (see the most current New York State Boater's Safety Guide). Use caution and best judgment if working from bridges. Be sure to park as far on the shoulder as possible. Use parking cones, wear reflective vests, and use truck emergency warning lights, and affix warning light to top of truck. Standard field procedures involving moderate lifting should be applied.
9. Equipment and supplies:
   YSI multiprobe sonde, 4 C batteries, profiling cable, YSI 650 data logger, field sheets.
10. Reagents and standards: None.
11. Reference Solution: None.
12. Sample collection, preservation, shipment and storage: NA.
13. Quality Control:
    The probes must be allowed to equilibrate. Data collected are reviewed by the field crew upon return for initial qualitative acceptability (do the data make sense). Final determination of data acceptability will be handled during analysis at a later time.
14. Calibration and standardization: see field SOP 315.
15. Procedure:
    I. Collecting a profile from a boat
       i. attach the YSI 650 datalogger to a fully calibrated YSI Multiprobe
       ii. remove the calibration cup and fit the sonde with a field cup
       iii. using the key pad, turn the unit on
       iv. from the main menu, select RUN and press enter
       v. lower the YSI multiprobe to the first depth interval [Note: the profile interval is system dependent].
       vi. gently shake to dislodge any debris, bubbles
       vii. it is absolutely critical that the unit be allowed to equilibrate before taking a measurement (depends on parameter stabilization times)
       viii. record measurements on the field sheet
    II. Collecting discrete measurements in a stream
       i. wade approximately mid-way into the stream channel (lower from a bridge if wading is not possible or collect from stream bank)
       ii. facing upstream, submerge the probes a few inches below the water surface
       iii. wait until readings stabilize
       iv. read and record data
16. Calculations: Raw data are converted to units of scientific measure internally by the data logger.
17. Method performance:

This procedure is in accordance with the manufacturer's recommendations.

18. Pollution prevention: This procedure has no discernible negative impact on the environment.
19. Data assessment and acceptance criteria for quality control measures:
    Assessment of results should be done on location. Acceptance criteria for quality control include consideration field conditions, presence of data points outside parameter detection range values, comparison to other data sources (i.e. ground truth), and field judgment in context of conditions and specific system.
20. Corrective actions for out-of-control or unacceptable data:
    If unacceptable data is determined to be a result of instrument malfunction, then instrument will be returned for repair. If unacceptable data is determined to be due to inappropriate use by the field crew, then a review of the procedure will be conducted to ensure the problem will not happen again. If necessary, the profile may need to be recollected.
21. Contingencies for handling out of control or unacceptable data:
    Identify data that fail QA/QC, record throughout data transfer to client. Analyze cause of unacceptable data (i.e. instrument error or interferences). Return instrument to manufacturer for repair and recalibration if deemed necessary.
22. Waste management: None.
23. References:
    - YSI Environmental Operations Manual revision J (3/2012), 1700/1725 Brannum Lane, Yellow Springs, OH 45387, www.ysi.com
    - YSI Sonde Calibration SOP 315

S-13 GEDDES BROOK, NINEMILE CREEK AND LCP FLOODPLAIN SEDIMENT SAMPLING AND PROCESSING

SECTION 1.0 SCOPE

These procedures are to be followed; any substantive modifications to the procedures shall be approved by the Field Team Leader. This SOP includes procedures to collect floodplain sediment as well as channel sediment samples as described in the Geddes Brook (2011b), Ninemile Creek (2018 and 2015), and LCP (2009a) OM&M Plans.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water sampling include: caution deploying and retrieving heavy equipment, slips, trips, falls, and the proper use of personal flotation devices (PFDs) and personal protective equipment (PPE). Gloves must also be worn at all times in the field. The type of glove may vary by task; this will be determined by field leader.

SECTION 3.0 SEDIMENT SAMPLE COLLECTION EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Not all materials and equipment included on the list may be necessary to complete the task.

- Lexan® Tubes
- Ponar
- PFDs
- Scoops
- Large ziplock bags
- Soil classification notes
- Field notebook/iPad
- Field forms
- Cellular phone
- Gloves (all types)

SECTION 4.0 SEDIMENT COLLECTING PROCEDURE

This section describes procedures for collecting sediment composite samples from locations described in the Geddes Brook, Ninemile Creek, and LCP OM&M Plans. If sampling with lexane tubes or via grab sampling, follow procedures detailed in Section 4.1. If sampling with a ponar, follow procedures detailed in Section 4.2. Note, ponars should only be utilized in soft substrates. Each composite sample will consist of five grab samples from the top 6 inches of sediment. If surface water samples are to be taken at the same location, they should be collected before the sediment samples. Sample locations will be previously staked out with a GPS unit.

4.1 Sampling Method- lexane or grab sampling

1. Record the water depth at each sample location on the field forms.
2. At each sediment sampling location, five grab samples will be collected from the 0-6 inches interval. Grab samples are to be collected within a 10 ft. radius of the designated sample location.
3. Sediment samples will be collected by driving a Lexan® sample tube equipped with an egg catcher (if needed) into the sediment to the desired depth.
4. The sample will be removed from the Lexan® tube using a sterile, dedicated scoop and placed in a large ziplock bag. Rocks and vegetative material will be discarded, and care taken to retain fine materials which tend to disperse when disturbed.
5. Sediment samples will be visually described for: 1) sediment type, 2) color, 3) texture, 4) grain size and shape, 5) visible evidence of staining, and 6) any other observations.
6. Sample locations will be located using a GPS unit.
7. Sample description, depth, and location will be recorded on the field forms.

4.2 Sampling Method – Ponar

Record the water depth at each sample location on the field forms.

1. Securely attach the ponar sampler to a cable or line of sufficient strength to accommodate the weight of the sampler and sample.
2. Set the mechanism on the sampler so the jaws are held in the open position.
3. Slowly lower the sampler over the side of the vessel. Maintain tension on the sampler to keep the jaw mechanism from prematurely closing.
4. After the sampler contacts the sediments on the bottom, relax the tension on the sampler to allow the jaw locking mechanism to release.
5. Place tension on the cable/line and slowly lift. This should cause the sampler jaws to close trapping the sample inside.
6. Slowly retrieve the sampler.
7. Hang the sampler above a pre-cleaned container of suitable size and composition (an inert material that will not interfere with or cause cross contamination).
8. Empty the contents of the sampler into the container.
9. Repeat the process until sufficient sample quantity has been recovered.
10. Pick objects such as wood debris, vegetation, and living organisms (clams etc.) from the sediment and discard.

11. Transfer the sediments to a designated container(s) or keep the sediment in the original container(s) and seal the container(s) and transport the sample(s) to the onshore sample processing area.
12. Sediment samples will be visually described for: 1) sediment type, 2) color, 3) texture, 4) grain size and shape, 5) visible evidence of staining, and 6) any other observations.
13. Sample description, depth, and location will be recorded on the field forms.

SECTION 5.0 SAMPLING PERSONNEL

The Project Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Project Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Project Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 6.0 SEDIMENT SAMPLE PROCESSING PRIOR TO LABORATORY RECEIPT

6.1 Equipment List

- PFDs
- Paper towels
- Hard hat (as needed) and safety glasses
- Digital camera
- Field notebook/iPad
- Cellular phone
- Plans with sampling locations
- Sample labels
- Re-sealable plastic bags (quart and gallon sizes)
- Sharpie pen
- Wet ice
- Coolers
- Work Gloves
- Nitrile gloves
- Chain of Custody forms
- Custody Seals
- Field forms
- Prior event field forms
- AHAs
- SOP
- OMM plan

6.2 Sediment Sample Processing Procedure

1. The five grab samples will be thoroughly mixed with a sterile scoop in a ziplock bag and then placed into the appropriate sample containers.
2. Composite and duplicate sediment samples and matrix spike/matrix spike duplicate/ matrix duplicate (MS/MSD/MD) samples will be prepared by mixing the sediment with a sterile, dedicated scoop in a ziplock bag and splitting the mixed sediment.

6.3 Sample Transport to Laboratory

Store the sediment at a temperature below 4 degrees Celsius and ship immediately on wet ice to the analytical laboratory. Provide Chain of Custody document with the shipment. Place custody seal on cooler before released to courier.

SECTION 7.0 REFERENCES

Parsons, 2011b. *100% Design Report for the Geddes Brook Interim Remedial Measure. Appendix E: Operation, Maintenance, and Monitoring Plan for the Geddes Brook Site.* Prepared for Honeywell, Syracuse, New York. February 2011.

Parsons. 2009a. *Operation, Maintenance, and Monitoring Plan for the LCP Bridge Street Site.* Prepared for Honeywell, Syracuse, New York. September 2009.

Parsons, 2018. *Maintenance, and Monitoring Plan for the Ninemile Creek Reach CD Site*. Prepared for Honeywell. Syracuse, New York, August 2018.

Parsons, 2015. *Ninemile Creek OM&M 2015 Surface Water, Soil, and Biota Sampling Work Plan.* Prepared for Honeywell. Syracuse, New York, September 2015.

SECTION 8.0 REVISIONS/REVIEWS

Doc Number: Rev No.: 0 Date: August 4, 2021

Reviewer: Parsons

What was changed: N/A

S-14 GEDDES BROOK, NINEMILE CREEK AND LCP SURFACE WATER SAMPLING AND PROCESSING

SECTION 1.0 SCOPE

These procedures are to be followed; any substantive modifications to the procedures shall be approved by the Field Team Leader. This SOP includes procedures to collect surface water samples as described in the Geddes Brook (2011b), Ninemile Creek (2015 and 2018), and LCP (2009a) OM&M Plans.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water sampling include: caution deploying and retrieving heavy equipment, slips, trips, falls, and the proper use of personal flotation devices (PFDs) and personal protective equipment (PPE). Gloves must also be worn at all times in the field. The type of glove by vary by task; this will be determined by field leader.

SECTION 3.0 SURFACE WATER SAMPLE COLLECTION EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Not all materials and equipment included on the list may be necessary to complete the task.

- PFDs
- Large ziplock bags
- Field notebook/iPad
- Field forms
- Cellular phone
- Gloves (all types)
- Water quality meter

SECTION 4.0 SURFACE WATER COLLECTING PROCEDURE

This section describes procedures for collecting surface water samples from locations described in the Geddes Brook, Ninemile Creek, and LCP OM&M Plans. Each sample will be analyzed for field parameters (temperature, pH, specific conductance, dissolved oxygen and oxidation-reduction potential (ORP)). If surface water samples are to be taken at the same location as sediment samples, they should be collected before the sediment

samples. Samples should be collected beginning at the downstream location and working upstream. Sample locations will be previously staked out with GPS unit.

4.1 Sampling Method

1. From this point forward, sample handling procedures will follow USEPA's "clean hands/dirty hands" protocols whenever handling materials that may come in contact with the sample. One person of the two person sampling crew will be designated to perform the "clean hands" duties, while the other will perform the "dirty hands" duties.
2. Both sampling personnel will put on two pairs of disposable gloves. The outer pair of gloves will be changed any time there is potential for the outer gloves coming in contact with potential contaminants.
3. Pre-cleaned sample containers will be pre-labeled and double bagged using resealable food storage bags, and placed in a clean, dedicated cooler. "Dirty hands" will open the cooler and the outer plastic bag containing the appropriate sample container (both should change gloves after handling the sampler and prior to opening the outer and inner bags). "Clean hands" will then open the inner plastic bag.
4. "Clean hands" will immerse the sample container without disturbing the sediment. If samples cannot be collected directly into the sample bottle, a decontaminated sample collection device may be used. Bottles should have zero headspace.
5. "Clean hands" will then place the cap back on the container, and place it inside the inner bag, and then place the inner bag inside the outer bag, held by "Dirty hands." "Dirty hands" will then close the outer bag, and place the double bagged container back in the cooler. This process will be repeated at each location.
6. COC procedures will be followed.
7. Measurements of temperature, pH, specific conductance, dissolved oxygen and ORP shall be taken by direct immersion of instrument probes into the water body. If direct measurement is not possible, these measurements shall be taken from water collected and placed in a field container. The results shall be recorded in on field forms.
8. Record the over-all depth of the water column (i.e., distance from the surface to the sediment bottom), as well as the depth at which the sample was collected (i.e., distance from the surface).
9. Sample description and location will be recorded in the field form.

SECTION 5.0 SAMPLING PERSONNEL

The Project Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Project Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Project Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 6.0 SURFACE WATER SAMPLE PROCESSING PRIOR TO LABORATORY RECEIPT

6.1 Equipment List

- PFDs
- Paper towels
- Safety glasses
- Digital camera
- Field notebook/iPad
- Cellular phone
- Plans with sampling locations
- Sample labels
- Re-sealable plastic bags (quart and gallon sizes)
- Sharpie pen
- Wet ice
- Coolers
- Work Gloves
- Nitrile gloves
- Chain of Custody forms
- Custody Seals
- Field forms
- Prior event field forms
- AHAs
- SOP
- OMM plan

6.2 Surface Water Sample Processing Procedure

1. Sample containers are pre-labeled prior to sampling.

6.3 Sample Transport to Laboratory

Store the samples at a temperature below 4 degrees Celsius and ship immediately on wet ice to the analytical laboratory. Provide Surface Water Chain of Custody document with the shipment. Place custody seal on cooler before released to courier.

SECTION 7 REFERENCES

Parsons, 2011b. *100% Design Report for the Geddes Brook Interim Remedial Measure. Appendix E: Operation, Maintenance, and Monitoring Plan for the Geddes Brook Site.* Prepared for Honeywell, Syracuse, New York. February 2011.

Parsons. 2009a. *Operation, Maintenance, and Monitoring Plan for the LCP Bridge Street Site.* Prepared for Honeywell, Syracuse, New York. September 2009.

Parsons, 2018. *Maintenance, and Monitoring Plan for Ninemile Creek*. Prepared for Honeywell. Syracuse, New York, August 2018.

Parsons, 2015. *Ninemile Creek OM&M 2015 Surface Water, Soil, and Biota Sampling Work Plan.* Prepared for Honeywell. Syracuse, New York, September 2015.

SECTION 8.0 REVISIONS/REVIEWS

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Reviewer: Parsons

What was changed: N/A

S-15 EARTHWORM COLLECTION AND PROCESSING

SECTION 1.0 SCOPE

These procedures are to be followed; any substantive modifications to the procedures shall be approved by the Field Team Leader. This SOP includes procedures to collect earthworms by hand digging with shovels and sorting through soils.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water sampling include: caution deploying and retrieving heavy equipment, slips, trips, falls, and the proper use of personal flotation devices (PFDs) and personal protective equipment (PPE). Gloves must also be worn at all times in the field. The type of glove by vary by task; this will be determined by field leader.

SECTION 3.0 EARTHWORM SAMPLE COLLECTION EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Not all materials and equipment included on the list may be necessary to complete the task.

- Hand shovel
- PFDs
- Balance for weighing samples
- Digital camera
- Field notebook/iPad
- Cellular phone
- Gloves (all types)

SECTION 4.0 EARTHWORM COLLECTING PROCEDURE

This section describes procedures for collecting benthic earthworms from locations described in the Geddes Brook (2011b) and Ninemile Creek (2015 and 2018) OM&M Plans. One composite sample will be collected from each location and analyzed (10-20 grams per sample).

4.1 Hand Shovels

Field teams will collect earthworms at target locations with shovels by the following procedures:

1. Overturn the top 12" of soil with a shovel (several shovel scoops)
2. While wearing nitrile gloves, sort through the soil extracting the earthworms by hand
3. Place collected earthworms in bucket for processing
4. Process earthworms retained for analysis according to Section 6.0

SECTION 5.0 SAMPLING PERSONNEL

The Project Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Project Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Project Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 6.0 EARTHWORM SAMPLE PROCESSING PRIOR TO LABORATORY RECEIPT

6.1 Equipment List

- PFDs
- Paper towels
- Safety glasses
- Digital camera
- Field notebook/iPad
- Cellular phone
- Balance for weighing samples
- Small baskets for weighing samples
- Sample labels
- Re-sealable plastic bags (quart and gallon sizes)
- Sharpie pen
- Wet ice
- Coolers
- Work Gloves
- Nitrile gloves
- Chain of Custody forms
- Custody Seals
- Field forms
- Prior event field forms

- AHAs
- SOP
- OMM plan

6.2 Earthworm Sample Processing Procedure

1. Each sample will be a minimum of 10 grams, with 20 grams or higher being the preferred quantity.
2. Rinse each sample with DI water to remove any residual exterior soil prior to weighing.
3. For each sample, record the total weight and number of earthworms on the field log. Take a photograph of one specimen (at least) per sample.
4. Place the entire sample into a re-sealable plastic bag and place bag into 8-oz jars.
5. Place label on jars covered by clear tape.
6. Place samples in a cooler on large quantities of wet ice if shipping directly to laboratory. If not shipping immediately, store samples in a freezer until shipment. Samples are not to be depurated prior to analysis.
7. Prior to shipping the samples, print the chain of custody form and include with the shipment in a ziplock bag.
8. Before sample is transferred to courier, place a custody seal on cooler.
9. One MS/MSD is required for each group of samples. After 20 samples, a MS/MSD is required for every additional set of 20 samples.

6.3 Sample Transport to Laboratory

Store the earthworms at a temperature below 4 degrees Celsius and ship immediately on wet ice to the analytical laboratory. Provide earthworm Chain of Custody document with the shipment. Place custody seal on cooler before released to courier.

SECTION 7.0 REFERENCES

Parsons, 2011b. *100% Design Report for the Geddes Brook Interim Remedial Measure. Appendix E: Operation, Maintenance, and Monitoring Plan for the Geddes Brook Site.* Prepared for Honeywell, Syracuse, New York. February 2011.

Parsons, 2018. *Maintenance, and Monitoring Plan for Ninemile Creek*. Prepared for Honeywell. Syracuse, New York, August 2018.

Parsons, 2015. *Ninemile Creek OM&M 2015 Surface Water, Soil, and Biota Sampling Work Plan.* Prepared for Honeywell. Syracuse, New York, September 2015.

SECTION 8.0 REVISIONS/REVIEWS

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What was changed: N/A

S-16 BENTHIC MACROINVERTEBRATE COLLECTION AND PROCESSING

SECTION 1.0 SCOPE

These procedures are to be followed; any substantive modifications to the procedures shall be approved by the Field Team Leader. Macroinvertebrates will be collected and shipped to laboratory for chemical analysis as described in the Geddes Brook (2011b) and Ninemile Creek (2015 and 2018) OM&M Plans. As detailed in this SOP, a grab sampler (e.g., modified van Veen, Ekman, Ponar), aquatic nets, and crayfish traps may be used to collect macroinvertebrates for the program depending on habitat type that is being sampled. This SOP includes procedures to collect macroinvertebrates with the use of a grab sampler, aquatic nets, and crayfish traps. The specific taxonomic group to be sampled will be based upon availability.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water sampling include: caution deploying and retrieving heavy equipment, slips, trips, falls, and the proper use of personal flotation devices (PFDs) and personal protective equipment (PPE). Gloves must be worn at all times in the field. Type of glove can vary by task; this will be determined by field leader.

SECTION 3.0 MACROINVERTEBRATES SAMPLE COLLECTION EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Since multiple procedures or alternate methods may be employed to achieve the objectives, not all materials and equipment included on the list may be necessary to complete the task.

- Aquatic nets
- Grab sampler (e.g., modified van Veen, Ekman, Ponar)
- Polypropylene sieve (mesh size = 600 µm)
- Crayfish traps
- PFDs
- Waders
- Balance for weighing samples
- Digital camera
- Field notebook/iPad
- Cellular phone

SECTION 4.0 MACROINVERTEBRATES COLLECTING PROCEDURE

This section describes procedures for collecting benthic macroinvertebrates from locations described in the Geddes Brook (2011b) and Ninemile Creek (2015 and 2018) OM&M Plans. Benthic organisms will be collected based on the presence of sufficient quantities. A grab sampler (e.g., modified van Veen, Ekman, Ponar) and aquatic nets may be used to collect benthic organisms. A sufficient number of individuals will be collected to obtain the required biomass for chemical analysis (10 to 20 grams per sample). Individual organisms will be composited (by species or at least by the next closest taxonomic group identified) in the field and/or laboratory.

4.1 Grab Sampler

When grab sampling, the follow steps should be taken:

1. Lower the petite ponar over the side of the boat with a cable or rope. Allow the sampler to freefall from the water surface to allow it to penetrate the bottom. The closing mechanism is activated upon reaching the bottom.
2. Retrieve the sampler. Check the sample for acceptability. A sample is considered acceptable if it is not over-filled with sediment, overlying water is present and not excessively turbid, the sediment surface is relatively flat, and the desired plant material has been obtained. Cut the above grade portion of the aquatic macrophytes at the base. Discard the below grade portion of the sample.
3. Place the sample in a 600 micron mesh bottomed plastic bucket held over the side of the boat. Rinse excess sediment from the sample and separate out the macroinvertebrates.

4.2 Aquatic Net

Aquatic nets can be used in many different ways to sample macroinvertebrates, two of the ways that will be utilized are kick sampling and dip netting.

- Kick Sampling: Place an aquatic net downstream of sampler and disturb the sediments in front of the net with foot. Continue this moving downstream at a diagonal. The contents collected in the net are emptied into pan of stream water and macroinvertebrates are separated out.
- Dip Net: Use net to skim vegetation through the water. It is inserted gently with the opening facing upwards, and a scooping action is carries out while pushing the net through the water to fish out the macroinvertebrates. Scooping should take place in areas with emergent vegetation, passing the net very closely to taller stems where most insects find shelter. Net contents are placed in pan of stream water and macroinvertebrates are separated out. Clean the net from unwanted debris and living material every 5-10 scoops.

4.3 Crayfish Trap

When setting crayfish traps, the follow steps should be taken:

1. Proceed to the appropriate station and record in a field log.
2. Assemble the trap. If bait will be used, the trap can be baited at this time.
3. Tie a long piece of rope onto the trap, and lower the trap out into the stream channel.

4. Secure the end of the line to a structure on the shoreline, and use surveyor flagging to mark where the line is tied.
5. Allow the trap to soak for the prescribed sampling period (e.g., 24–48 hours).
6. After 24-48 hours, pull the trap to the water surface by using the line, and bring the trap on to bank.
7. Open the trap, and transfer the captured crayfish to the collection buckets.
8. Process crayfish in accordance with Section 6.0.

Process macroinvertebrates retained for analysis according to Section 4.0.

SECTION 5.0 SAMPLING PERSONNEL

The Project Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Project Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Project Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 6.0 BENTHIC MACROINVERTEBRATE SAMPLE PROCESSING PRIOR TO LABORATORY RECEIPT

6.1 Equipment List

- PFDs
- Waders
- Paper towels
- Hard hat (as needed) and safety glasses
- Digital camera
- Field notebook/iPad
- Cellular phone
- Balance for weighing samples
- Small baskets for weighing samples
- Plans with sampling locations
- Sample labels
- Sharpie pen
- Re-sealable plastic bags (quart and gallon sizes)
- Wet ice
- Coolers
- Work Gloves
- Nitrile gloves
- Chain of Custody forms
- Custody Seals

- Field forms
- Prior event field forms
- AHAs
- SOP
- OMM plan

6.2 Macroinvertebrate Sample Processing Procedure

1. Check what species were sampled at the location during prior sampling events and attempt to use the same species. If the same species are not present, then attempt to use species of similar levels and feeding habits.
2. Each sample will be a minimum of 10 grams, with 20 grams or higher being the preferred quantity. Samples will be comprised of individuals from the same taxonomic grouping.
3. For each sample, record the total wet weight of each group of macroinvertebrates on the field log. If the sample is comprised of less than 10 individuals, weights of all individuals will be recorded in addition to the total weight of the sample. Take a photograph of one specimen (at least) per sample.
4. Place the entire sample into a re-sealable plastic bag, place this in a glass jar (if provided/required by the lab) and place in a cooler on large quantities of wet ice or into a freezer (these previously bagged in ziplock bags).
5. Prior to shipping the samples, print the chain of custody form and include with the shipment in a ziplock bag.
6. Before sample transfer to courier, be sure to place a custody seal on cooler

6.3 Sample Transport to Laboratory

Store the macroinvertebrates at a temperature below 4 degrees Celsius and ship immediately on wet ice to the analytical laboratory. If not being shipped immediately, store in a freezer (below 0 degrees Celsius). Provide macroinvertebrates Chain of Custody document with the shipment. Place custody seal on cooler before released to courier

SECTION 7.0 REFERENCES

Parsons, 2011b. *100% Design Report for the Geddes Brook Interim Remedial Measure. Appendix E: Operation, Maintenance, and Monitoring Plan for the Geddes Brook Site.* Prepared for Honeywell, Syracuse, New York. February 2011.

Parsons, 2018. *Maintenance, and Monitoring Plan for Ninemile Creek*. Prepared for Honeywell. Syracuse, New York, August 2018.

Parsons, 2015. *Ninemile Creek OM&M 2015 Surface Water, Soil, and Biota Sampling Work Plan.* Prepared for Honeywell. Syracuse, New York, September 2015.

SECTION 8.0 REVISIONS/REVIEWS

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S-17 GEDDES BROOK, NINEMILE CREEK AND LCP FISH COLLECTION AND PROCESSING

SECTION 1.0 SCOPE

These procedures are to be followed; any substantive modifications to the procedures shall be approved by the Field Team Leader.

Several methods may be used to collect fish for the program. This SOP includes procedures to collect fish by electrofishing, angling, seine nets, and/or minnow traps. Use of each method will be dependent on species and life stages being targeted; a combination of methods likely will be necessary to obtain the required species.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water and lake sampling include: caution deploying and retrieving heavy equipment, slips, trips, falls, and the proper use of personal flotation devices (PFDs) and personal protective equipment (PPE). The use of electrofishing equipment involves potential hazards related to the high voltage output. Given that water is an excellent conductor of electricity, the operator of the electrofishing equipment (SUNY ESF) must observe certain precautions to avoid injury. For example, the acceptable voltage range for electroshocking is 300 to 400 volts, and the acceptable current range is 19 to 23 amps based on experience from previous investigations. All personnel participating in electroshocking activities must wear high voltage gloves.

SECTION 3.0 FISH SAMPLE COLLECTION EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Since multiple procedures or alternate methods may be employed to achieve the objectives, not all materials and equipment included on the list may be necessary to complete the task.

- Backpack Electroshocker
- Angling Equipment
- Seine net
- Minnow trap
- High voltage gloves
- PFDs
- Waders
- Hard hat (as needed) and safety glasses
- Measuring board
- Fish holding tub
- Portable pH, temperature and conductivity meters

- Balance for weighing samples
- Fish holding tub
- Digital camera
- Field notebook/iPad
- Cellular phone
- Portable temperature and conductivity meter

SECTION 4.0 FISH COLLECTING PROCEDURE

This section describes procedures for collecting fish from locations described in the Geddes Brook (2011b), Ninemile Creek (2015 and 2018), and LCP (2009a) OM&M Plans, respectively. Fish samples will be collected using seine nets, angling equipment, minnow traps, and/or electrofishing. Samples collected will include sport fish and small prey fish, depending on the site. For small prey fish samples, a sufficient number of individual specimens will be collected to obtain the required biomass for chemical analysis (40 to 60 grams per sample). Individual specimens will be composited by species in the field and/or laboratory for analysis.

4.1 Electrofishing

Electrofishing uses electrical currents to immobilize fish for capture. Electrofishing is less effective in deeper waters, where fish can swim and avoid the current, so this method will be limited to areas that are less than 4 meters [13.2 ft.] deep, or were field crews can walk depending on the depth of the stream. The following outlines the procedures for electrofishing:

1. Personnel performing the electroshocking will wear appropriate health and safety gear (rubber boots/waders, rubber gloves, PFD).
2. Measure the water conductivity and temperature to determine the appropriate operating voltage and amperage.
3. Adjust the output voltage and amperage dials until the desired output setting is obtained without harming fish. Use pulsed output to reduce stress on fish.
4. Collect the fish with dip nets and place in bucket of water for processing.
5. Release all unselected fish following processing.
6. Process fish retained for analysis according to Section 6.0.

4.2 Angling

Angling efforts will follow all rules and regulations set forth by the NYSDEC. Each sampler must have a valid NYS fishing license. All undesired fish will be released immediately. Fish will be processed for analysis according to Section 6.0.

4.3 Sampling with a Seine Net

For shallow areas, a bag seine will be used to collect juvenile fish for abundance estimates and prey fish tissue samples. The bag seine is typically used in shallow water where the net wall can extend from the surface of the water to the bottom. It is useful in the capture of near-shore species or for species that use the near-shore area

seasonally or daily. In addition, the substrate needs to be relatively smooth so that the lead line of the seine drags along the bottom of the river preventing fish escapement. The fish are herded into the net as it is swept through the water. Seining will be conducted by a minimum of two people. The following outlines the procedures for seine netting (based on NYSDEC 1989):

4.3.1 Sampling

1. Proceed to the appropriate station and record in a field log.
2. Prior to entering the water stretch the bag seine out on shore and remove any material lodged in the mesh. Inspect the net for holes and make repairs, if necessary.
3. One person begins extending the seine perpendicular to the shoreline until the net is straightened out or the water becomes too deep. Be sure bag is fully deployed and not tangled.
4. One person holds the on-shore brail stationary while the off shore person sweeps or walks the brail towards shore. A third person walks behind the bag to dislodge any snags if the seine becomes stuck. As the person holding the offshore brail approaches shore, the two ends are worked together to beach the seine while maintaining the integrity of the bag section and keeping the lead line on the bottom.
5. Fish are removed from the net and placed into holding buckets for identification. Be sure to pick through any debris captured in the net to retrieve all fish.
6. Stretch out the seine on shore and remove any material lodged in the net. Check the entire seine for fish stuck in the mesh. To prevent inadvertent transportation of fish between sites, any fish remaining in the net need to be removed prior to moving to the next site.
7. Process fish in accordance with Section 6.0.

4.4 Minnow trap sampling

A minnow trap is used as a passive sampling device to capture juvenile fish as well as the adult individuals of small fish species. Fish are captured when they swim into the trap through a funnel-shaped opening that makes escape difficult. The trap is generally set in shallow nearshore areas. The trap can be deployed with bait inside (bread) to attract fish or without bait. Fish may be attracted to the trap by other fish that are already captured in it.

4.4.1 Sampling

1. Proceed to the appropriate station and record in a field log.
2. Assemble the trap. If bait will be used, the trap can be baited at this time.
3. Tie a long piece of rope onto the trap, and lower the minnow trap out into the stream channel, or place it at the edge of habitat along the shoreline or adjacent to habitat structure (e.g., a downed tree limb).
4. Secure the end of the line to a structure on the shoreline, and use surveyor flagging to mark where the line is tied.
5. Allow the trap to soak for the prescribed sampling period (e.g., 24–48 hours).
6. After 24-48 hours, pull the trap to the water surface by using the line, and bring the trap on to bank.
7. Open the trap, and transfer the captured fish to the collection buckets.
8. Process fish in accordance with Section 6.0.

4.5 Trapnet sampling

A trap net is used as a passive sampling device to capture fish as they swim along the shoreline. A trap net consists of a leader line (23 m [75.4 ft.] length), two wings (11.5 m [37.7 ft.] each), and a series of hoops; the entire net consists of 0.635 cm [0.25 in.] stretch mesh. The net is set perpendicular to and facing the shoreline. When fish encounter the leader line, they are directed offshore into the mouth of the net, through the hoops, and into the end of the net. As fish move through the series of hoops, escape becomes increasingly difficult. Fish may be attracted to the net by other fish that are already captured in it. This method will be utilized in Ninemile Creek only.

4.5.1 Station selection

1. Proceed to the appropriate station and record in field log.
2. Record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface where net will be located.

4.5.2 Setting the net

1. Anchor the shoreward end of the leader line near the shoreline or attach it to the shoreline by tying it to a fixed object on shore (e.g., tree).
2. Extend the leader line out into the water and perpendicular to shore, until it is taut.
3. Extend each wing at a 45 to 90 degree angle to the leader line. This can be done either by boat or by wading, depending on the water depth and substrate characteristics.
4. Anchor the lower ends of both wings with anchors and attach buoys to the upper ends of the wings. Adjust the buoy lines so that the buoys are floating and the lines are relatively taut.
5. Extend the hoops of the trap away from shore in line with the leader line and pull on the end of the net until all of the hoops are upright.
6. Close the end of the net with a piece of line.
7. Attach an anchor to the end of the net to keep it submerged and attach a buoy to the anchor to mark the location of the end of the net. Record the depth below the water surface of the far end of the net.
8. Allow the net to soak (i.e., fish) for the prescribed sampling period (e.g., 24 to 48 hours).

4.5.3 Sample Collection

1. Arrive at the buoy at the end of the net and pull the buoy and its anchor into the boat.
2. Retrieve the hoops in sequence, while moving toward shore.
3. Starting at the mouth of the net, shake the captured fish into the closed end of the net.
4. Once all captured fish are in the end of the net, remove the piece of line from the end of the net and empty fish into the collection buckets.
5. If sampling will continue at the collection site, reset the trap according to steps 3 through 8 above for setting a trap net.

Process fish according to procedures in 4.1 (above). If fish are being retained for tissue assessment, record water quality data (temperature, pH, dissolved oxygen, conductivity) at the near surface location where the net was placed. Fish not required for other analyses will be released.

SECTION 5.0 SAMPLING PERSONNEL

The Project Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Project Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Project Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 6.0 FISH SAMPLE PROCESSING PRIOR TO LABORATORY RECEIPT

6.1 Equipment List

- Digital camera
- Field notebook/iPad
- Cellular phone
- Paper towels
- Balance for weighing samples
- Small baskets for weighing forage fish
- Plans with sampling locations
- Sample labels
- Resealable plastic bags (quart and gallon sizes)
- Foil
- Sharpie pen
- Wet ice
- Coolers
- Nitrile gloves
- Chain of Custody forms
- Field forms
- SOP
- OMM plan(s)

6.2 Fish Sample Processing Procedure

1. Check what species were sampled at the location during prior sampling events and attempt to use the same species and size ranges. If the same species are not present, then attempt to use species of similar trophic levels and feeding habits.
2. Samples will meet the following criteria for their respective grouping:

    a. Each sport fish sample will meet the follow criteria:
        - >6 inches for Channel Catfish and Brown Trout
        - >12 inches for Smallmouth Bass

- >4 inches for Pumpkinseed/Bluegill Sunfish
- >7 inches for Brown Bullhead

If not one of the species listed above, fish will be of legal size.

b. Each prey fish sample will be minimum of 40 grams, with 60 grams or higher being the preferred quantity depending on mass requirements for the analyses being conducted.

3. For each sample, record the total length of each fish and weight (total composite weight for prey fish and weight of each individual sportfish collected) on the field log. Take a photograph of one specimen (at least) per sample.
4. If a subset of samples are being analyzed for organic parameters (i.e., PCB Aroclors, dioxins/furans, lipids), then:
   a. For sport fish, select the species that will be analyzed for the additional analyses; the species should be consistent with previous years and with work plan requirements, as practical. If selecting a subset of the species, try to select the largest individual(s) for organic analysis to ensure that there is enough mass to conduct all the necessary analyses.
   b. For small prey fish, select the samples with the highest total mass, as practical, from the appropriate sample locations dictated by the work plan to ensure that there is enough mass to conduct all the necessary analyses.
5. Wrap fish in clean foil (shiny side out) and attach an identification label that includes the fish tag number, date, sample type and location sampled.
6. Place the entire sample into a re-sealable plastic bag (place bag in a jar if provided/ required by the lab), label the bag or jar with corresponding label, and place in a cooler on large quantities of wet ice or into freezer.
7. Prior to shipping the samples, print the chain of custody form and include with the shipment in a ziplock bag.

The analytical laboratory will prepare fillets, for adult sportfish, in accordance with the NYSDEC's SOP PrepLab (May 28, 2014).

6.3 Sample Transport to Laboratory

Store the fish on wet ice immediately after collection. If shipping to the laboratory the same day as collection, ship on wet ice. If not being shipped to the laboratory the day of collection, store at a temperature below 4 degrees Celsius prior to shipping. Once ready to ship to the analytical laboratory immediately place on wet ice (keeping ice in ziplock bags). Provide the Fish Chain of Custody document with the fish shipment.

SECTION 7.0 REFERENCES

Parsons, 2018. *Maintenance, and Monitoring Plan for Ninemile Creek*. Prepared for Honeywell. Syracuse, New York, August 2018.

Parsons, 2015. *Ninemile Creek OM&M 2015 Surface Water, Soil, and Biota Sampling Work Plan.* Prepared for Honeywell. Syracuse, New York, September 2015.

Parsons, 2011b. *100% Design Report for the Geddes Brook Interim Remedial Measure. Appendix E: Operation, Maintenance, and Monitoring Plan for the Geddes Brook Site.* Prepared for Honeywell, Syracuse, New York. February 2011.

Parsons. 2009a. *Operation, Maintenance, and Monitoring Plan for the LCP Bridge Street Site.* Prepared for Honeywell, Syracuse, New York. September 2009.

SECTION 8.0 REVISIONS/REVIEWS

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S-18 SMALL MAMMAL COLLECTION AND PROCESSING

SECTION 1.0 SCOPE

These procedures are to be followed; any substantive modifications to the procedures shall be approved by the Field Team Leader.

This SOP includes procedures to collect small mammals from locations described in the Geddes Brook and Ninemile Creek OM&M Plans. Collection methods include both live and snap traps. Snap traps are the preferred method however, a combination of methods may be necessary to obtain the required samples.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for sampling include: caution deploying and retrieving heavy equipment, stepping in the sight of lines or cables, slips, trips, falls, handling traps, handling live and dead animals, and the proper use of personal flotation devices (PFDs) as necessary and personal protective equipment (PPE). Do not overload any vessel and load vessels evenly so they are not prone to capsizing. These safety considerations apply to the vessel and sampling crews whenever working on the water.

SECTION 3.0 SMALL MAMMAL SAMPLE COLLECTION EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Since multiple procedures or alternate methods may be employed to achieve the objectives, not all materials and equipment included on the list may be necessary to complete the task.

- Leather gloves
- Nitrile gloves
- Weight scale
- Snap traps
- Sherman live traps
- Digital camera
- Field notebook/iPad
- Flags
- Sharpie pen
- Field data sheets
- Cellular phone

SECTION 4.0 SMALL MAMMAL TRAPPING PROCEDURE

This section describes procedures for collecting small mammals for tissue analysis. These techniques are generally useful for the collection of mammals ranging in body size from a shrew to a field mouse. The methods described in this SOP include both live collection and kill collection techniques. The SOP discusses the use of live traps and snap traps.

4.1 Equipment

The following is a list of typical equipment used for the collection of small mammals:

- Sherman live traps (or equivalent)
- Snap traps (or equivalent)
- Bait balls (peanut butter, rolled oats, and sunflower seeds and/or corn meal)
- Brightly colored wire flags or wooden stakes
- Clipboard and data sheets
- Small mammal identification book
- Copy of applicable trapping and salvage permits and scientific location permits
- Site map with site locations overlay
- Scale
- Weighing bag or Ziploc® bags
- Extra 4 in. × 4 in. waxed paper squares
- Appropriate safety equipment as required by the health and safety plan.

4.2 Personnel

Only personnel trained to use small mammal traps, and whose names are listed on the appropriate permits, are authorized to capture and handle small mammals. All required research protocols, federal regulations, and other applicable regulatory guidelines should be studied before initiating trapping operations. Personnel without previous experience should be under the guidance and direct supervision of an experienced trapper.

4.3 Collection Methods and Trap Types

4.3.1 Grid/Trap Line Marking

Individual traps at a station should be placed in locations that sample various microhabitat features because microhabitat differences have been shown to influence small mammal occurrence. For example, traps should be set at the bases of trees and shrubs, at the edge of the shrub canopy, in the open, in microtine runways, alongside fallen trees, in short and tall grass, and in disturbed areas of forbs and shrubs. The beginning and end of trap lines, the corners of grids, and individual stations should be marked whenever possible. Generally, the fewer markers the better to avoid attracting predators (ground and aerial) that may cue on the markers, which would thereby increase mortality in the trapping area and influence the density/ abundance/occurrence estimations. If wire flags are used, the flag should be trimmed to a 1-in. width to reduce flapping. A color visible to humans but not readily visible (and therefore an attractant) to wildlife should also be used. An alternative to the use of wire flags is to use painted wooden stakes, willow stems, or rebar driven into the ground to mark the

station center, with only the top few inches painted. In wooded habitats, surveyor flagging may be tied to the vegetation to mark the station center. All grid and trap line locations should be marked on field site maps to aid relocation and provide a permanent record of where trapping occurred and what trapping method was used. If a global positioning system unit is available, readings of the beginning and end markers of a trapline or the corners of the grid should be logged.

4.3.2 Trap Functioning

Each trap should be cleaned and checked for proper functioning before placing it in the field. When trapping is being conducted to address small mammal tissue contamination or bioaccumulation, or where the hantavirus is of concern, all traps should be cleaned and disinfected before placement at a station or before moving to a different station. Disinfection of traps is discussed in the health and safety plan. All urine and fecal materials should be washed off. Traps may be disassembled for cleaning beneath the treadle mechanism by removing the wires from selected trap sides, permitting easy access to the trap interior. Treadles on live traps should release doors with only very light fingertip pressure on the treadle or a light tap on the top of the trap. Sensitivity of the mammal trap is varied by pulling forward or pushing back the treadle lock mechanism. Snap traps should be checked to ensure that all parts are securely fastened so that when the trap is sprung, the trap does not disassemble. Trap sensitivity is adjustable on all snap traps. To adjust the sensitivity of museum special snap traps, bow (i.e., bend) or straighten the holding bar that passes across the snap bar and inserts into the bait treadle (bowing the holding bar increases sensitivity, straightening the holding bar decreases sensitivity).

4.3.3 Bait

Dry baits are readily available and easy to use. Rolled oats or horse feeds, such as Purina Omelene, make good dry baits. Dry baits may not be as effective as moist baits, but this may be advantageous depending on study objectives. Care should be taken when using live traps to ensure that dry bait does not prevent the treadle from working properly. Bait balls are very attractive to a wide variety of small mammals ranging from shrews to raccoons. Bait balls are made by mixing peanut butter, rolled oats, and sunflower seeds and/or cornmeal. Peanut butter should first be warmed until easily stirred, then the remaining ingredients should be added. This mixture is then allowed to cool. A small amount of the peanut butter mixture (approximately the size of an M&M® Peanut candy) is spooned into the middle of a 4 in. x 4 in., waxed paper square. The waxed paper is folded around the bait ball and the ends are twisted (so that the bait ball looks like a Hershey's® Kiss). Snap traps can be baited with the mixture above or with pure peanut butter.

4.3.4 Trap Placement

The following procedures should be used to place traps:

1. Clear the immediate area where each trap will be placed of grass and other ground clutter so that each trap sets firmly on the ground. You may level the ground, but do not disturb an area much larger than the size of the trap.
2. Check to be sure that when the door of a live trap is set open, there is no wobble as the animals step into the entrance of the trap. For snap traps, ensure that the entire platform sits firmly on the ground. If the trap moves when a small mammal begins to enter, it may retreat and thereafter avoid the trap.
3. If wind or a steep slope causes trap instability, anchor each trap with a U-shaped piece of #12 wire, open-end down, that straddles the center of each trap. Force the wire ends into the ground to prevent each trap from being moved. For large snap traps (i.e., rat traps), attach a small screw eye to the back edge of the trap, attach a length of wire or rope (i.e., 12–18 in.), and attach the second end to a large nail or spike. The

nail or spike is driven into the ground to secure the trap in the event the animal is caught but not immediately killed and attempts to escape.

4. If using dry bait, place a handful of bait inside the trap, turn the trap upside down, and shake it so that the bait is on the opposite side of the treadle, then quickly turn the trap right side up. The dry bait should now be on the treadle. Be sure the bait is on the treadle and not under it. Too much bait under the treadle will hamper operation of the trap. If using bait balls to bait traps, determine which is the front end of the trap by pressing open each door in turn and looking inside. The front of the trap is the end that has the metal door catch on the floor of the trap. Then hold the twisted ends of a bait ball, and push the ball through the top of the back door. Once it is inside the trap, pull the ball back toward you. The bait ball will catch the inside the trap door and pull it shut.
5. If temperatures below 5 °C are expected or extended periods of rain are anticipated, place a wad of bedding material (polyester fiberfill or similar nonabsorbent material) in each trap to serve as nesting material. This step will help insulate animals from potentially fatal cold weather.

4.3.5 Trap Checking

If traps are left open all day, they should be checked at least twice daily. Heavy rain, cold, or extreme heat can kill trapped animals; trap checks should be performed as expeditiously as possible. Extra bait should be carried during trap checks. The suspension of trapping due to inclement weather will be at the discretion of designated field personnel. Any time trapping efforts are suspended, entrance doors on live traps should be shut and snap traps deactivated. All traps should be closed or deactivated before any scheduled days off.

4.3.6 Animal Handling and Euthanizing

Review the health and safety plan for specific protective requirements before handling animals. The only acceptable form of euthanasia is by placing animal in a CO2 chamber.

1. A shut door may indicate a capture. To check, (with leather gloves) hold the trap with the baited end of the trap facing the ground. Gently press the front door open only as far as necessary to determine if an animal is inside.
2. Place the unopened trap with live animal inside the chamber.
3. Add CO2 or begin CO2 reaction using baking soda and vinegar.
4. Close lid of container and wait a minimum of 20 minutes.
5. Ensure animal is dead prior to opening trap then open one end and invert over the sample bottle.
6. Record the weight.

4.3.7 Trap Cleanup

Due to the risk of hantavirus in small mammal populations across the country, any traps that have been used should be treated as if they contain hantavirus. Risk of hantavirus is greatest in closed air environments. Therefore, traps should be transported in an open-air vehicle such as the back of a pickup truck or a trailer. If this is not possible, the traps should be bagged in large plastic bags, and care should be taken not to tear the bags while placing the traps in the vehicle. Alternatively, traps can be washed in the field provided a means of transporting wastewater is available. Once traps are transported to an area for washing, all traps should be washed with soap and water, decontaminated with bleach, and rinsed thoroughly whether traps were used in a treated (e.g., contaminated) or an untreated area. Traps should then be allowed to air dry before they are packed away. Refer to the health and safety plan for further precautions regarding hantavirus and small mammal

handling. Traps from treated sites should be washed with soap and water, decontaminated with bleach, air dried, and packed as described in the health and safety plan.

SECTION 5.0 SAFETY PRECAUTIONS

1. Disposable latex or nitrile gloves must be worn at all times when handling small mammals and/or samples.
2. Hands must be washed after removing gloves.
3. Disinfect all surfaces coming in contact with samples after they are used. Suitable disinfectants include a bleach/water solution, alcohol, or commercial products such as Lysol®.
4. Workers who become ill or who develop a febrile or respiratory illness within 45 days of the last potential exposure should immediately seek medical attention and inform the attending physician of the potential occupational risk of hantavirus infection. The physician should contact local health authorities promptly if hantavirus-associated illness is suspected. A blood sample should be obtained and forwarded through the state health department to the Centers for Disease Control for hantavirus antibody testing.

SECTION 6.0 REFERENCES AND OTHER SOURCES

Albers, P.H., G. Linder, and J.D. Nichols. 1990. Effects of tillage practices and carbofuran exposure on small mammals. J. Wildl. Manage. 54(1):135–142.

Boonstra, R., and F.H. Rodd. 1984. Efficiency of pitfalls versus live traps in enumeration of populations of Microtus pennsylvanicus. Can. J. Zool. 62(5):758–765.

Boonstra, R., F.H. Rodd, and D.J. Carleton. 1982. Effect of Blarina brevicauda on trap response of Microtus pennsylvanicus. Can. J. Zool. 60(3):438–442.

Boonstra, R., and C.J. Krebs. 1976. The effect of odour on trap response in Microtus townsendii. J. Zool. 180:467–476.

Calhoun, J.B., and J.U. Casby. 1958. Calculation of home range and density of small mammals. Public Health Monogr. No. 55.

Calhoun, J.B. 1959. Population dynamics of vertebrates: revised sampling procedures for the North American Census of Small Mammals (NACSM). Release No. 10. Admin. Publ. U.S. Department of Health, Education, and Welfare, Public Health Service, National Institutes of Mental Health.

Call, M.S. 1989. Rodents and insectivores. pp. 429–452. In: Inventory and Monitoring of Wildlife Habitat. A.Y. Cooperrider, R.J. Boyd, and H.R. Stuart (eds). U.S. Department of the Interior, Bureau of Management Service Center, Denver, CO.

Chabreck, R.H., B.U. Constantin, and R.B. Hamilton. 1986. Use of chemicals and repellents during small mammal trapping. Southwestern Nat. 31(1):109–110.

Parsons, 2011b. 100% Design Report for the Geddes Brook Interim Remedial Measure. Appendix E: Operation, Maintenance, and Monitoring Plan for the Geddes Brook Site. Prepared for Honeywell, Syracuse, New York. February 2011.

Getz, L.L. 1971. Microclimate, vegetation cover, and local distribution of the meadow vole. Trans. Illinois Acad. Sci. 9–21.

Jett, D.A., and J.D. Nichols. 1987. A field comparison of nested grid and trapping web density estimators. J. Mamm. 68(4):888–892.

Merritt, J.F., and J.M. Merritt. 1980. Population ecology of the deer mouse (Peromyscus maniculatus) in the Front Range of Colorado. Ann. Carnegie Mus. Nat. Hist. 49(7):113–130.

Rogers, L.E., and J.D. Hedlund. 1980. A comparison of small mammal populations occupying three distinct shrub-steppe communities in eastern Oregon. Northwest Sci. 54(3):183–186.

Rowley, M.H., J.J. Christian, D.K. Basu, M.A. Pawlikowski, and B. Paigen. 1983. Use of small mammals (voles) to assess a hazardous waste site at Love Canal, Niagara Falls, New York. Arch.

Environ. Contam. Toxicol. 12:383–397.

Thomas, R.E., and E.D. Bellis. 1980. An eye-lens weight curve for determining age in Microtus pennsylvanicus. J. Mamm. 61:561.

White, G.C., D.R. Anderson, K.P. Burnham, and D.L. Otis. 1982. Capture-recapture and removal methods for sampling closed populations. LA-8787-NERF, Los Alamos National Laboratory, Los Alamos, NM.

SECTION 7.0 REVISIONS/REVIEWS

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S-19 NINEMILE CREEK TRANSECT SURVEY

SECTION 1.0 SCOPE

These procedures are to be followed; any substantive modifications to the procedures shall be approved by the Field Team Leader.

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. All employees must follow all the safety requirements that are in the corresponding AHAs.

SECTION 3.0 TRANSECT SURVEY EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Since multiple procedures or alternate methods may be employed to achieve the objectives, not all materials and equipment included on the list may be necessary to complete the task.

- Boat
- Oars
- Trolling motor
- Rope
- GPS unit
- PFDs
- Waders
- Digital camera
- Field notebook/iPad
- Cellular phone

SECTION 4.0 DATA COLLECTING PROCEDURE

This section describes procedures for surveying the Ninemile Channel and the Geddes Brook channel and wetland connections.

4.1 System Check/Control Point Check In/Check Out

Survey control points, established by Thew Associates, are sited around the perimeter of all work areas. When work is started under a particular work order, the operator is first prompted to check into a control point to check the system, set up on one of the control points and hit the measure key, the unit will indicate if it is within tolerance. If the measurement is within tolerance, take a photograph of the screen for documentation. If the

measurement is out of tolerance, bring attention to management. At a minimum, check in at the beginning of each day.

4.2 Ninemile Creek Transect Survey

Transects will be surveyed with GPS unit across the channel at Stations agreed upon in the Ninemile OM&M Plan (2018). These survey readings will be compared with the elevation and composition of the surface material that existed at the end of construction as well as to data from the prior event.

1. Pre load Ninemile Creek station lines onto GPS
2. Minimum of a four employees is required to perform this task.
3. At appropriate stationing, two team member will hold boat in place (from channel bank)with rope attached to boat, 2nd member will be holding GPS rod in place and finally the 3rd member will take the GPS shot on the remote screen. Additional personnel (if available) can aid in steadying boat in place.
4. Start surveying at one side of the channel and work your way across to the other side, taking GPS shots every 3 ft. to 5 ft. and as close to the station line as possible.
5. At each station record in field notebook/iPad the composition of the channel materials
6. Once one location is completed, work your way downstream to next station and repeat same process as above, until all locations are surveyed.

Upon complete field survey, data is uploaded and compared to previous data.

4.3 Geddes Brook Channel and Wetland Connection Survey

Elevations of the Geddes Brook channel (one location) and wetland connections (5 locations) will be surveyed with a GPS unit at sill log locations for the wetland connection and on the mouth of Geddes Brook for the channel.

1. Pre load sill log and channel locations into GPS unit.
2. Use GPS unit to stakeout to each location.
3. Once on the location, record on GPS unit the elevation of the sill log or channel.
4. Once elevation is recorded for one location, stakeout to next location and repeat step above.

Upon complete field survey, data is uploaded and compared to previous data.

SECTION 5.0 SAMPLING PERSONNEL

The Project Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Project Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Project Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 6.0 REFERENCES

Parsons, 2018. *Maintenance, and Monitoring Plan for Ninemile Creek*. Prepared for Honeywell. Syracuse, New York, August 2018.

SECTION 7.0 REVISIONS/REVIEWS

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Reviewer: Parsons

What was changed: N/A

S-20 TRIBUTARY SURFACE WATER AND RAINWATER SAMPLING AND PROCESSING

SECTION 1.0 SCOPE

These procedures are to be followed; and any substantive modifications to the procedures shall be approved by the Field Team Leader. This Standard Operating Procedure (SOP) includes procedures to collect surface water in tributaries and rainwater samples as described in the 2021 Onondaga Lake and Tributary Surface Water Monitoring for PCBs Memo (Parsons 2021).

SECTION 2.0 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each day and as new activities are conducted. The designated safety officer shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for near-water sampling include: caution deploying and retrieving heavy equipment, slips, trips, falls, and the proper use of personal flotation devices (PFDs) and personal protective equipment (PPE). Gloves must also be worn at all times in the field. The type of glove may vary by task; this will be determined by field leader.

SECTION 3.0 SURFACE WATER SAMPLE COLLECTION EQUIPMENT LIST

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP. Not all materials and equipment included on the list may be necessary to complete the task.

- PFDs
- Large ziplock bags
- Field notebook/iPad
- Field forms
- Cellular phone
- Powder-free gloves
- Water quality meter
- 0.5 L/500 mL Teflon dipper
- Amber glass bottles (2-1 L, 2.5 L) with fluorocarbon-lined caps
- Stainless steel funnels (31 cm diameter)
- HPLC grade acetone
- Distilled or deionized water

SECTION 4.0 SURFACE WATER COLLECTING PROCEDURE

This section describes procedures for collecting surface water samples from locations described in the 2021 Onondaga Lake and Tributary Surface Water Monitoring. Each sample will be analyzed for field parameters (temperature, pH, specific conductance, dissolved oxygen and oxidation-reduction potential (ORP)). If more than one sample is to be taken in a tributary, the sample should be collected beginning at the downstream location and working upstream. Sample locations will be previously staked out and will depend primarily on accessibility.

4.1 Grab Sampling Method (Tributaries)

1. Pre-cleaned sample containers will be pre-labeled and placed in a clean, dedicated cooler.
2. Slowly enter the tributary from downstream and face upstream. Allow time for sediment to settle. Immerse the capped sample container to a depth of roughly one half the water depth to fill. Discard water to the downstream. Repeat three times. Following three rinses, repeat and retain water in the jar. Avoid sampling resuspended sediment. Hold the bottle at a small upward angle, uncap it to fill, then re-cap before raising it through the water surface. If samples cannot be collected directly into the sample bottle, a decontaminated sample collection device may be used[2]. Should the device be utilized, multiple (2) dips will be composited directly into the bottle. Bottles should have zero or very little headspace.
3. Place inside cooler. Repeat procedure at next location, using a fresh set of gloves.
4. COC procedures will be followed.
5. Measurements of temperature, pH, specific conductance, dissolved oxygen and ORP shall be taken by direct immersion of instrument probes into the water body. If direct measurement is not possible, these measurements shall be taken from water collected and placed in a field container. The results shall be recorded in paper or electronic field forms.
6. Record the over-all depth of the water column (i.e., distance from the surface to the sediment bottom), as well as the depth at which the sample was collected (i.e., distance from the surface).
7. Sample description and location will be recorded in the field forms.

4.2 Rainwater Collection

1. Rainwater collection stations will be set up approximately 24 hours prior to an anticipated rain event.
2. Each collector will consist of 1.0 L narrow-mouth amber glass bottles topped with a 31 cm diameter (or similar size commercially available) stainless steel funnel, washed with HPLC quality grade acetone and then with DI water. To minimize potential evaporation or sills, the funnel will be secured through use of a funnel stand, and aluminum foil will be wrapped around the bottle neck.
3. Collection set up will be placed on an elevated flat surface, at least 4 feet above the ground. Six bottles will be deployed in an attempt to obtain a large enough sample of rainwater.
4. Samples will be collected within 6 hours of the end of the rain event.
5. Sample bottles will be combined into one composite sample in a 2.5 L amber glass bottle. If composite sample has enough volume to fill two 1 L amber glass bottles, split composite evenly between two bottles.

1. A Teflon dipper (0.5 L/500 mL in size) is recommended for use in this case. The device will be rinsed three times before use (similar to the glassware) and decontaminated between sites utilizing a triple rinse with HPLC grade acetone rinse and deionized water.

6. If composite sample does not contain a large enough sample volume, store and refrigerated at ~4ºC. The above process will be repeated until there is enough volume for a complete 1 L sample. Samples may also be composited at the laboratory.

SECTION 5.0 SAMPLING PERSONNEL

The Project Manager is responsible for assigning appropriate field personnel to be responsible for the various site activities. The Project Manager is also responsible for assuring that this and any other appropriate procedures are followed by field personnel. Field personnel assigned to the various site activities are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure or nonconformance to the Project Manager. Only qualified field personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and health and safety training.

SECTION 6.0 SURFACE WATER SAMPLE PROCESSING PRIOR TO LABORATORY RECEIPT

6.1 Equipment List

- Paper towels
- Safety glasses
- Digital camera
- Field notebook/iPad
- Cellular phone
- Plans with sampling locations
- Sample labels
- Sharpie pen
- Wet ice
- Coolers
- Work (cut resistant) Gloves
- Nitrile gloves
- Chain of Custody forms
- Custody Seals
- Field forms
- Prior event field forms
- AHAs
- SOP

6.2 Surface Water Sample Processing Procedure

Sample containers are pre-labeled prior to sampling. Samples are to be chilled on wet ice until shipped to the laboratory.

6.3 Sample Transport to Laboratory

Store the samples at a temperature below 4 degrees Celsius and ship immediately on wet ice to the analytical laboratory. Provide Surface Water Chain of Custody document with the shipment. Place custody seal on cooler before released to courier.

SECTION 7.0 REFERENCES

Parsons. 2021. 2021 Onondaga Lake and Tributary Surface Water Monitoring for PCBs Memo. July 2021.

SECTION 8.0 REVISIONS/REVIEWS

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STANDARD OPERATING PROCEDURE
Water-Level Measurements

I. Purpose and Scope

The purpose of this procedure is to provide a guideline for the measurement of the depth to groundwater in monitoring wells, where a second phase of floating liquid (e.g., gasoline) is not encountered. This SOP includes guidelines for discrete measurements of static water levels and does not cover the use of continuously recording loggers.

II. Equipment and Materials

- Electronic water level meter, Solinst or equivalent, with a minimum 100-foot tape; the tape should have graduations in increments of 0.01 feet or less

III. Procedures and Guidelines

Verify that the unit is turned on and functioning properly. Slowly lower the probe on its cable into the well until the probe just contacts the water surface; the unit will respond with a tone or light signal. Sight across the top of the locking well casing adjacent to the measuring point, recording the position of the cable when the probe is at the water surface. The measuring point will be a standardized surveyed location on the top of each well casing, adjacent to the lock hasp, indicated by a notch, paint mark, or similar method. Measure the distance from this point to the closest interval marker on the tape, and record the water level reading in the log book.
Measure and record the three following additional readings: (1) the depth of the well; (2) the depth from the top of the casing to the top of the well riser; and (3) the distance to the surface of the concrete pad or to ground. Measurements are to be taken with respect to the measuring point on the top of the well casing. The depth of the well may be measured using the water-level probe with the instrument turned off.

IV. Attachments

None.

V. Key Checks and Preventative Maintenance

Prior to each use, verify that the battery is charged by pressing the test button on the water-level meter. Verify that the unit is operating correctly by testing the probe in distilled or deionized water. Leave the unit turned off when not in use.

STANDARD OPERATING PROCEDURE
Low-Flow Groundwater Sampling from Monitoring Wells

I. Purpose and Scope

This procedure presents general guidelines for the collection of groundwater samples from monitoring wells using low-flow purging and sampling procedures. Operations manuals should be consulted for specific calibration and operating procedures.

II. Equipment and Materials

- Flow-through cell with inlet/outlet ports for purged groundwater and watertight ports for each probe
- Meters to monitor pH, specific conductance, turbidity, dissolved oxygen, oxidation-reduction potential (ORP), and temperature (e.g., Horiba® U-22 or similar)
- Water-level indicator
- In-line disposable 0.45µ filters (QED® FF8100 or equivalent)
- Adjustable-rate, positive-displacement pump, submersible, or peristaltic pump
- Generator
- Disposable polyethylene tubing
- Plastic sheeting
- Well-construction information
- Calibrated bucket or other container and watch with second indicator to determine flow rate
- Sample containers
- Shipping supplies (labels, coolers, and ice)
- Field book

III. Procedures and Guidelines

A. Setup and Purging

1. For the well to be sampled, information is obtained on well location, diameter(s), depth, and screened interval(s), and the method for disposal of purged water.
2. Instruments are calibrated according to manufacturer's instructions.
3. The well number, site, date, and condition are recorded in the field logbook.
4. Plastic sheeting is placed on the ground, and the well is unlocked and opened. All decontaminated equipment to be used in sampling will be placed only on the plastic sheeting until after the sampling has been completed.
5. All sampling equipment and any other equipment to be placed in the well is cleaned and decontaminated before sampling in accordance with SOP *Decontamination of Personnel and Equipment*.

6. Water level measurements are collected in accordance with SOP *Water Level Measurements* and the total depth of the well is measured.
7. Attach and secure the polyethylene tubing to the low-flow pump. Lower the pump slowly into the well and set it at approximately the middle of the screen. Place the pump intake at least 2 feet above the bottom of the well to avoid mobilization of any sediment present in the bottom. Preferably, the pump should be in the middle of the screen.
8. Insert the measurement probes into the flow-through cell. The purged groundwater is directed through the cell, allowing measurements to be collected before the water contacts the atmosphere.
9. Start purging the well at 0.2 to 0.5 liters per minute. Avoid surging. Purging rates for more transmissive formations could be started at 0.5 to 1 liter per minute. The initial field parameters of pH, specific conductance, dissolved oxygen, ORP or Eh, turbidity, and temperature of water are measured and recorded in the field logbook.
10. The water level should be monitored during purging, and, ideally, the purge rate should equal the well recharge rate so that there is little or no drawdown in the well (i.e., less than 0.5 feet). The water level should stabilize for the specific purge rate. There should be at least 1 foot of water over the pump intake so there is no risk of the pump suction being broken, or entrainment of air in the sample. Record adjustments in the purge rate and changes in depth to water in the logbook. Purge rates should, if needed, be decreased to the minimum capabilities of the pump (0.1 to 0.2 liters per minute) to avoid affecting well drawdown.
11. During purging, the field parameters are measured frequently (every 3 to 5 minutes) until the parameters have stabilized. Field parameters are considered stabilized when measurements meet the following criteria:
    - pH: within 0.1 pH units
    - Temperature: within 1°Celsius
    - Specific conductance: within 3 percent
    - Dissolved oxygen: within 10 percent
    - Turbidity: within 10 percent or as low as practicable given sampling conditions
    - ORP: within 10 mV

B. Sample Collection

Once purging has been completed, the well is ready to be sampled. The elapsed time between completion of purging and collection of the groundwater sample from the well should be minimized. Typically, the sample is collected immediately after the well has been purged, but this is also dependent on well recovery.

Samples will be placed in bottles that are appropriate to the respective analysis and that have been cleaned to laboratory standards. Each bottle typically will have been previously prepared with the appropriate preservative, if any.

The following information, at a minimum, will be recorded in the logbook:

1. Sample identification (site name, location, and project number; sample name/number and location; sample type and matrix; whether the sample is filtered or not; time and date; sampler's identity)
2. Sample source and source description
3. Field observations and measurements (appearance, volatile screening, field chemistry, sampling method), volume of water purged prior to sampling, number of well volumes purged, and field parameter measurements
4. Sample disposition (preservatives added; laboratory sent to, date and time sent; laboratory sample number, chain-of-custody number, sample bottle lot number)

The steps to be followed for sample collection are as follows:

1. The flow-through cell will be removed prior to filling sample bottles.
2. The cap is removed from the sample bottle, and the bottle is tilted slightly.
3. The sample is slowly discharged from the pump so that it runs down the inside of the sample bottle with a minimum of splashing. The pumping rate should be reduced to approximately 100 ml per minute when sampling VOCs.
4. Samples may be field filtered before transfer to the sample bottle. Filtration must occur in the field immediately upon collection. Inorganics, including metals, are to be collected and preserved in the filtered form as well as the unfiltered form. The recommended method is through the use of a disposable in-line filtration module (0.45-micron filter) using the pressure provided by the pumping device for its operation.
5. Samples for analysis for volatile organic compounds should be collected first, if such samples are required.
6. Adequate space is left in the bottle to allow for expansion, except for VOC vials, which are filled to overflowing and capped.
7. The bottle is capped, then labeled clearly and carefully.
8. Samples are placed in appropriate containers and, if necessary, packed with ice in coolers as soon as practical.

C. Additional remarks

1. If the well goes dry during purging, wait until it recovers sufficiently to remove the required volumes to sample all parameters. It may be necessary to return periodically to the well but a particular sample (e.g., large amber bottles for semivolatile analysis) should be filled at one time rather than over the course of two or more visits to the well.
2. It may not be possible to prevent drawdown in the well if the water-bearing unit has sufficiently low permeability. If the water level was in the screen to start with, do not worry about it because there is no stagnant water in the riser above the screen to begin with.
   If the water level in the well is in the riser above the screen at the beginning of purging, then be sure you pump out sufficient volume

from the well to remove the volume of water in the riser above the screen. For a 2-inch diameter well, each foot of riser contains 0.163 gallons; for a 4-inch riser, each foot of riser contains 0.653 gallons; for a 6-inch riser, each foot of riser contains 1.47 gallons.
Alternatively, the water in the riser above the screen can be removed by lowering the pump into the well until the pump intake is just below the water level, starting the pump, running it at a low rate, and slowly lowering the pump as the water level in the riser declines. This approach can be terminated when the water level reaches the top of the screen, at which time the stagnant water in the riser has been removed. This may not be a practical approach for dedicated sampling equipment. As with typical low-flow sampling, the flow rate should be kept as low as practicable.

3. There may be circumstances where a positive-displacement or submersible pump cannot be used. An example is at isolated, hard-to-reach locations where the required power supply cannot be brought. In this case, a peristaltic pump may be used. Samples can be collected by the procedures described above for all but those for VOC analysis. The water to be placed in the vials for VOC analysis should not be run through the peristaltic pump but instead should be collected by the following:
   - Stop the pump when it is time to collect the VOC sample.
   - Disconnect the tubing upstream from the pump (a connector must be installed in the line to do this).
   - Holding a finger over the end of the tubing to keep the water in the tubing, remove the tubing from the well. Be sure that the tubing does not contact other than clean surfaces.
   - Place the end of the tubing that was in the well into each VOC vial and fill the vial by removing the finger from the other end of the tube.
   - Once the vials are filled, return the tubing to the well and collect any other samples required.
4. Nondedicated sampling equipment is removed from the well, cleaned, and decontaminated in accordance with SOP *Decontamination of Personnel and Equipment*. Disposable polyethylene tubing is disposed of with PPE and other site trash.

IV. Attachments

White paper on reasons and rationale for low-flow sampling.

V. Key Checks and Preventative Maintenance

- The drawdown in the well should be minimized as much as possible (preferably no more than 0.5 to 1 foot) so that natural groundwater-flow conditions are maintained as closely as possible.
- The highest purging rate should not exceed 1 liter per minute. This is to keep the drawdown minimized.

- Stirring up of sediment in the well should be avoided so that turbidity containing adsorbed chemicals is not suspended in the well and taken in by the pump.
- Overheating of the pump should be avoided to minimize the potential for losing VOCs through volatilization.
- Keep the working space clean with plastic sheeting and good housekeeping.
- Maintain field equipment in accordance with the manufacturer's recommendations. This will include, but is not limited to:
    - Inspect sampling pump regularly and replace as warranted
    - Inspect quick-connects regularly and replace as warranted
    - Verify battery charge, calibration, and proper working order of field measurement equipment prior to initial mobilization and daily during field efforts

Attachment to the SOP on Low-Flow Sampling Groundwater Sampling from Monitoring Wells
White Paper on Low-Flow Sampling

EPA recommends low-flow sampling as a means of collecting groundwater samples in a way that minimizes the disturbance to the natural groundwater flow system and minimizes the introduction of contamination into the samples from extraneous sources. The following are details about these issues.

When a pump removes groundwater from the well at the same rate that groundwater enters the well through the screen, the natural groundwater-flow system around the well experiences a minimum of disturbance. Some disturbance is bound to occur because you are causing groundwater to flow to the well in a radial fashion that otherwise would have flowed past it. However, the resulting low-flow sample provides the most-representative indication we can get of groundwater quality in the immediate vicinity of the well.

Normally, when a well is pumped at an excessive rate that drops the water level in the well below the water level in the aquifer, the water cascades down the inside of the well screen when it enters the well. The turbulence from this cascading causes gases such as oxygen and carbon dioxide to mix with the water in concentrations that are not representative of the native groundwater and are higher than expected. This causes geochemical changes in the nature of the water that can change the concentrations of some analytes, particularly metals, in the groundwater sample, not mention it's effect on the dissolved oxygen levels that then will be measured in the flow-through cell. Such turbulence also may cause lower-than-expected concentrations of volatile organic compounds due to volatilization.

For wells in which the water level is above the top of the screen, the water up in the riser is out of the natural circulation of the groundwater and, therefore, can become stagnant. This stagnant water is no longer representative of natural groundwater quality because its pH, dissolved-oxygen content, and other geochemical characteristics change as it contacts the air in the riser. If we minimize the drawdown in the well when we pump, then we minimize the amount of this stagnant water that is brought down into the well screen and potentially into the pump. As a result, a more-representative sample is obtained.

Typically, wells contain some sediment in the bottom of the well, either as a residue from development that has settled out of the water column or that has sifted through the sand pack and screen since the well was installed. This sediment commonly has adsorbed on it such analytes as metals, SVOCs, and dioxins that normally would not be dissolved in the groundwater. If these sediments are picked up in the groundwater when the well is disturbed by excessive pumping, they can:

- Make filtering the samples for metals analysis more difficult
- Add unreasonably to the measured concentration of SVOCs and other organic compounds

The SOP for low-flow sampling has been modified recently and should be consulted for additional information about low-flow sampling and ways of dealing with wells in which the water level cannot be maintained at a constant level.

STANDARD OPERATING PROCEDURE
Field Measurement of pH, Specific Conductance, Turbidity, Dissolved Oxygen, ORP, and Temperature Using the Horiba® U-22 with Flow-through Cell

I. Purpose and Scope

The purpose of this procedure is to provide a general guideline for using the Horiba® U-22 for field measurements of pH, specific conductance, turbidity, dissolved oxygen, oxidation-reduction potential (ORP), and temperature of groundwater samples. The operator's manual should be consulted for detailed operating procedures.

II. Equipment and Materials

- Horiba® U-22 Water Quality Checker with flow-though cell
- Distilled water in squirt bottle
- Horiba® U-22 Auto-Calibration Standard Solution

III. Procedures and Guidelines

A. Parameters and Specifications:

Parameter	Range of measurement	Accuracy
PH	0 - 14 pH	+/- 0.1 pH units
Specific	0 – 100 mS/cm	+/- 3 % full scale
Turbidity	0 – 800 NTU	+/- 5 % full scale
Dissolved	0 - 19.9 mg/l	+/- 0.2 mg/l
Temperature	0 - 55 ºC	+/- 1.0 ºC
ORP	-1999 mv - +1999 mv	+/- 15 mV
Salinity	0 - 4 %	+/- 0.3 %

B. Calibration:

Prior to each day's use, clean the probe and flow-through cell using deionized water and calibrate using Horiba® Standard Solution. Calibration procedure:

1. Fill the calibration beaker to about 2/3 with the standard solution.
2. Fit the probe into the beaker. All the parameter sensors will now be immersed in the standard solution except the D.O. sensor; the D.O. calibration is done using atmospheric air.
3. Turn power on.
4. Press CAL key to put the unit in the calibration mode.
5. Wait a moment, and the upper cursor will gradually move across the four auto-calibration parameters one by one: pH, COND, TURB, and DO. When the calibration is complete, the readout will briefly show END. The instrument is now calibrated.
6. If the unit is calibrated properly, pH will read 4.0 +/- 3%, conductivity will read 4.49 =/- 3%, and turbidity will read 0 +/- 3%

C. Sample Measurement:

As water passes through the flow-through Cell, press MEAS to obtain reading; record in the field notebook.

lV. Key Checks and Preventive Maintenance

- Calibrate meter
- Clean probe with deionized water when done
- Refer to operations manual for recommended maintenance
- Check batteries, and have a replacement set on hand

Note: The turbidity meter with the Horiba® U-22 often provides inaccurate measurements (readings of –10 or 999); it is recommended that a separate turbidity meter be used for field measurements.

STANDARD OPERATING PROCEDURE
Decontamination of Personnel and Equipment

I. Purpose

To provide general guidelines for the decontamination of personnel, sampling equipment, and monitoring equipment used in potentially contaminated environments.

II. Scope

This is a general description of decontamination procedures.

III. Equipment and Materials

- Demonstrated analyte-free, deionized water (specifically, ASTM Type II water)
- Distilled water
- Potable water; must be from a municipal water supplier, otherwise an analysis must be run for appropriate volatile and semivolatile organic compounds and inorganic chemicals (e.g., Target Compound List and Target Analyte List chemicals)
- 2.5% Liquinox® and water solution
- Concentrated pesticide grade methanol (DO NOT USE ACETONE)
- Large plastic pails or tubs for Liquinox® and water, scrub brushes, squirt bottles for Liquinox® solution, methanol and water, plastic bags and sheets
- DOT approved 55-gallon drum for disposal of waste
- Phthalate-free gloves
- Decontamination pad and steam cleaner/high pressure cleaner for large equipment

IV. Procedures and Guidelines

A. PERSONNEL DECONTAMINATION

To be performed after completion of tasks whenever potential for contamination exists, and upon leaving the exclusion zone.

1. Wash boots in Liquinox® solution, then rinse with water. If disposable latex booties are worn over boots in the work area, rinse with Liquinox® solution, remove, and discard into DOT-approved 55-gallon drum.
2. Wash outer gloves in Liquinox® solution, rinse, remove, and discard into DOT-approved 55-gallon drum.

3. Remove disposable coveralls ("Tyveks") and discard into DOT-approved 55-gallon drum.
4. Remove respirator (if worn).
5. Remove inner gloves and discard.
6. At the end of the work day, shower entire body, including hair, either at the work site or at home.
7. Sanitize respirator if worn.

B. SAMPLING EQUIPMENT DECONTAMINATION—GROUNDWATER SAMPLING PUMPS

Sampling pumps are decontaminated after each use as follows.

1. Don phthalate-free gloves.
2. Spread plastic on the ground to keep hoses from touching the ground
3. Turn off pump after sampling. Remove pump from well and place pump in decontamination tube, making sure that tubing does not touch the ground
4. Turn pump back on and pump 1 gallon of Liquinox® solution through the sampling pump.
5. Rinse with 1 gallon of 10% methanol solution pumped through the pump. (DO NOT USE ACETONE).
6. Rinse with 1 gallon of tap water.
7. Rinse with 1 gallon of deionized water.
8. Keep decontaminated pump in decontamination tube or remove and wrap in aluminum foil or clean plastic sheeting.
9. Collect all rinsate and dispose of in a DOT-approved 55-gallon drum.
10. Decontamination materials (e.g., plastic sheeting, tubing, etc.) that have come in contact with used decontamination fluids or sampling equipment disposed of in DOT-approved 55-gallon drums.

C. SAMPLING EQUIPMENT DECONTAMINATION—OTHER EQUIPMENT

Reusable sampling equipment is decontaminated after each use as follows.

1. Don phthalate-free gloves.
2. Before entering the potentially contaminated zone, wrap soil contact points in aluminum foil (shiny side out).
3. Rinse and scrub with potable water.
4. Wash all equipment surfaces that contacted the potentially contaminated soil/water with Liquinox® solution.
5. Rinse with potable water.
6. Rinse with distilled or potable water and methanol solution (DO NOT USE ACETONE).
7. Air dry.
8. Rinse with deionized water.
9. Completely air dry and wrap exposed areas with aluminum foil (shiny side out) for transport and handling if equipment will not be used immediately.

10. Collect all rinsate and dispose of in a DOT-approved 55-gallon drum.

11. Decontamination materials (e.g., plastic sheeting, tubing, etc.) that have come in contact with used decontamination fluids or sampling equipment will be disposed of in DOT-approved 55-gallon drums.

D. HEALTH AND SAFETY MONITORING EQUIPMENT DECONTAMINATION

1. Before use, wrap soil contact points in plastic to reduce need for subsequent cleaning.
2. Wipe all surfaces that had possible contact with contaminated materials with a paper towel wet with Liquinox® solution, then a towel wet with methanol solution, and finally three times with a towel wet with distilled water. Dispose of all used paper towels in a DOT-approved 55-gallon drum.

E. SAMPLE CONTAINER DECONTAMINATION

The outsides of sample bottles or containers filled in the field may need to be decontaminated before being packed for shipment or handled by personnel without hand protection. The procedure is:

1. Wipe container with a paper towel dampened with Liquinox® solution or immerse in the solution AFTER THE CONTAINERS HAVE BEEN SEALED. Repeat the above steps using potable water.
2. Dispose of all used paper towels in a DOT-approved 55-gallon drum.

F. HEAVY EQUIPMENT AND TOOLS

Heavy equipment such as drilling rigs, drilling rods/tools, and the backhoe will be decontaminated upon arrival at the site and between locations as follows:

1. Set up a decontamination pad in area designated by the Navy
2. Steam clean heavy equipment until no visible signs of dirt are observed. This may require wire or stiff brushes to dislodge dirt from some areas.

V. Attachments

None.

VI. Key Checks and Items

- Clean with solutions of Liquinox®, methanol, and distilled water.
- Do not use acetone for decontamination.
- Drum all contaminated rinsate and materials.
- Decontaminate filled sample bottles before relinquishing them to anyone.

Standard Operating Procedure
Packaging and Shipping Procedures

I. Low-Concentration Samples

A. Prepare coolers for shipment:

- Tape drains shut.
- Affix "This Side Up" labels on all four sides and "Fragile" labels on at least two sides of each cooler.
- Place mailing label with laboratory address on top of coolers.
- Fill bottom of coolers with about 3 inches of vermiculite.

B. Arrange decontaminated sample containers in groups by sample number. Consolidate VOC samples into one cooler to minimize the need for trip blanks.

C. Affix appropriate adhesive sample labels to each container. Protect with clear label protection tape.

D. Seal each sample bottle within a separate ziplock plastic bag or bubble wrap, if available. Tape the bag around bottle. Sample label should be visible through the bag.

E. Arrange sample bottles in coolers so that they do not touch.

F. If ice is required to preserve the samples, cubes should be repackaged in zip-lock bags and placed on and around the containers.

G. Fill remaining spaces with vermiculite.

H. Complete and sign chain-of-custody form (or obtain signature) and indicate the time and date it was relinquished to Federal Express or the courier.

I. Separate copies of forms. Seal proper copies (traffic reports, packing lists) along with a return address label within a large zip-lock bag and tape to inside lid of cooler.

J Close lid and latch.

K. Carefully peel custody seals from backings and place intact over lid openings (right front and left back). Cover seals with clear protection tape.

L. Tape cooler shut on both ends, making several complete revolutions with strapping tape. **Do not** cover custody seals.

M. Relinquish to Federal Express or to a courier arranged with the laboratory. Place air bill receipt inside the mailing envelope and send to the sample documentation coordinator along with the other documentation.

II. Medium- and High-Concentration Samples:

Medium- and high-concentration samples are packaged using the same techniques used to package low-concentration samples, with several additional restrictions. First, a special air bill including a Shipper's Certification for Restricted Articles is required. Second, "Flammable Liquid N.O.S." or "Flammable Solid N.O.S." (as appropriate) labels must be placed on at least two sides of the cooler. Third, sample containers are packaged in metal cans with lids before being placed in the cooler, as indicated below:

- Place approximately ½ inch of vermiculite in the bottom of the can.
- Position the sample jar in the zip-loc bag so that the sample tags can be read through the plastic bag.
- Place the jar in the can and fill the remaining volume with vermiculite.
- Close the can and secure the lid with metal clips.
- Write the traffic report number on the lid.
- Place "This Side Up" and "Flammable Liquid N.O.S." or "Flammable Solid N.O.S." (as appropriate) labels on the can.
- Place the cans in the cooler.
- For medium concentration samples, ship samples with ice or "blue ice" inside the coolers. (Double bag ice in zip-lock plastic bags.)

III. Special Instructions for Shipping Medium and High Concentration Samples by Federal Express

A. Label cooler as hazardous shipment:

- Write shipper's address on outside of cooler. If address is stenciled on, just write "shipper" above it.
- Write or affix sticker saying "This Side Up" on two adjacent sides.
- Write or affix sticker saying "ORM-E" with box around it on two adjacent sides. Below ORM-E, write NA#9188.
- Label cooler with "Hazardous Substance, N.O.S." and "liquid" or "solid," as applicable.

B. Complete the special shipping bill for restricted articles.

- Under Proper Shipping Name, write "Hazardous Substance, N.O.S." and "liquid" or "solid," as applicable.
- Under Class, write "ORM-E.
- "Under Identification No., write NA No. 9188.

C. For high concentration samples, ship samples with "blue ice" only inside coolers.

STANDARD OPERATING PROCEDURE L-1A: NITROGEN, NITRATE +NITRITE, NITRITE (AS N; NO_X, NO_2)

Nitrogen, Nitrate + Nitrite, Nitrite (as N; NOx, NO_2).....SOP 239

1) Test Method: Nitrogen, Nitrate + Nitrite, Nitrite, SM 4500-NO_3 F, 22nd Edition

2) Applicable Matrix or Matrices:

Drinking, surface and saline waters, domestic and industrial wastes.

3) Limit of Detection and Quantification:

The instrument manufacturer reports a method detection limit of 0.001 mg/L, the applicable range of the method is 0.01-2.0mg/L. During any quarter in which samples are being analyzed, verify the LOD by preparing a minimum of two spiked samples in separate batches, using the same spiking concentration as your calculated LOD. At least once every thirteen months, recalculate the MDL_s and MDL_b using historical QC data from the last twenty four months. Refer to EPA document 821-R-16-006 Revision 2 Section 4 (f) for the acceptance criteria of verified MDL.

4) Scope and Application:

This method pertains to the determination of nitrate & nitrite in surface and saline waters as well as domestic and industrial wastes.

5) Summary of Test Method:

Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Nitrite alone can be determined by removing the cadmium column; nitrate may be determined by subtraction.

6) Definitions:

Nitrate + Nitrite are defined in Equation 1.

(Eq. 1) NOx = NO2 + NO3

Where:

NO_x - Nitrate + Nitrite; directly measured in laboratory

NO_2 - Nitrite; directly measured in laboratory

NO_3 = Nitrate; calculated by difference by rearranging equation 1 to solve for NO_3 (Equation 2).

(Eq. 2) NO3 = NOx – NO2

Chelate- Is a complex chemical molecule between certain metals with a ligand, where the metal forms a bond with at least two or more atoms of the ligand (bi- or multi-dentate).

Reduce- To decrease the valence of (an atom) by adding electrons, or to remove oxygen from (a compound), or to add hydrogen to (a compound), or to change to a metallic state by removing nonmetallic constituents.

Also defined in this SOP are other nitrogen constituents found in the Allstock solution. Ammonia (NH_3) is measured directly in the laboratory (SOP 238).

7) Interferences:

- Residual chlorine can interfere by oxidizing the cadmium column.
- Low results could be obtained for samples that contain high concentrations of iron, copper, or other metals. In this method, EDTA is added to the buffer to reduce this interference.
- Samples that contain large concentrations of oil and grease will coat the surface of the cadmium.
- Sample turbidity may interfere. Turbidity is removed by filtration through a 0.45µm pore diameter PES filter prior to analysis.

8) Safety:

Always wear safety goggles, gloves and lab coats when handling acids or other toxic substances. Use hoods for mixing solutions that produce fumes. If you spill concentrated acids, bases or other toxic chemicals notify the technical director immediately. The following chemicals may be highly toxic or hazardous. Handle with extreme caution at all times: Sodium Hydroxide, Sulfuric Acid, and Phosphoric Acid.

9) Equipment and Supplies:

- Flow Injection Analysis (FIA) system (Lachat Instruments QuikChem 8500 Series 2)
  - RP-150 series Reagent Pump
  - Lachat XYZ Auto Sampler: ASX 280 Series
  - 520nm optical filter
  - Nitrate/Nitrite QuikChem Method 10-107-04-1-C
  - Omnion software and computer
  - assorted pump tubes as described in instrument manual
  - reagent bottles and instrument waste bottles
  - Lachat repair and maintenance kit
- sampling/standard vials, diluting cups
- Eppendorf pipettes
- assorted volumetric flasks
- assorted graduated cylinders
- calibrated top loading balance

10) Reagents and Standards:

10.1 Preparation of Reagents

Degassing Reagents: Preparation of reagents a day in advance (reagents will outgas as they come to room temperature) and the use of backpressure loops on the chemistry manifolds will normally prevent air spikes from occurring. If air spikes become a problem, degas all solutions except the standards by vacuum filtration.

1. **15N Sodium Hydroxide-** Add 150 g NaOH very slowly to 250 mL type II water. CAUTION: The solution will get very hot, cool in an ice water bath while swirling until dissolved. Cool and store in a plastic bottle.
2. **Ammonium Chloride buffer, pH 8.5-** In a 1 L volumetric flask, dissolve 85 g ammonium chloride (NH_4Cl) and 1.0 g disodium ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA \cdot 2H_2O$) in ~800 mL type II water. Dilute to the mark and invert to mix. Adjust the pH to 8.5 with 15N NaOH. *Alternatively*, in a hood, add 500 mL type II water, 105 mL concentrated hydrochloric acid (HCl), 95 mL ammonium hydroxide (NH_4OH), and 1.0 g EDTA to a 1 L volumetric flask. CAUTION: fumes are produced, dilute to the mark and invert to mix. Adjust the pH to 8.5 with 15N NaOH.
3. **Sulfanilamide Color Reagent-** To a 1 L volumetric flask, add ~600 mL type II water. Then add 100 mL of 85% phosphoric acid (H_3PO_4), 40 g sulfanilamide, and 1.0 g N-(1-naphthyl)ethylenediamine dihydrochloride (NED). Shake to wet, and stir for 30 min to dissolve. Dilute to the mark and invert to mix. Store in a dark bottle, this reagent is stable for 30 days.
4. **Carrier and Diluent for Preserved Samples**- In a 2 L volumetric flask containing about 1 L of Type II water, dilute 4 mL of concentrated sulfuric acid (H_2SO_4). Dilute to the mark with Type II water and invert until mixed. This is used to make standards and dilutions via the auto dilutor when running preserved samples. *If samples are not preserved, use Type II water as carrier and diluent.*
5. **Cupric Sulfate Solution:** In a 1L volumetric flask with ~800 mL type II water, add 2.0 g of cupric sulfate ($CuSO_4 \cdot 5H_2O$, FW 249.69). Stir until dissolved, dilute to the mark and invert to mix. *Holding time 3 months. Used to regenerate the cadmium column.*

10.2 Preparation of Standards

Stock 1000mgN/L standards should be kept in amber bottles and stored at 6^oC when not in use. Holding time is 3 months.

1. **Stock NH_3 1000 mgN/L Standard**
   a. Ammonium Sulfate - Place 4.717g of ammonium sulfate dried at 110^{o}C for 2 hours ($H_8O_4N_2S$; FW: 132.14) into a 1L volumetric flask. Dilute to the mark with type II water and invert to mix.
   b. Ammonium Chloride: Place 3.819g ammonium chloride dried at 110^{o}C for 2 hours (NH_4Cl; FW: 53.49) into a 1L volumetric flask. Dilute to the mark with type II water and invert to mix.
2. **Stock NO_2 1000 mgN/L Standard**: Only needed if running NO_2 and NO_x concurrently: place 6.076g of Potassium nitrite (KNO_2; MW: 85.10) dried at 110^{o}C into 1L flask. Dilute to volume with Type II water.
3. **Stock NO_3 1000 mgN/L Standard**: Only needed if running NO_2 and NO_x concurrently: place 7.218g of Potassium nitrate (KNO_3; MW: 101.10) dried at 110^{o}C into 1L flask. Dilute to volume with Type II water.

4. **All Stock*** - Pipette 0.1 mL of NO_2^- standard 1000mg/L, 0.4 mL of NO_3^- standard 1000mg/L and 0.5 mL of T-NH_3 Standard 1000mg/L into a 500 mL volumetric flask. **Made daily.** *NOTE: *NH_3 standard only needed if running both channels concurrently, omit from all stock if only running NO_x channel. The resulting final concentration for this stock is 1000µg/L NH_3 and NO_x and 200µg/L NO_2.*

5. **Reference All Stock*** - Made from commercially purchased standards. Pipette 0.2 mL of NO_2^- standard (1000ppm), 0.5 mL of NO_3^- standard (1000ppm), and 0.913 mL of T-NH_3 standard (1000ppm) into a 250 mL volumetric flask with approximately 100 mL of Type II water. Fill to volume and mix well. **Made daily**. **The Lachat is programmed to do a 10x dilution on this stock which results in a final concentration of 300µgN/L NH3, 80µgN/L NO2, and 280µgN/L NOx.*

6. **MS/LCS Spike Allstock** - Place 0.3 mL of Stock NO_2^- 1000mg/L Standard, 1.2 mL of Stock NO_3^- 1000mg/L, and 1.5 mL of Stock NH_3 1000mg/L Standard into a 100mL flask. Dilute to volume with Type II water and invert to mix. *Holding time: 3 months*

7. **LCS** - Place ~ 50 mL of Type II water into 100 mL volumetric flask. Pipette 1.0 mL of spiking solution into flask and fill to line using Type II water. **Make daily**.

8. **Matrix Spike (MS)** - Place ~ 15 mL of designated sample into 25 mL volumetric flask. Pipette 250 µL of MS/LCS Spike Allstock into flask and fill to line using designated sample. **Make daily.**

10.3 Standard Curve Preparation:
The Stock solutions listed above are used to prepare the Low range "All Stock" solution's described below. **Made daily.** *NOTE: *only needed if running both channels concurrently, omit unneeded analyte from all stock if only running singular channel.*

All Stock* Prepare in **500mL** Type II water

Analyte	Low Range (nominal value)
NO2	0.1mL (200 µg/L)
NO3	0.4m (1000 µg/L)
NH3	0.5mL (1000 µg/L)

Table 1: Standard Stock and Standard Curve used for running T-NH_3, NO_2^- and NO_x^- as prepared by Lachat Auto dilutor*

Standard Type	LOW RANGE CALIBRATION CURVE Nominal Concentration		
	NO_2^- µgN/L	NO_x^- µgN/L	T-NH_3 µgN/L
All Stock	200	1000	1000
STD 0	0	0	0
STD 1	2	20	20
STD 2	5	50	50
STD 3	10	100	100
STD 4	20	200	200
STD 5	40	500	500
STD 6	100		

** Occasionally a different volume of a solution may be made. If this occurs, the volume made will contain proportional quantities of component constituents as outlined here.*

11) Sample Collection, Preservation, Shipment and Storage:

Samples are filtered either in situ using flipmate style PES 0.45µm filters or after they arrive at the lab through PES 0.45µm filters, then transferred to a clean plastic bottle. *For NO_x ONLY: If samples cannot be run within 7 days they should be preserved with 11N sulfuric acid to a pH of ≤ 2 and stored at 6°C, NO_2 samples should **not** be preserved.* **Holding time** for NO_x & NO_2 samples is 2 days from sample collection unpreserved and 28 days preserved (NO_x only).

12) Quality Control:

Analyze one ICV, ICB, LCS, and REF at the beginning of every run before samples are analyzed. Duplicates, CCVs, and CCBs are run every ten samples. Matrix Spike samples are run every 20 samples. A Matrix spike duplicate should be run ~every 200 samples. Record results on QC charts and be sure they are within the acceptable limits.

UFI's QC parameters are outlined in the Method Performance Section. They are monitored on a variety of levels; by the analyst(s), the Laboratory Director, and the Quality Assurance Officer, as needed. In addition, basic knowledge of the characteristic features of the limnological systems may be used to aid in auditing QC data.

13) Calibration and Standardization:

Standards are placed at the start of every sample run. The Omnion software which is used for data collection from the Lachat QuikChem 8500 calculates and plots the calibration data. The "r" for the standards curve should be no less than 0.995 and the residual error of each point should be no more than ±10%, except for the lowest point which should be no more than ±30%.

14) Procedure:

14.1 Instrument stabilization

Before starting up the Lachat QuikChem 8500, visually inspect that the tubing located under each of the platens is not flat, kinked, or cracked. If so, replace **all tubes** within that analysis. Follow the chart below when replacing tubes. *Record tube replacement and any other maintenance actions in the Lachat maintenance log.* Reagents may be made prior to instrument start up or during initial set up. Samples to be run must be completely thawed. All NO_x & NO_2 samples should be filtered upon arrival to the lab as described in filtering SOP 114.

Analysis	Color	Reagents used
All (One tube for Both)	green/green	Sample
All	purple/purple	sampler wash pull off water
T-NH_3	orange/orange	DCIC
T-NH_3	white/white	Salicylate
T-NH_3	black/black	Ammonia GD Buffer
T-NH_3	grey/grey	Ammonia Acceptor
T-NH_3	red/red	Alkaline Donor
T-NH_3	red/red	Carrier
NO_x	orange/orange	Carrier
NO_x	black/black	Color Reagent
NO_x	blue/yellow	NO_x Buffer

a) Fill Diluent Container with fresh Type II water or acidic carrier
b) Fill Start up bottle with Type II water and place all pump tubes into it
c) Turn on power strip to turn on instrument, autosampler will initialize and peristaltic pump will start to pump water through the lines. Turn on computer.
d) Pause peristaltic pump and put the ammonium chloride buffer tube into the buffer solution, start pump again and allow the instrument to flush with buffer. Cover each

reagent bottle with parafilm. Pause the pump and put the carrier and then color reagent tubes into their respective solutions. Start the pump again to allow reagents to flush through the system. Turn the column on by turning the black valve to the open position (Column is turned ON for NO_x, but kept OFF for NO_2). Do **NOT** let DI or air pump through the column, **only** buffer. **NOTE: Buffer always needs to be put on the instrument first in order to prevent precipitates from forming in the lines.**

e) Open Omnion software and open the appropriate method (NO_x or NO_2). A message will pop up asking you to allow the heater to heat to 60°C for ammonia if you are running ammonia with NO_x, choose yes.

f) Pause the peristaltic pump to conserve reagent while you prepare your calibrants, quality control samples and sample table.

14.2 Preparing calibrants and quality control samples:

a) Fill a standard vial with prepared All Stock solution and place in position S1 in the back of the sampler rack.

b) Fill a standard vial with the prepared LCS sample and place in position S2 of the sampler rack.

c) Fill a standard vial with prepared REF stock solution and place in position S3.

d) Fill standard vial with prepared CCV (if not making CCVs with dilutor) and place in position S4.

e) Fill standard vial with CCB (Type II water) and place in position S5.

f) Fill standard vial with cupric sulfate solution and place in position S6 (only if running NOx by itself).

g) Fill the fourth sample rack with glass sample vials for standard prep, QC prep and sample dilutions.

h) The Method screen will have a sample table window, method editor/results table window, an ammonia peak window (if applicable), and a NOx peak window. Edit the sample table by clicking in each cell, entering relevant sample ID number and hitting enter (cell will not update unless you hit enter). Do this for all sample IDs.

i) For samples with duplicates, click on the sample type, a drop down menu will pop up, select duplicate set. For samples with matrix spikes, select spike set and for MSDs select spiked duplicate set.

j) When finished with samples, highlight the CCV and CCB columns and right click. Select the Define DQM set option at the bottom of the options. A table will open to select 'after every N samples', make N=10 and also check off close end of run. You may also add a "column clean" step to the DQM (injects Cupric sulfate solution) if running NO_x by itself.

k) Pour samples into sample vials and place in sampling tray starting with position 1 (samples will be loaded front to back and left to right). Samples can be loaded up through cup 270.

l) Prime the dilutor by going to configuration→autosamplers and remove any air bubbles. Click preview to preview the baseline. Once a stable baseline is achieved, click the start button and the instrument will start making the

standard curve. Once all QC passes, samples will be run.

14.3 Shut down

When the run is finished, the sample table will go back to being unhighlighted (finished samples are highlighted in grey as the instrument goes through them).

a) Pause the pump and put the color reagent tube into Type II water to begin rinsing. After about one minute, put the carrier tube into the type II water.
b) After the system has flushed out the other reagents, put the buffer tube into Type II water to flush. (Be sure that the cadmium column is taken off-line before doing this).
c) Take all tubes out of water and allow air to flush through the system. Unclick the pump tube cartridges.
d) Remove all used sample and dilution vials from autosampler.

14.4 Exporting data

a) An excel file will have exported for the run into the data folder on the computer for ease of data transfer to the database/parsers.

b) To print a report with calibration and QC pass/fail data on it go to Tools→Custom Report in the Omnion software.

    1. A report will pop up; click the yellow Format icon in the toolbar and a custom report format table will pop up. Got to the table tab and check the boxes for rep#, autodilution factor, detection time, analyte properties, cup number, peak height, and peak area. Go to the charts tab and check the boxes for calibration and DQM tests to be included in the report, click apply and then close.

15) Data analysis and Calculations:

The Omnion software performs the necessary calculations for NO_x & NO_2.

16) Method Performance:

Refer to UFI Controlled Document No. 12 for LOD, LOQ and control limits.

17) Pollution Prevention and Waste Management:

It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. For most natural water systems, this procedure has no negative impact on the environment. Refer to MSDS for proper chemical use and disposal procedures. If any hazardous waste is generated, it is disposed of according to UFI's chemical waste disposal practices.

Table 2: QA\QC for NO_x & NO_2 Analysis

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Initial Calibration Verification	A known concentration of standard solution analyzed at the beginning of the run	1st sample of every batch	ICV

Initial Calibration Blank	Type II water containing all reagents in the same proportion as those in calibration standards and samples	2nd sample of every batch	ICB
Laboratory Control Sample	A spike of known concentration to Type II water	One per sample batch	LCS
Reference	A standard solution of known concentration, made from either a different lot # reagent, a different manufacturer, or another method (dissolving a solid)	One per sample batch	REF
Method Blank	Type II water that undergoes the same procedure as samples	One per sample batch	MB
Duplicate	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP
Continuing Calibration Verification	A standard solution of known concentration, analyzed throughout the course of the run and at the end of every run.	Every 10 samples, and at the end of sample batch, followed by a CCB	CCV
Continuing Calibration Blank	Type II water containing all reagents in the same proportion as those in calibration standards and samples	Every 10 samples, and at the end of every sample batch, preceded by a CCV	CCB
Matrix Spike	A spike of known concentration added to sample matrix	Every 20 samples or one per batch if less than 20 samples	MS
Matrix Spike Duplicate	Same as above, repeated	One per month or ~250 samples	MSD

18) Data Assessment and Acceptance Criteria for Quality Control Measures:

Record results from all quality control samples onto the QC file. The control charts are designed so that the mean is displayed through the middle, with an upper and lower warning limit, and an upper and lower control limit. The warning and control limits are calculated from the previous year's data. The process should be shut down for troubleshooting if one or more of the following occur:

- a single action outside the control limit
- 2 out of 3 consecutive measurements between the warning and control limit
- 7 consecutive measurements above or below the mean
- 6 consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located
- an obvious nonrandom pattern

All data that falls outside stated control limits are appropriately flagged. Refer to UFI Controlled Document No. 12 for flags and their meaning.

19) Corrective Actions for Out-of-Control or Unacceptable Data:

If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. If 2 out of 3 consecutive measurements are between the warning and control limits then causes should be investigated and a Corrective Action Report may be initiated (see Quality Manual for C.A.R. protocol). Based on the Laboratory Directors judgement a comment may be inserted in the comment section of affected data packet. If a cause is found, then a corrective action must be initiated and fully documented.

20) Contingencies for Handling Out-of-Control or Unacceptable Data:

If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is insufficient sample, data should be flagged with an explanation of the circumstances.

21) References:

APHA 2012. Standard Methods for the examination of water and wastewater. 22nd Edition American Public Health Association. Washington D.C.

Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

Lachat Instruments. Determination of Nitrate/Nitrite in drinking, surface and wastewaters by flow injection analysis (QuikChem Method 10-107-04-1-C). July 14, 2008. Lachat Instruments, Loveland CO.

Lachat Operations Manual. Available from Lachat Instruments, 5600 Lindbergh Drive, Loveland, CO 80536

Omnion Operations Manual. Available from Lachat Instruments, 5600 Lindbergh Drive, Loveland, CO 80536

22) Tables, Diagrams, Flowcharts and Validation Data

See attached analyte specific training document for training procedure.

Table 3. Quality Control Acceptance Limits for Nitrate (NO_x) Analysis

Nitrate (NOx) Quality Control Acceptance Limits		
QC	**Nominal**	**Acceptance Range**
ICV/CCV	250.00	± 10% (225.00 - 275.00)
ICB/CCB	0.00	<10
LCS/MS/MSD	150.00	± 15% (127.50 - 172.50)
REF	280.00	± 15% (238.00 - 322.00)
LOD	10.00	N/A
MB	0.00	<15
DUP	-	± 15%

Table 4. Quality Control Acceptance Limits for Nitrite (NO_2) Analysis

Nitrite (NO2) Quality Control Acceptance Limits		
QC	**Nominal**	**Acceptance Range**
ICV/CCV	50.00	± 10% (45.00 - 55.00)
ICB/CCB	0.00	<2
LCS/MS/MSD	30.00	± 15% (25.50 – 34.50)
REF	80.00	± 15% (68.00 - 92.00)
LOD	2.00	N/A
MB	0.00	<3
DUP	-	± 15%

STANDARD OPERATING PROCEDURE L-1B: NITROGEN, TOTAL AMMONIA (AS N; tNH_3)

UPSTATE FRESHWATER INSTITUTE LABORATORY METHODS MANUAL
224 Midler Park Drive, Syracuse, NY 13206

Nitrogen, Total Ammonia (as N; tNH_3) .....SOP 238

1) Test Method: Nitrogen, Total Ammonia SM 4500-NH_3 H, 22nd Edition

2) Applicable Matrix or Matrices:

Drinking, surface and saline waters, domestic and industrial wastes.

3) Limit of Detection and Quantification:

The instrument manufacturer reports a method detection limit of 0.002 mg/L, the applicable range of the method is 0.01-20mg/L. During any quarter in which samples are being analyzed, verify the LOD by preparing a minimum of two spiked samples in separate batches, using the same spiking concentration as your calculated LOD. At least once every thirteen months, recalculate the MDL_s and MDL_b using historical QC data from the last twenty four months. Refer to EPA document 821-R-16-006 Revision 2 Section 4 (f) for the acceptance criteria of verified MDL.

4) Scope and Application:

This method pertains to the determination of ammonia in surface and saline waters as well as domestic and industrial wastes.

5) Summary of Test Method:

The sample containing ammonium is injected into a continuously flowing carrier stream by means of an injection valve, and mixed with a continuously flowing stream of an alkaline solution. The ammonia is separated from the matrix in a diffusion cell across a hydrophobic semi-permeable membrane and absorbed by a flowing acceptor stream.

When ammonia in the acceptor is heated with salicylate and DCIC in an alkaline phosphate buffer, an emerald green color is produced which is proportional to the ammonia concentration. The color is intensified by the addition of sodium nitroprusside. Heat is used to aid ammonia from the donor in passing into the acceptor, in particular for the low level concentrations.

6) Definitions:

Total ammonia (T-NH_3) dissociates in water to form free ammonia and ammonium (Equation 1).

$$\text{(Eq. 1)} T\text{-}NH_3 = NH_4^+ + NH_3$$

Where:

$T\text{-}NH_3$ = total ammonia measured directly in the laboratory according to this SOP.
NH_4^+ = ammonium (protonated form of ammonia).
NH_3 = free ammonia.

This dissociation is a function of pH and temperature. These two forms are not directly measured in the laboratory, however they can be calculated through the use of equilibrium chemistry, pH and temperature and T-NH_3.

Also defined in this SOP are other nitrogen constituents found in the Allstock solution. Nitrate + Nitrite (NO_x) and nitrite (NO_2) are measured directly in the laboratory (SOP 239).

7) Interferences:

- Calcium and magnesium ions may be present in concentrations sufficient to cause precipitation problems during analysis. An EDTA or sodium citrate solution can be used to prevent the precipitation of calcium and sodium ions.
- Lauryl sulfate, detergents, oil and grease can cause low ammonia recoveries by wetting the gas diffusion membrane.

8) Safety:

Always wear safety goggles, gloves and lab coats when handling acids or other toxic substances. Use hoods for mixing solutions that produce fumes. If you spill concentrated acids, bases or other toxic chemicals notify the technical director immediately. The following chemicals may be highly toxic or hazardous. Handle with extreme caution at all times: Sodium Hydroxide, Sodium Nitroprusside, Sulfuric acid, and DCIC.

9) Equipment and Supplies:

- Flow Injection Analysis (FIA) system (Lachat Instruments QuikChem 8500 Series 2)
  - RP-150 series Reagent Pump
  - Lachat XYZ Auto Sampler: ASX 280 Series
  - 660nm optical filter
  - Ammonia QuikChem Method Rev. 2.0 10-107-06-5-J
  - Omnion software and computer
  - assorted pump tubes as described in instrument manual
  - reagent bottles and instrument waste bottles
  - Lachat repair and maintenance kit
- sampling/standard vials, diluting cups
- Eppendorf pipettes
- assorted volumetric flasks
- assorted graduated cylinders
- calibrated top loading balance

10) Reagents and Standards:

10.1 Preparation of Reagents

Degassing Reagents: Preparation of reagents a day in advance (reagents will outgas as they come to room temperature) and the use of backpressure loops on the chemistry manifolds will normally prevent air spikes from occurring. If air spikes become a problem, degas all solutions except the standards by vacuum filtration.

1. **Sodium Phenolate:** In a 1L volumetric flask, dissolve 88mL of 88% liquefied phenol into ~600mL DI water. While stirring, slowly add 32g NaOH. Cool, dilute to the mark, and invert to mix. Do NOT degas this reagent. *Prepare fresh every 3 to 5 days. Discard reagent when it is dark brown as it will affect the baseline on*

the Lachat. ***CAUTION: Phenol causes severe burns and is rapidly absorbed into the body through the skin, wear gloves.***

2. **Sodium Hypochlorite:** In a 500mL volumetric flask, dilute 159mL 8.25% sodium hypochlorite (store bought bleach) to the mark with DI water. Invert to mix. *Prepare fresh daily.*
3. **Sodium Nitroprusside:** In a 1L volumetric flask, dissolve 3.5g sodium nitroprusside (sodium nitroferricyanide) Dilute to the mark with DI water and invert to mix. *Prepare fresh every 1 to 2 weeks.*
4. **1M Sodium Hydroxide Solution:** In a 1L volumetric flask, dissolve 40g NaOH in ~900mL DI water. Mix to dissolve, dilute to the mark with DI water.
5. **Buffer for Non Acid Preserved Samples:** In a 1L volumetric flask, dissolve 50g EDTA and 225mL 1M Sodium Hydroxide in ~700mL DI water. Mix until dissolved and dilute to the mark with DI water. *Prepare fresh monthly.*
6. **Buffer for Acid Preserved Samples:** In a 1L volumetric flask, dissolve 50g EDTA and 254mL 1M Sodium Hydroxide in ~700mL DI water. Mix until dissolved and dilute to the mark with DI water. *Prepare fresh monthly.*
7. **Sulfuric Acid Diluent for Carrier and Standards:** In a 1L volumetric flask, add ~800mL DI water and 2mL concentrated sulfuric acid. Dilute to the mark, invert to mix. *Prepare fresh weekly.*

10.2 Preparation of Standards

Stock 1000mgN/L standards should be kept in amber bottles and stored at 6°C when not in use. Holding time is 3 months.

1. **Stock NH_3 1000 mgN/L Standard**
   a. Ammonium Sulfate: Place 4.717g of ammonium sulfate dried at 110°C for 2 hours ($H_8O_4N_2S$; FW: 132.14) into a 1L volumetric flask. Dilute to the mark with type II water and invert to mix.
   b. Ammonium Chloride: Place 3.819g ammonium chloride dried at 110°C for 2 hours (NH_4Cl; FW: 53.49) into a 1L volumetric flask. Dilute to the mark with type II water and invert to mix.
2. **Stock NO_2 1000 mgN/L Standard**: Only needed if running NO_2 and NO_x concurrently: place 6.076g of Potassium nitrite (KNO_2; MW: 85.10) dried at 110°C for 2 hours into 1L flask. Dilute to volume with Type II water.
3. **Stock NO_3 1000 mgN/L Standard**: Only needed if running NO_2 and NO_x concurrently: place 7.218g of Potassium nitrate (KNO_3; MW: 101.10) dried at 110°C for 2 hours into 1L flask. Dilute to volume with Type II water.
4. **All Stock***: Pipette 0.1 mL of NO_2^- standard 1000mg/L, 0.4 mL of NO_3^- standard 1000mg/L and 0.5 mL of T-NH_3 Standard 1000mg/L into a 500 mL volumetric flask. **Made daily.** *NOTE: *NH_3 standard only needed if running both channels concurrently, omit from all stock if only running NO_x channel. The resulting final concentration for this stock is 1000µg/L NH_3 and NO_x and 200µg/L NO_2.*

5. **Reference All Stock*:** Made from commercially purchased standards. Pipette 0.2 mL of NO_2^- standard (1000ppm), 0.5 mL of NO_3^- standard (1000ppm), and 0.913 mL of T-NH_3 standard (1000ppm) into a 250 mL volumetric flask with approximately 100 mL of Type II water. Fill to volume and mix well. **Made daily**. **The Lachat is programmed to do a 10x dilution on this stock which results in a final concentration of 300µgN/L NH3, 80µgN/L NO2, and 280µgN/L NOx.*

6. **MS/LCS Spike Allstock**: Place 0.3 mL of Stock NO_2^- 1000mg/L Standard, 1.2 mL of Stock NO_3^- 1000mg/L, and 1.5 mL of Stock NH_3 1000mg/L Standard into a 100mL flask. Dilute to volume with Type II water and invert to mix. *Holding time: 3 months*
7. **LCS**: Place ~ 50 mL of Type II water into 100 mL volumetric flask. Pipette 1.0 mL of spiking solution into flask and fill to line using Type II water. **Made daily**.
8. **Matrix Spike (MS)**: Place ~ 15 mL of designated sample into 25 mL volumetric flask. Pipette 250 µL of MS/LCS Spike Allstock into flask and fill to line using designated sample. **Made daily.**

*10.3 Standard Curve Preparation**:***
The Stock solutions listed above are used to prepare the Low range "All Stock" solution's described below. **Made daily.** *NOTE: *only needed if running both channels concurrently, omit unneeded analyte from all stock if only running singular channel.*

All Stock* Prepare in **500mL** Type II water

Analyte	Low Range (nominal value)
NO2	0.1mL (200 µg/L)
NO3	0.4m (1000 µg/L)
NH3	0.5mL (1000µg/L)

Table 1: Standard Stock and Standard Curve used for running T-NH_3, NO_2 and NO_x^- as prepared by Lachat Auto dilutor*

Standard Type	LOW RANGE CALIBRATION CURVE Nominal Concentration		
	NO_2^- µgN/L	NO_x^- µgN/L	T-NH_3 µgN/L
All Stock	200	1000	1000
STD 0	0	0	0
STD 1	2	20	20
STD 2	5	50	50
STD 3	10	100	100
STD 4	20	200	200
STD 5	40	500	500
STD 6	100		

** Occasionally a different volume of a solution may be made. If this occurs, the volume made will contain proportional quantities of component constituents as outlined here.*

11) Sample Collection, Preservation, Shipment and Storage:

Samples are filtered either in situ using flipmate style PES 0.45µm filters or after they arrive at the lab through PES 0.45µm filters, then transferred to a clean plastic bottle. If samples cannot be run within 7 days they should be preserved with 11N sulfuric acid to a pH of ≤ 2 and stored at 6°C. **Holding time** for T-NH_3 samples is 7 days from sample collection unpreserved and 28 days preserved.

12) Quality Control:

Analyze one ICV, ICB, LCS, and REF at the beginning of every run before samples are analyzed. Duplicates, CCVs, and CCBs are run every ten samples. Matrix Spikes are run every 20 samples. A Matrix spike duplicate should be run ~every 200 samples. Record results on QC charts and be sure they are within the acceptable limits.

UFI's QC parameters are outlined in the Method Performance Section. They are monitored on a variety of levels; by the analyst(s), the Laboratory Director, and the Quality Assurance Officer, as needed. In addition, basic knowledge of the characteristic features of the limnological systems may be used to aid in auditing QC data.

13) Calibration and Standardization:

Standards are placed at the start of every sample run. The Omnion software which is used for data collection from the Lachat QuikChem 8500 calculates and plots the calibration data. The "r" for the standards curve should be ≥0.995 and the residual error of each point should be ≤ ±10%, except for the lowest point which should be ≤ ±30%.

14) Procedure:

14.1 Instrument stabilization

Before starting up the Lachat QuikChem 8500, visually inspect that the tubing located under each of the platens is not flat, kinked, or cracked. If so, replace **all tubes** within that analysis. Follow the chart below when replacing tubes. *Record tube replacement and any other maintenance actions in the Lachat maintenance log.* Reagents may be made prior to instrument start up or during initial set up. Samples to be run must be completely thawed. All TNH_3 samples should be filtered upon arrival to the lab as described in filtering SOP 114.

Analysis	Color	Reagents used
All (One tube for Both)	green/green	Sample
All	purple/purple	sampler wash pull off water
$T\text{-}NH_3$	orange/orange	DCIC
$T\text{-}NH_3$	white/white	Salicylate
$T\text{-}NH_3$	black/black	Ammonia GD Buffer
$T\text{-}NH_3$	grey/grey	Ammonia Acceptor
$T\text{-}NH_3$	red/red	Alkaline Donor
$T\text{-}NH_3$	red/red	Carrier
NO_x	orange/orange	Carrier
NO_x	black/black	Color Reagent
NO_x	blue/yellow	NO_x Buffer

a) Fill Diluent Container with fresh Type II water or acidic carrier
b) Fill Start up bottle with Type II water and place all pump tubes into it
c) Turn on power strip to turn on instrument, autosampler will initialize and peristaltic pump will start to pump water through the lines. Turn on computer.
d) Pause peristaltic pump and put ammonia buffer tube into the buffer solution, start pump again and allow the instrument to flush with buffer. Pause the pump and put the DCIC, alkaline donor, carrier, and ammonia acceptor tubes into their respective solutions, start the pump again to allow reagents to flush through the system. Pause the pump one last time to put the salicylate (color) tube into the reagent, start pump again and let the salicylate flush through the system. When all reagents are running through the system the second mixing coil on the manifold (closest to the computer) will be a faint yellow color. Cover each reagent bottle with parafilm. **NOTE: Buffer always needs to be put on the instrument first in order to prevent precipitates from forming in the lines.**

e) Open Omnion software, and open up the appropriate Ammonia/NOx method. A message will pop up asking you to allow the heater to heat to 60°C for ammonia, choose yes.

f) Pause the peristaltic pump to conserve reagent while you prepare your calibrants, quality control samples and sample table.

14.2 Preparing calibrants and quality control samples:

a) Fill a standard vial with prepared All Stock solution and place in position S1 in the back of the sampler rack.

b) Fill a standard vial with the prepared LCS sample and place in position S2 of the sampler rack.

c) Fill a standard vial with prepared REF stock solution and place in position S3.

d) Fill a standard vial with prepared CCV (if not making CCVs with dilutor) and place in position S4.

e) Fill standard vial with CCB (Type II water) and place in position S5.

f) Fill the fourth sample rack with glass sample vials for standard prep, QC prep and sample dilutions.

g) The Method screen will have a sample table window, method editor/results table window, an ammonia peak window, and a NOx peak window (if applicable). Edit sample table by clicking in each cell, entering relevant sample ID number and hitting enter (cell will not update unless you hit enter). Do this for all sample IDs (skip over duplicates and matrix spikes).

h) For samples with duplicates, click on the sample type, a drop down menu will pop up, select duplicate set. For samples with matrix spikes, select spike set and for MSDs select spiked duplicate set.

i) When finished with samples, highlight the CCV and CCB columns and right click. Select the Define DQM set option at the bottom of the options. A table will open to select 'after every N samples', make N=10 and also check off close end of run.

j) Pour samples into sample vials and place in sampling tray starting with position 1 (samples will be loaded front to back and left to right). Samples can be loaded up through cup 270.

k) Prime the dilutor by going to configuration→autosamplers and remove any air bubbles. Click preview to preview the baseline. Once a stable baseline is achieved, click the start button and the instrument will start making the standard curve. Once all QC passes, samples will be run.

14.3 Shut down

When the run is finished, the sample table will go back to being unhighlighted (finished samples are highlighted in grey as the instrument goes through them).

a) Pause the pump and put the color reagent tube into Type II water to begin rinsing. After about one minute, when the color reagent is visibly rinsed from the mixing coil, put the carrier, DCIC, and alkaline donor tubes into type II water, waiting about one minute between each tube.

b) After the system has flushed out the other reagents, put the buffer tube into Type II water to flush. (*Be sure that the cadmium column is taken off-line before doing this if running NO_x simultaneously*).

c) Take all tubes out of water and allow air to flush through the system. Unclick the pump tube cartridges.
d) Remove all used sample and dilution vials from the autosampler.

14.4 Exporting data

a) An excel file will have exported for the run into the data folder on the computer for ease of data transfer to data entry templates. Rename this file as Lachat_2019juliandate in the raw data folder on the server under the applicable nitrogen analyte.

b) To print a report with calibration and QC pass/fail data on it go to Tools→Custom Report in the Omnion software.

    a. A report will pop up; click the yellow Format icon in the toolbar and a custom report format table will pop up. Got to the table tab and check the boxes for autodilution factor, detection time, cup number, peak height, and peak area. Go to the charts tab and check the boxes for calibration to be included in the report, click apply and then close.

15) Data analysis and Calculations:
The Omnion software performs the necessary calculations for T-NH_3.

16) Pollution Prevention and Waste Management:
It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. For most natural water systems, this procedure has no negative impact on the environment. Refer to MSDS for proper chemical use and disposal procedures. If any hazardous waste is generated, it is disposed of according to UFI's chemical waste disposal practices.

17) Method Performance:
Refer to UFI Controlled Document No. 12 for LOD, LOQ and control limits.

Table 2: QA\QC for NH_3 Analysis

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Initial Calibration Verification	A known concentration of standard solution analyzed at the beginning of the run	1st sample of every batch	ICV
Initial Calibration Blank	Type II water containing all reagents in the same proportion as those in calibration standards and samples	2nd sample of every batch	ICB
Laboratory Control Sample	A spike of known concentration to Type II water	One per sample batch	LCS

Reference	A standard solution of known concentration, made from either a different lot # reagent, a different manufacturer, or another method (dissolving a solid)	One per sample batch	REF
Method Blank	Type II water that undergoes the same procedure as samples	One per sample batch	MB
Duplicate	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP
Continuing Calibration Verification	A standard solution of known concentration, analyzed throughout the course of the run and at the end of every run.	Every 10 samples, and at the end of sample batch, followed by a CCB	CCV
Continuing Calibration Blank	Type II water containing all reagents in the same proportion as those in calibration standards and samples	Every 10 samples, and at the end of every sample batch, preceded by a CCV	CCB
Matrix Spike	A spike of known concentration added to sample matrix	Every 20 samples or one per batch if less than 20 samples	MS
Matrix Spike Duplicate	Same as above, repeated	One per month or ~250 samples	MSD

18) Data Assessment and Acceptance Criteria for Quality Control Measures:

Record results from all quality control samples onto the QC file. The control charts are designed so that the mean is displayed through the middle, with an upper and lower warning limit, and an upper and lower control limit. The warning and control limits are calculated from the previous year's data. The process should be shut down for troubleshooting if one or more of the following occur:

- a single action outside the control limit
- 2 out of 3 consecutive measurements between the warning and control limit
- 7 consecutive measurements above or below the mean
- 6 consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located
- an obvious nonrandom pattern

All data that falls outside stated control limits are appropriately flagged. Refer to UFI Controlled

Document No. 12 for flags and their meaning.

19) Corrective Actions for Out-of-Control or Unacceptable Data:

If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. If 2 out of 3 consecutive measurements are between the warning and control limits then causes should be investigated and a Corrective Action Report may be initiated (see Quality Manual for C.A.R. protocol). Based on the Laboratory Directors judgement a comment may be inserted in the comment section of affected data packet. If a cause is found, then a corrective action must be initiated and fully documented.

20) Contingencies for Handling Out-of-Control or Unacceptable Data:

If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is insufficient sample, data should be flagged with an explanation of the circumstances.

21) References:

APHA 2012. Standard Methods for the examination of water and wastewater. 22nd Edition American Public Health Association. Washington D.C.

Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

Lachat Instruments. Determination of ammonia by flow injection analysis (QuikChem Method 10-107-06-5-J). January 16, 2015. Lachat Instruments, Loveland CO.

Lachat Operations Manual. Available from Lachat Instruments, 5600 Lindbergh Drive, Loveland, CO 80536

Omnion Operations Manual. Available from Lachat Instruments, 5600 Lindbergh Drive, Loveland, CO 80536

22) Tables, Diagrams, Flowcharts and Validation Data

See attached analyte specific training document for training procedure.

Table 3. Quality Control Acceptance Limits for Ammonia (tNH_3) Analysis

Ammonia (tNH3) Quality Control Acceptance Limits		
QC	**Nominal**	**Acceptance Range**
ICV/CCV	250.00	± 10% (225.00 – 275.00)
ICB/CCB	0.00	<10
LCS/MS/MSD	150.00	± 15% (127.50 - 172.50)
REF	300.00	± 15% (255.00 - 345.00)
LOD	10.00	N/A
MB	0.00	<15
DUP	-	± 15%

STANDARD OPERATING PROCEDURE L-1C: PHOSPHORUS, ORTHOPHOSPHATE (SOLUBLE REACTIVE PHOSPHORUS AS P; SRP)

Phosphorus, Orthophosphate (Soluble Reactive Phosphorus as P; SRP)…….SOP107

1) Test Method: Phosphorus, Soluble Reactive SM 4500-P E, 22nd Edition

2) Applicable Matrix or Matrices:
Drinking, surface and saline waters, domestic and industrial wastes.

3) Limit of Detection and Quantification:
During any quarter in which samples are being analyzed, verify the LOD by preparing a minimum of two spiked samples in separate batches, using the same spiking concentration as your calculated LOD. At least once every thirteen months, recalculate the MDL_s and MDL_b using historical QC data from the last twenty four months. Refer to EPA document 821-R-16-006 Revision 2 Section 4 (f) for the acceptance criteria of verified MDL.

Table 1: Phosphorus low range

Approx. [P range] µg/L	Light Path (cm)
0-50	10

4) Scope and Application:
This method covers the determination of SRP in drinking, surface, and saline waters, domestic and industrial wastes.

5) Summary of Test Method:
Ammonium molybdate and potassium antimonyl tartrate react in an acid medium with orthophosphate to form a heteropoly acid (phosphomolybdic acid) that is reduced to an intensely colored molybdenum blue by ascorbic acid. The separation of phosphorus into its various forms is defined analytically but the analytical differentiations have been selected so that they may be used for interpretive purposes. Filtration through a **0.45µm PES** filter or a 10µm membrane filter separates dissolved from suspended forms of phosphorus. No claim is made that filtration through a 0.45µm filter is a true separation of suspended and dissolved forms of phosphorus, it is merely a convenient and replicable analytical technique designed to make a gross separation. Filtration through a 10µm filter aids in the determination of suspended and dissolved forms of phosphorus for limnological comparability studies.

6) Definitions:

SRP - All orthophosphorus present in dissolved form which passes through a 0.45µm filter.

SRP 10- All orthophosphorus present in dissolved form which passes through a 10µm filter.

7) Interferences:

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

8) Safety:

Always wear safety goggles, gloves and lab coats when handling acids or other toxic substances. Use hoods for mixing solutions that produce fumes. If you spill concentrated acids, bases or other toxic chemicals notify the technical director immediately.

9) Equipment and Supplies:

- spectrophotometer for use at 880nm
- nitric acid washed glassware*
- reagents listed in this SOP
- pipettes and tips
- quartz cuvette cell (10cm)
- filtering apparatus
- 0.45µm mixed Polyethersulfanone PES
- 10µm polycarbonate filter
- calibrated top loading and analytical balance
- plastic trays

**All glassware should be washed with [1:1] Nitric Acid: Type II water and rinsed three (3) times with Type II water. Glassware should be dried upside down to prevent contamination.*

10) Reagents and Standards:

a. <u>5N Sulfuric acid</u> – Pour 280mL concentrated H_2SO_4 slowly into ~1000mL of Type II water in a 2000mL, class A, volumetric flask. Allow it to come to room temperature in an ice bath, then dilute to volume with Type II water.

b. <u>Potassium antimony tartrate solution</u> – Dissolve 1.3715g $K(SbO)C_4H_4O_6 \bullet 1/2H_2O$ in 400mL Type II water in a 500mL, class A, volumetric flask. Once dissolved, dilute to volume with Type II water.

c. <u>Ammonium molybdate solution</u> - Dissolve 40g (NH4)6Mo7O24•$4H_2O$ in 800mL Type II water in a 1000mL, class A, volumetric flask. Once dissolved, dilute to volume with Type II water.

d. <u>Ascorbic acid -0.1M</u> – Dissolve 8.8g ascorbic acid in 400mL Type II water in a 500mL, class A, volumetric flask. Once dissolved, dilute to volume. *The solution is stable for 7 days at 0-6°C but ideally keep at 4°C if possible.*

e. Mixed reagent – THIS SOLUTION IS ONLY STABLE FOR 4 HOURS. The chemicals for the mixed reagent should be added in this order: sulfuric acid, potassium antimonyl tartrate, ammonium molybdate, and ascorbic acid. Mix the above reagents in the following proportions:

Proportional mix of reagents for Phosphorus analysis

Mixed Reagent (mL)	No. of Samples	5N H_2SO_4 (mL)	P.A.T (mL)	Ammonium Molybdate (mL)	Ascorbic acid (mL)
100	12+4	50	5	15	30
200	25	100	10	30	60
300	37+4	150	15	45	90
400	50	200	20	60	120
500	62+4	250	25	75	150
600	75	300	30	90	180

f. Stock Phosphate solution, Commercially Purchased 100,000µgP/L– Ricca Phosphate Phosphourus Standard, 100ppm P. Cat #5856.5-16

g. Stock Phosphate solution 100µgP/L – dilute 1mL of 100,000µg/L stock to 1 liter with DI Water in a 1000mL, class A, volumetric flask

h. Stock Phosphate solution 1000µgP/L – dilute 10mL of 100,000µg/L stock to 1 liter with DI Water in a 1000mL, class A, volumetric flask

i. Stock phosphate Reference - 1,000µgP/L – dilute 0.5mL of Phosphate (PO_4^{3-}) as P to 500mL with Type II water in a 500mL, class A, volumetric flask.

j. Stock phosphate Spike - 5,000µgP/L – dilute 25mL of Phosphate (PO_4^{3-}) as P to 500mL with Type II water in a 500mL, class A, volumetric flask.

k. LCS/MS - pour 50mL of Type II water or sample water into beaker and spike with 100µL of the stock spike solution (5,000µgP/L). Nominal concentration is 10µgP/L.

l. Reference (REF): Pour 48mL of Type II water into a beaker and add 2.0mL of stock reference solution (1,000µgP/L). Nominal concentration is 40µgP/L.

m. ICV/CCV: pour 48.75mL of Type II water into a beaker and add 1.25mL of stock phosphate solution (1,000µgP/L). Nominal concentration is 25µgP/L.

n. ICB/CCB - pour 50mL of Type II water into a beaker.

o. Method Blank (MB) - pour 50mL of filtered Type II water into a beaker.

p. Blank Reagent- Mixed in the same proportions as the mixed reagent, substituting Type II water for the PAT and Ascorbic Acid.

Table 3: Phosphorus Reagent Naming System

Reagent	UFI Name	Bench Use	Ingredients
Stock Phosphate solution (50,000µgP/L)	**p50,000 Stock + JD***	Primary Stock Solution	Potassium Phosphate Monobasic ACS, Type II water
Stock Phosphate Solution (100µgP/L)	**p100 Stock + JD**	Calibrations, ICV, CCV	p50,000 stock, Type II water
Stock Phosphate Solution (1000µgP/L)	**p1000 Stock + JD**	Calibrations ICV, CCV	p50,000 stock, Type II water
Stock Phosphate Solution (10,000µgP/L)	**p10,000 Stock + JD**	Calibrations ICV, CCV	p50,000 stock, Type II water
Stock Phosphate Reference (1000µgP/L)	**pREF +JD**	Phosphorus Reference	Phosphate (PO_4 as P) NIST certified 1000µg/mL, Type II water
Stock phosphate Spike (5000µgP/L)	**pSPIKE + JD**	Phosphorus LCS/MS	Phosphate (PO_4 as P) NIST certified 1000µg/mL, Type II water
Sulfuric Acid Solution (11N)	**pH2SO4 (11N) + JD**	Digestion/Preservation	H_2SO_4, Type II water
11N Nitric/ Sulfuric Acid	**pH2SO4 (11N + HNO3) + JD**	**TIP Digestion**	H_2SO_4, HNO_3, Type II water
Sulfuric Acid Solution (5N)	**pH2SO4 + JD**	Mixed Reagent/pH adjusting	H_2SO_4,, Type II water
Ammonium Molybdate Solution	**pAMM + JD**	Mixed Reagent	Ammonium Molybdate, Type II water
Potassium Antimonyl Tartrate Solution	**pPAT +JD**	Mixed Reagent	Potassium Antimonyl Tartrate, Type II water
Ascorbic Acid Reagent	**pAA + JD**	Mixed Reagent	Ascorbic Acid, Type II water
Blank Reagent	**pBLANK + JD**	Turbidity Blank	pAMM, pH_2SO_4,, Type II water
Sodium Hydroxide Solution (1N)	**pNaOH + JD**	pH adjusting	NaOH, Type II water
Sodium Hydroxide Solution (6N)	**pNaOH (6N) + JD**	pH adjusting	NaOH, Type II water
Phenolphthalein Indicator Aq. Solution	**pPhen + JD**	pH adjusting	Phenolphthalein Disodium Salt, Type II water
Nitric Acid Wash	**pHNO_3 + JD**	General Glassware Acid Rinse	HNO_3, Type II water

**JD = Julian Date*

Below is a chart of the 6 standards used for the creation of the SRP50 curve. All standards are created using 100µg/L, 1000µg/L, or 10,000µg/L standard stock solutions. Use the standard stock solutions in combination with Type II water, so that the desired concentration is achieved, and the resulting total volume of a single standard is 50mL.

Table 4: SRP-50 Standard curve preparation in 50mL

Standard Concentration (µgP/L)	mL of 100µgP/L	mL of 1000µgP/L	mL of 10,000µgP/L
2	1.0	0.1	n/a
10	5.0	0.5	0.05
20	10.0	1.0	0.10
30	15.0	1.5	0.150
40	20.0	2.0	0.200
50	25.0	2.50	0.250

**Occasionally a different volume of a solution may be made. If this occurs, the volume made will contain proportional quantities of component constituents as outlined here.*

11) Sample Collection, Preservation, Shipment and Storage:

Samples should be filtered upon collection, or immediately upon arrival at the Laboratory, and analyzed within 48 hours of sampling time. SRP samples are refrigerated at 0-6^{0}C until analyzed. SRP samples are filtered through a PES 0.45µm filter. Filter SRP 10 samples through a 10µm membrane filter. Filters should be washed by soaking in distilled water for 24hrs before use; they may contribute significant amounts of phosphorus to samples containing low concentrations of phosphate. Rinse filters before use. ALL GLASSWARE NEEDS TO BE ACID WASHED AND PLACED UPSIDE DOWN ON DRYING RACKS AFTER USE. Filtering apparatus should also be acid washed as needed. Soluble Reactive Phosphorus samples, either sent to UFI, or sampled by UFI, should not be preserved. **Holding time is 48 hours from sample collection.**

12) Quality Control:

UFI's QC parameters are outlined in the Method Performance Section. They are monitored on a variety of levels; by the analyst(s), the Laboratory Director, and the Quality Assurance Officer as needed. In addition, basic knowledge of the characteristic features of the limnological systems may be used to aid in auditing QC data.

13) Calibration and Standardization:

A minimum of 6 standards should be prepared, using Type II water, bracketing the sample concentration. For the SRP/SRP10 test we prepare 6 standards for the curve calibration (see Table 3, section 10: Reagents and Standards). The spectrophotometer can be set up to run standards, produce linear regression statistics, and read sample concentration (see below). As a NELAC requirement, the "r" for the standard curve should be 0.995 or greater; however a correlation coefficient of 0.999 or greater is more desirable.

14) Procedure:

Measure 50mL of filtered sample (see section 11) into a clean, acid washed beaker. Prepare QC as described in section 10 so that the total volume equals 50 mL.

Add 8mL of mixed reagent and mix thoroughly. After at least 10 minutes, but no more than 30 minutes, measure the standards and samples in the spec at 880nm.

SRP10 samples should have a corresponding Blank to correct for turbidity. Measure a second 50mL aliquot of 10µm filtered sample to receive the Blank reagent.

Turbidity blanks must be hit with 8mL of Blank reagent. There is no time limit on the Blank reagent.

Most samples can be run, undiluted, on the 0-50µg/L curve using the 10cm cell. If a sample's concentration is above 50µg/L, the sample will be diluted using Type II water and a graduated cylinder to fall within the curve.

<u>To Use The Lambda 35 Spectrophotometer:</u>

a) Allow spectrophotometer to warm up for 20-30minutes prior to analysis (see Perkin Elmer manual for spectrophotometer operation).
b) Open the Perkin Elmer UV WIN Lab software and select the SRP method.
c) Fill the 10cm quartz cell with the prepared auto zero (Type II water and mixed reagent), place it in the spec, and click the "Auto Zero" button. After you have done this, the screen should read "0.000 A" in the upper right hand corner of the software.
d) Select the sample table tab and fill in the sample numbers and QC in the order you will be running them (software requires QC to be labeled sequentially ie. CCV1, CCV2, ect.)

e) Start the run and measure your initial QC first, you can press cancel on the run to 'pause' it and check your QC results at anytime, the instrument only shows you absorbance on the run screen.
f) Pour samples in cuvette and press "ok" on the prompt that pops up on the screen, do this for each sample, running your QC samples when necessary (see section 16, below).
g) When analysis is complete export the data into a folder on the desktop then move it into the SRP raw data folder in aquadog. Print and attach the curve and data printout to the data page. Close the software and turn off spec. Absorbance guidelines for standards are given under section 23 below.

C<u>reating the Calibration Curve:</u> Curves are to be updated on a weekly basis, or whenever lot numbers for the standards or color reagents change.

a. Create your standards for SRP/SRP10 using the chart listed in Table 3, section 10. Follow the same procedure as sample preparation, hit them with reagent, and wait at least 10 minutes.
b. The software is set to force a recalibration every 7 days, so when you start the method it will prompt for the curve standards as your first 'samples'. As mentioned above, you can press 'cancel' at anytime to view the residuals and R value on the curve before continuing the run.
b. Be sure to include all curve information in data packet when the run is finished.

15) Data analysis and Calculations:

Concentration calculations are done by the spectrophotometer.

16) Method Performance:

UFI laboratory adheres to the following chart for identifying and running QC samples. Each type of sample may not be applicable to every analysis. QC samples are run, as possible, following the chart below.
Refer to UFI Controlled Document No. 12 for LOD, LOQ and control limits

Table 5: QA\QC for SRP/SRP 10 Analysis

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Initial Calibration Verification (25µgP/L)	A known concentration of standard solution analyzed at the beginning of the run	1st sample of every batch	ICV
Initial Calibration Blank	Type II water containing all reagents in the same proportion as those in calibration standards and samples	2nd sample of every batch	ICB

Laboratory Control Sample (10µgP/L)	A spike of known concentration to Type II water	One per sample batch	LCS
Reference (40µgP/L)	A standard solution of known concentration, made from either a different lot # reagent, a different manufacturer, or another method (dissolving a solid)	One per sample batch	REF
Method Blank	Type II water that undergoes the same procedure as samples	One per sample batch	MB
Duplicate	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP
Continuing Calibration Verification (25µgP/L)	A standard solution of known concentration, analyzed throughout the course of the run and at the end of every run.	Every 10 samples, and at the end of sample batch, followed by a CCB	CCV
Continuing Calibration Blank	Type II water containing all reagents in the same proportion as those in calibration standards and samples	Every 10 samples, and at the end of every sample batch, preceded by a CCV	CCB
Matrix Spike (10µgP/L)	A spike of known concentration added to sample matrix	Every 20 samples or one per batch if less than 20 samples	MS
Matrix Spike Duplicate (10µgP/L)	Same as above, repeated	One per month or ~250 samples	MSD

17) Pollution Prevention:

It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. For most natural water systems, this procedure has no negative impact on the environment.

18) Data Assessment and Acceptance Criteria for Quality Control Measures:

Record results from all quality control samples onto the QC file. The control charts are designed so that the mean displayed through the middle, with an upper warning limit, a lower warning limit, an upper control limit and a lower control limit. The warning and control limits are calculated from the previous year's data. The process should be shut down for trouble shooting if one or more of the following occur:

- a single action outside the control limit
- 2 out of 3 consecutive measurements between the warning and control limit
- 7 consecutive measurements above or below the mean

- 6 consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located
- an obvious nonrandom pattern

All data that falls outside stated control limits are appropriately flagged. Refer to UFI Controlled Document No. 12 for flags and their meaning.

19) Corrective Actions for Out-of-Control or Unacceptable Data:

If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. If 2 out of 3 consecutive measurements are between the warning and control limits then causes should be investigated and a Corrective Action Report may be initiated (see Quality Manual for C.A.R protocol). Based on the Laboratory Directors judgement a comment may be inserted into the comment section of effected data packet. If a cause is found, then a corrective action must be initiated and fully documented.

20) Contingencies for Handling Out-of-Control or Unacceptable Data:

If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is insufficient sample, data should be flagged with an explanation of the circumstances.

21) Waste Management:

Refer to MSDS for proper chemical use and disposal procedures. If any hazardous waste is generated, it is disposed of according to UFI's chemical waste disposal practices.

22) References:

APHA 2012. Standard Methods for the examination of water and wastewater. 22nd Edition American Public Health Association. Washington D.C.

Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data:

See attached analyte specific training document for training procedure.

Table 6: Approximate SRP absorptions

10 cm Cell	
Concentration (µgP/L)	**Absorption**
0.3	0.003
1	0.006
2	0.012
3	0.018
5	0.030
7	0.042
10	0.060
20	0.120
50	0.300
100	0.600
125	0.750

Table 7. Quality Control Acceptance Limits for Soluble Reactive Phosphorus (SRP) Analysis

Soluble Reactive Phosphorus (SRP) Quality Control Acceptance Limits		
QC	**Nominal**	**Acceptance Range**
ICV/CCV	25.00	± 10% (22.50 - 27.50)
ICB/CCB	0.00	< 0.55
LCS/MS/MSD	10.00	± 15% (8.50 - 11.50)
REF	40.00	± 15% (34.00 - 46.00)
LOD	1.00	N/A
MB	0.00	< 0.83
DUP	-	± 15%

STANDARD OPERATING PROCEDURE L-1E: SOLIDS, TOTAL SUSPENDED (AH FILTERS; TSS_AH)

UPSTATE FRESHWATER INSTITUTE LABORATORY METHODS MANUAL
224 Midler Park Drive, Syracuse, NY 13206

Solids, Total Suspended (AH filters; TSS_AH)……..SOP 101

1) Test Method: Solids, Total Suspended SM 2540 D, 22nd Edition

2) Applicable Matrix or Matrices:

Drinking, surface and saline waters, slurries (sediment traps), domestic and industrial wastes

3) Limit of Detection and Quantification:

Published limit is 2.5 mg of filtered residue according to Standard Methods for examination of water and wastewater.

4) Scope and Application:

Drinking, surface and saline waters, domestic and industrial wastes

5) Summary of Test Method:

A well-mixed sample is filtered through a pre-ash weighed glass fiber filter and the residue retained on the filter is dried to a constant weight at 103-105°C for 24 hours. Filtered residue is to be between 2.5 mg and 200 mg. Sample results outside of these values are to be qualified as "estimated". Samples resulting in residue greater than 200 mg should be reanalyzed using a smaller volume. The increase in weight represents the total suspended solids.

6) Definitions:

Total Suspended Solids- The portion of the total solids retained by a filter.

Desiccant- Any material, such as calcium oxide or silica gel, which has a high affinity for water, generally it is used as a drying agent.

Desiccator- Any chamber which holds desiccant and is utilized to keep material goods free from atmospheric humidity

7) Interferences:

Because excessive residue on the filter may form a water-entrapping crust, limit the sample size to that yielding no more than 200 mg dried residue. For samples high in dissolved solids thoroughly rinse the inside of the filtration apparatus filter holder to ensure removal of dissolved materials. Prolonged filtration times resulting from filter clogging may produce high results due to increased colloidal materials captured on the clogged filter.

8) Safety:

No hazardous materials are required for this test. Proper laboratory procedures should be followed at all times.

9) Equipment and Supplies:

- glass fiber filters: **934-AH (47mm, 1.5µm**)
- aluminum dishes
- vacuum filter apparatus and vacuum pump set at **7inches Hg or 3.5psi**
- calibrated analytical balance weights (**100 mg, 1g and 10g**)
- calibrated certified weights (**1g, 500mg, 100mg, 10mg**)
- tongs and forceps
- tray
- pipettes, graduated cylinders
- drying oven set at **103-105^{0}C**
- muffle oven set at **550^{0}C**
- desiccator with fresh desiccant

10) Reagents and Standards:

Not applicable**,** certified calibration weights are used daily to standardize analytical balances (see Appendix A, Balance, Analytical).

11) Sample Collection, Preservation, Shipment and Storage:

Samples should be kept cool and in the dark prior to processing.

Holding time is 7 days from sample collection.

12) Quality Control:

UFI's QC parameters are outlined in the Method Performance Section. They are monitored on a variety of levels; by the analyst(s), the Laboratory Director, and the Quality Assurance Officer as needed. In addition, basic knowledge of the characteristic features of the limnological systems may be used to aid in auditing QC data. Care should be taken to ensure samples are removed from oven for their final weight in sufficient time (24 hours) to reanalyze if necessary within the 7 day holding time.

13) Calibration and Standardization:

Analytical balances are calibrated annually by a certified technician. Weekly internal calibrations are done using a certified standard weight set, and daily or as needed the calibration is checked using the 100 mg, 1g and 10g weights. Observations are printed and recorded in the balance bench sheet. Solids analyst should check to make sure weights have been checked on the day solids are weighed out by referencing the balance bench sheet. If the log is not filled out refer to Metrology analyst.

14) Procedure:

I. Pre-ashing Filters

i. Use forceps to handle filters and weighing dishes at ALL times.

ii. Place filter onto filter apparatus. Apply vacuum and wash filter with about 60mL Type II water, continue suction until the filter is dry.

iii. Remove filter and place filter into a clean, labeled aluminum pan.

iv. Dry filter (and pan) in oven for ***at least 1 hour at 103-105°C***.

v. Ash dried filters at ***550°C for 15-20 minutes***.

vi. Remove filters (and pan) from furnace and allow cooling in desiccators until analysis.

II. Sample Analysis

i. Reference the analytical balance calibration sheet to check that the analytical balance has been calibrated on the day solids are weighed out. If the balance has not been calibrated checked, do so by weighing out 100 mg, 1g and 10g certified weights, record observed weights values in the analytical balance clipboard.

ii. Assign and weigh out each individual pan for a specific sample, record the pan ID (located on bottom of pan) on solids bench sheet along with the initial weight of filter and pan.

iii. Place weighed filter onto filter apparatus, wet filter with Type II water if necessary to seat filter onto apparatus. Screw top onto apparatus and turn on pump apply no more than 7inches Hg or 3.5psi of pressure.

iv. Mix sample thoroughly via gentle inversion, record total volume filtered in the bench sheet.

v. Filter sample through the filter apparatus, washing down the sides of the pipette or graduated cylinder, to add any remaining sediment to the filter. Wash down the sides of the filtering apparatus receiver to assure all solids are washed onto the filter.

vi. Remove top receiving funnel and stop suction, carefully remove the filter from the apparatus (using forceps) and place back into the aluminum dish it was initially weighed in.

vii. Weigh cooled filters with aluminum dish on analytical balance, record weights as 103-105°C weight on bench sheet.

viii. Dry for 12-24 hours in 103-105°C ovens, start 12-24 hours period once oven has reached 103-105°C document in the oven log book.*****

Note: *Based on the results from a weight study done on 05/01/2014 it was deemed unnecessary to weigh and dry filters repeatedly to a constant weight.* ***As long as the samples are put into an oven that remains closed for at least 12 hours (overnight) filters only need to be weight once to achieve a TSS result. If however other "wet" samples are placed into the oven during that 12 hour period then the samples must remain in oven for an additional 12 hours without opening oven.*** *Care should be taken to ensure samples are removed from oven for their final weight in sufficient time (24-48 hours) to reanalyze if necessary within the 7 day holding time.*

*****If volatile suspended solids are to be determined, after the TSS weight has been measured place the samples in the 550°C muffle furnace for 1 hour and then cool and weigh a final time for VSS calculation.

III. Data Entry

i. Run Sheet - Unlike, parsed data non-parsed data is time consuming and can contain errors if the analyst isn't careful. In order to make it effective and less time consuming, the analyst will need to run the analytes one of two ways.

1. The analyst will run the analytes based on the order assigned by the Amended Chain of Custody.
    a. In the event that a run contains multiple Amended Chains of Custody, the analyst should identify where each COC ends within their run and enter the data in sections.
2. The analyst will run the analytes in numeral order based on their Order ID.
    a. Used the Order ID of each sample to arrange them in numerical order.

ii. The key point is that, ***Sample Master will always arrange all samples in numerical order based on the Order ID***. If the analyst enters data for multiple days but ran the data based on the order of each Amended Chains of Custody, then the samples will be mixed and will not follow the analyst run sheet.

IV. Entering Data in Sample Master

i. On the run sheet, count how many CCV's/CCB's, DUPS, MS/MDS, Method Blanks there are and make note of it.

ii. Create a QC batch in Sample Master. Write down the QC Batch ID on the QC Batch ID line in the bench sheet.

1. How to create QC Batch:
    a. Go to the second module and click "**Create QC Batch**"
    b. Enter the Order ID's for each sample that is on your run in the **Order ID** field (click the plus sign to enter a list of ID numbers)
    c. Enter the test in the test field/drop-down, then click "**Retrieve**"
    d. Mark all of the samples by clicking the plus sign, then click "**New**" to generate a new QC Batch ID
    e. A window will pop up, enter the analysis date, click "**Advanced"**

f. Write down the QC Batch ID at the top of the run sheet
g. Count the QC params in the sequence and add/subtract items according to the numbers counted for each QC on the run sheet; click "**Close**" then click "**Yes**"

iii. Go to the second module and click "**Result Entry.**" In the QC Batch ID field/drop-down menu, select your Batch ID. Click "**Retrieve.**"

iv. In the top left corner of click "**Results to Enter**" under the display section.

1. Enter the ***analysis date*** under the analysis date column. To copy and paste the date to the rest of the cells, hover over the analysis date column and highlight it, then click "**Ctrl + W,**" the whole column should automatically fill with the analysis date.
2. Click "**Show Result Calculations,**" a new "**Measured Result**" column should appear.
3. Enter your results under the "**Measure Result**" column; ensure that the results entered correspond to the appropriate sample.
4. Review the data carefully and ensure there are no typos, if any comments were made on the run sheet address them. Be sure to include dilution information along with its corresponding qualifier/report flag, F2.
5. Now that the data has been reviewed, highlight all the data under the corresponding tabs using the "+" sign.
6. Under the ribbon, click "**Edit**", from the drop-down menu select "**Calculate Marked**"
7. The calculated data will move into the "**Results to Validate**" section, while the entered results will stay behind. Highlight the rest of the data under the corresponding tabs using the "+" sign and move the data from "Results to Enter" to "Result to Validate" by clicking "**Enter**" and from "Results to Validate" to "Results to Approve" by clicking "**Validate.**"
8. When the samples are moved into the "**Results to Approve**" tab, check the flags and make sure they make sense. If the flagging is being done incorrectly, delete the flags and flag the samples correctly.
9. Finally, check that the ***%Rec*** and the ***%RPD*** are calculated. If there are results that are white and not filled with gray, yellow, or red, click "**Edit**", from the drop down menu select "**Calculate Marked QC Recoveries.**"
10. If either the percent recoveries or the flagging are not being calculated correctly or at all. Inform the laboratory director and give Sample Master a call.

v. To print the report and corresponding control charts for the data packets

1. Go to the second module and click "**Custom Reporting**". Enter your QC Batch ID's and click "**Retrieve**"
2. Mark all of the samples in the list. In the Report drop-down, choose the report named "**COA Basic with Surrogate and QC**". Click preview in the ribbon, then open the print dialog to print.
3. To print the control charts go to the fourth module and click "**Control Charts**"
4. For Matrix Type select "**Liquid.**" Using the drop-down select the test and the instrument used to run the test. Enter the time frame for your control charts under Analysis Date.
    a. The time frame for the control charts should span in a monthly basis. This allows the analyst to be able to see any changes or possible trends. If the analyst chooses for the time frame to span among several months, this can make the data difficult to visually check or see trends forming.
    b. Certain analytes will be prone to having more QC than others such as phosphorus or nitrogen while others will have a limited amount such as alkalinity, this occurs due to the volume of samples ran for each test. Since alkalinity has a lower number of samples its control charts can and should expand over several months in order to properly see any trends or changes occurring.
5. Only print Control Charts for your initial QC and ongoing QC, these may vary among test. Keep in mind that not all tabs apply to every test. If you click on a particular tab and the analyte name disappears under Parameter, it is likely that this category does not apply to the analyte.
6. Click the "**Standard**" tab; manually unselect all of the QC type except for the CCV. Click "**Retrieve.**"
7. In this new window, click the "**Plus Sign"** to select all the results
8. In the ribbon click "**Preview/Chart**", click "**Yes**". Click "**Print Dialog**". Under Print Range, click "**Pages**" enter from 1 to 1.
9. Follow Steps (*3-9*) for the remaining initial and ongoing QC (CCV, CCB, REF, LOD, Method Blanks, Duplicates, MS/MSD, etc.)

Note: Do not save any changes! If when creating QC charts you happen to click or change something by accident inform the lab director or the lead analyst. Saving changes will alter with the limits in place.

vi. When submitting the final report should include the following:

1. Custom Reporting with Stamp of Date Enter along with analyst initials
2. Analytes Control Charts
3. Printed Report/Data from Instrument
4. Original run sheet
5. Chains of Custody of all samples analyze in the run

Analytes	Corresponding Control Charts
Alkalinity	REF, DUP
Chloride	CCV, CCB, LCS, MS, MSD, REF, MB, DUP
Chlorophyll A	CCV, CCB, MB, DUP
Color	REF, DUP
Conductivity	CCV, REF, DUP
Dissolved Oxygen	No Control Charts Needed
FSS/TSS/VSS	MB, DUP
pH	CCV, REF, DUP
Sediment Traps	MB
Silica	CCV, CCB, LCS, MS, MSD, REF, MB, DUP
Turbidity	REF, DUP
UV254	CCV, CCB, MB, DUP

15) Calculations:

(Eq. 1) TSS = (A – B) * 1000/ C

Where: TSS = Total Suspended Solids (mg/L)
A = weight of dried residue, pan and filter (g)
B = weight of pan and filter (g)
1000 = conversion factor for converting from gram to mg
C = volume of sample (L)

16) Method Performance:

UFI laboratory follows the following chart for identifying and running QC samples. Each type of sample may not be applicable to every analysis. QC Samples are run, as possible, following the chart below. Refer to UFI Controlled Document 012 for LOD, LOQ and control limits.

Table 1: QA\QC for TSS_AH Analysis

QC Sample Type	Description/Definition	Frequency Performed	Abbreviation
Method Blank	Type II water that undergoes the same procedure as samples	One per sample batch	MB
Duplicate (see method deviations)	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP

17) Pollution Prevention:

Filters may be placed in the trash once analysis is finalized. Filtrate may be discarded down the drain. For most natural water systems, this procedure has no negative impact on the environment.

18) Data Assessment and Acceptance Criteria for Quality Control Measures:

Record results from all quality control samples onto the QC file. The control charts are designed so that the mean displayed through the middle, with an upper warning limit, a lower warning limit, an upper control limit and a lower control limit. The warning and control limits are calculated from the previous year's data. The process should be shut down for trouble shooting if one or more of the following occur:

- a single action outside the control limit
- 2 out of 3 consecutive measurements between the warning and control limit
- 7 consecutive measurements above or below the mean
- 6 consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located
- an obvious nonrandom pattern

All data that falls outside stated control limits are appropriately flagged. Refer to UFI Controlled Document No. 12 for flags and their meaning.

19) Corrective Actions for Out-of-Control or Unacceptable Data:

If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. If 2 out of 3 consecutive measurements are between the warning and control limits then causes should be investigated and a Corrective Action Report may be initiated (see Quality Manual for C.A.R protocol). Based on the Laboratory Directors judgement a comment may be inserted into the comment section of affected data packets. If a cause is found, then a corrective action must be initiated and fully documented.

20) Contingencies for Handling Out-of-Control or Unacceptable Data:

If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is insufficient sample, data should be flagged with an explanation of the circumstances.

21) Waste Management:

Used filters may be discarded in the trash. Filtrate may be discarded down the drain.

22) References:

APHA 2012. Standard Methods for the examination of water and wastewater. 22nd Edition American Public Health Association. Washington D.C.

Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data

See attached analyte specific training document for training procedure.

Table 2: TSS Constant weight study (conducted on 5/1/14)

Sample ID	initial weight time taken: 10:26	subsequent weight time taken: 12:56	RPD
13	1.5153	1.5167	-0.092348
18	1.5795	1.58	-0.031651
19	1.5185	1.5139	-0.026425
6	1.5496	1.5501	-0.032261
80	1.5414	1.5416	-0.012974
3	1.5043	1.5036	0.046544
20	1.5043	1.5036	0

Table 3. Quality Control Acceptance Limits for Total Suspended Solids (TSS_AH) Analysis

Total Suspended Solids (TSS) Quality Control Acceptance Limits		
QC	**Nominal**	**Acceptance Range**
ICV/CCV		
ICB/CCB		
LCS/MS/MSD		
REF		
LOD		
MB	0.00	< 1.25
DUP		± 5%

24) Method deviations:

i. For freshwater systems additional sample volume may be needed to achieve the 2.5mg filter residue minimum, however, sample volume cannot exceed 1 liter.

ii. Sediment-trap samples duplicates are not analyzed. The samples are collected in triplicate and assessed for precision. This is due to the nature of the trap which results in a small sample volume.

STANDARD OPERATING PROCEDURE L-1F: TURBIDITY (Tn_L)

Turbidity (Tn_L)…….....SOP 222

1) Test Method: Turbidity, raw or acidified SM 2130B, 22nd Edition

2) Applicable Matrix or Matrices:

Drinking, surface and saline waters, domestic and industrial wastes.

3) Limit of Detection and Quantification:

Refer to UFI Controlled Document No. 12 (attached). Once a year immediately following determination of LOD/LOQ values and before running any samples an LOD and LOQ verification must be performed. A solution with a concentration that is approximately 2X the determined LOD must be analyzed once to obtain a value that is greater than zero. A solution with a concentration that is approximately 2X the determined LOQ must be analyzed once to obtain a value that is evaluated against the method's LCS criteria and must fall within the acceptance limits for recovery.

4) Scope and Application:

Drinking, surface and saline waters, domestic and industrial wastes.

5) Summary of Test Method:

This method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions. The greater the intensity of scattered light, the higher the turbidity of the sample. A formazin polymer is used as the reference turbidity standard suspension.

6) Definitions:

Turbidity- The cloudiness or haziness of a fluid caused by individual particles (suspended solids) that are generally invisible to the naked eye, similar to smoke in air. In water bodies such as lakes, rivers and reservoirs, high turbidity levels can reduce the amount of light reaching lower depths, which can inhibit growth of submerged aquatic plants and consequently affect species which are dependent on them.

7) Interferences:

Rapidly settling coarse sediments, dirty glassware, the presence of air bubbles and vibrations can cause false results. Color due to dissolved substances will absorb light and can cause false low turbidities. Addition of acid and subsequent measurement can determine calcium carbonate turbidity (raw turbidity – acidified turbidity).

8) Safety:

Always wear safety goggles, gloves and lab coats when handling acids or other toxic substances. Use hoods for mixing solutions that produce fumes. If you spill concentrated acids, bases or other toxic chemicals notify the technical director immediately.

9) Equipment and Supplies:

1. Turbidimeter (HACH 2100AN)
   - Hach filter module for turbidity (Cat. No. 30312-00)
   - Hach sample cells and caps for ratio turbidimeters (Cat. No. 20849-00)
2. StablCal Calibration set for HACH 2100AN (Cat. 26595-05)
   - contains 6 sealed vials of <0.1, 20, 200, 1000, 4000, 7500NTU
3. Class A titration burette
4. silicone oil
5. 100mL volumetric flask
6. automatic pipettes and tips
7. Kim wipes

10) Reagents and Standards*:

1. Gelex Secondary Silica Gel Standards – purchased from HACH (set of 6).
2. Reference Formazin Turbidity Standard (4000NTU) – Commercially supplied (CAS# 100-97-0).
3. Reference 100NTU – Pipette 2.5mL of reference 4000NTU Turbidity Standard into a 100mL volumetric flask. Dilute to the mark with type II water and invert to mix. **Made Daily.**
4. Sulfuric Acid Titrant Solution (0.02N) for acidified turbidities only (see Alkalinity SOP # 103)

**Occasionally a different volume of a solution may be made. If this occurs, the volume made will contain proportional quantities of component constituents as outlined here.*

11) Sample Collection, Preservation, Shipment and Storage:

Samples should be kept cool and in the dark. Measurements should be made as soon as possible to prevent particles from breaking apart or coagulating.

Holding time is 48 hours from sample collection.

12) Quality Control:

UFI's QC parameters are outlined in the Method Performance Section. They are monitored on a variety of levels; by the analyst(s), the Laboratory Director, and the Quality Assurance Officer as needed. In addition, basic knowledge of the characteristic features of the limnological systems may be used to aid in auditing QC data.

13) Calibration and Standardization:

The electronic and optical design of the HACH 2100AN Turbidimeter provides long-term stability and minimizes the need for frequent calibration. Calibration is done monthly by following the calibration procedure in Section 3; pg. 22 in the HACH instrument manual.

With each use, calibration is verified using prepared Gelex Secondary Standards. If the reading in the range of use is not within 10% of the standard assigned value (see below), recalibrate using the StablCal Calibration kit.

I. **TO CALIBRATE** (Performed *Monthly*)*:

a. Verify the instrument is set for NTU mode, ratio on and automatic ranging. Check to make sure the turbidity filter module is inserted in the filter assembly and the instrument is in the turbidity mode (this is evident if the LED display reads NTU in the right corner.
   › To place instrument in turbidity mode, press *flow* then *units* until NTU is displayed.
b. Press <**CAL/ZERO**> (the annunciator lights and the small LED digits in the mode display flashes 00. The NTU value of the dilution water used in the previous calibration is displayed).
c. Fill a clean sample cell to the white line (~30mL) with Type II water. Wipe the cell clean and apply a thin film of silicone oil.
d. Place the sample cell into the cell holder; close the cell cover (install all matched vials with the orientation mark aligned with the cell holder reference mark).
e. Press <**ENTER**> (the instrument display will count down from 60 to 0 and then makes a measurement. This result is stored and used to calculate a correction factor for measurement of all NTU standards. If reading of dilution water is > 0.5 NTU an E1 error is displayed at the end of calibration).
f. The instrument automatically increments to the next standard, displays the expected NTU value (e.g. 20NTU), and the standard number 02 is shown in the mode display. Remove the sample cell from the cell holder.
g. Apply a thin film of silicone oil onto the surface of the 20NTU formazin standard and place into the cell holder, close the cell cover.
h. Press<ENTER> (the instrument display will count down from 60 to 0 and then makes a measurement. The instrument applies a correction factor to compensate for the turbidity of the dilution water).
i. Continue to follow steps f-h with the remaining primary turbidity standards of 200, 1000, 4000, and 7500.
j. Displayed standard number will increment back to 00 and the previously measured value of the dilution water is displayed.
k. Press <**CAL/ZERO**> (the instrument makes calculations based on the new calibration data and returns the instrument to the measurement mode).
l. If E1 or E2 appears in the display, an error occurred during calibration. Prepare new standards and recalibrate the instrument. Make sure the standards are fresh and well mixed. Also make sure the dilution water is < 0.5 NTU.
m. To review calibration data press <**CAL**> and then use the up arrow to scroll through the standards. Press <**PRINT> to** print all the calibration data. Press <**UNITS/EXIT**> to return to the operating mode.

II. **Setting The GELEX Standard Values**

a. Going from lowest to highest, wipe the GELEX vial clean, apply a thin film of silicone oil on its surface. Place the GELEX vial in the sample compartment aligning the orientation mark with the sample cell compartment orientation mark. Close the cell cover, once the measurement is made, mark the "actual" reading from the instrument on the top of the GELEX vial with label tape. Do this for all the GELEX standards.

Note- To exit calibration procedure at any time WITHOUT changing any stored value press <UNITS/EXIT**>*

14) Procedure:

I. **Initial Quality Control**

a. Measure and record all 6 Gelex silica gel standards, if values are within 10% of the set values obtained from the calibration procedure then proceed with the following QC measurements.
b. ICV- Use 3rd GELEX standard as ICV/CCV
c. ICB-fill a clean cuvette with Type II water, wipe dry with Kim wipes. Place in turbidimeter and press ENTER, record results.
d. REF-fill clean cuvette with 100NTU working reference solution, cap and wipe dry with Kim wipes. Place in turbidimeter and press ENTER, record results.
e. LOD- Use 2nd GELEX standard as LOD

II. **To Run A Sample- (non-acidified/total turbidity)**

a. Carefully invert sample to mix, DO NOT SHAKE, tiny air bubbles will form and interfere with accurate turbidity measurements.

b. Fill the clean and rinsed glass cell with sample, wipe dry with Kim wipes and place into instrument following proper orientation. Press<**ENTER**>; record reading in proper data sheet once instrument has printed.

III. **Reporting A Sample**

Turbidity readings should be reported as follows:

Turbidity Range NTU	**Report to the Nearest NTU**
0-1.0	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1000	50
>1000	100

Note: When comparing water treatment efficiencies, do not estimate turbidity more closely than specified above. Uncertainty and discrepancies in turbidity measurements make it unlikely that results can be duplicated to greater precision than specified.

IV. Data Entry

a. Run Sheet - Unlike, parsed data non-parsed data is time consuming and can contain errors, if the analyst isn't careful. In order to make it effective and less time consuming, the analyst will need to run the analytes one of two ways.

   i. The analyst will run the analytes based on the order assigned by the Amended Chain of Custody.

      1. In the event that a run contains multiple Amended Chains of Custody, the analyst should identify where each COC ends within their run and enter the data in sections.

   ii. The analyst will run the analytes in numeral order based on their Order ID.

      1. Used the Order ID of each sample to arrange them in numerical order.

   iii. The key point is that, ***Sample Master will always arrange all samples in numerical order based on the Order ID***. If the analyst enters data for multiple days but ran the data based on the order of each Amended Chain of Custody, then the samples will be mixed and will not follow the analyst run sheet.

b. Entering Data in Sample Master

   i. On the run sheet, count how many CCV's/CCB's, DUPS, MS/MDS, Method Blanks there are and make note of it.

   ii. Create a QC batch in Sample Master. Write down the QC Batch ID on the QC Batch ID line in the bench sheet.

      1. How to create QC Batch:

         a. Go to the second module and click "**Create QC Batch**"
         b. Enter the Order ID's for each sample that is on your run in the **Order ID** field (click the plus sign to enter a list of ID numbers)
         c. Enter the test in the test field/drop-down, then click "**Retrieve**"
         d. Mark all of the samples by clicking the plus sign, then click "**New**" to generate a new QC Batch ID
         e. A window will pop up, enter the analysis date, click "**Advanced"**
         f. Write down the QC Batch ID at the top of the run sheet
         g. Count the QC params in the sequence and add/subtract items according to the numbers counted for each QC on the run sheet; click "**Close**" then click "**Yes**"

iii. Go to the second module and click "**Result Entry.**" In the QC Batch ID field/drop-down menu, select your Batch ID. Click "**Retrieve.**"

iv. In the top left corner of click "**Results to Enter**" under the display section.
    1. Enter the ***analysis date*** under the analysis date column. To copy and paste the date to the rest of the cells, hover over the analysis date column and highlight it, then click "**Ctrl + W,**" the whole column should automatically fill with the analysis date.
    2. Click "**Show Result Calculations,**" a new "**Measured Result**" column should appear.
    3. Enter your results under the "**Measure Result**" column; ensure that the results entered correspond to the appropriate sample.
    4. Review the data carefully and ensure there are no typos, if any comments were made on the run sheet address them. Be sure to include dilution information along with its corresponding qualifier/report flag, F2.
    5. Now that the data has been reviewed, highlight all the data under the corresponding tabs using the "+" sign and move the data from "Results to Enter" to "Result to Validate" by clicking "**Enter**" and from "Results to Validate" to "Results to Approve" by clicking "**Validate.**"
    6. When the samples are moved into the "**Results to Approve**" tab, check the flags and make sure they make sense. If the flagging is being done incorrectly, delete the flags and flag the samples correctly.
    7. Finally, check that the ***%Rec*** and the ***%RPD*** are calculated. If there are results that are white and not filled with gray, yellow, or red, click "**Edit**", from the drop down menu select "**Calculate Marked QC Recoveries.**"
    8. If either the percent recoveries or the flagging are not being calculated correctly or at all. Inform the laboratory director and give Sample Master a call.

v. To print the report and corresponding control charts for the data packets
    1. Go to the second module and click "**Custom Reporting**". Enter your QC Batch ID's and click "**Retrieve**"
    2. Mark all of the samples in the list. In the Report drop-down, choose the report named "**COA Basic with Surrogate and QC**". Click preview in the ribbon, then open the print dialog to print.
    3. To print the control charts go to the fourth module and click "**Control Charts**"

4. For Matrix Type select "**Liquid.**" Using the drop-down select the test and the instrument used to run the test. Enter the time frame for your control charts under Analysis Date.
    a. The time frame for the control charts should span in a monthly basis. This allows the analyst to be able to see any changes or possible trends. If the analyst chooses for the time frame to span among several months, this can make the data difficult to visually check or see trends forming.
    b. Certain analytes will be prone to having more QC than others such as phosphorus or nitrogen while others will have a limited amount such as alkalinity, this occurs due to the volume of samples ran for each test. Since alkalinity has a lower number of samples its control charts can and should expand over several months in order to properly see any trends or changes occurring.
5. Only print Control Charts for your initial QC and ongoing QC, these may vary among test. Keep in mind that not all tabs apply to every test. If you click on a particular tab and the analyte name disappears under Parameter, it is likely that this category does not apply to the analyte.
6. Click the "**Standard**" tab; manually unselect all of the QC type except for the CCV. Click "**Retrieve.**"
7. In this new window, click the "**Plus Sign"** to select all the results
8. In the ribbon click "**Preview/Chart**", click "**Yes**". Click "**Print Dialog**". Under Print Range, click "**Pages**" enter from 1 to 1.
9. Follow Steps (*3-9*) for the remaining initial and ongoing QC (CCV, CCB, REF, LOD, Method Blanks, Duplicates, MS/MSD, etc.)

Note: Do not save any changes! If when creating QC charts you happen to click or change something by accident inform the lab director or the lead analyst. Saving changes will alter with the limits in place.

vi. When submitting the final report should include the following:
    1. Custom Reporting with Stamp of Date Enter along with analyst initials
    2. Analytes Control Charts
    3. Printed Report/Data from Instrument
    4. Original run sheet
    5. Chains of Custody of all samples analyze in the run

Analytes	Corresponding Control Charts
Alkalinity	REF, DUP
Chloride	CCV, CCB, LCS, MS, MSD, REF, MB, DUP
Chlorophyll A	CCV, CCB, MB, DUP
Color	REF, DUP
Conductivity	CCV, REF, DUP
Dissolved Oxygen	No Control Charts Needed
FSS/TSS/VSS	MB, DUP
pH	CCV, REF, DUP
Sediment Traps	MB
Silica	CCV, CCB, LCS, MS, MSD, REF, MB, DUP
Turbidity	REF, DUP
UV254	CCV, CCB, MB, DUP

15) Data analysis and Calculations:

HACH 2100AN automatically calculates the corrected turbidity value of a sample.

Acidified turbidity measurements are usually run on a sample once an alkalinity measurement is complete and must be corrected for the volume of acid used in the titration according to the following formula:

$$\text{(Eq. 1) } Tn_{ac} = (A + B / 100) * Tn$$

Where:

Tn_{ac} = Acidified turbidity (NTU)
A = Volume of sample used in alkalinity titration (requires 100 mL)
B = Volume of acid used in alkalinity titration
Tn = Raw turbidity (non acidified) (NTU)

16) Method Performance:

UFI laboratory follows the following chart for identifying and running QC samples. Each type of sample may not be applicable to every analysis. QC samples are run, as possible, following the chart below. Refer to UFI Controlled Document No. 12 for LOD, LOQ and control limits.

Table 1: QA\QC for Turbidity/Acidified Turbidity Analysis

QC Sample Type	Description/Definition	Frequency Performed	Abbreviation
Initial Calibration Verification	A known concentration of standard solution analyzed at the beginning of the run	1st sample of every batch	ICV
Initial Calibration Blank	Type II water containing all reagents in the same proportion as those in calibration standards and samples	2nd sample of every batch	ICB
Reference (100NTU)	A standard solution of known concentration, made from either a different lot # reagent, a different manufacturer, or another method (dissolving a solid)	One per sample batch	REF
Duplicate	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP
Continuing Calibration Verification	A standard solution of known concentration, analyzed throughout the course of the run and at the end of every run.	Every 10 samples, and at the end of sample batch, followed by a CCB	CCV
Continuing Calibration Blank	Type II water containing all reagents in the same proportion as those in calibration standards and samples	Every 10 samples, and at the end of every sample batch, preceded by a CCV	CCB

17) Pollution Prevention:

It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. For most natural water systems, this procedure has no negative impact on the environment.

18) Data Assessment and Acceptance Criteria for Quality Control Measures:

Record results from all quality control samples onto the QC file. The control charts are designed so that the mean displayed through the middle, with an upper warning limit, a lower warning limit, an upper control limit and a lower control limit. The warning and control limits are calculated from the previous year's data. The process should be shut down for trouble shooting if one or more of the following occur:

- a single action outside the control limit
- 2 out of 3 consecutive measurements between the warning and control limit
- 7 consecutive measurements above or below the mean
- consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located an obvious nonrandom pattern

All data that falls outside stated control limits are appropriately flagged. Refer to UFI Controlled Document No. 12 for flags and their meaning.

19) Corrective Actions for Out-of-Control or Unacceptable Data:

If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. If 2 out of 3 consecutive measurements are between the warning and control limits then causes should be investigated and a Corrective Action Report may be initiated (see Quality Manual for C.A.R protocol). Based on the Laboratory Directors judgement a comment may be inserted in comment section of effected data packet. If a cause is found, then a corrective action must be initiated and fully documented.

20) Contingencies for Handling Out-of-Control or Unacceptable Data:

If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is insufficient sample, data should be flagged with an explanation of the circumstances.

21) Waste Management:

Refer to MSDS for proper chemical use and disposal procedures. If any hazardous waste is generated, it is disposed of according to UFI's chemical waste disposal practices.

22) References:

APHA 2012. Standard Methods for the examination of water and wastewater. 22nd Edition American Public Health Association. Washington D.C.

Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

Model 2100AN Laboratory Turbidimeter Instruction Manual. 1999. HACH Company, Colorado.

23) Tables, Diagrams, Flowcharts and Validation Data

See attached analyte specific training document for training procedure.

Table 2. Quality Control Acceptance Limits for Turbidity (Tn_L) Analysis

Turbidity (Tn_L) Quality Control Acceptance Limits		
QC	**Nominal**	**Acceptance Range**
ICV/CCV		± 10%
ICB/CCB		<0.4
LCS/MS/MSD		± 15%
REF	100.00	± 15% (85.00 - 115.00)
LOD	2	
MB		
DUP		± 15%

Note: *Quality control acceptance limits will vary according to the nominals determined after calibration.*

STANDARD OPERATING PROCEDURE L-1G: SOLIDS, FIXED, SUSPENDED, VOLATILE SUSPENDED (AH FILTERS; FSS_AH, VSS_AH)

UPSTATE FRESHWATER INSTITUTE LABORATORY METHODS MANUAL
224 Midler Park Drive, Syracuse, NY 13206

Solids, Fixed Suspended, Volatile Suspended (AH filters; FSS_AH, VSS_AH)……SOP 202

1) Test Method: Solids, Fixed Suspended, Volatile Suspended SM 2540 E, 22nd Edition

2) Applicable Matrix or Matrices:

Drinking, surface and saline waters, slurries (sediment traps), domestic and industrial wastes.

3) Limit of Detection and Quantification:

Refer to UFI Controlled Document No. 12 (attached). Limits are published in Standard Methods for examination of water and wastewater.

4) Scope and Application:

Drinking, surface and saline waters, domestic and industrial wastes.

5) Summary of Test Method:

The residue from total solids or total suspended solids is ignited to a constant weight at 550°C for 1 hour. The remaining solids represent fixed total or fixed suspended solids, while the weight lost on ignition is the volatile solids. Volatile solids are a rough determination of organic matter present in the sample.

6) Definitions:

Fixed solids- is the term applies to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature.

Volatile solids- the weight of solids lost upon ignition.

7) Interferences:

Negative errors in the volatile solids may be produced by loss of volatile matter during drying. Determination of low concentrations of volatile solids in the presence of high fixed solids concentrations may be subject to considerable error.

8) Safety:

No hazardous materials are required for this test. Care should be exercised when handling samples around the muffle furnace, high temperatures are used and burns can occur. Heat protective gloves should be used when placing samples in and out of the furnace.

9) Equipment and Supplies:

- glass fiber filters: **934-AH (47mm, 1.5µm**)
- aluminum dishes
- vacuum filter apparatus and vacuum pump set at 7inches Hg or 3.5psi
- calibrated analytical balance and certified weights (10g, 1g and 100mg; 1g, 500mg, 100mg and 10mg)
- tongs and forceps

- tray
- graduated cylinders
- drying oven set at 103-105^{o}C
- muffle oven set at 550^{o}C
- desiccator with desiccant
- minute timer

10) Reagents and Standards:

Not applicable**,** certified calibration weights are used daily to standardize analytical balances (see Appendix A: Balance, Analytical).

11) Sample Collection, Preservation, Shipment and Storage:

Samples should be kept cool and in the dark prior to processing.

Holding time is 7 days from sample collection.

12) Quality Control:

UFI's QC parameters are outlined in the Method Performance Section. They are monitored on a variety of levels; by the analyst(s), the Laboratory Director, and the Quality Assurance Officer as needed. In addition, basic knowledge of the characteristic features of the limnological systems may be used to aid in auditing QC data.

13) Calibration and Standardization:

Analytical balances are calibrated annually by a certified technician. Weekly internal calibrations are done using a certified standard weight set, and daily or as needed, the calibration is checked using the 10g, 1g and 100mg weights. Solids analyst should check to make sure weights have been checked on the day solids are weighed out by referencing the balance log book. If the log is not filled out refer to Metrology analyst.

14) Procedure:

I. **Preparation of filter**

a. *Use forceps to handle filters and weighing dishes at ALL times*.

b. Place filter onto filter apparatus. Apply vacuum and wash filter with about 60mL Type II water, continue suction until the filter is dry.

c. Remove filter and place filter into a clean, labeled aluminum pan.

d. Dry filter (and pan) in oven for ***at least 1 hour*** at ***103-105°C***.

e. Ash dried filters at ***550°C for 15-20 minutes***.

f. Remove filters (and pan) from furnace and allow cooling in desiccators until analysis.

II. **Sample Analysis**

a. Reference the analytical balance clipboard to check that the balance has been calibrated on the day solids are weighed out. If the balance has not been calibrated, calibrate the balance by weighing out 10g, 1g and 100mg certified weights, record results on clipboard.

b. Assign and weigh out each pan to a particular sample, record the pan ID (located on bottom of pan) on the solids datasheet along with the initial weight of filter and pan.

c. Place weighed filter onto filter apparatus, wet filter with Type II water if necessary to seat filter onto apparatus. Screw top onto apparatus and turn on pump apply no more than 7inches Hg or 3.5psi of pressure.

d. Mix sample thoroughly by gentle inversion, allow sample to settle for 10 seconds and then measure sufficient volume of sample with appropriate graduated cylinder, record total volume filtered on datasheet.

e. Filter sample through the filtration apparatus, use deionized water to wash down the sides of the graduated cylinder and filtration apparatus. This insures the collections of all sediments in the sample are collected by the filter.

f. Remove top of receiving funnel, stop suction and carefully remove the filter from the apparatus (using forceps) and place it back into the aluminum dish it was initially weighed in.

g. Dry for 12-24 hours in 103-105°C ovens, start 12-24 hours period once oven has reached 103-105°C documents the oven used its temperature and the time the samples were placed in and out of the oven.

h. Weigh cooled filters with aluminum dish, record weights as 103-105°C weight on datasheet.

i. Place cooled weighed filter (with pan) into 550°C muffle furnace for 1 hour.

j. Remove filters (with pan) and cool to room temperature in desiccator.

k. Weigh a final time for VSS and FSS calculations, enter weights in data sheet under 550°C column.

Note: Given our experience and knowledge of the fresh water system's in NYS there is little reason to reweigh samples once dried in the muffle oven because complete carbon combustion has already occurred. If the analyst suspects poor reproducibility due to insufficient carbon combustion, the issue should be brought to the Laboratory Directors attention and the samples should be placed back into the muffle furnace for another hour, reweighed and results compared.

III. **Data Entry**

a. Run Sheet - Unlike, parsed data non-parsed data is time consuming and can contain errors if the analyst isn't careful. In order to make it effective and less time consuming, the analyst will need to run the analytes one of two ways.

i. The analyst will run the analytes based on the order assigned by the Amended Chain of Custody.

1. In the event that a run contains multiple Amended Chains of Custody, the analyst should identify where each COC ends within their run and enter the data in sections.

ii. The analyst will run the analytes in numeral order based on their Order ID.

1. Used the Order ID of each sample to arrange them in numerical order.

iii. The key point is that, ***Sample Master will always arrange all samples in numerical order based on the Order ID***. If the analyst enters data for multiple days but ran the data based on the order of each Amended Chains of Custody, then the samples will be mixed and will not follow the analyst run sheet.

b. Entering Data in Sample Master

i. On the run sheet, count how many CCV's/CCB's, DUPS, MS/MDS, Method Blanks there are and make note of it.

ii. Create a QC batch in Sample Master. Write down the QC Batch ID on the QC Batch ID line in the bench sheet.

1. How to create QC Batch:

a. Go to the second module and click "**Create QC Batch**"
b. Enter the Order ID's for each sample that is on your run in the **Order ID** field (click the plus sign to enter a list of ID numbers)
c. Enter the test in the test field/drop-down, then click "**Retrieve**"
d. Mark all of the samples by clicking the plus sign, then click "**New**" to generate a new QC Batch ID
e. A window will pop up, enter the analysis date, click "**Advanced"**
f. Write down the QC Batch ID at the top of the run sheet
g. Count the QC params in the sequence and add/subtract items according to the numbers counted for each QC on the run sheet; click "**Close**" then click "**Yes**"

iii. Go to the second module and click "**Result Entry.**" In the QC Batch ID field/drop-down menu, select your Batch ID. Click "**Retrieve.**"

iv. In the top left corner of click "**Results to Enter**" under the display section.

1. Enter the ***analysis date*** under the analysis date column. To copy and paste the date to the rest of the cells, hover over the analysis date column and highlight it, then click "**Ctrl + W,**" the whole column should automatically fill with the analysis date.
2. Click "**Show Result Calculations,**" a new "**Measured Result**" column should appear.
3. Enter your results under the "**Measure Result**" column; ensure that the results entered correspond to the appropriate sample.
4. Review the data carefully and ensure there are no typos, if any comments were made on the run sheet address them. Be sure to include dilution information along with its corresponding qualifier/report flag, F2.
5. Now that the data has been reviewed, highlight all the data under the corresponding tabs using the "+" sign.
6. Under the ribbon, click "**Edit**", from the drop-down menu select "**Calculate Marked**"
7. The calculated data will move into the "**Results to Validate**" section, while the entered results will stay behind. Highlight the rest of the data under the corresponding tabs using the "+" sign and move the data from "Results to Enter" to "Result to Validate" by clicking "**Enter**" and from "Results to Validate" to "Results to Approve" by clicking "**Validate.**"
8. When the samples are moved into the "**Results to Approve**" tab, check the flags and make sure they make sense. If the flagging is being done incorrectly, delete the flags and flag the samples correctly.
9. Finally, check that the ***%Rec*** and the ***%RPD*** are calculated. If there are results that are white and not filled with gray, yellow, or red, click "**Edit**", from the drop down menu select "**Calculate Marked QC Recoveries.**"

10. If either the percent recoveries or the flagging are not being calculated correctly or at all. Inform the laboratory director and give Sample Master a call.

v. To print the report and corresponding control charts for the data packets
    1. Go to the second module and click "**Custom Reporting**". Enter your QC Batch ID's and click "**Retrieve**"
    2. Mark all of the samples in the list. In the Report drop-down, choose the report named "**COA Basic with Surrogate and QC**". Click preview in the ribbon, then open the print dialog to print.
    3. To print the control charts go to the fourth module and click "**Control Charts**"
    4. For Matrix Type select "**Liquid.**" Using the drop-down select the test and the instrument used to run the test. Enter the time frame for your control charts under Analysis Date.
        a. The time frame for the control charts should span in a monthly basis. This allows the analyst to be able to see any changes or possible trends. If the analyst chooses for the time frame to span among several months, this can make the data difficult to visually check or see trends forming.
        b. Certain analytes will be prone to having more QC than others such as phosphorus or nitrogen while others will have a limited amount such as alkalinity, this occurs due to the volume of samples ran for each test. Since alkalinity has a lower number of samples its control charts can and should expand over several months in order to properly see any trends or changes occurring.
    5. Only print Control Charts for your initial QC and ongoing QC, these may vary among test. Keep in mind that not all tabs apply to every test. If you click on a particular tab and the analyte name disappears under Parameter, it is likely that this category does not apply to the analyte.
    6. Click the "**Standard**" tab; manually unselect all of the QC type except for the CCV. Click "**Retrieve.**"
    7. In this new window, click the "**Plus Sign"** to select all the results

8. In the ribbon click "**Preview/Chart**", click "**Yes**". Click "**Print Dialog**". Under Print Range, click "**Pages**" enter from 1 to 1.
9. Follow Steps (*3-9*) for the remaining initial and ongoing QC (CCV, CCB, REF, LOD, Method Blanks, Duplicates, MS/MSD, etc.)

Note: Do not save any changes! If when creating QC charts you happen to click or change something by accident inform the lab director or the lead analyst. Saving changes will alter with the limits in place.

vi. When submitting the final report should include the following:
1. Custom Reporting with Stamp of Date Enter along with analyst initials
2. Analytes Control Charts
3. Printed Report/Data from Instrument
4. Original run sheet
5. Chains of Custody of all samples analyze in the run

Analytes	Corresponding Control Charts
Alkalinity	REF, DUP
Chloride	CCV, CCB, LCS, MS, MSD, REF, MB, DUP
Chlorophyll A	CCV, CCB, MB, DUP
Color	REF, DUP
Conductivity	CCV, REF, DUP
Dissolved Oxygen	No Control Charts Needed
FSS/TSS/VSS	MB, DUP
pH	CCV, REF, DUP
Sediment Traps	MB
Silica	CCV, CCB, LCS, MS, MSD, REF, MB, DUP
Turbidity	REF, DUP
UV254	CCV, CCB, MB, DUP

15) Calculations:

(Eq. 1) VSS = (A – B) * 1000 / C

(Eq. 2) FSS = (B – D) * 1000 / C

Where:

VSS = Volatile Suspended Solids (mg/L)
FSS = Fixed Suspended Solids (mg/L)
A = weight of dried residue, pan and filter (105°C) (g)
B = weight of dried residue, pan and filter after ignition at 550°C (g)
C = volume of sample filtered (L)
D = Initial weight of pan and filter (g)
1000=conversion factor for converting from g to mg

16) Method Performance:

UFI laboratory follows the following chart for identifying and running QC samples. Each type of sample may not be applicable to every analysis. QC samples are run, as possible, following the chart below. Refer to UFI Controlled Document No. 12 for LOD, LOQ control limits.

Table 1: QA\QC for VSS/FSS_AH Analysis.

QC Sample Type	Description/Definition	Frequency Performed	Abbreviation
Method Blank	Type II water that undergoes the same procedure as samples	One per sample batch	MB
Duplicate	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP

17) Pollution Prevention:

Filters may be placed in the trash once analysis is finalized. Filtrate may be discarded down the drain. For most natural water systems, this procedure has no negative impact on the environment.

18) Data Assessment and Acceptance Criteria for Quality Control Measures:

Record results from all quality control samples onto the QC file. The control charts are designed so that the mean displayed through the middle, with an upper warning limit, a lower warning limit, an upper control limit and a lower control limit. The warning and control limits are calculated from the previous year's data. The process should be shut down for trouble shooting if one or more of the following occur:

- a single action outside the control limit
- 2 out of 3 consecutive measurements between the warning and control limit

- 7 consecutive measurements above or below the mean
- 6 consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located
- an obvious nonrandom pattern

All data that falls outside stated control limits are appropriately flagged. Refer to UFI Controlled Document No. 12 for flags and their meaning.

19) Corrective Actions for Out-of-Control or Unacceptable Data:

If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. If 2 out of 3 consecutive measurements are between the warning and control limits then causes should be investigated and a Corrective Action Report may be initiated (see Quality Manual for C.A.R protocol). Based on the Laboratory Directors judgement a comment may be inserted into the comment section of effected data packet. If a cause is found, then a corrective action must be initiated and fully documented

20) Contingencies for Handling Out-of-Control or Unacceptable Data:

If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is insufficient sample, data should be flagged with an explanation of the circumstances.

21) Waste Management:

Used filters may be discarded in the trash. Filtrate may be discarded down the drain.

22) References:

APHA 2012. Standard Methods for the examination of water and wastewater. 22nd Edition American Public Health Association. Washington D.C.

Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York

23) Tables, Diagrams, Flowcharts and Validation Data

See attached analyte specific training document for training procedure.

Table 2: TSS Constant weight study (conducted on 5/1/14)

Sample ID	initial weight time taken: 10:26	subsequent weight time taken: 12:56	RPD
13	1.5153	1.5167	-0.092348
18	1.5795	1.58	-0.031651
19	1.5185	1.5139	-0.026425
6	1.5496	1.5501	-0.032261
80	1.5414	1.5416	-0.012974
3	1.5043	1.5036	0.046544
20	1.5043	1.5036	0

Table 3. Quality Control Acceptance Limits for Fixed Suspended Solids (FSS_AH) Analysis

Fixed Suspended Solids (FSS_AH) Quality Control Acceptance Limits		
QC	**Nominal**	**Acceptance Range**
ICV/CCV		
ICB/CCB		
LCS/MS/MSD		
REF		
LOD		
MB	0.00	< 1.25
DUP		± 5%

Table 4. Quality Control Acceptance Limits for Volatile Suspended Solids (VSS_AH) Analysis

Volatile Suspended Solids (VSS_AH) Quality Control Acceptance Limits		
QC	**Nominal**	**Acceptance Range**
ICV/CCV		
ICB/CCB		
LCS/MS/MSD		
REF		
LOD		
MB	0.00	< 1.25
DUP		± 5%

STANDARD OPERATING PROCEDURE L-2A: MERCURY IN AQUEOUS, SOLIDS AND TISSUE SAMPLES BY EPA 7471A, 7470A, AND 245.1 REV 3 BY COLD VAPOR AA

AND

PREPARATION OF SOLIDS BY EPA 7471A OR B FOR MERCURY ANALYSIS

eurofins	Always check on-line for validity. **Mercury in Aqueous, Solid and Tissue Samples by EPA 7471A, 7471B, 7470A, and 245.1 rev 3 by Cold Vapor AA**	Level: **Work Instruction**
Document number: **T-MET-WI7965**		
Old Reference: **1-P-QM-WI-9015067**		
Version: **20**		Organisation level: **5-Sub-BU**
Approved by: **X6TJ** Effective Date **27-APR-2022**	Document users: **6_EUUSLA_Metals_Hg Analysis, 6_EUUSLA_Metals_Hg Analysis Verifiers, 6_EUUSLA_Metals_Management**	Responsible: **5_EUUSLA_Metals_Manager**

Revision Log

Revision	20	**Effective Date**: This Version
Section	**Justification**	**Changes**
Revision Log	Formatting requirement	Removed revision logs up to the previous version
Header	Clarification	Update to reflect current company name
Procedure B.2.c.	Clarification	Updated to reflect current process
Sample Analysis 3. 4. and 6.	Current Process	Updated to reflect current process

Revision	19	**Effective Date**: Nov 24,2020
Section	**Justification**	**Changes**
Revision Log	Formatting requirement	Removed revision logs up to the previous version
Throughout Document	Current Practice	Updated QC IDs
LIMS ID	New procedure	Added new LIMs method IDs
Cross Reference	Update	Added Do Not Use Form and verification SOP
Basic Principals	Current Process	Updated to reflect current process
Sample Collection, Preservation, and Handling	Method Required	Added information regarding preservation hold time
Apparatus and Equipment	Addition	Added products used for analysis
Reagents and Standards	Clarification	Added note about deviation from method
Calibration	Update	Criteria has been moved to new SOP and removed wording of old LIMs
Procedure	Update/Enhancement	Added direction for new LIMs and feature in Envoy
Sample Analysis	Update	Updated to current practice
Calculations	Enhancement	Add units to water sample
Quality Assurance/Quality	Update	change to reference Verification SOP

Control 2		
Data Review	Update	Updated to reflect current practice
Instrument Repair and Maintenance	Enhancement	Added Q-E*QA-FRM6871*

Reference

1. Test Methods for Evaluating Solid Wastes, SW-846 Method 7470A, September 1994

2. Test Methods for Evaluating Solid Wastes, SW-846 Method 7471B, February 2007.

3. Test Methods for Evaluating Solid Wastes, SW-846 Method 7471A, September 1994

4. Method 245.1 (rev. 3), Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectroscopy, USEPA 600/R-94/111 May 1994.

5. *Chemical Hygiene Plan*, current version.

Cross Reference

Document	Document Title
T-MET-WI11948	Preparation of Solids by EPA 7471A or B for Mercury Analysis
T-MET-WI11924	Digestion of Aqueous Samples by SW-846 Method 7470A
T-MET-WI26740	Digestion of Aqueous Samples for Mercury by EPA 245.1
T-MET-WI9084	Preparation of Mercury Solutions and Standards
QA-SOP11178	Demonstrations of Capability
QA-SOP11901	Instrument Maintenance and Calibration
QA-SOP11892	Determining Method Detection Limits and Limits of Quantitation
QA-SOP11896	Establishing Control Limits
QA-SOP11886	Processing Regulatory Compliance (i.e. SDWA, NPDES) Samples
QA-FRM6871	Do Not Use - Environmental
T-MET-WI35797	Metals Data Verification Process

Scope

This method is used for determination of mercury in aqueous and solid samples. The optimum concentration range for this method is 0.2 to 5.0 ppb.

Matrices - EPA 7470A and EPA 245.1 are applicable to water analysis. EPA 7471A and EPA 7471B are applicable to soil and tissue analysis. EPA 245.1 is applicable to drinking water analysis.

Method Detection Limits (MDLs) are based on annual statistical evaluation of laboratory data and are subject to change. The current MDLs and RLs are maintained in the LIMS, and are subject to change without notification.

Basic Principles

The Leeman Labs Mercury Analyzer utilizes continuous flow technology with drying of the sample vapor for the analysis of mercury by automated vapor generation. The reaction for the mercury analysis is a simple reduction reaction. The mercury is reduced with stannous chloride to liberate mercury metal and Tin (IV) chloride. An inert gas is used to sweep the volatile mercury into the absorption cell in the optical path of the atomic absorption spectrophotometer. The dry vapor enters one path of the optical cell, which has been optimized for fast response (small diameter), and sensitivity (long length).

Mercury is measured using a solid state detector with a wide dynamic range and a mercury source that delivers a stable source of emission at 254 nm. The signal is referenced to the simultaneous absorbance of air through direct view of the lamp. The system adds Stannous chloride to the samples via a "Y" connection in the pump tubing. The peristaltic pump then carries the sample/stannous mix to the liquid gas separator. Argon gas is bubbled through the liquid and used to transport the volatile mercury into the detector. The mercury is reduced with stannous chloride to liberate mercury metal and Tin (IV) chloride.

Definitions

1. CRA - Low Level Check Standard

2. MSA – Method of Standard Additions

3. SPLP - Synthetic Precipitation Leaching Procedure

4. TCLP – Toxicity Characteristic Leaching Procedure

5. QC Type Designators:

    a. BKG – unspiked background sample

    b. DUP – Sample Duplicate

c. MS – sample spike

d. MSD – Sample spike duplicate

e. MB –Preparation Blank (Water/ Solid). Equivalent to a Method Blank (MB)

f. LCS/LCSD - Laboratory Control Sample/Laboratory Control Sample Duplicate

Interferences
Potassium permanganate is added to samples to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Take care to ensure that free chlorine is absent before the mercury is reduced and swept into the cell by using an excess of hydroxylamine sulfate (or chloride) reagent.

Copper has been reported to interfere; however, copper concentrations as high as 10 mg/kg had no effect on recovery of mercury from spiked samples.

Safety Precautions and Waste Handling
All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations.

See *Chemical Hygiene Plan* for general information regarding employee safety, waste management, and pollution prevention.

Preparing samples for inorganic analysis involves working with concentrated acids and other chemicals which are dangerous if not handled carefully:

Nitric acid (HNO3) – This acid can cause skin burns. Add nitric acid to samples in a hood to avoid exposure to toxic fumes.

Sulfuric acid (H2SO4) – This acid is a strong oxidizing agent and can cause severe burns. Sulfuric acid spills are extremely slippery, adding to the danger. Always use in a fume hood. Never mix with concentrated HCl or concentrated KMNO4 to avoid a violent reaction (explosive splattering and extreme heat).

Hydrochloric acid (HCl) – This acid can cause skin burns. Never mix HCl with concentrated H2SO4 to avoid a violent reaction. Always use in a fume hood.

When diluting strong acids, never add water to acid; always add acid to water.

Store concentrated acids in the prep room acid lockers. Only acids are to be stored in these lockers. (Store solvents in the flammable liquid storage cabinet.) Some concentrated acids are kept in the acid reagent bottles on prep room counters. Fill reagent bottles in an operating fume hood using caution to avoid spills.

Perform acid digestions in hoods that are turned on and have active alarms. Notify a supervisor immediately if the hood is malfunctioning or the alarm sounds. Samples that contain dust may be hazardous. Open in a fume hood.

Samples that may contain cyanide require special precautions to avoid exposure to hydrogen cyanide gas. Contact your supervisor prior to adding acid. Always open these samples and add the acid in a hood.

Use spill pillows to absorb large acid spills (small spills are cleaned with wet paper towels.) Use SPILL-X-A powder or equivalent to neutralize any remaining acid and then rinse the area thoroughly with water.

Dispose of acid waste properly. Collect all acid digestions, waste solutions, and expired reagent solutions in waste containers. When the acid waste containers are full, a designated acid waste handler transfers the waste to the acid neutralization tank.

Personnel Training and Qualifications
All personnel performing this procedure must have documentation of reading, understanding, and agreeing to follow the current version of this SOP and an annual documented Demonstration of Capability (DOC) which is maintained in the analyst's training records.

Initially, each analyst performing the instrumental analysis must work with an experienced analyst for a period of time until they can independently calibrate the instrument, use the system to set up sequences, perform the calculations, interpret raw data, and enter data into the LIMS. Proficiency is measured through documented audits of the tasks listed and over checking of data as well as an Initial Demonstration of Capability (IDOC).

The IDOC consists of four laboratory control samples that are carried through all steps of the analysis and meet the defined acceptance criteria. The criteria include the calculation of mean accuracy and standard deviation. Various options are available for a DOC and can include four laboratory control samples or one blind sample. Refer to *QA-SOP11178* for more guidance on these options.

Sample Collection, Preservation, and Handling
Aqueous samples are collected in plastic or glass containers, preserved to a pH of <2 with nitric acid. Samples must be analyzed within 28 days of collection.
NOTE: Regulatory Drinking Water samples (EW) are collected in 1-L plastic or glass containers and must be analyzed by EPA 245.1. Drinking water samples are not analyzed for dissolved mercury.

Solid samples are collected in glass containers and stored at 0° to 6°C not frozen. Samples must be analyzed within 28 days of collection.

Dissolved Mercury: Samples to be analyzed for soluble mercury requiring filtration at the lab must be submitted unpreserved. The sample is run through a 0.45 micron filter within 5 days of receipt and are collected in plastic containers and preserved to a pH of <2 with HNO3.

Samples must be held for 16 hours following preservation and checked again prior to processing.

Store sample digestates in plastic bottles at room temperature. Store standards and digestates separately.

Apparatus and Equipment

1. Hydra II Mercury Analyzer
2. Leeman Labs Envoy software – a windows based program to help navigate the software.
3. 15-mL graduated polypropylene screw cap tubes (certified ± 1%)
4. 10-mL sterile disposable syringes
5. 25-mm syringe filters, PTFE, 0.45-µm
6. 40-mL clear glass VOA vials and lids
7. 50-mL polypropylene containers and covers (digestion vessels for block digestion) - certified clean and Class A equivalent

Reagents and Standards

A. Store all standards and reagents in polyethylene or glass containers at room temperature. Label the container with the solution name, lot number, date prepared, the expiration date, the initials of the person preparing the solution, and the storage conditions.

NOTE: Standard/ spiking concentration and reagent vendors are subject to change without notification.

B. Reagents use the following or equivalent:

1. Nitric acid, 70.0% to 71.0% HNO3, Fisher Trace Metal Grade reagent, 1.428 g/mL; Store in glass container at room temperature. Follow manufacturer's expiration date.
2. Sodium chloride, NaCl, J.T. Baker, Certified ACS. Store in plastic container at room temperature. Follow manufacturer's expiration date.
3. Hydroxylamine hydrochloride, NH2OH·HCl, J.T. Baker, Certified ACS. Store in plastic container at room temperature. Follow manufacturer's expiration date.
4. Reagent Water
5. Stannous chloride solution, 10% SnCl, Baker Analyzed reagent, ACS. Store in plastic container at room temperature. Follow manufacturer's expiration date.
6. Hydrochloric acid, HCl, 36.5% to 38.0%, Fisher Trace Metal Grade reagent, 1.194 g/mL or equivalent. Store in glass container at room temperature. Follow manufacturer's expiration date.

C. For the preparation of calibration blanks, ICBs, CCBs, calibration standards, ICVs, CCVs, CRAs, Method Blanks, LCSs and Matrix Spikes solutions, see Form *T-MET-WI9084*.

D. General solutions - See Form *T-MET-WI9084*.

NOTE: Method states to use Sulfuric acid when making Stannous Chloride, however, manufacture requires HCl. The lab practices this deviation in order to maintain instrument performance.

Calibration

Leeman Labs Hydra II Mercury Analyzer

1. The software program has been developed to check the correlation coefficient of the curve, run appropriate ICV and CCVs at proper intervals, and check the percent recoveries of the ICV and CCVs.
2. Due to the instrument software limitations, the calibration blank is included in the correlation coefficient calculation.
3. A recalibration and reread of any associated samples is required for any checks that fall outside the windows.
4. For the frequency, acceptance criteria and corrective action see SOP *T-MET-WI35797*
5. For the preparation of calibration standards, see *T-MET-WI9084*.
6. The calibration is part of each run shown in the LIMs system

Procedure

A. Sample Digestion

1. Aqueous samples are digested by EPA 7471A/B according to SOP *T-MET-WI11924*.
2. Aqueous samples are digested by EPA 245.1 according to SOP *T-MET-WI26740*.
3. Solid samples are digested according to SOP *T-MET-WI11948*.

B. Leeman Labs Hydra II Mercury Analyzer Operation

1. Instrument Setup

a. Turn ON the power to the instrument (switch in the back) and computer.

b. Ensure that Argon supply is set to 15 psi.

c. Double click the Envoy icon on the desktop to initialize the instrument software.

d. Put on the peristaltic pump cassettes. Do not over tighten. At the end of shift, remove them from the pump.

e. Place levers in the 1 o-clock position to avoid stalling the pump. Do not fully tighten at this point.

f. Check that the rinse bottle is full and Luer connections are tight. Only a 'light' finger tightening is required. Refill the rinse tank with a 2.0% Hydrochloric Acid (HCl) solution. For preparation of 2.0% HCl solution, see *T-MET-WI9084*.

g. Check that the 10% stannous chloride bottle is full and Luer connections are tight. Only a 'light' finger tightening is required. For preparation of 10% stannous chloride, see *T-MET-WI9084*.

h. Click the start icon on the Tool Bar to turn on the peristaltic pump and press the green play button.

i. Check to see that the lamp, pump and gas turn on. If necessary, open the Method/Instrument Control Panel and turn them on and set appropriate parameters.

j. When the pump is turning, tighten the cassettes by lowering the levers to a horizontal position. Allow 20 minutes for lamp and pump equilibration.

a) There is an option to use Chart Recorder which displays when the instrument is optimized. To utilize this feature follow these steps
   i. Observe Instrument
   ii. Stabilization Tools
   iii. Chart Recorder : resize window to ~1200 seconds or 10mins.

k. Inspect all system connections for leaks.

l. The system is now ready to be optimized for automated analysis.

2. Autosampler and Run Setup

a. Clear previous analyses
   i. Analysis Tab
   ii. Tools
   iii. Database Manger
   iv. Create Archive

b. Scan the samples from their label that is on the sample itself into the Envoy program under the Sequence Tab
   i. Select Sequence
   ii. New
   iii. Select correct rack size
   iv. Scan samples in order

c. Check QC
   i. Method Tab
   ii. QC control checks tab
   iii. Modify QC as needed to set pass/fail flags

d. Press Run Sequence (Test tube rack icon): The calibration and sequence will run automatically with CCV and CCB every 10 analyses.

e. The results of the calibration and samples can be observed in the Analysis Tab.

Sample Analysis

1. Filtering Samples

a. Samples that are cloudy or have particulate suspended in solution must be filtered prior to analysis.

b. Difficult matrix samples or samples with limited volume may be filtered using a 10-mL sterile disposable syringe fitted with a 0.45 um PTFE syringe filter.

c. If any samples are filtered, the MB and the LCS on the batch must be filtered.

d. Document all filtrations on the run cover sheet.

2. Dilutions

a. Dilute samples with appropriate matrix matching solution when necessary to yield a response that falls within the calibration range.

b. Stop run if sample is above 4.5ppb. Rinse system and dilute sample immediately. Reanalyze. If the subsequent sample analyzed after an over range sample has a detection, reanalyze the subsequent sample as well.

c. Report the results for the least dilute sample where the concentration measured is within the acceptable calibration range.

3. Data Export: follow the below step by step instructions
   On the instrument
   a. Analysis Tab
   b. Report Tab
   c. Select Statisics
   d. Select Load
   e. Select TALS Export
   f. Select OK
   g. Check all data on this run
   h. Select Report
   i. Select CSV File
      1.Name CSV file (2034301MO7)
   j. Select Save
   k. Open IDAT sequence shortcut on desktop
   l. Highlight and copy run file
   m. Open TALS import file on desktop and paste run

4. Attach raw data to run: follow the step by step instructions
   On the instrument
   a. Analysis Tab
   b. Report Tab
   c. Select Detailed
   e. Select Load
   f. Select Detailed TALS
   g. Select OK
   h. Check all data on this run
   i. Select report
   j. Select CSV file
      1.Name CSV file (2034301MO7)
   k. Select Save

NOTE: Do not paste this report into the TALS import file.

5. See Data Review section for when data is in LIMs system. See SOP *T-MET-WI35797* for final data review.

6. Shutdown

   a. Place Stannous Chloride and rinse tubing into 2% HCl for minimum of 5 minutes.

   b. Place tubing into reagent water for a minimum of 5 minutes

   c. Remove tubing from reagent water to allow the aspirating of air for a minimum of 5 minutes.

   Never leave bottle of Stannous Chloride and rinse connected to the instrument if the pump clamps are released because siphoning can occur and cause damage to the instrument.

NOTE: Do not turn off power switch to instrument on a daily basis.

Calculations

1. Final Result

   a. Water sample (ug/L)

$$\text{Instrument Reading} \times \frac{\text{Dilution Volume}}{\text{Aliquot Volume}} \times \frac{\text{Final Volume}}{\text{Sample Volume}}$$

   b. Solid sample (mg/kg)

$$\text{Instrument Reading} \times \frac{\text{Dilution Volume}}{\text{Aliquot Volume}} \times \frac{\text{Final Volume}}{\text{Sample Weight (grams)}}$$

2. Relative percent different (RPD)

$$RPD = \frac{S - D}{(S + D)/2} \times 100$$

Where:

S = first sample value

D = duplicate sample value

3. Spike recovery

$$\%\ Recovery = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = spiked sample result

SR = sample result

SA = spike added

4. Correlation Coefficient

$$r = \frac{\sum XY - \frac{\sum X \sum Y}{N}}{\sqrt{(\sum X^2 - \frac{(\sum X)^2}{N})(\sum Y^2 - \frac{(\sum Y)^2}{N})}}$$

Where :

X = the known concentration

Y = the instrument response

N = the total number of data points

5. Serial Dilution

$$\%\ Difference = \frac{(5 \times SDR) - SR}{SR} \times 100$$

Where:

SDR = serial dilution result

SR = sample result

6. Methods of standard additions (MSA)

Take 4 identical aliquots of the same sample. Leave one unspiked. Spike the other 3 aliquots with different levels of a standard solution. Add blank solution to sample aliquots so that the final volume is the same for all. Use small volumes of spiking solution to avoid diluting the sample more than 10%. Analyze the 4 aliquots and record the instrument readings in absorbance. Use the readings and spike values to find the slope and x- and y- intercepts. The x- intercept is the result.

$$\text{Slope} = m = \frac{\sum x_i y_i - (\sum x_i \sum y_i)/n}{\sum x_i^2 - (\sum x_i)^2/n}$$

$$\text{Y-Intercept} = b = \bar{y} - m\bar{x}$$

$$\text{Result} = -\frac{b}{m}$$

$$\text{Correlation Coefficient} = r = \frac{\sum\{(x_i - \bar{x})(y_i - \bar{y})\}}{\sqrt{\left[\sum (x_i - \bar{x})^2\right]\left[\sum (y_i - \bar{y})^2\right]}}$$

The correlation coefficient (r) for the least squares fit must be ³0.995. If the r value is <0.995, the MSA must be repeated at the same dilution. If the r value is again low, the result with the higher r value is verified and both are flagged with a "+" in the data package. If the r value is <0.990, the sample is run at an interference dilution to overcome matrix effects. This usually requires a raised limit of quantitation. If a client requests a particular limit of quantitation that prohibits further dilution, then the sample is repeated at the same dilution and the best of the two results is verified.

Statistical Information/Method Performance
Generate MDLs and LOQs according to *QA-SOP11892*. The department supervisor maintains annual study data.

QC limits for MS/MSD, and LCS/LCSD are established through statistical analysis of historical data. The limits are maintained in the LIMS for the relevant analysis numbers.

The department supervisor requests that a Quality Assurance Specialist update to the LIMS as needed. Update the department database via a download from the LIMS.

Quality Assurance/Quality Control
Batch Quality Control

1. For the preparation and concentrations of Batch Quality Control see *T-MET-WI9084*.

2. For the frequency, acceptance criteria and corrective action see *T-MET-WI35797*.

3. For EPA 7470A, 7471A, and 7471B, a digestion batch is up to 20 samples. Each batch must contain a MB, LCS, BKG, DUP, MS and MSD (an LCSD is used if there is insufficient sample for an MSD).

4. For EPA 245.1 Rev 3, a digestion batch is up to 10 samples. Each batch must contain a MB, LCS, BKG, DUP, and MS (an LCSD is used if there is insufficient sample for an MSD).

Data Review

1. To view imported analytical batch in the LIMS, follow these steps:
    a. Go to Analyst
    b. Choose Analyst Desktop II
    c. Select the instrument where the data is pulled from on the left hand side by expanding the Instrument option
    d. Data will be listed with a designated analytical batch number given by the LIMs system under the instrument where it was analyzed.
    e. Record this designated analytical batch number on prep batch paperwork.

2. How to complete 1st level review of analytical batch
    a. Once analytical batch is located from following steps in #1 double click to open the batch
    b. Choose Edit button
    c. When asked if data should be processed choose No
    d. Edit Standards/Batch QC
        i. Scan calibration standards from prep batch sheet
    e. If PDS is on analytical run enter PDS data
        i. Go to the Reagents tab at the bottom
        ii. Scan lot number of spike used in PDS
        iii. Enter volume of spike used for PDS. Normally this would be 0.1mL to a final volume of 10mL
        iv. Go to Worksheet Tab and enter a final volume for the PDS. Normally, this would be 10mL
    f. Calculate Results
        i. Go to Samples Results Tab

ii. Highlight all samples by using Ctrl + L
iii. Right click and choose Identify
iv. Once samples are and calibration and all identified it is always a good practice to recalculate by hitting F6

g. Evaluate the Results
i. Go to the Sample List tab
ii. Either look at each line individually to ensure calibration and data are valid or filter by job number and evaluate data
iii. Look for recoveries in the spiked calibration as well as the batch QC
iv. Look for contamination in blanks
v. Look for E flags for samples that need to be diluted. If they were diluted check that the dilution makes sense.

h. Enter Batch Information
i. Prior to saving batch right click and chose View Batch Information or press Ctrl + 1
a. If you try to save batch without going to this screen the program will prompt you
ii. Enter analyst
iii. Enter Stannous Chloride ID lot #
iv. Enter tube lot #s if dilutions were made, filtering of samples occurred, or PDS was used
v. Enter lot number of filters used
vi. Hit Ok to save

i. Attach Raw Data
i. Go to IDAT Sequence folder \\lldata\Env\IDAT-Sequences
ii. Find the analytical run by searching the unique run number given to it by the analyst.
iii. Double Click on file once located
iv. Once file is open, Save As pdf file and name the file the analytical run number give to the data by the LIMs system.
v. Open Sharefile in Google Chrome
vi. Go into the Personal Folder and choose Browse Files
vii. Find File and select Upload
viii. Once uploaded into Sharefiles go into the analytical batch in the LIMs system and choose Docs button at top
ix. Right click and select Add New Document
x. Select the document in the Personal Folder in Sharefiles and hit Select
xi. Hit OK and now the raw data file is attached into the analytical batch

j. 1st level data
i. Once data has been confirmed by analyst to be valid and the raw data is attached go to Sample List tab
ii. Highlight calibration and samples that are valid (if all samples Ctrl +L to highlight)
iii. Either do Ctrl + Shift + 1 to turn status to 1st Level or right click, Review Sample, Choose 1st Level Review

Instrument Maintenance and Repair

A. Routine Maintenance

1. Replace the pump tubing as needed under normal daily usage.
a. Inspect tygon supply lines for discoloration and cloudiness
b. Check peri-pump lines for flattening

2. As needed for foamy samples, replace liquid/gas separator
a. Remove and rinse the clear front panel
b. For severe foam replace entire gas box module

3. If liquid has entered the optical cell, check the optical cell and windows, and if needed, clean the optical cell.

a. Wipe the optical cell with a soapy solution (one drop of liquid Ivory soap to 500 mL reagent water) and warm tap water.

b. Rinse with reagent water and dry. To speed the drying of the optical cell, connect the heater plug to the optical cell with the windows off for several minutes.

c. Clean the quartz windows with methanol and a piece of lens paper.

4. Document any maintenance in the Mercury maintenance logbook located next to the instrument.

NOTE: Detailed instructions for the maintenance and troubleshooting of the Leeman Labs Mercury Analyzer can be found in the Leeman Labs Hydra II Mercury Analyzer Manual.

B. Taking an instrument/analysis out of service/returning an instrument/analysis to service.

NOTE: In the event of an equipment failure, perform the steps in SOP *QA-SOP11901*:

1. Document the nature of the failure in the maintenance logbook.

2. Document how and when the defect was discovered.

3. Notify a supervisor or experienced analyst to determine a person who can decide on appropriate action to take.

4. The instrument must be clearly tagged as Out of Service. The tag must be printed from Q-E*QA-FRM6871* contain the following information:

a. Date taken out of service.

b. Employee who took the instrument out of service.

c. Reason for tagout.

5. The date taken out of service and the date returned to service must be documented in the logbook.

6. Document any corrective action that was taken and the result of that corrective action (i.e., system calibration within specifications, etc.) to bring the equipment back into service.

7. Supervisory personnel must perform a documented evaluation and review of instrumentation/equipment where a major or uncommon failure has occurred to assess the potential impact the failure could have on the calibration and/or qualification of the instrument.

8. After a repair, document whether the function has been fixed. Calibration or verification activities are to be performed before the instrumentation is put back into service.

QA-FRM6871 Do Not Use - Environmental
QA-SOP11178 Demonstrations of Capability
QA-SOP11886 Processing Regulatory Compliance (i.e. SDWA, NPDES) Samples
QA-SOP11892 Determining Method Detection Limits and Limits of Quantitation
QA-SOP11896 Establishing Control Limits
QA-SOP11901 Instrument Maintenance and Calibration
T-MET-WI11924 Digestion of Aqueous Samples by SW-846 Method 7470A
T-MET-WI11948 Preparation of Solids by EPA 7471A or B for Mercury Analysis
T-MET-WI26740 Digestion of Aqueous Samples for Mercury by EPA 245.1
T-MET-WI35797 Metals Data Verification Process
T-MET-WI9084 Preparation of Mercury Solutions and Standards

End of document

Version history

Version	Approval	Revision information	
18	29.JUL.2019		
19	24.NOV.2020		
20	27.APR.2022		

eurofins	Always check on-line for validity. **Preparation of Solids by EPA 7471A or B for Mercury Analysis**	Level: **Work Instruction**
Document number: **T-MET-WI11948**		
Old Reference: **1-P-QM-WI-9015161**		
Version: **21**		Organisation level: **5-Sub-BU**
Approved by: **XL3S** Effective Date **13-MAY-2021**	Document users: **6_EUUSLA_Metals_Hg Prep, 6_EUUSLA_Metals_Hg Prep Verifiers, 6_EUUSLA_Metals_Management**	Responsible: **5_EUUSLA_Metals_Manager**

Revision Log

	Revision: 21	**Effective date:** This version
Section	**Justification**	**Changes**
Revision Log	Formatting requirement	Removed revision logs up to the previous version
LIMS ID	Enhancement	Added TALS Method IDs
Appartus and Equipment	Reflects current procedure	Removed references to LLENS
Reagents and Standards	Enhancement	Clarified acid manufacturer. removed g/mL. Added "or equivalent".
Procedure	Reflects current procedure	Enter weight as 1, add actual weight to Comments
Quality Assurance/Quality Control	Reflects current procedure	Corrected QC names

Revision:	20	**Effective Date:**	This version
Section	**Justification**	**Changes**	
Revision Log	Formatting requirement	Removed revision logs up to the previous version	
Throughout SOP	Update	Updated SOP references to D4 titles	
Procedure	Reflects current procedure	Added step 15 about Hydroxlamine	

Reference

1. Test Methods for Evaluating Solid Wastes, SW-846 Method 7471A, Rev. 1, September 1994.

2. Test Methods for Evaluating Solid Wastes, SW-846 Method 7471B, Rev. 2, February 2007
3. *Chemical Hygiene Plan*, current version.

Cross Reference

Document	Document Title
T-MET-WI7965	Mercury in Aqueous, Solid and Tissue Samples by Cold Vapor AA
T-MET-WI9084	Working Instructions for Preparation of Mercury Solutions and Standards

Scope
This procedure is used to prepare soil, sediment, sludge, oil, tissue and wipe samples for the measurement of mercury by atomic absorption cold vapor technique following SW-846 7471A or 7471B protocol. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix. Samples that require additional homogenization are addressed on a case-by-case basis and homogenized by the Sample Support Group (Department 6055).

Basic Principles
Samples are digested with aqua regia and potassium permanganate to oxidize mercury compounds to mercuric ions and eliminate possible interference from sulfide. Samples high in chlorides require additional permanganate. At the time of analysis, excess permanganate is reduced with sodium chloride/hydroxylamine hydrochloride. Mercuric ions are reduced to mercury metal using stannous chloride. Mercury measurement is performed using mercury cold vapor technique.

Reference Modifications
To increase efficiency, polypropylene containers are used in place of BOD bottles. Prior to analysis (after excess potassium permanganate is reduced with sodium chloride/hydroxylamine hydrochloride solution) samples are adjusted to 100 mL in volumetric flasks. This allows aliquots to be taken as required for analysis; aliquots cannot be taken when BOD bottles are used. No impact on the quality of the data generated using this modification has been observed.

Interferences
Not applicable to this procedure.

Safety Precautions and Waste Handling

All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations.

See *Chemical Hygiene Plan* for general information regarding employee safety, waste management, and pollution prevention.

Preparing samples for inorganic analysis involves working with concentrated acids and other chemicals which are dangerous if not handled carefully:

Nitric acid (HNO_3) – This acid can cause skin burns. Add nitric acid to samples in a hood or use the designated dispensing equipment to avoid exposure to toxic fumes.

Hydrochloric acid (HCl) – This acid can cause skin burns. Never mix HCl with concentrated H_2SO_4 to avoid a violent reaction. Always use in a fume hood or use the designated dispensing equipment.

When diluting strong acids, never add water to acid; always add acid to water.

Store concentrated acids in the prep room acid lockers. Only acids are to be stored in these lockers. (Store solvents in the flammable liquid storage cabinet.) Some concentrated acids are kept in the acid reagent bottles on prep room counters. Fill reagent bottles in an operating fume hood using caution to avoid spills.

Perform acid digestions in hoods that are turned on and have active alarms. Notify a supervisor immediately if the hood is malfunctioning or the alarm sounds.

Samples that contain dust may be hazardous. Open in a fume hood.

When a hazardous flag is added indicating possible cyanide, special precautions are required to avoid exposure to hydrogen cyanide gas. Contact your supervisor prior to adding acid. Always open these samples and add the acid in a hood.

Use spill pillows to absorb large acid spills. (Small spills are cleaned with wet paper towels.) Use SPILL-X-A powder or equivalent to neutralize any remaining acid and then rinse the area thoroughly with water. Spill pillows and SPILL-X-A are stored on the prep room shelf.

Dispose of acid waste properly. Collect all acid digestions, waste solutions, and expired reagent solutions in waste containers. When the acid waste containers are full, a designated acid waste handler transfers the waste to the acid neutralization tank.

Personnel Training and Qualifications

All personnel performing this procedure must have documentation of reading, understanding, and agreeing to follow the current version of this SOP and an annual documented Demonstration of Capability (DOC) which is maintained in the analyst's training records.

Initially, each employee performing this digestion procedure must work with an experienced employee for a period of time until they can independently set up batches and perform the necessary steps outlined in this procedure.

Proficiency is measured through an Initial Demonstration of Capability (IDOC) that consists of four laboratory control samples (LCS) that are carried through all steps of the analysis and meet the defined acceptance criteria. The criteria include the calculation of mean accuracy and standard deviation. Various options are available for a DOC and can include four LCS's or one blind sample.

Sample Collection, Preservation, and Handling

Samples are collected in either glass or plastic containers with no preservatives. They must be stored at 0° to 6°C, not frozen and digested and analyzed within 28 days of collection.

Digested samples are stored in plastic containers at room temperature. Store samples, standards, and digested samples separately.

Apparatus and Equipment

1. Polypropylene containers (digestion vessels) - Certified clean and Class A equivalent
2. Balance, capable of reading 0.1 mg
3. Polypropylene covers, (digestion vessel covers)
4. Chemware Ultra-Pure PTFE boiling stones, or equivalent
5. Environmental Express HotBlock (block digestor), adjustable and capable of maintaining a temperature of 95° ± 1°C

Reagents and Standards

A. Store all prepared standards and reagents in glass or polyethylene bottles at room temperature. Label the bottle with the solution name, lot number, date prepared, the expiration date, the initials of the person preparing the solution, and the storage conditions.

B. Standard/ spiking concentration and reagent vendors are subject to change without notification.

C. Reagents - Follow manufacturer's storage conditions and expiration date. If no expiration date is provided, re-evaluate annually or set a one year expiration date. Use the following or equivalent:

1. Hydrochloric acid, 36.5% to 38.0% HCl, JT Baker Trace Metal Grade reagent
2. Nitric acid, 70.0% to 71.0% HNO_3, JT Baker. Trace Metal Grade reagent
3. Potassium permanganate, $KMNO_4$, Fisher or equivalent. Certified ACS.
4. Sodium chloride, NaCl, J.T. Baker or equivalent. Certified ACS.
5. Hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$, J.T. Baker or equivalent. Certified ACS.
6. 1000 mg/L Hg standard solution, Inorganic Ventures or equivalent.

D. Working instructions for the preparation of mercury solutions and standards are contained within *T-MET-WI9084*. This form includes shelf life and storage conditions.

1. Hg intermediate standard (10 mg/L).
2. Hg intermediate standard (1.0 mg/L).
3. 40 ppb Hg Water Standard.
4. 100 ppb Hg Soil Standard.
5. Potassium permanganate solution (5%).
6. Aqua regia.
7. Sodium chloride/hydroxylamine hydrochloride solution.

E. Adjust all additions according to final solution volume if larger or smaller volumes are needed. Thoroughly mix the solution after diluting to volume.

Calibration
Not applicable to this procedure.

Block Digestor Instructions
1. Turn block digestor on by pressing rocker switch located on the cord.
2. Wait about 8 seconds until controller display indicates current block temperature.
3. Press and hold STAR (*) key.
4. The display shows the Set Point Temperature.
5. The digits can be changed to the desired value by pressing the up and down arrow keys while holding the (*) key.
6. Confirm Control Point temperature is set to the block temperature that provides 95° ± 1°C sample temperature.

NOTE: See HotBlock Control Point Temperature Logbook to obtain control point temperature setting for the HotBlock being used for digestion. If necessary, adjust Control Point temperature to the proper setting.

Procedure
1. Turn block digestor on and allow block to reach the Control Point setting that provides 95° ± 1°C sample temperature.
2. Weigh three aliquots, ~ 0.2000g each, taken from three different areas (combined 0.6000 to 0.6500 g to the nearest 0.0001 g) of a well-mixed, as-received sample into a polypropylene digestion vessel.
    a. Add 0.6000g to 0.6499g of Chemware Ultra-Pure PTFE boiling stones to the vessel for the MB and LCS.
    b. Enter the MB weight as 1.0 g with final volume of 100 mL and the LCS weight as 1.0 g with final volume 100 mL in the LIMS. In the notes section, record the actual weight in grams of boiling stones used.
3. Matrix exceptions:
    a. Samples with a liquid consistency: increase weight to 1 g (1.00 to 1.05 g).
    b. Oil samples: weigh 0.2000 g to 0.2500 g (to the nearest 0.0001 g) of sample and add 0.2000 g to 0.2499 g of Teflon Chips to the MB and LCS container. Enter the blank weight as 0.2000 to 100.0000 final volume, and the LCS weight as 1.0000 to 100.0000 final volume in LIMS.
    c. Wipes: one blank media each must be used for the batch MB, the LCS, and the LCSD. Use reagent water to rinse any particulate matter from the wipe container into the vessel containing the wipe before digesting. Digest wipes in their own batch.
    d. Tissue samples: spike the LCS, LCSD in the same manner as the matrix spike and matrix spike duplicate (Refer to *T-MET-WI9084*). Digest tissue samples in their own batch.
4. For sample batch quality control preparation, spiking procedures and concentration levels see *T-MET-WI9084*.
5. All spiking must be performed prior to starting the digestion procedure.

6. Add about 5 mL reagent water and about 5 mL of aqua regia solution.

7. Place sample containers in block digestor, bring to 95°C ± 1°C and heat approximately 2 minutes. (Place a calibrated thermometer in batch blank container.)

8. Remove sample containers from block and allow to cool.

9. Add 50 mL of reagent water and 15 mL of 5% $KMnO_4$ solution and mix by carefully swirling the container.

    a. Add additional portions of 5% $KMnO_4$ solution (in 5-mL increments, up to as much as 25 mL), if necessary, until the purple color persists for at least 15 minutes.

    b. Add the same amount of $KMnO_4$ solution to entire digestion batch.

    c. If the maximum amount of 25 mL of 5% $KMnO_4$ solution was added and the purple color did not persist for at least 15 minutes, then contact group leader, further dilutions are required. A comment must be placed on the batch sheet documenting the reason for the dilution.

10. Transfer sample containers to block digestor.

11. Place a calibrated thermometer in batch blank container.

12. Put a polypropylene cover on each container.

13. When the thermometer indicates 95° ± 1°C, continue heating for 30 minutes.

14. Remove sample containers from digestion block and allow to cool.

15. Add 6 mL of sodium chloride/hydroxylamine hydrochloride solution to reduce excess permanganate. Adjust volume to the 100 mL mark with reagent water, seal container with screw cap and mix.

16. The sample is now ready for analysis.

Calculations
Not applicable to this procedure.

Statistical Information/Method Performance
Not applicable to this procedure.

Quality Assurance/Quality Control

Each digestion batch (up to 20 samples) must contain a method blank (MB), LCS, and either an unspiked background sample, duplicate (DU), matrix spike (MS), matrix spike duplicate (MSD) or an LCS/LCSD.

Refer to *T-MET-WI7965* for sample batch quality control requirements, acceptance criteria, and corrective action.

T-MET-WI7965 Mercury in Aqueous, Solid and Tissue Samples by EPA 7471A, 7471B, 7470A, and 245.1 rev 3 by Cold Vapor AA
T-MET-WI9084 Preparation of Mercury Solutions and Standards

End of document

Version history

Version	Approval	Revision information	
19	19.JUL.2016		
20	06.MAR.2019		
21	13.MAY.2021		

STANDARD OPERATING PROCEDURE L-2B: DETERMINATION OF METHYL MERCURY IN VARIOUS MATRICES BY CV-GC-AFS

eurofins | Frontier Global Sciences	**Document Title:** Determination of Methyl Mercury in Various Matrices by CV–GC–AFS	**Eurofins Document Reference:** EFAFS-T-AFS-SOP2808

Eurofins Document Reference	EFAFS-T-AFS-SOP2808	**Revision**	8
Effective Date	11/6/2020	**Status**	Final
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Local Document Level	Level 3		
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Local Document Category	NA		

Prepared by	Bryn Fada
Reviewed and Approved by	Terri Torres and Patrick Garcia-Strickland

Table of Contents

1 Revision Log:

Revision: 8	**Effective Date:** This version	
Section	**Justification**	**Changes**
2.12, 2.13	Required	Updated references
3	Required	Added link to CHP/Standard SOP
5.3	Required	Added Ethyl Hg to Scope
8.2	Updated	Batch consist of 3 method blanks, 1 LCS/LCSD, and 1 MS/MSD per 10 samples
8.13	Updated	Removed reference to MDN blanks
9.2	Updated	Removed reference to bubblers
9.7	Updated	Removed section no longer relevant and renumbered subsequent sections
10.1/10.2	Required	Updated
12.1.1/13.2	Updated	Removed section no longer relevant and renumbered subsequent sections
13.10	Updated	Removed reference to bubblers
14.1.1	Required	Added pipette rinse
14.2-14.4	Updated	Removed info regarding the receipt, prep, and storage of standards and added link to new standard SOP. Renumbered sections.
15.3	Updated	Removed procedure for manual Tekran 2500 and renumbered subsequent sections
15.3.3 - 15.3.12	Required	Added acetate buffer and renumbered subsequent sections
16	Updated	Removed all sections describing procedure for manual Tekran 2500 and renumbered subsequent sections. Automated Tekran 2700 is now used exclusively. Troubleshooting table was also rewritten to apply to 2700 only
17	Required/Clarification	Changed "ICB" to "IBL" and clarified equations for calculations
17.1	Updated	Replaced all mentions of Peak Height to Peak Area as measured by 2700
18.1	Required	Referenced new MDL requirements
19.2	Updated	Removed reference to bubblers
19.4/11	Required	Removed requirement for (MD)
Appendix C	Required	Added Ethyl Hg method modifications

2 Reference:

2.1 EPA Method 1630 Draft Method. January 2001.

2.2 Bloom, N.S. Ultra-Clean Sample Handling, Environmental Lab 1995, March/April, 20.

2.3 Bloom, N.S. Determination of Picogram Levels of Methyl Mercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapour Atomic

Fluorescence Detection. Can. J. Fish. Aq. Sci. 1989, 46, 1131.

2.4 Bloom, N.S.; M. Horvat; C.J. Watras Results of the International Mercury Speciation Intercomparison Exercise. Water Air Soil Pollution 1995, 80, 1257.

2.5 Bloom, N.S.; Crecelius, E.A. Determination of Mercury in Seawater at Sub-nanogram per Liter Levels. Mar. Chem. 1983, 14, 49.

2.6 Bloom, N.S.; Fitzgerald, W.F. Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection. Anal. Chem. Acta. 1988, 208, 151.

2.7 Gill, G.A.; Fitzgerald, W.F. Mercury Sampling of Open Ocean Waters at the Picogram Level. Deep Sea Res. 1985, 32, 287.

2.8 Horvat, M.; Bloom, N.S.; Liang, L. A Comparison of Distillation with Other Current Isolation Methods for the Determination of Methyl Mercury Compounds in Low Level Environmental Samples Part 2, Water. Ana.l Chem. Acta. 1993, 282, 153.

2.9 Liang, L.; Bloom, N.S.; Horvat, M. Simultaneous Determination of Mercury Speciation in Biological Materials by GC/CVAFS after Ethylation and Room Temperature Precollection. Clin. Chem. 1994, 40, 602.

2.10 Bloom, N.S.; Horvat, M.; Watras, C.J. "Results of the International Mercury Speciation Intercomparison Exercise," Wat. Air. Soil Pollut., 1995, 80, 1257.

2.11 Chemical Hygiene Plan, Eurofins Frontier Global Sciences, current version

2.12 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.13 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019.

2.14 Tekran Model 2700 User Manual and Analytical Guides, Rev 1.01 May 2011

3 Cross Reference:

Document	Document Title
EFQA-Q-QM-QM5805	*QA Manual*
EFHS-S-HS-12066	*Chemical Hygiene Plan*
EFQA-Q-QD-SOP10098	*Procedure for Determining IDLs, MDLs, LODs, PQLs, LOQs, OPRs, IQs, OQs, and PQs*
EFQA-R-MT-SOP2710	Balance Verification, Calibration and Maintenance
EFQA-R-EQ-SOP2711	Pipette Verification, Calibration and Maintenance
EFAFS-S-SB-SOP5132	Cleaning of Sampling Equipment and Bottles
EFTM-T-TM-SOP2839	*Stock and Prepared Standards*
EFSR-S-CS-SOP2794	Ultra Clean Aqueous Sample Collection
EFAFS-T-AFS-SOP2986	KOH/Methanol Digestion of Solids for Methyl Mercury
EFAFS-T-AFS-SOP2797	Distillation of Aqueous Samples for Methyl Mercury Analysis

Document	Document Title
EFQA-P-DR-SOP2801	Data Review and Validation
EFAFS-T-AFS-SOP5134	Preparation of Sediments by Acidic KBr Extraction into Methylene Chloride for Determination of Methyl Mercury
EFAFS-S-T-SOP2806	Preparation of Tenax- and Carbo-Traps for Methyl Mercury and Dimethyl Mercury Analysis
EFSR-P-SP-SOP2811	Sample Preservation and Sub-Sampling
EFHS-S-HS-SOP2991	Waste Disposal Procedure for Client Sample Waste

4 Purpose:

4.1 This Standard Operating Procedure (SOP) is designed to ensure that reproducible and traceable procedures are followed in the standardization of the methyl mercury (MeHg) analyzers and in the analysis of samples for monomethyl mercury (MeHg or MMHg), as well as to establish the bounds wherein data will be considered acceptable.

5 Scope:

5.1 This SOP provides for the determination of monomethyl mercury (CH_3Hg) in a wide range of matrices including, but not limited to, aqueous, biological, and geological media. Methyl mercury is measured by Cold Vapor-Gas Chromatography-Atomic Fluorescence Spectrometry (CV-GC-AFS) and is calculated by comparing the instrument response of samples to that of standards.

5.2 This method is designed for the determination of methyl mercury in the range of 0.05-4.0ng/L (ppt) or 0.05-5.0 ng/g (ppb). Application may be extended to higher levels by selection of a smaller sample size, as long as the instrument value (intensity) remains within the calibration curve.

5.3 This SOP also provides for the determination of ethyl mercury in a wide range of matrices including, but not limited to, aqueous, biological, and geological media. Ethyl mercury is measured by Cold Vapor-Gas Chromatography-Atomic Fluorescence Spectrometry (CV-GC-AFS) and is calculated by comparing the instrument response of samples to that of standards.

6 Basic Principles:

6.1 All aqueous samples should be prepared according to *EFAFS-T-AFS-SOP2797*. Sediments/soils are prepared by *EFAFS-T-AFS-SOP5134*. Tissues are prepared by *EFAFS-T-AFS-SOP2986*.

6.2 An aliquot of prepared sample is pH adjusted to 4.9 with acetate buffer and ethylated in a closed purge vessel by the addition of sodium tetraethyl borate ($NaBEt_4$). The volatile Hg(0) and ethyl derivatives of CH_3Hg and labile Hg(II), (methyl ethyl and diethyl methyl mercury), are purged from solution by purging with N_2 onto a graphitic carbon (Carbotrap®) or adsorptive polymer (Tenax®) trap. This trap is dried and then placed into an analytical train and the analytes are thermally desorbed from the trap into an inert gas stream. They are then separated by a GC column, passed through a pyrolitic column (which converts the organomercury forms to detectable elemental mercury) and then into the cell of a Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) for detection. Peak height is measured with a strip chart recorder, or captured electronically, and all results are entered into an excel spreadsheet.

6.3 For dissolved CH3Hg, samples are filtered through a 0.45-µm capsule filter prior to distillation.

7 Reference Modifications:

7.1 No significant modifications were made to this method.

8 Definitions:

8.1 Analytical Run – the continuous analysis of one or more batches. An analytical run requires a 5-point calibration curve, ICV/OPR, ICB, and CCV/CCB every ten samples. An analytical run must conclude with an OPR/CCB.

8.2 Batch – no more than 20 client samples grouped for preparation. *3* MBLK, 1 LCS/*LCSD* (or BS/BSD) and 1 MS/MSD are prepared per 10 samples.

8.3 Calibration Standards (CAL) – a series of standards that will be used to calibrate the instrument, made from a PDS. A calibration blank plus at least five different concentrations are required, beginning with one at PQL concentration.

8.4 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.5 Control Limit (CL) – the limit of the range of acceptability for the quality control samples

8.6 Initial Calibration Verification (ICV/OPR) – a standard used to check initial calibration and is prepared from a SDS. This standard is run at mid-level concentration and verifies instrument calibration. It is always followed by an ICB.

8.7 Initial and Continuing Calibration Blank (ICB and CCB) for evaluation of instrument drift, sensitivity, and contamination. ICB must be analyzed directly after the ICV, and the CCBs every 10 samples immediately after CCVs. ICB and CCBs must individually be less than one-half of the Practical Quantitation Limit.

8.8 Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS and LCSD) – a sample containing a known concentration of methyl mercury that is used to monitor complete method performance. The preferred LCS is a matrix matched Certified Reference Material (CRM), but a blank spike meets the requirement as well. In LIMS, the LCS is always referred to as a Blank Spike (BS), whether it is matrix matched or not.

8.9 Method Duplicate (MD) – a second separate sample, taken from the same source sample and analyzed in the laboratory separately at the request of the client. A MSD may be used as a duplicate.

8.10 Matrix Spikes and Matrix Spike Duplicates (MS/MSD): The purpose of analyzing matrix spikes and matrix spike duplicates (MS/MSD) of a matrix representative sample per each batch is to demonstrate the performance of the analytical method in a particular sample matrix, and to recognize matrix interference. To prepare a MS/MSD for MMHg, predetermined quantities of the analyte are added to a sample matrix before distillation of samples.

8.11 May: This action, activity, or procedural step is optional.

8.12 May Not: This action, activity, or procedural step is prohibited.

8.13 Method Blank (BLK) or Preparation Blank (PB): Method blanks consist of the same

reagents used to digest the samples, in the same volume or proportion, and are carried through the complete sample preparation and analytical procedure.

8.14 Method Detection Limit (MDL) – the limit derived from an exercise as described in 40 CFR, Part 136, Appendix B. The exercise produces a defined value that is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.15 Ongoing Precision and Recovery (OPR) – a standard that is prepared from a secondary source stock standard. This standard is analyzed at 0.5 ng/L and verifies instrument calibration.

8.16 Practical Quantization Limit (PQL) – the minimum concentration that can be reported quantitatively. The PQL is often described as 1-10 times higher than MDL. EFGS defines the PQL as the lowest concentration that can achieve 70-130 % recovery from the reproducibility of ten replicate sample preparations. The PQL is the upper Control Limit for the ICB, CCB, and MBLK (Prep blank); i.e. these QC standards must be lower in concentration than PQL. In LIMS, the PQL is given the term MRL.

8.17 Primary Dilution Standard (PDS) – a standard that is used to make a series of calibration standards for this method. It is prepared from a SSS of arsenic.

8.18 Quality control sample (QCS)—A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process. This sample is analyzed within a batch as an LCS and is performed on a quarterly basis.

8.19 Stock Standard Solution (SSS) – a standard of analyte that is purchased from a certified source for the preparation of working standards.

8.20 Secondary Dilution Standard (SDS) – a sample of standard from an alternate SSS, used to prepare the ICV, CCV, MS, and MSD standards, and for IDOC/CDOC.

8.21 Shall: This action, activity, or procedure is required.

8.22 Should: This action, activity, or procedure is suggested, but not required.

8.23 Stock Standard Solution – a standard of analyte purchased from a certified source for the preparation of working standards.

9 Interferences:

9.1 Only clean fluoropolymer or borosilicate glass containers, with fluoropolymer line caps, should be used for samples, standards, and reagents, because Hg vapors can diffuse into, or out of other materials, resulting in results that are biased high or low.

9.2 BrCl will oxidize nearly all forms of mercury; therefore, pipettes used to aliquot BrCl or bubblers used/cleaned with BrCl should never be used for methyl mercury analysis.

9.3 Samples preserved with nitric acid (HNO_3) cannot be analyzed for methyl mercury as the analyte is partially decomposed in the distillation step by this reagent. Special care should be taken when sharing glassware with the Trace Metals group to ensure that all traces of nitric acid have been rinsed from the glassware prior to use for standard or reagent creation or storage.

9.4 Methyl mercury analysis is pH sensitive and distillation can cause acidification of samples; therefore, it is essential that the pH of the distillates be adjusted by the addition of acetate buffer. Each distillate must be tested for pH before analysis. This is done when distillation is complete and the pH is measured and recorded on the bench sheet and/or in the logbook (LOG-HG-026 Sample Digestion Logbook). The laboratory technician ensures that the pH paper is not directly placed into the sample. The optimum pH for the distillate is 3.5-7. For pH <3.0, the sample will be analyzed, but should be re-distilled if sufficient sample volume remains. This shall be entered as a comment in the MMO notes in LIMS.

9.5 Distilled methyl mercury results are corrected using an empirically derived efficiency factor. This factor is based upon historical data that reflects methyl mercury losses inherent to this procedure.

9.6 Because tissue digests prepared with a KOH/methanol digestion are basic, 600 µL of acetate buffer must be added to adjust the pH of the solution in the bubbler. Also, it is recommended that aliquot sizes no greater than 100 µL of the tissue digest be analyzed, unless otherwise instructed by a project manager or Group Leader.

9.7 Free chlorine interferes and must be removed using ascorbic acid

10 Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to the Chemical Hygiene Plan *(CHP) EFHS-S-HS-QP12066.* This includes, but is not limited to, laboratory coat, *apron, eye protection, face shield and protective gloves.*

10.2 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Therefore, every chemical must be treated as a potential health hazard. Exposures shall be reduced as much as possible. *Analysts and technicians are expected to familiarize themselves with the characteristics and risks of each chemical they work with by referring to the SDS located at:*

https://msdsmanagement.msdsonline.com/company/5c1df5b3-747d-4789-8104-42457dc3a3e5/

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Eurofins Frontier will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 CAUTION: Sodium tetraethyl borate is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. To discard unused portions of ethylating agent and empty bottles, place into a large beaker of 1N HCl in the fume hood. Triethylboron will bubble off to the air where it is eventually oxidized to harmless boric acid. Boil the acid down to ½ volume to destroy residues before discarding as acid waste.

CAUTION: Fill empty tetraethyl borate vial and cap quickly with water and gently place in specified waste beaker in fume hood. Tetraethyl borate can spontaneously combust upon contact with air.

10.5 Chronic Hg exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability, and nervousness. Organo-mercurials may cause permanent brain damage. Because of the toxicological and physical properties of CH_3Hg, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

10.6 It is recommended that the laboratory purchase a dilute standard solution of CH_3Hg for this method. If primary solutions are prepared, they shall be prepared in a hood, and a NIOSH/MESA-approved toxic gas respirator shall be worn when high concentrations are handled.

10.7 Facility—when samples known or suspected to contain high concentrations of CH_3Hg are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak-proof, or in a fume hood demonstrated to have adequate airflow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazard except in an accident.

10.8 Personal hygiene – hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

10.9 Effluent vapors – the effluent from the CV-AFS should pass through either a column of activated charcoal or a trap containing gold or sulfur to amalgamate or react with Hg vapors.

10.10 See Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.11 Pollution prevention information can be found in the current Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.12 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to *EFHS-S-HS-SOP2991* (waste disposal), which provides instruction on dealing with laboratory and client waste.

11 Personnel Training and Qualifications:

11.1 An analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source before being qualified to analyze samples without supervision. Continuing DOC will be maintained and monitored via performance on CRMs and other QC samples, as well as obtaining acceptable results on proficiency testing exercises.

11.2 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.3 All employees must read the Quality Manual (*EFQA-Q-QM-QM5805*) and complete the annual Ethics training.

11.4 All training documents including IDOCs, CDOCs, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employees training file for ten years after the employee is no longer working for Eurofins Frontier Global Sciences.

11.5 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous goods, are stored by the Health and Safety Officer for ten years after the employee is no longer working for Eurofins Frontier Global

Sciences.

12 Sample Collection, Preservation, and Handling:

12.1 Samples are collected into rigorously cleaned (according to *EFAFS-S-SB-SOP5132*) fluoropolymer bottles (with fluoropolymer caps) or borosilicate glass bottles with fluoropolymer lined caps. Bottles should be tightly sealed, and care must be taken to minimize headspace within the sample bottle. Acid preserved samples are stable for at least six months, if kept in the dark and cool.

12.2 Collect samples using clean sampling techniques, according to *EFSR-S-CS-SOP2794*.

12.3 Freshwater samples are preserved to 0.4% HCl. Saline samples are preserved to 0.2% H_2SO_4. See *EFSR-P-SP-SOP2811* (sample preservation). Samples may be shipped to the laboratory unpreserved if they are (1) collected in appropriate bottles, (2) filled to the top with no head space, capped tightly, and (4) maintained at 0-4°C from the time of collection until preservation. The samples must be acid-preserved within 48 hours of sampling.

12.4 After preservation, aqueous samples are stored in a secure refrigerator until distillation. After distillation, aqueous samples are stored in the refrigerator until disposal. Tissue and sediment samples are stored in a secured, designated freezer before and after preparation.

13 Apparatus and Equipment:

13.1 LIMS – Element, version 6 or higher; Computer – Windows XP, 7 or 8 with MS Excel

13.2 Recorder: Any integrator or multi-range chart recorder with 0.1-5.000 mV input and variable speeds is acceptable. Data capture software may also be used.

13.3 Tenax® Traps: Borosilicate, silanized quartz tubes filled with low mercury adsorptive polymer material and plugged with silanized glass wool. Refer to *EFAFS-S-T-SOP2806* (analytical trap preparation for methyl mercury) for specifics regarding Tenax- and Carbotrap® construction and verification.

13.4 Carbotraps®: Borosilicate, silanized quartz tubes filled with low mercury Carbotrap® material and plugged with silanized glass wool. Refer to *EFAFS-S-T-SOP2806* (analytical trap preparation for methyl mercury) for specifics regarding Tenax- and Carbotrap® construction and verification.

13.5 Atomic Fluorescence Spectrophotometer (AFS): To achieve the low detection levels and small, interference-free sample aliquots claimed by this method, a very sensitive (IDL < 1 pg Hg) AFS detector with a 257.3 nm lamp is required. Such systems can be built in-lab or purchased from Tekran Inc. (Toronto, Ontario).

13.6 Flow Meter/Needle Valve: Capable of controlling and measuring gas flow to the purge vessel at 200-500 mL/minute.

13.7 Teflon Fittings: Connections between components and columns are made using 6.4-mm O.D. Teflon FEP tubing and Teflon friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with 3.2-mm O.D. Teflon tubing due to its greater flexibility.

13.8 Isothermal GC Unit: A 1.3-m packed GC column is made to the following specification (Supelco Inc. custom product): The column is made of 0.25-in. O.D. borosilicate glass

column tubing with 4-mm I.D. bore. The tube is formed into an 8-cm diameter coil of 1.0-m length with two 15-cm arms extending in parallel up from the coil. The column is silanized, and packed with 1 m (in the coil section only) of preconditioned 60/80 mesh 15% OV-3 on Chromasorb WAW-DMSC, held in place with silanized glass wool plugs. The column is held in a small temperature-controlled isothermal oven made from a heating mantle (Glass-Col TM-580) interfaced with a Cole Parmer Digi-Sense temperature controller. The column is held at a constant temperature of 100□2□C using the temperature controller.

13.9 Pyrolytic Organomercury Breakdown Column: This column consists of a 20-cm length of 7-mm O.D. by 4.5-mm I.D. quartz tubing with the central 10 cm packed with quartz wool. The column is wrapped with 1.5 m of 22-gage Nichrome wire that is electrically heated to about 700□C (bright orange) with 30-34 volts from an autotransformer.

13.10 Nitrogen (N_2): Grade 4.5 (standard laboratory grade) nitrogen, which can be further purified of mercury using a gold or iodated carbon trap located in line between the gas output and *the analyzer gas input.*

13.11 Argon (Ar): No less than Grade 4.7 (high purity grade) argon that has been further purified by the removal of mercury using a gold or iodated carbon trap that is located in line between the gas output and the analyzer gas input.

13.12 Pipettes: Calibrated variable pipettes with a range of 10 µL – 5 mL. Used to make solutions and sample dilutions. Pipettes are to be calibrated weekly according to *EFQA-R-EQ-SOP2711*.

13.13 Analytical balance - capable of accurately weighing to the nearest 0.01 g, calibrated according to *EFQA-R-MT-SOP2710*. The balance must have been calibrated earlier in the date and a calibration sticker shall be in place on the balance.

13.14 Volumetric flasks - class A and cleaned according to *EFAFS-S-SB-SOP5132*. Make sure to use volumetric flasks designated for methyl mercury use only. These flasks should be filled with MQ and preserved with 5% Baker HCl if they are not to be used immediately after cleaning.

13.15 Glass bottles: Borosilicate glass I-Chem bottles can be used to store samples, standards and reagents.

13.16 Tekran 2700 with autosampler: Automated MHg system that utilizes the purge and trap system. See Instrument Software Inventory *EFQA-S-IT-WI7061*

13.17 Teflon (Fluoropolymer) bottles: Teflon bottles that have been cleaned for methyl mercury use can be used to make and store the Acetate Buffer and to store standards and samples.

13.18 Sample Digestion Logbook.

13.19 CV-GC-AFS instrument Log

14 Reagents and Standards:

14.1 Reagent Water: 18-MO ultrapure deionized water starting from a pre-purified (distilled, R.O., etc.) source is used. To remove any remaining trace metals and organics, an activated carbon cartridge is placed between the final ion exchange bed and the 0.2-µm filter. The reagent water is tested for trace metal and mercury concentrations on a weekly basis and must test less than the PQL to be in-control.

14.1.1 Rinse bottle labelled:

Speciation Rinse, MQ only

To be used for all speciation analysis: As, DMHg, CrVI, HgO, MMHg, Se and any other type of speciation analysis. Anything that requires us to evaluate an oxidation state of any metal.

14.2 Hydrochloric acid: Trace-metal purified reagent HCl containing less than 5 pg/mL Hg. CH3Hg is not stable in concentrated acid, so the acid does not need to be tested for CH3Hg. The acid used at Eurofins Frontier shall be lot sequestered and tested below 5 pg/mL Hg prior to being used. The acid is entered into LIMS with an expiration date of three years and a copy of the Certificate of Analysis (CoA) shall be on file with the Quality Assurance department.

14.3 Sulfuric acid: Trace-metal purified reagent H2SO4 containing less than 5 pg/mL Hg. CH3Hg is not stable in concentrated acid, so the acid does not need to be tested for CH3Hg. The acid used at Eurofins Frontier shall be lot sequestered and tested below 5 pg/mL Hg prior to being used. The acid is entered into LIMS with an expiration date of three years and a copy of the Certificate of Analysis (CoA) shall be on file with the Quality Assurance department.

14.4 Methyl Mercury Stock and Prepared Standards:

14.4.1 See SOP *EFTM-T-TM-SOP2839* for information regarding the receipt, documentation, preparation, and storage of purchased and prepared standards used by EFGS.

14.4.2 Methyl Mercury Stock Solutions are purchased from Absolute Standards (100 ug/mL Hg, Primary) and Alfa Aesar (799 ug/mL Hg, Secondary). Alternate vendors may be used, providing that one primary and at least one secondary source are used.

14.4.3 Spiking Standard, 1000 ng/mL: a PDS made from Absolute Primary Stock Standard. Use 1.0 mL of the stock standard into 100 mL reagent water containing 0.5% Glacial Acetic and 0.2% HCl. Expiration date is currently set at 12 months or when the stock standard expires, whichever is shorter. Test this standard by making a 1000X dilution, and then placing 100 µL into an assumed aliquot of 50 mL. Enter 1000 into the Dilution column in the excel spreadsheet. The true value is 2000 ng/L.

14.4.4 Spiking Standard, 100 ng/mL: a PDS made from Absolute Primary Stock Standard. Use 0.100mL of the stock standard into 100mL reagent water containing 0.5% Glacial Acetic and 0.2% HCl. Expiration date is currently set at 12 months or when the stock standard expires, whichever is shorter. Test this standard by making a 100X dilution, and then placing 100µL into an assumed aliquot of 50 mL. Enter 100 into the Dilution column of the excel spreadsheet. The true value is 200 ng/L.

14.4.5 Spiking Standard, 10 ng/mL: a PDS made from Absolute Primary Stock Standard. Use 0.010mL of the stock standard into 100mL reagent water containing 0.5% Glacial Acetic and 0.2% HCl. Expiration date is currently set at 12 months or when the stock standard expires, whichever is shorter. Test this standard by making a 10X dilution, and then placing 100 µL into an assumed aliquot of 50 mL. Enter 10 into the Dilution column of the excel spreadsheet. The true value is 20 ng/L.

14.4.6 Calibration Standard, 1.0 ng/mL: made from the 100 ng/mL PDS (Absolute): Use 2.5 mL of the 100 ng/mL Absolute standard to 250 mL of reagent water containing 0.5% Glacial

Acetic and 0.2% HCl. This standard is also used for the BS/BSDs, and MS/MSDs. Expiration date is currently set at 3 months, or when the stock standard expires, whichever is shorter. Test this standard by placing 100 µL into an assumed aliquot of 50 mL. The true value is 2.0 ng/L.

14.4.7 Calibration Standard, 0.05 ng/mL: made from the 100 ng/mL PDS (Absolute): Use 0.125 mL of the 100 ng/mL Absolute standard to 250 mL of reagent water containing 0.5% Glacial Acetic and 0.2% HCl. This standard may also be used for the BS/BSDs and MS/MSDs if a lower spike level is desired. Expiration date is currently set at 3 months, or when the stock standard expires, whichever is shorter. Test this standard by placing 100 µL into an assumed aliquot of 50 mL. The true value is 0.10 ng/L.

14.4.8 Initial Calibration Verification, 1.0 ng/mL: made from SDS (Alfa Aesar or equivalent): Use 50 µL of the secondary stock standard to 50 mL of reagent water containing 0.5% Glacial Acetic Acid and 0.2% HCl. Expiration date is currently set at 3 months, or when the stock standard expires, whichever is shorter. Test this standard by placing 50 µL into an assumed aliquot of 50 mL.

14.5 Ethylating Agent: CAUTION: Sodium tetraethyl borate is toxic, gives off toxic gases (triethylboron) and is spontaneously combustible. To discard unused portions of ethylating agent and empty bottles, place into a large beaker of 1N HCl in the fume hood. Triethylboron will bubble off to the air where it is eventually oxidized to harmless boric acid. Boil the acid down to ½ volume to destroy residues before discarding as acid waste.

14.5.1 Procedure: Locate the 125 mL Teflon ethylating agent bottle in freezer in the methyl lab. Rinse bottle 3X with reagent water. Fill bottle with 100 ml of reagent water. Add 2 g reagent grade KOH. Shake vigorously until the KOH pellets have completely dissolved. Put solution in the freezer and leave to cool until crystals just start to form. Meanwhile, gather about 15 of the 5 ml ethylating agent vials and dump the used ethylating agent into the specified waste beaker found in the fume hood. Rinse the vials and let them dry under the clean hood on new blotter paper. Be sure to complete the following step under the fume hood with clean blotter paper on the counter. Remove crystallized KOH solution from the freezer and place in hood. Open tetraethyl borate vial with a new razor blade and wipe off excess wax before removing cap. Upon opening, immediately pour the contents of the tetraethyl borate vial into the KOH solution. CAUTION: Fill empty tetraethyl borate vial and cap quickly with water and gently place in specified waste beaker in fume hood. Tetraethyl borate can spontaneously combust upon contact with air. Shake the 125 mL Teflon bottle well and then pour approximately 4 mL into each of the dry 5 ml vials. Cap and freeze the vials until needed. Do not over fill the 5 mL vials, as they could expand during freezing. The frozen bottles will keep for at least a week. If any doubt arises about the quality of the ethylating agent, make a new batch, as the old material often gives good results for standards, but not for environmental samples. Do not use NaBEt4 solid or solutions if they have a yellow color.

14.5.2 Ethylating agent is identified by the lot number of the solid reagent (see section 9.1.3 for entering neat reagents). The working reagent is remade every two weeks. The solution shall be stored in freezer.

14.6 Acetate Buffer: Fill a 1 L bottle ¾ full with reagent water. Add 196.3 g CH3COOK (2 moles potassium acetate). Add 120.1 g acetic acid (2 moles). Add 0.5 ml ethylating agent. Shake and let sit about 20 minutes. Purge with Nitrogen overnight. The reagent shall be entered into LIMS.

14.6.1 Alternatively (using sodium acetate if potassium acetate is not available): Fill 1 L bottle ½ full with reagent water. Add 272 g sodium acetate and let dissolve. Add 118 mL glacial acetic acid. Dilute to 1 L with reagent water. Add 0.5 ml ethylating agent. Purge with Nitrogen overnight.

14.6.2 Acetate Buffer is given a default expiration of six months, or the expiry of the parent reagents, whichever is sooner.

14.6.3 Acetate buffer is tested by ethylating 600 uL of reagent during an analytical run. The default aliquot entered into the Excel file is 50 mL. The warning limit for the ethylating agent is 0.025 ng/L. If the reagent tests above the control limit, it can be repurged or remade prior to retesting. Only one analytical replicate is necessary.

14.7 L-Ascorbic Acid: reagent grade

14.8 2.5% Ascorbic acid

15 Calibration:

15.1 The calibration sequence determines the range of sample concentrations that are reportable. The calibration sequence starts with the instrument blank level (IBL) followed by a 5-point curve using the methyl mercury calibration standard solutions. The five points are: 0.0025 ng (0.05 ng/L), 0.010 ng (0.20 ng/L), 0.050 ng (1.0 ng/L), 0.100 ng (2.0 ng/L), and 0.200 ng (4.0 ng/L).

15.1.1 Additional calibration points may be added later in the run to extend this range, as long as all calibration QC criteria in Section 19 are met. This is only acceptable when sample volume is exhausted and re-preparation and re-analysis is not possible. This must be narrated in the work order and client report.

15.2 Immediately following the standard calibration curve, an Initial Calibration Verification (ICV/OPR) standard is analyzed. The ICV/OPR standard is made from a secondary source (see section 14.3.8). Following the ICV/OPR, an Initial Calibration Blank (ICB) is analyzed.

15.3 To calibrate the MHg 2700 instrument setup, follow the protocols below:

15.3.1 Ensure instrument and computer have been powered up. The system should be on for 30 minutes before calibration analysis is started.

15.3.1.1 Open the software of the instrument with the short cut on the desktop.

15.3.1.2 Open a new worksheet under the EPA 1630 method.

15.3.2 While the system is stabilizing grab eight of septa vials and label them with IBL, CAL1, CAL2, CAL3, CAL4, CAL5, ICV1 and ICB.

15.3.3 Add approximately 50 mL reagent water to each vial.

15.3.4 Using the 0.050 ng/mL MeHg calibration standard solution, add 50 µL and 200 µL to the vials labeled CAL1 and CAL2. Then using the 1.0 ng/mL MeHg calibration standard solution, add 50 µL, 100 µL and 200 µL CAL3, CAL4 and CAL5. Add 50 µL of the ICV solution to vial labeled ICV.

15.3.5 Add 300 uL of acetate buffer to each vial. Ensure the solution level is far enough away from the probe inlet at the top of vial (approximately 2 centimeters).

15.3.6 The ICB and IBL only contain water, buffer, and ethylating agent.

15.3.7 Remove ethylating agent from the freezer, and check to insure that the liquid to ice ratio is approximately 50%. Add 40.0 µL of the ethylating agent to each vial , immediately returning the ethylating agent to the freezer. Seal vials right after the ethylating has been added to each.

15.3.8 Swirl vials and allow reaction to occur for 30 minutes.

15.3.9 After 30 minutes the system is allowed to start analyzing, Ensure that each vial is placed into the autosampler in consecutive order. Enter the vials into the software as SEQ-ICB, SEQ-CAL1, SEQ-CAL2 and so on. Reference the location of each in the software. The system should start off with a clean cycle.

15.3.10 To start the run click on run worksheet. For the initiation of the run the “run worksheet” portion should be selected with method “clean” for cleans and “psample10” for sample analysis. Click ok and the run with commence. Each clean with take 6 minutes and each sample analysis will take 10.5 minutes.

15.3.11 The instrument will evaluate the each peak and determine speciation of the peaks as well. The integration of the peaks in reported on the worksheet.

15.3.12 The system will stop if no sample IDs are placed in the next row for analysis.

16 Procedure:

16.1 Instrument Start Up

16.1.1 Ensure the instrument has been on for one hour to stabilize before running calibration curve. If instrument was left on overnight no waiting period is necessary.

16.1.2 Open the Tek MDS software on the computer. Evaluate the PG2 reading to be ~7.5 psig and the PG3 reading to be ~15 psig.

16.1.3 On the front of the instrument ensure the status of the five icons (General System, Tekran USB, Detector, Syringe and Liquid Detector) to be within operational requirements.

16.1.3.1 General System icon is the form of a computer and should be green or yellow.

16.1.3.2 Tekran USB icon is the universal USB symbol and should be green.

16.1.3.3 Detector icon is the letter "D" with an arrow under it pointing right and should be green.

16.1.3.4 Syringe icon is a syringe plunger and should be red. The syringe function of the instrument has been disable.

16.1.3.5 Liquid Detector icon is a water drop and should not be present on the display.

16.1.3.6 If any of these icons are not the color indicated then there is an issue with the instrument and this should be investigated before the instrument is used.

16.2 Analyzing Aqueous Samples

16.2.1 Grab 60mL septa vials for each samples/batch QC in the distillation batch.

16.2.2 Label each vial with the unique LIMS sample ID.

16.2.3 Pour the prepared sample into the 60mL septa vial. Add 40µL of the 2.5% ascorbic acid to the sample, shake and let sit for 5 minutes.

16.2.4 Add 300µL of the acetate buffer and 40µL of the ethylating agent. Shake the contents and let sit for 30 minutes before analysis.

16.3 Analyzing Sediment Extractions

16.3.1 Grab 60mL septa vials for each samples/batch QC in the distillation batch.

16.3.2 Label each vial with the unique LIMS sample ID.

16.3.3 Pour the prepared sample into the 60mL septa vial. Add 300µL of the acetate buffer and 40µL of the ethylating agent to the sample, shake and let sit for 30 minutes before analysis.

16.4 Analyzing Tissue Digests

16.4.1 Grab 60mL septa vials for each samples/batch QC in the distillation batch.

16.4.2 Label each vial with the unique LIMS sample ID and dilution.

16.4.3 Add approximately 50mL of RO water to the vial.

16.4.4 Add the sample aliquot to the vial. Add 600µL of the acetate buffer and 40µL of the ethylating agent to the sample, shake and let sit for 30 minutes before analysis.

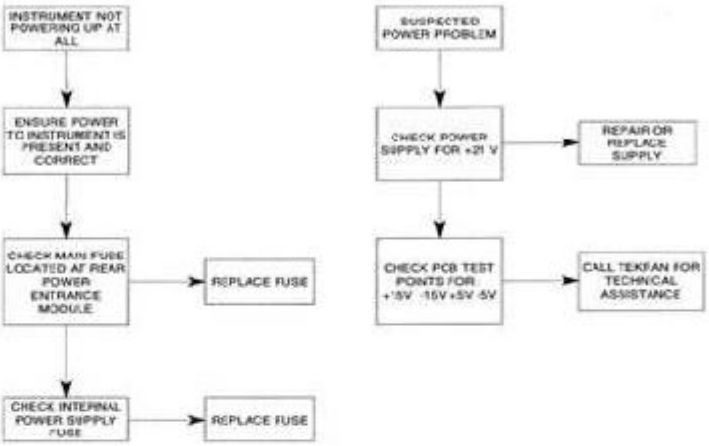
16.4.4.1 When aliquoting from the digestion it is important to take into account the volatile nature of the solution. To ensure an accurate volume pull the sample into the pipette tip multiple times until no more air is released during discharge.

16.5 Troubleshooting

16.5.1 The following is a summary of common troubleshooting techniques. This is not an all-inclusive list of what may be done to deal with analytical issues. Consultation with the group leader is preferred when performing these corrective actions. Analysts are encouraged not to rely on this guideline. Instead, this document should be used as a learning tool. Analysts should be actively striving to learn about troubleshooting as well as creative, productive ways of dealing with analytical issues.

TEKRAN

INSTPOW.ABC\TopChart



Issue	**Usually Identified by:**	**Potential resolution/investigation**
Poor calibration curve (the first time)	Poor Relative Standard Deviation (RSD) control limit >15%	-Halt analysis. Investigate. -First, determine if there was any physical reason why the curve may have failed. (i.e., poor trap connections, questionable bubbler seal, heating coil not hot enough, improper pipette techniques, fluctuations in argon flow, etc.). *-If there is one point in the curve that skews the rest of the points, rerun this point and name it SEQ-CAL6.* *-If the poor curve is not due to one standard, but to several, the curve must be reanalyzed.*
Failing CCV/CCB	*Analyte detect in CCB or* poor CCV standard recovery (Control limit: 75-125%)	-Halt analysis. Investigate. -Check all physical possibilities (see calibration failure) *-Rerun 2 replicates of failed CCB or CCV. Both must pass to continue analysis. If any fail, instrument must be recalibrated.*
Poor analytical accuracy recoveries	MS/MSD recoveries greater than 130% or lower than 65%	*-Determine if samples are qualifiable with QA flow charts (may require checking physical sample if homogeneity is a concern). Follow the Qualifier Flow Charts to see if reanalysis is necessary, or if result may be qualified.* *-Check all physical possibilities. Check calculations.* *-Rerun MS/MSD again, ideally at the same aliquot, if possible (but reserving volume for further reanalysis, if this second set fails).* -If recoveries are good, consider it good. (Most likely a physical reason that was not observed at the time and could not be noticed after the fact) -If recoveries are poor, *run an as/asd within the batch to fulfill QC requirements.*
Poor analytical precision	*Failing MD* (RPD greater than 25%)	-Determine if samples are qualifiable with QA flow charts (may require checking physical sample if homogeneity is a concern). Follow the Qualifier Flow Charts to see if reanalysis is necessary, or if result may be qualified. -If reanalysis is necessary for digests, *rerun both the parent and the duplicate digestate.* -For digestates, double-check that the correct weight information in the Calib/QC page is entered, then re-analyze. -After re-analysis, if the RPD is still poor, there is *likely* a homogeneity issue. *Run an AD (analytical duplicate) within the batch to fulfill QC requirements.*
Discrepancies between work order, bench sheet and physical samples.	Differences in #of samples or types of analysis. Unusual QC requirements	-General rule-Don't start until you know what exactly you are doing. Conflicts should be dealt with at the beginning of your analysis. -When in doubt ask, usually the project managers. They are the easiest and best way to find out what is truly going on.

17 Calculations:

17.1 Methyl Mercury in Water

17.1.1 Only *IBL* is being used to correct the peak height values from the strip chart.

17.1.2 The average calibration factor (A) is calculated using the peak height values and known concentration of methyl mercury. The calibration points are first corrected by subtraction of the IBL. Then the individual calibration point response is divided by the expected concentration of methyl mercury. The average calibration factor is determined from all calibration points and used to convert sample response to concentration.

17.1.3 Average the results for the preparation blanks (PB), from the peak heights of at least three preparation blanks.

17.1.4 To calculate methyl mercury in waters (ng/L), use the following equations.

MeHg Initial Result (ng/L) = $[[[[(\text{Peak Height})-B]/A]*D_S/E]-[[(PB)-B/A]*D_B/E]/D_S$

MeHg Final Reported Result (ng/L) = $[[(\text{MeHg Initial Result})*D*[V_f/V_i]$

Where:

B is the peak height of the *IBL*.

A is the calculated average calibration factor (in units/(ng/L)).

V_f is the final prepared volume of the sample analyzed in mL.

V_i is the initial prepared volume of the sample analyzed in mL.

D_S is the instrumental dilution of the sample compared to the volume of the calibration points.

D_B *is the instrumental dilution of the blanks compared to the volume of the calibration points.*

PB is the average *peak areas* of the preparation blanks.

If the sample is not being prep blank corrected, the $[[(PB)-B]/A]*D_B/E$ term equals 0.

E is the empirically-derived efficiency factor

17.2 Methyl Mercury in Solids:

17.2.1 To calculate methyl mercury in a solid digestion or extraction (ng/g), use the following equations:

MeHg Initial Result (ng/L) = $[[[[(\text{Peak Height})-B]/A]*D_S]-[[(PB)-B]/A]*D_B]/D_S$

MeHg Final Result (ng/g) = $[[(\text{MeHg Initial Result})*D*[V_f/V_i]$

Where:

B is the peak height of the IBL.

A is the calculated average calibration factor (in (ng/L)/units).

V_f is the final prepared volume of the sample analyzed in mL.

V_i is the initial prepared mass of the sample analyzed in mg.

D_S is the instrumental dilution of the sample compared to the volume of the calibration

points.

D_B *is the instrumental dilution of the blanks compared to the volume of the calibration points.*

PB is the average final result of the preparation blanks in ng/L.

E is the empirically-derived efficiency factor

17.2.2 To calculate methyl mercury in a solid distillation (ng/g), use the following equations:

MeHg Initial Result (ng/L) = [[[[(Peak Height)-B]/A]*D_S/E]-[[(PB)-B/A]*D_B/E]/D_S

MeHg Final Result (ng/g) = [[(MeHg Initial Result)*D*[V_f/V_i]

Where:

B is the average bubbler blank peak height or peak area.

A is the calculated average calibration factor (in (ng/L)/units).

V_f is the final prepared volume of the sample analyzed in mL.

V_i is the initial prepared mass of the sample analyzed in mg.

D_S is the instrumental dilution of the sample compared to the volume of the calibration points.

D_B *is the instrumental dilution of the blanks compared to the volume of the calibration points.*

PB is the average final result of the preparation blanks in ng/L.

E is the empirically-derived efficiency factor

18 Statistical Information/Method Performance:

18.1 The Method Detection Limit (MDL) is determined according to 40 CFR Part 136 Section B and *EFQA-Q-QD-SOP10098.*

18.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as the lowest calibration point which must have a recovery between 65-135%. The PQL is determined by running ten replicate samples with a concentration that will produce a recovery of 65-135%. When possible the same samples from section 18.1 are used to generate this data. The PQL is referred to as the Method Reporting Limit (MRL) in LIMS.

18.3 Using clean handling and reagents low in mercury, the following LOD and PQL levels are attainable:

18.3.1 For distilled waters (*EFAFS-T-AFS-SOP2797*): PQL is 0.050 ng/L, LOD is 0.26 ng/L

18.3.2 For extracted sediments (*EFAFS-T-AFS-SOP5134*): PQL is 0.050 ng/g, LOD is 0.15 ng/g

18.3.3 For digested tissues (*EFAFS-T-AFS-SOP2986*): PQL is 2.00 ng/g, LOD is 0.50 ng/g

18.4 Current LODs and PQLs are stored at: *\\tacorp\Corp\QA\QA_Facilities\Seattle-QA\EFGS-QA\Method-Limits-MDLs-IDLs.*

18.5 The method detection limit (MDL) listed in Table 1 in method EPA 1630 and the quality control acceptance criteria listed in Table 2 in EPA 1630 were validated in four laboratories. In addition, the techniques in this method have been inter-compared with

other techniques for low-level CH3Hg determination in water in the International Mercury Speciation Inter-comparison Exercise (reference 15 in EPA 1630, this SOP 2.10).

18.6 Eurofins Frontier has been participating in inter-comparison studies when available, since there are no proficiency studies available for methyl mercury analysis.

19 Quality Assurance/Quality Control:

19.1 An analytical batch is defined as 20 or fewer client samples. QC samples such as: BLKs, BS/BSD, ICV, ICB, CCVs, CCBs, or matrix QC (MD, MS, or MSD) are excluded.

19.2 One CCV/CCB must be performed every 10 analytical runs.

19.3 One MS/MSD pair must be analyzed for every 10 samples. For a batch up to 20, two sets of MS/MSDs must be analyzed. MS/MSDs are spiked according to the work order instructions or the default spiking level. Samples are spiked by lab assistants during preparation, not by analysts. The true value of spikes will change if a smaller sample mass is digested.

19.3.1 For aqueous samples, the general MS/MSD spiking level is 0.045 ng of methyl mercury into 45 mL of sample (1.0 ng/L). Client samples can be spiked at higher or lower concentrations depending on historical data, specified by the Project Manager or Senior Analyst.

19.3.2 For soil/sediment samples, the default spiking level is 2.5 ng of methyl mercury into 0.5 g of sample (5.0 ng/g).

19.3.3 For tissue samples, the default spiking level is 20 ng of methyl mercury into 0.250 g of sample (80 ng/g).

19.4 A matrix duplicate (MD) is prepared with each batch. Upon request, a matrix triplicate (MT) may be performed. MD and MT samples should be analyzed using the same sample aliquots as the ambient sample. The MSD may serve as the MD.

19.5 One matrix specific CRM must be performed in duplicate with each batch (BS/BSD in LIMS).

19.5.1 Due to the lack of a CRM for methyl mercury in water, one BS/BSD must be analyzed per analytical batch. The spiking levels may vary depending upon the client, and will be performed during preparation. Refer to work order, project managers, senior analyst, or group leader for specific spiking levels. The default spike addition for BS/BSD is 0.045 ng of methyl mercury into 45mL of reagent water (1.0ng/L). The BS/BSD goes through the same sample preparation procedure as the samples.

19.6 Three preparation blanks must be performed with each batch.

19.7 At the end of the analytical day, a CCV (OPR) standard and a CCB must be analyzed.

19.8 Analysts are to verify QC sample results in “real-time” as they come off the instrument. This allows for correction of any analytical problems immediately.

19.9 Results that fall out of acceptable criteria range may be qualified using the flowcharts in *EFQA-P-DR-SOP2801* (data review).

19.10 In most cases, the acceptance criteria listed below must be met in order for a data set to be considered valid. Of particular importance to the client is Eurofins Frontier’s position that a single non-compliant result on a QC sample does not automatically invalidate a

data set. Data points initially noted on the analysis day's spreadsheet as invalid for known reasons may be discarded if a rerun is performed during the same analysis day.

19.11 Quality Control Limits for Determination of Methyl Hg

QC Item	EFGS Acceptance Criteria*	Different from EPA Method 1630 Criteria
Calibration Factor RSD	</=15%	
Low Standard Recovery	65-135% recovery	
ICV/CCV/OPR (0.5 ng/L)	67-133% recovery	No CCV required
MD	One MD required per analytical day, ≤ 35 RPD	No MD required
MS/MSD	Water: 65-130% recovery with RPD ≤ 35 Tissue: 65-130% Rec. RPD ≤ 35 Sediment: 65-130% Rec. RPD ≤ 35 Frequency of one MS/MSD per 10 samples or per client request	
Blank Spikes and Digested CRM (QCS) (BS/BSD)	Water 70-130% Rec. RPD ≤ 25 Tissue LCS/LCSD 70-130% Rec. RPD ≤ 25 Sediment LCS/LCSD 70-130% RPD ≤ 25	Ongoing Precision and Recovery Standard required at the beginning and end of each run, 67-133% recovery 1 BS only per 1630
ICB (Ethylation Blanks) The value is used to blank correct the standard curve.	< PQL	A single Ethylation Blank is analyzed with each analytical run.
CCB (Ethylation Blanks) are required after each CCV and OPR.	< PQL	CCBs not required
Preparation Blanks (see below for DoD requirements)	Minimum of 3. Mean less <0.045 ng/L Standard deviation <0.015 ng/L Other matrices individually less < PQL	

19.12 For DoD samples, the method blank will be considered to be contaminated if:

19.12.1 The concentration of any target analyte in the blank exceeds 1/2 the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);

19.12.2 The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or

19.12.3 The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

19.12.3.1 If the 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.

19.13 Initial precision and recovery (IPR) – to establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.

19.13.1 Analyze four replicates of at 0.5 ng/L.

19.13.2 Using the results of the set of four analyses, compute the average percent recovery (X), and the standard deviation of the percent recovery (s) for CH3Hg.

19.13.3 It the average percent recovery is within 69-131% and the standard deviation is less than 31%, the IPR is acceptable. This IPR is equal to the IDOC that is required per TNI standards

20 Corrective Action:

20.1 The quality control data gathered throughout the analytical day provides an indication of overall data quality. Therefore, corrective action is required if quality assurance measures are outside of acceptable limits. First, a careful re-examination of the data entry and calculations is performed to assure that there are no numerical errors. The project manager is informed of the data issue. The analyst will decide what corrective action, including reruns, is warranted. The analyst is responsible for creating re-extracts in LIMS and alerting the Group Leader that reanalysis is necessary. The Quality Assurance Officer has the final say in what corrective action is to be performed.

20.2 If insufficient sample volume remains to repeat analysis for samples analyzed after the last acceptable CCV/OPR, provide a narrative explanation in the work order (in the MMO section) and/or on the data review checklist. Estimated values must be flagged in LIMS and in the report to the client.

20.3 The above corrective actions apply only to events which have unknown causes. If the analyst is aware of the cause, no corrective action is necessary other than reanalyzing the sample and documenting appropriately.

20.4 If an MS/MSD fails, an AS/ASD should be analyzed, if possible. The AS/ASD should be spiked 1 to 5 times the ambient concentration.

20.5 If an MD/MT fails, and the sample concentration is greater than 5 times the PQL and the difference is less than 1 times the ambient sample and the duplicate should be reanalyzed for confirmation, if possible. The undigested sample should be inspected for

heterogeneity, and a note made in the work order (MMO) and/or data review checklist. A poor RPD may be qualified according to the Data Qualifier Flowcharts included in *EFQA-P-DR-SOP2801* (data review).

20.6 Continuing Calibration Verification (CCV): if a recovery falls outside acceptance criteria, re-calibrate the instrument and reanalyze all affected samples since the last acceptable CCV or immediately analyze two additional CCVs. If both CCVs are within acceptance criteria, the samples may be reported without reanalysis and the analysis of the next bracket may continue beginning with a CCB.

20.6.1 If either of the two CCVs fails, the analysis must be terminated, the problem resolved, the instrument re-calibrated and then all of the affected samples since the last acceptable CCV reanalyzed.

21 List of Attachments:

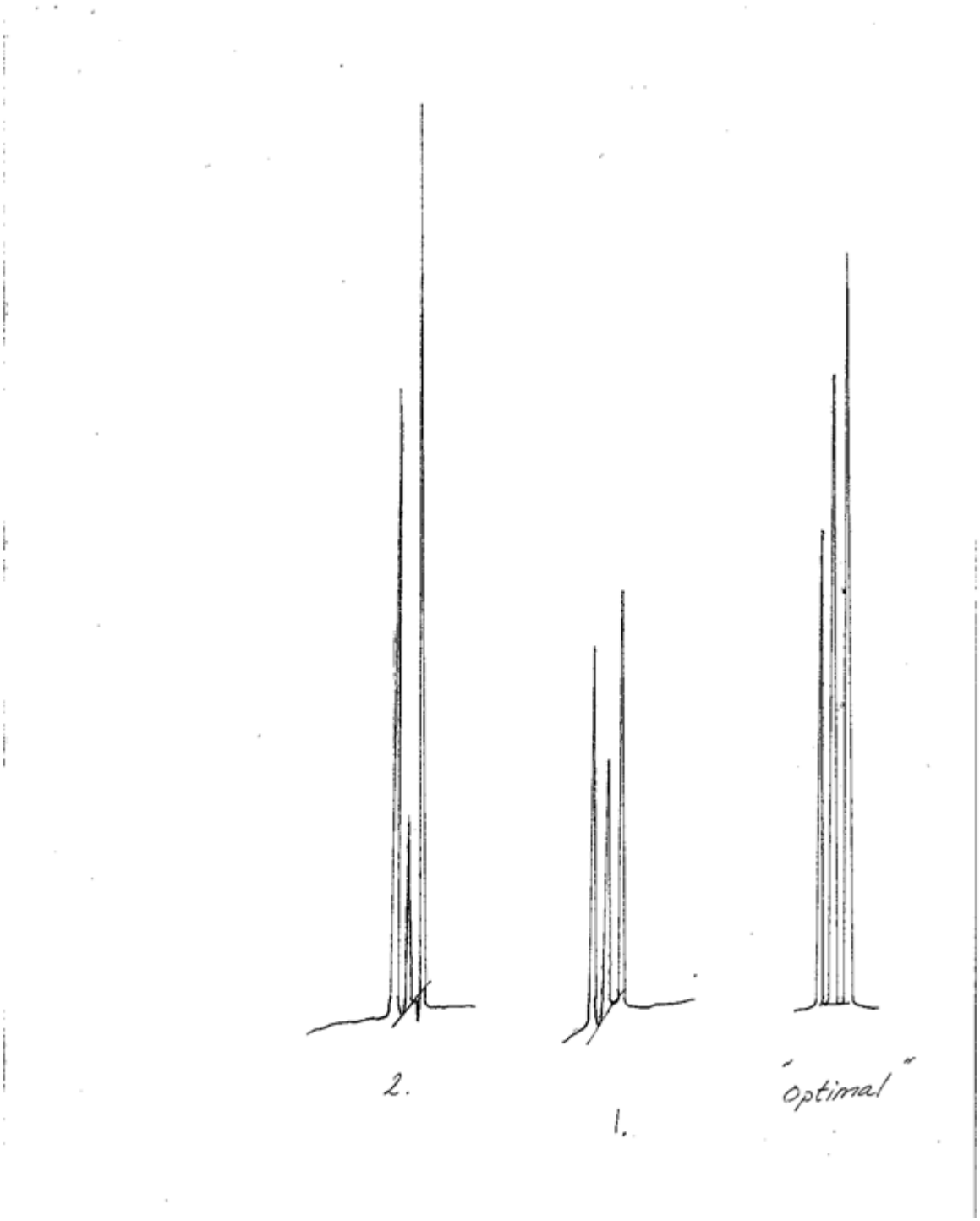
Appendix A: Illustration of Peak Shapes

Appendix B: Example - CV-GC-AFS Instrument Maintenance Log

Appendix C: Determination of Ethyl Mercury

Appendix A

Illustration of Peak Shapes



Appendix B

Example – CV-GS-AFS Instrument Maintenance Log

Date		1)	2)	3)	4)	5)	6)	7)
Analyst								
Check lamp (note voltage)								
Adjust lamp (note voltage)								
Optimized lamp								
KOH cleaned bubbler								
Removed trap (note trap #)								
Trap set								
Ar flow (at wall)								
Ar flow through instrument								
Shut down procedure								
1)								
2)								
3)								
4)								
5)								
6)								
7)								

Appendix C
Determination of Ethyl Mercury

1 Purpose

1.1 To outline the standard, reagent and procedural differences needed in EFAFS-T-AFS-SOP2808 to adapt the procedure to the analysis of water samples for ethyl mercury. Due to the high concentration of mercury in these samples, the samples are not distilled prior to analysis. The minimum dilution on these samples is 500-fold.

2 Apparatus and Equipment:

2.1 Program ETF for Tekran 2700: For ethyl mercury analysis, the program ETF used for this analysis is "psample15" supplied by the instrument manufacturer.

3 Reagents and Standards:

3.1 Propylating Agent: Sodium Tetrapropylborate (Made with the same process as the ethylating agent).

3.1.1 Vendor is Ryan Scientific Inc

3.2 Primary Standard: Ethyl Hg (5.0585 µg/g of C2H5Hg) or 4.4184 µg/g as Hg

3.2.1 Vendor is Applied Isotope Technologies, Inc (PN-30017.A1)

3.3 Calibration Standards: Two different level of standards are used for the calibration

3.3.1 High level standard is a 2500x of the parent source (Cal3 is 20µL in 50mL, Cal4 is 50µL in 50mL and Cal5 is 200µL in 50mL)

3.3.2 Low Level standard is a 50x of the High level Standard (Cal1 is 200µL in 50mL and Cal2 is 400µL in 50mL)

4 Procedure

4.1 Follow EFAFS-T-AFS-SOP2808 with the following modifications

4.1.1 Propylating agent is used instead of ethylating agent. When it's necessary to switch from one agent to another, a reverse purging of the sample line and probe is recommended to ensure the previous agent is removed from the system.

4.1.2 Calibration of the instrument is described in section 3.3.

4.1.3 There is no secondary standard for ethyl mercury, so the primary is used for CCVs. Ethyl mercury is present in the MHg-ICV standard, so CCVs for each analyte are analyzed separately.

4.1.4 A retention time study was performed on three different calibrations on three different days. The retention time window calculated for ethyl mercury from this study is 199 to 266 seconds. This retention window needs to be applied to the ethyl mercury analysis.

4.1.5 MS/MSDs can be spiked with MHg and EHg standards.

5 Calculations

5.1 The standard MHg analysis calculations apply to these samples. Since the samples are not distilled, an efficiency factor is not applied.

5.2 The recovery limits established for MHg are applied to this analysis.

Version history

Version	Approval	Revision information
6	30.OCT.2015	
7	20.MAY.2016	
7.1	31.JAN.2017	
8	3.NOV.2020	

STANDARD OPERATING PROCEDURE L-2C: DETERMINATION OF TOTAL MERCURY IN VARIOUS MATRICES BY FI-AFS

eurofins	Always check on-line for validity.	Level: Standard Operating Procedure
Document number: **EFGS-T-AFS-SOP2822**	**Determination of Total Mercury in Various Matrices by FI-AFS**	
Old Reference: **FGS-121**		
Version: **7.3**		Organisation level: **4-Business Unit**
Approved by: **FH5J, GW2R** Effective Date: **12-MAY-2023**	Document users: **EFGS_AFS, EFGS_S-and-R Element, EFGS_TraceMetal**	Responsible: **EFGS_SMM**

1) Revision Log:

Revision: 7.2D	**Effective Date:** This version	
Section	**Justification**	**Changes**
16.3.2	Required	Corrected preservation time for aqueous samples

2) Reference:

2.1 EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, 2002.

2.2 Method 1669, "Method for Sampling Ambient Water for Determination of Metals at EPA Ambient Criteria Levels," U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303), 401 M Street SW, Washington, DC 20460, April 1995 with January 1996 revisions.

2.3 Bloom, N.S.; Ultra-Clean Sample Handling, Environmental Lab 1995, March/April, 20.

2.4 Bloom, N.S.; Horvat M., and Watras C.J. Results of the International Mercury Speciation Intercomparison Exercise. Wat. Air Soil Pollut. 1995, 80, 1257.

2.5 Bloom, N.S.; Crecelius, E.A. Determination of Mercury in Seawater at Sub-nanogram per Liter Levels.Mar.Chem.1983, 14, 49.

2.6 Bloom, N.S.; Crecelius, E.A. Distribution of Silver, Lead, Mercury, Copper, and Cadmium in Central Puget Sound Sediments Mar. Chem 1987, 21, 377-390.

2.7 Bloom, N.S.; Fitzgerald, W.F. Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection. Anal. Chem. Acta. 1988, 208, 151.

2.8 Cossa, D.; Couran, P. An International Intercomparison Exercise for Total Mercury in Seawater. App.Organomet. Chem.1990, 4, 49.

2.9 Fitzgerald, W.F.; Gill, G.A. Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis. Anal. Chem. 1979, 15, 1714.

2.10 Gill, G.A.; Fitzgerald, W.F. Mercury Sampling of Open Ocean Waters at the Picogram Level Deep Sea Res.1985, 32, 287.

2.11 Chapter NR 149, Lab Certification and Registration, Wisconsin Administrative Code.

2.12 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.13 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019.

3) Cross Reference:

Document	Document Title
EFGS-Q-QM-QM5805	QA Manual
CA-Q-S-006	Detection and Quantitation Limits
EFGS-Q-QD-SOP2710	Class 1 Weight Calibration, Balance Verification, Calibration & Maintenance
EFGS-Q-QD-SOP41510	Volumetric Verification and Pipette and Dispenser Operation & Maintenance
EFGS-S-SB-SOP5139	Cleaning of Sampling Equipment and Bottles
EFGS-S-CS-SOP2794	Ultra-Clean Aqueous Sample Collection
EFGS-T-TM-SOP2839	Stock and Prepared Standards
EFGS-T-AFS-SOP2985	Digestion of Gas/Air Samples Collected on FSTM Traps
EFGS-T-AFS-SOP2800	Digestion of KCL Traps for Total Mercury
EFGS-T-AFS-SOP2795	Digestion of Tissues for Total Mercury Analysis Using Nitric and Sulfuric Acids (70:30)
EFGS-P-DR-SOP2801	Data Review and Validation and Monthly Logbooks Reviews
EFGS-T-TM-SOP2837	Total Recoverable Metals Digestion for Animal or Plant Tissues
EFGS-T-AFS-SOP2807	Preparation of Solid Samples for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion
EFGS-S-HS-SOP2991	Waste Disposal Procedures for Client Sample Waste
EFGS-T-TM-SOP2821	HF/HNO3/HCl Bomb Digestion of Sediments, Soils, Rocks, and Bayer Process Solids and Slurries for Mercury, followed by Repeated HNO3 Evaporation

4) Purpose:

4.1 This standard operating procedure (SOP) describes a method for the determination of total mercury (Hg) in a wide range of matrices including, but not limited to, aqueous, biological, and geological media. Total mercury is measured by Flow Injection Atomic Fluorescence Spectrometry and is calculated on a concentration (ppt) basis by comparing the instrument response of samples to the instrument response of standards.

4.2 This SOP is designed to ensure that reproducible traceable procedures are followed in the standardization of the total mercury analyzers and in the analysis of samples for total mercury, as well as to establish the limits wherein data will be considered acceptable.

5) Scope:

5.1 This method is designed for the determination of mercury in the typical range of 0.5-80 ng/L (ppt). Samples with mercury concentrations outside the designated calibration range can only be analyzed at a dilution.

5.2 This SOP describes a method of the determination of mercury species in aqueous and solid matrices (biological tissue, plant tissue, nutraceutical, etc.).

6) Basic Principles:

6.1 Total mercury analyses are split into two categories: waters and solids. For analysis of aqueous samples, a dilution (up to 1x) of oxidized sample is added to a 50mL vial. If less than 30mL of sample is used, the sample is diluted to a final volume of at least 30mL with 1% BrCl. For solids, a appropriate dilution (based on specific preparation method) is made of the digested sample by pipetting into a 50mL vial and diluting it to 50mL with 1% BrCl. In the case of waters and solids, the final volume is neutralized with 50 uL of 25% hydroxylamine-hydrochloride (NH2OH-HCl). Approximately 20mL of sample is aspirated by an auto sampler (Please refer to Figure 1 for a detailed system flow diagram of the Tekran 2600 analysis system). This sample is then mixed with 3% stannous chloride ($SnCl_2$) which reduces Hg^{2+} ions to Hg^0 before introduced to the top of a phase separator.

6.2 As sample travels down the phase separator, Hg^0 is liberated by a counter-current flow of ultra-pure argon (or nitrogen). This mercury then travels through a soda-lime acid vapor trap and a switching valve (V2) and amalgamates onto the fixed gold quartz trap. Following primary amalgamation, V2 is triggered which switches on the flow of pure argon through the sample trap. At the same time, the gold quartz trap is heated and mercury is released into the pure argon gas stream. The mercury passes through a second switching valve (V1) and amalgamates onto a pure gold "analytical trap." The analytical trap is then heated and V1 is switched, which introduces the mercury into the AFS detector. All event timing and peak integration is carried out via a PC running TekMDS-2 software running the EPA 1631 "Sample" event timing file (ETF).

(NOTE: This method may also be run using 15ml vials and selecting the appropriate ETF with in the TekMDS-2 software. Sample must fill the vial up to the 15ml mark. All other procedures, reagent concentrations, and dilutions should be kept the same.)

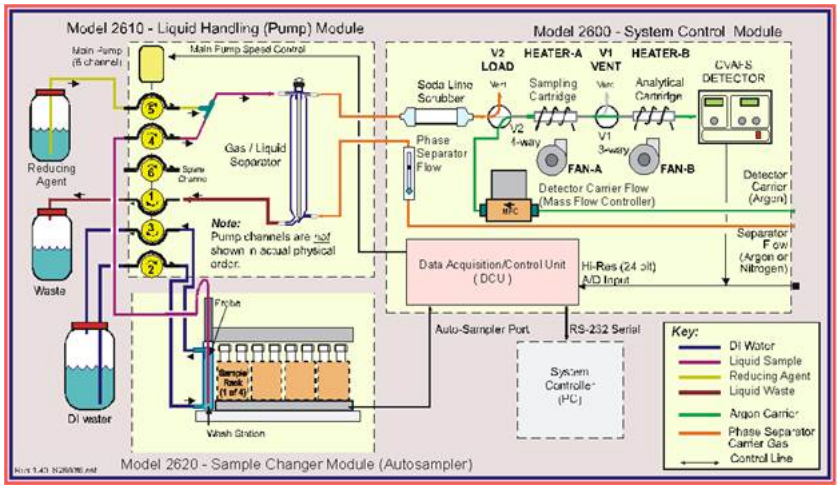


Figure 1 - Tekran 2600 Flow Diagram

7) Reference Modifications:
7.1 There were no significant modifications made to this method.

8) Definitions:
8.1 Analytical Duplicate (AD): A representative sample (that yielded a result within the calibration curve) is analyzed a second time during the analytical run. The second analysis should be at the same aliquot as the original.

8.2 Analytical Run – The continuous analysis of one or more batches during the same 12 hour-shift. Each analytical day requires 3 IBLs (instrument blank levels), a minimum five-point calibration curve, ICV, and CCV/CCB every ten sample injections following the initial calibration. An analytical day must conclude with a CCV/CCB. An analytical run may conclude with a CCVH and CCB.

8.3 Analytical Spike and Analytical Spike Duplicate (AS/ASD): A representative sample is selected and spiked, with a dilution of the primary source, during the analytical run, at a target concentration of 1-5X the ambient concentration of the sample. These QC samples are used to indicate sample matrix effects on the analyte of interest. Non-detectable samples are spiked at 5x the MRL/PQL.

8.4 Batch: 20 client samples or less grouped for preparation. See Quality Assurance Section for batch requirements.

8.5 Calibration Standards (CAL) – a series of non-zero standards that will be used to calibrate the instrument, made from a primary source stock standard. Three calibration blanks plus at least five different concentrations are required, beginning with one at PQL concentration or lower.

8.6 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.7 Continuing Calibration Verification (CCV): A dilution of the OPR standard resulting in an instrumental concentration of 5.0ng/L. This standard is analyzed every 10 analyses after the ICV, and determines whether the instrument is maintaining calibration.

8.8 Continuing Demonstration of Capability (CDOC): Acceptable performance on a PT sample or a new IDOC or a set of four (4) consecutive blank spike or laboratory control sample aliquots [prepared according to a method by an analyst or technician that are analyzed by the same or different analyst or technician according to a method] that meet established and documented criteria for precision and accuracy to assess the ongoing proficiency of the analysts or technicians.

8.9 Control Limit (CL) – the limit of the range of acceptability for the quality control samples

8.10 Equipment Blank (EB): Reagent water processed through the sampling devices and placed in a sample container prior to using the equipment to collect samples and used to demonstrate that the sampling equipment is free from contamination.

8.11 Field Blanks (FB): A sample of reagent water placed in a sample container in the field and used to demonstrate that samples have not been contaminated by sample collection or transport activities. EPA-1631E recommends the analysis of at least one field blank per 10 samples collected at the same site at the same time. It is recommended to analyze these blanks before analyzing the client samples in the batch.

8.12 Initial Calibration Verification (ICV) –A dilution of the OPR standard resulting in an instrumental concentration of 5.0 ng/L. This standard is run immediately following the calibration curve and verifies instrument calibration.

8.13 Initial Precision and Recovery (IPR) – A dilution or digestion of a secondary source resulting in an instrumental concentration of 5.0 ng/L mercury.

8.14 Instrument Blank Level and Continuing Calibration Blank (IBL and CCB) for evaluation of instrument drift, sensitivity and contamination. At least 3 IBLs must be analyzed before the first calibration standard, and

the CCBs every 10 samples immediately after CCVs.

8.15 Initial Demonstration of Capability (IDOC): A set of four (4) blank spike or laboratory control sample aliquots prepared according to a method by an analyst or technician at the concentration specified by the group manager (or if unspecified, to a concentration of one (1) to four (4) times the limit of quantitation) that are analyzed by the same or a different analyst or technician according to a method. The mean and standard deviation of the four results are calculated and compared to established and documented criteria for precision and accuracy to assess the initial proficiency of the analysts or technicians before they independently process client samples.

8.16 Laboratory Control Sample (LCS and LCSD) or Quality Control Sample (QCS): A sample (and duplicate) containing a known concentration of mercury that is used to monitor complete method performance. The preferred LCS is a matrix matched Certified Reference Material (CRM), but a blank spike meets the requirement also. In LIMS, the LCS is always referred to as a Blank Spike (BS), whether it is matrix matched or not.

8.17 Limit of Detection (LOD) – The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%. The LOD shall be at least 2 times but no greater than 4 times the DL for multiple analyte methods or 2 times but no greater than 3 times the DL for single analyte methods.

8.18 Limit of Quantitation (LOQ) – equal to PQL (practical quantitation limit) or reporting limit (RL) and verified on a quarterly basis by spiking at or below the LOQ and showing a recovery within method specified control limits for laboratory control samples.

8.19 LIMS: Laboratory Information Management System. Computer software used for managing samples, standards, and other laboratory functions.

8.20 May: This action, activity, or procedural step is optional.

8.21 May Not: This action, activity, or procedural step is prohibited.

8.22 Matrix Spike (MS) and Matrix Spike Duplicate (MSD): A representative sample is selected and spiked with a dilution of the primary source at a known concentration. The MS and MSD are run through the entire analytical process just as the samples are. These QC samples will indicate sample matrix effects on the analyte of interest.

8.23 Method Blank (MB)=): For waters, reagent water that is prepared and analyzed in a manner identical to that of samples. For digested solids, preparations blanks consist of the same reagents used to digest the samples, in the same volume or proportion and are carried through the complete sample preparation and analytical procedure. Boiling chips are used as a blank matrix for solids. Preparation blanks are referred to as BLK in LIMS.

8.24 Method Detection Limit (MDL): A limit derived from 40 CFR, Part 136, Appendix B. This method produces a defined value that is the minimum concentration that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.25 Method Duplicates/Method Triplicates (MD/MT): A second or third separate sample dilution, taken from the same source sample, prepared and analyzed in the laboratory separately.

8.26 Reagent water: 18 MΩ minimum, reagent water starting from a pre-purified (distilled, Reverse Osmosis, etc.) source.

8.27 Must: This action, activity, or procedural step is required.

8.28 Ongoing Precision and Recovery (OPR): A dilution of a secondary source resulting in an instrumental concentration of 5.0 ng/L mercury.

8.29 PM: Project Manager.

8.30 Primary Source: The stock standard used to make the calibration standard. Procedural Method: A method where standards and samples are run through the analytical procedure exactly the same. By NELAC definition, this SOP is a procedural method.

8.31 Secondary Source: The stock standard used to make the OPR standard

8.32 Shall: This action, activity, or procedure is required.

8.33 Should: This action, activity, or procedure is suggested, but not required.

8.34 Stock Standard Solution (SSS) – a standard of analyte that is purchased from a certified source for the preparation of working standards.

8.35 Total mercury: As defined by this method, all bromine monochloride-oxidizable mercury forms and species found in aqueous solutions. This includes, but is not limited to, Hg2+, Hg0, strongly organo-complexed Hg(II) compounds, adsorbed particulate Hg(P), and several tested covalently bound organomercurials (i.e. CH3HgCl, (CH3)2Hg, and C6H5HgOOCCH3). The recovery of mercury bound within microbial cells may require additional preparation steps (i.e. UV oxidation, or oven digestion).

8.36 Travel or Trip Blank (TB): A sample of reagent water placed in a sample container in the laboratory and used to demonstrate that samples have not been contaminated by transport activities.

8.37 Wash Station Blank (WSB) – a "blank" that is aspirated from the instrument rinse station (0.5% BrCl). At least three WSBs are used at the beginning of analysis to assess overall cleanliness of the system/reagents. WSBs may also be used mid-run to flush the system after running a high level sample, or check the mercury levels in the wash station.

8.38 High Calibration Verification (CCVH) – At the conclusion of an analytical run, a high calibration verification (CCVH) may be analyzed and must be followed by a CCB. If this CCVH recovers within the limits set for standard CCVs, the calibration range of the instrument may be extended to the concentration of the CCVH. Any sample following a sample whose concentration is between the top calibration point and CCVH may only be reported if their concentration is below the reporting limit or 10 times greater than the concentration of the CCB that followed the CCVH.

9) Interferences:

9.1 Due to high levels of acid and halogens (i.e. bromide) in digested solids, it is recommended that these digestates be analyzed at a 10x dilution or higher.

9.2 Improperly adjusted pump tubing can cause the phase separator to fill with sample. In extreme situations, the overflow can back up into instrument causing damage to the traps and switching valves. Care must be taken to insure the pump tubing tension is properly set. DO NOT OVER TIGHTEN**.**

9.3 The minimum digestate dilution that should be analyzed if HF acid, FSTM material, or coal is present in significant concentrations is a 50x dilution. Samples prepared according to *EFGS-T-TM-SOP2821* are diluted before analysis, therefore a 10x dilution is the minimum.

9.4 Water vapor has the potential to create recovery interferences. To prevent interference from water, ensure that soda-lime pre-traps and gold traps remain dry.

9.5 The presence of high concentrations of silver and/or gold can cause SnCl2 to precipitate out of solution and adhere to the tubing and/or phase separator walls. High concentrations of these metals can sometimes be found in the matrix spike samples from the digestion sets that are shared with the trace metals group.

9.6 Analysis of samples containing high concentrations of strong acids (>2%) can cause passivation of the sample trap and lead to low bias/recoveries. When analyzing samples containing >2% strong acid (at the instrument), the analyst should verify that passivation is not an issue by running a Hg spike into MQ water containing a similar concentration of acid. If the spike recovers low (<90%) passivation may be an issue and the sample may need to be diluted.

9.7 If elemental Hg is spilled in the facility, contamination can occur to all uncapped reagents and those not stored in gas-impermeable containers. See Appendix 1 for instructions on analysis post elemental Hg spill.

10) Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to the Chemical Hygiene Plan (*EFGS-S-HS-12066*). This includes, but is not limited to, laboratory coat, eye protection and protective gloves.

10.2 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Chemists should refer to the SDS (Safety Data Sheets) located at https://msdsmanagement.msdsonline.com/company/5c1df5b3-747d-4789-8104-42457dc3a3e5/ for each chemical they are working with.

10.2.1 Note: Use particular caution when preparing and using BrCl, as it releases extremely irritating, corrosive fumes similar in effect to free chlorine. Always handle this reagent in an approved fume hood.

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Eurofins Frontier will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 Hydrochloric acid: Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer). Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering. For more information see SDS.

10.5 See Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.6 Pollution prevention information can be found in the current Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.7 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to SOP *EFGS-S-HS-SOP2991* "Waste Disposal Procedure for Client Sample Waste," which provides instruction on dealing with laboratory and client waste

11) Personnel Training and Qualifications:

11.1 An analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source before being qualified to analyze samples without supervision. Continuing DOC will be maintained and monitored via performance on CRMs and other QC samples, as well as obtaining acceptable results on proficiency testing exercises.

11.2 The analyst/laboratory technician must have read this SOP and other relevant SOPs and have the training documented on the applicable form(s). The analysis may be questioned on SOP by supervisor(s) and/or trainers.

11.3 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.4 All employees must read the Quality Manual (*EFGS-Q-QM-QM5805*) and complete annual Ethics training.

11.5 All training documents including IDOCs, CDOCs, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employees training file for ten years after the employee is no longer working for Eurofins Frontier Global Sciences.

11.6 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous goods, are stored by the Health and Safety Officer for ten years after the employee is no longer working for Eurofins Frontier Global Sciences.

12) Sample Collection, Preservation, and Handling:

12.1 Aqueous samples are collected in rigorously cleaned fluoropolymer (e.g. Teflon) bottles and caps (as described in *EFGS-S-SB-SOP5139* "Cleaning of Sampling Equipment and Bottles for Mercury Analysis"). Certified clean glass bottles with fluoropolymer lids may be used if mercury is the only analyte of interest.

12.1.1 Aqueous samples are preserved upon receipt with 0.2N BrCl that has tested low in mercury. Samples are typically preserved to 2% BrCl v/v, but may require further oxidation due to high levels of organic matter or mercury. Refer to *EFGS-T-AFS-SOP2992* "Mercury in Water by Oxidation".

12.2 Solid samples may be collected in glass, high density polyethylene, or fluoropolymer jars.

12.2.1 Solid samples are preserved by freezing upon receipt.

12.3 Impinger solutions preserved with nitric acid or containing potassium permangante (this category includes proficiency testing samples) need to be preserved with BrCl to insure the complete oxidation of organic species.

12.4 All samples should be collected utilizing clean techniques, so as not to cross-contaminate samples with mercury. See *EFGS-S-CS-SOP2794* "Ultra Clean Aqueous Sample Collection" and EPA Method 1669 for aqueous sample techniques.

13) Apparatus and Equipment:

13.1 LIMS – TALS; Computer – Windows 7, 8, or 10

13.2 Tekran TekMDS-2 software (see instrument software log *EFGS-S-IT-WI17061*).

13.3 Tekran Model 2600 System Control Module. This module contains dual stage pre-concentration/desorption units, a high resolution analogue to digital converter, and a high sensitivity AFS Detector (IDL<1pg).

13.4 Tekran Model 2610 Pump Unit. This module contains a precision 6 channel peristaltic pump with optical speed feedback. Speed may be varied manually or under computer control. The pump head has three four-roller channels to providing high pumping rates for wash station circulation and waste removal, and three eight-roller channels to providing slower/low pulse delivery of $SnCl_2$ and sample (one extra channel).

13.5 Model 2620 Auto-Sampler – a specially modified Gilson Model 223 auto-sampler, includes reticulating wash station and allows for automatic sample handling with the 2600 analysis system.

13.6 50mL polypropylene vials with screw caps, manufactured by CPI International (Item No: 4092-450MP). Equivalent pre-cleaned and/or tested vials, graduated (class A) to 50mL may also be used.

13.7 Three-stop tubing, various inner diameters of Marprene for $SnCl_2$ (1.02mm), for wash station fill (2.38mm), wash station drain (2.79mm), and phase separator drain (2.79mm) Three-stop silicone tubing (2.05mm) is used for sample feed.

13.8 Teflon Fittings and FEP tubing (1/16" ID) of various sizes and lengths. This tubing is used for the sample probe, $SnCl_2$, phase separator, wash station, drain lines, and between gold traps.

13.9 Soda-Lime trap. This is a 14cm long, 1.1cm diameter glass tube filled with reagent grade, non-indicating 8-14 mesh soda-lime ($Ca(OH)_2$+NaOH) aggregates packed between portions of silanized glass wool. This trap is purged of mercury using a ultra-pure argon gas stream for at least 20 minutes. After purging, the trap is installed and the system rinsed with 3% $SnCl_2$ reductant and 0.5% BrCl wash station for approximately 5 minutes.

13.10 Phase separator – manufactured by Tekran. The phase separator facilitates laminar fluid flow of liquid sample over a frosted rod counter-current to a stream of ultra-pure argon gas at approximately 400mL/min.

13.11 Gold-Coated Quartz Sand Trap ("sample trap") – manufactured by Tekran or made in house, heated from 0% to 100%, 8 Amp maximum.

13.12 Pure Gold Bead Trap ("analytical trap") – manufactured by Tekran, heated from 0% to 100%, 8 Amp maximum.

13.13 Pipettes: Calibrated variable pipettes with a range of 5 µL – 10 mL. These are used to make solutions and sample dilutions. Pipettes are to be calibrated weekly according to SOP *EFGS-Q-QD-SOP41510* or daily if DOD samples are analyzed.

13.14 Analytical Balance – capable of accurately weighing to the nearest 0.1mg, and able to tare at least one gram. The analytical balances are verified for accuracy on a daily basis according to *EFGS-Q-QD-SOP2710*, "Balance Verification, Calibration and Maintenance.

14) Reagents and Standards:

14.1 Reagent Water: 18-MΩ ultra pure deionized water starting from a pre-purified (distilled, reverse osmosis, etc.) source is used. To remove any remaining trace metals and organics, an activated carbon cartridge is placed between the final ion exchange bed and the 0.2-µm filter. Reagent water used in the mercury lab is checked weekly for total mercury concentrations, and must test below 0.25ng/L.

14.2 Concentrated (36-38% weight basis) Trace-Metal Grade Hydrochloric Acid (HCl): This HCl is lot-tested (analyzed like a water sample) at an 100x dilution. This reagent must test below 0.25ng/L. Do not prep blank correct.

14.3 Concentrated (69%-70% weight basis) Trace-Metal Grade Nitric Acid (HNO_3): Trace metal purified reagent-grade nitric acid is pre-analyzed and lot sequestered. Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent should be from a lot number that has been previously tested to be low for the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to the same as the manufacturer's expiration date.

14.3.1 Nitric Acid, 5%

14.3.1.1 Rinse bottle labelled:
Metals Rinse, 5% HNO3
To be used for CV-AFS (THg only) and ICPMS preps/analysis.

14.4 0.2N Bromine Monochloride (BrCl):

14.4.1 2.5 L of concentrated trace-metal grade HCl (14.2) is added to a 2.5 L glass jug. To this, 27 g of KBr is added and the bottle is inverted. The solution then sits overnight allowing for the KBr to be dissolved .

14.4.2 38 g of $KBrO_3$ (certified to be low in Hg) is slowly added to the acid. When all of the $KBrO_3$ is added, the solution should go from yellow to red to orange. **CAUTION: This process generates copious amounts of free halogens (Cl_2, Br_2, BrCl) which are released from the bottle. Add the $KBrO_3$ SLOWLY in a properly operating fume hood.**

14.4.3 Loosely cap the bottle and allow to sit for 1 hour in a fume hood before tightening. Once tightly capped, invert bottle to make sure all of the solids goes into solution.

14.4.3.1 The expiration time for this reagent is set by default to six months in LIMS. As there is no suggested holding time in EPA method 1631E, the holding time can be extended as long as the primary reagents have not expired. The mercury concentration of the BrCl is monitored through the preparation of water preparation blanks. Bottles of 0.2N BrCl suspected to be contaminated should never be used for analysis.

14.4.3.2 All 0.2N BrCl bottles should be tested before use. To test, add 50 µL of 25% hydroxylamine-HCl to a 50 mL vial. Add 1.0 mL of the 0.2N BrCl to this same vial and dilute to 50mL with reagent water. This reagent must test below 0.25ng/L (do not prep blank correct). Analyze at least one replicate per bottle.

14.4.3.3 0.5% BrCl Rinse Solution: 30mL concentrated low-level mercury BrCl into 6,000mL of reagent water.

14.4.3.4 1.0% BrCl Solution: 10 mL of 0.2N BrCl brought to 1,000 mL final volume with reagent water.

14.4.3.5 2.0% BrCl Solution: 20 mL of 0.2N BrCl brought to 1,000 mL final volume with reagent water.

14.5 50% Hydroxylamine-HCl: Dissolve 500g of NH_2OH-HCl in reagent water and bring the volume up to 1L. Shake vigorously to ensure all added salt goes into solution. This solution may be purified by adding of 1mL of 50% $SnCl_2$ solution (14.6) and purging overnight at approximately 500 mL/min with ultra-pure argon. The working reagent is a 25% solution that is made by adding one part reagent water to one part 50% hydroxylamine hydrochloride. This reagent must test below 0.25ng/L.

14.5.1 To test the 50% Hydroxylamine-HCl solution, add 0.1 mL of the 50% reagent to a 50mL vial, dilute to 50mL with reagent water, and analyze like a normal water sample. This reagent must test below 0.25 ng/L (do not prep blank correct). Analyze one replicate per bottle.

14.6 50% Stannous Chloride ($SnCl_2$): Add 1000 g $SnCl_2 \bullet 2H_20$ to a thoroughly-rinsed 2.5 L glass bottle (a funnel made with weighing paper is extremely helpful here). Using a pump dispenser, add 600 mL concentrated trace-metal grade HCl (14.2) to this bottle. Bring the solution to a final volume of 2 L and mix thoroughly and carefully. This solution should be purged overnight with ultra-pure argon to remove all traces of mercury. Store this solution in a fume hood and keep it tightly capped. The working reagent is a 3% solution that is made by diluting 150mL of 50% $SnCl_2$ to 2.5L with reagent water.

14.6.1 To test the Stannous Chloride (SnCl2), add 0.3 mL of the 50% reagent to a 50 mL vial, dilute to 50 mL with reagent water, and analyze like a normal water sample. This reagent must test below 0.25 ng/L (do not prep blank correct). Analyze one replicate per bottle.

14.6.2 The expiration time for this reagent by default is set to six months in LIMS. As there is no suggested holding time in EPA method 1631E, the holding time can be extended as long as the primary reagent has not expired.

14.7 Total Mercury Stock and Prepared Standards: Alternate volumes of any of these standards may be prepared so long as the ratio of the components is kept constant.

14.7.1 See SOP *EFGS-T-TM-SOP2839* for information regarding the receipt, documentation, preparation, and storage of purchased and prepared standards.

14.7.2 Total Mercury Stock Standard Solution (Stock): Certified mercury standard purchased from High Purity Standards (1000 µg/mL (1 000 000 ng/mL) primary source) or Absolute Standards (100 µg/mL (100 000 ng/mL) secondary source), or any equivalent standard. If standards of differing concentrations are purchased, it is the analyst's responsibility to ensure the recipes for reagents 14.7.3 through 14.7.8 are altered appropriately.

14.7.3 100,000 ng/mL Spiking Standard: If made from the Primary Stock Standard (High Purity, or equivalent vendor). Dilute 10 mL of the stock standard to 100 mL RO water containing 2 % BrCl in a volumetric flask. (Can also be made by preserving Secondary Stock Standard to 2% BrCl). Expiration date is currently set at 6 months or when the stock standard expires, whichever is shorter.

14.7.4 10,000 ng/mL Spiking Standard: If made from the Primary Stock Standard (High Purity, or equivalent vendor). Dilute 1.0 mL of the stock standard to 100 mL RO water containing 2 % BrCl in a volumetric flask. If made from Secondary Stock Standard dilute 10mL of stock standard to 100mL with RO water containing 2% BrCl. Expiration date is currently set at 6 months or when the stock standard expires, whichever is shorter.

14.7.5 1,000 ng/mL Spiking Standard: If made from the Primary Stock Standard. Dilute 0.250 mL of the stock standard to 250 mL RO water containing 2 % BrCl. If made from Secondary Stock Standard, dilute 2.5mL of stock standard to 250mL with RO water containing 2% BrCl. Expiration date is currently set at 6 months or when the stock standard expires, whichever is shorter.

14.7.6 100 ng/mL Spiking Standard: Made from a stock standard or dilution of a stock standard with a concentration of 100,000 ng/mL. Dilute 0.100 mL of the 100,000 ng/mL dilution to 100 mL RO water containing 2 % BrCl. Expiration date is currently set at 3 months or when the stock standard expires, whichever is shorter.

14.7.7 Calibration Standard (10 ng/mL): Must be made from a dilution of the Primary Stock Standard. Typically made by diluting 0.5mL of a 10,000 ng/mL Primary Spiking Standard to 500 mL of RO water containing 2 % BrCl. Transfer to one 1000 mL glass or Teflon bottle. The calibration standard is considered stable for three months or until the stock standard expires.

14.7.8 OPR Standard (10 ng/mL): Must be made from a dilution of a Secondary Spiking Standard. Typically made by diluting 1.0mL of a 1000ng/mL Secondary Spiking standard to 100mL with RO water containing 2% BrCl.

14.7.9 Initial Calibration Verification (ICV): This solution is made daily. To make 500 mL of ICV solution, add 500 µL of 25% hydroxylamine-HCl solution to approximately 100 mL of water in a 500 mL volumetric flask. Add 10 mL of 0.2N BrCl and swirl to reduce the BrCl to dilute acid. Finally, add 250 µL of OPR standard (14.7.8) and carefully bring to a final volume of 500 mL. The (nominal) mercury concentration of this solution should be 5.0 ng/L. The expiration date of this solution should match that of the OPR standard used to prepare it.

14.7.10 Continuing Calibration Verification (CCV): The ICV solution (14.7.9) is to be used for all CCV injections throughout an analytical run.

14.7.11 Argon Grade 4.7 or better (ultra high-purity grade) – argon that has been further purified by the removal of mercury using a gold trap that is located in line between the gas output and the analyzer gas input.

15) Calibration:

15.1 The calibration sequence consists of three IBLs followed by a minimum 5-point calibration curve using the calibration factors method. Usual concentrations are 0.5ppt, 1.0ppt, 5.0ppt, 20.0ppt, and 80.0ppt, analyzed from lowest to highest. The calibration must include a point at 0.5 ppt or lower. Additionally, the analyst may include points above 80.0 ppt so long as they can demonstrate carryover is not present for any matrix that will be analyzed. After the chosen calibration standards are analyzed, an ICV/OPR (5.0 ppt) is injected and the calibration is assessed before any client samples are run.

15.1.1 Three IBLs are prepared by adding 50mL of 2.0% BrCl to a sample vial. The uncorrected response of these IBLs must be under 0.5ppt once the calibration factor has been determined. If it is higher, then analysis should be halted and the cause determined (reagent contamination is a common cause).

15.1.2 Calibration standards at or above 5.0 ppt should be created as stock solutions in a manner similar to how the ICV solution is created in 14.7.9. To create solutions at concentrations lower than 5.0 ppt, it is recommended that the analyst dilute their most concentrated stock solution. Below is an example of how a set of calibration standards (0.5 ppt, 1.0 ppt, 5.0 ppt, 20.0 ppt, 40.0 ppt) might be created:

- 0.5 ppt: Created as a dilution of the 40.0 ppt stock solution. Add 50 µL of 25% hydroxylamine-HCl to a 50 mL vial. To this, add 625 µL of 40.0 ppt stock solution and bring to 50 mL final volume using 2.0% BrCl.
- 1.0 ppt: Created as a dilution of the 40.0 ppt stock solution. Add 50 µL of 25% hydroxylamine-HCl to a 50 mL vial. To this, add 1250 µL of 40.0 ppt stock solution and bring to 50 mL final volume using 2.0% BrCl.
- 5.0 ppt: Created as a stock solution. To make 500 mL of 5.0 ppt stock solution, add 500 µL of 25% hydroxylamine-HCl solution to approximately 100 mL of water in a 500 mL volumetric flask. Add 10 mL of 0.2N BrCl and swirl to reduce the BrCl to dilute acid. Finally, add 250 µL of 10.0 ng/mL primary standard (14.7.7) and carefully bring to a final volume of 500 mL.
- 20.0 ppt: Created as a stock solution. To make 500 mL of 20.0 ppt stock solution, add 500 µL of 25% hydroxylamine-HCl solution to approximately 100 mL of water in a 500 mL volumetric flask. Add 10 mL of 0.2N BrCl and swirl to reduce the BrCl to dilute acid. Finally, add 1000 µL of 10.0 ng/mL primary standard (14.7.7) and carefully bring to a final volume of 500 mL.
- 80.0 ppt: Created as a stock solution. To make 500 mL of 40.0 ppt stock solution, add 500 µL of 25% hydroxylamine-HCl solution to approximately 100 mL of water in a 500 mL volumetric flask. Add 10 mL of 0.2N BrCl and swirl to reduce the BrCl to dilute acid. Finally, add 4000 µL of 10.0 ng/mL primary standard (14.7.7) and carefully bring to a final volume of 500 mL.

15.2 Once the instrument is calibrated and the ICV/OPR and three IBLs are analyzed and passing, the instrument is operational. The sample concentrations must fall within the range of the calibration standards or be diluted and reanalyzed, unless a high calibration verification has been added to the analytical run.

15.3 The calibration of this system and calculation of sample results are performed using units of concentration (ppt or ng/L).

16) Procedure:

16.1 Pre-analysis and Organization:

16.1.1 Prior to analyzing samples it is imperative to reference LIMS for all project specific information, such as QC requirements, suggested dilutions, project manager information, and specifics regarding spike levels.

16.1.2 The analyst should then locate samples and check the work order in LIMS for notes about specific project requirements.

16.1.3 The analyst should compare the sample IDs to the work order and see that the samples are accounted for, and notify the project manager of any discrepancies in analysis required, sample identification, etc.

16.1.4 All mercury analyses receive a unique dataset identifier and LIMS assigned sequence number. The dataset ID is comprised of the instrument type and number, the date and the calibration number for that day. The format is as follows: THg26001-130216-1, where "THg "refers to a total mercury analysis; "26001" refers to Tekran 2600 instrument number 1; 130216 refers to the date (February 16, 2013 in the YYMMDD format); and "1" refers to the first calibration of the day. The sequence number is assigned by LIMS when the data gets imported into LIMS. The alpha-numeric code is based on the following format: 3B02001, where the 3 refers to the year (2013), the "B" is the month (A= January, B=February…L=December), "02" is the day of the month (February 2nd) and the final 3 digits is the nth sequence created on that particular year/month/day combination.

16.1.5 In general the analyst should organize their samples in the order listed on the bench sheet. The first samples analyzed should be the preparation blanks, then the LCS if analyzing solid samples, followed by actual samples. If possible, run total and dissolved samples side by side to facilitate verification that total concentration is greater than dissolved concentration. See QA section.

16.2 Instrument Start Up:

16.2.1 If necessary, prepare the soda-lime trap. The soda-lime trap should be changed at least every three analytical days.

16.2.2 Start the TekMDS software and check to make sure the computer is communicating with the instrument and the autosampler. Load a new work sheet and begin to enter the sample IDs into the run. Take care to insure that the appropriate autosampler position and dilution are entered correctly into the worksheet.

16.2.3 Empty the waste carboy in accordance with EFHS-S-HS-SOP2991 "Waste Dumping Procedure for Client Sample Waste.

16.2.4 Fill rinse basin with a fresh solution of 0.5% BrCl and refill 3% $SnCl_2$ container.

16.2.5 Check tubing for wear and re-index or replace as needed. Clamp all tubing/cassettes onto pump head and adjust tension. Do not over-tighten.

16.2.5.1 Insure that there are no kinks in reagent or waste lines.

16.2.6 Turn the pump on to "local" and check flow of all reagents, including flow through the sample probe from the wash station and flow of SnCl2 into phase separator. Adjust tension on tubing, if necessary. Be sure that the waste line is flowing well and waste does not back-up into the phase separator! This can often be prevented by loosening the tension on the tubing for both the phase separator drain and the wash station drain. Allow it to run with reagents for 20 minutes.

16.2.7 All analytical runs should begin with at least two "clean" cycle to "blank" the gold traps, followed by three wash station blanks (WSB) to assure that the system is free of mercury.

16.2.8 Set pump back to "remote" to start the run.

16.2.9 Note: It is important to check the flow, reagent levels, and waste carboy level throughout the analytical run. If a reagent is low in volume, it can be refilled mid-run. Similarly, the waste carboy should be emptied mid-run, if necessary. The SnCl2 and sample flow (tension on tubing) cannot be changed mid-run as it may affect instrument response. For this reason, it is important to verify proper sample/reagent flow prior to beginning analysis.

16.3 Batching and Analyzing Aqueous Samples:

16.3.1 All analysts will show Initial Precision and Recovery (IPR) by analyzing four secondary spikes at 5.0ng/L. The spikes need to recover between 79-121% with an RSD < 21%.

16.3.2 All aqueous samples should be preserved with BrCl at least 16 hours prior to analysis. In the event a sample requires further oxidation prior to analysis, additional BrCl is added and the sample is not analyzed for at least 24 additional hours. In special cases where rush turn-around-time is required and an oxidation period of less than 24 hours may be used, the analyst should consult a supervisor for approval. The supervisor must be able to confirm (based on past experience) that the particular matrix type is completely oxidized before analysis.

16.3.3 It is recommended that all known field, equipment, and trip blanks should be analyzed before any other sample types.

16.3.4 For all samples, ensure an appropriate dilution is selected prior to vialing (refer to LIMS, historical data, minimum dilutions, etc.).

16.3.5 When preparing dilutions, use calibrated pipettes to dispense the aliquots into the 50mL vials. Dilute the sample to a final volume of 50mL with 2% BrCl and neutralize with 50µL of 25% NH2OH-HCl. The sample should turn from a yellowish color to a clear/cloudy solution, depending on the matrix. Be sure to note any sample dilutions onto the bench sheet for cross referencing during peer review. Note that the analyst may choose a smaller final volume (no less than 30 mL) so long as the ratio of sample to 25% NH2OH-HCl is preserved (e.g. 40 µL of 25% NH2OH-HCl for a 40 mL final volume). Note that volumetric verification at each final volume must be performed for every lot of tube received.

16.3.6 If a 1x dilution of a water sample is possible, the sample first must be thoroughly homogenized. Then, 50 mL of sample is poured directly into 50mL vial already containing 50 µL of 25% NH_2OH-HCl. The analyst may choose to use a smaller volume of sample (no less than 30 mL) so long as the ratio of sample to 25% NH_2OH-HCl is preserved (e.g. add 30 mL of sample to 30 µL of 25% NH_2OH-HCl).

16.3.7 Load sample vials into the auto sampler. Verify that the correct vial is in the proper position relative to the analysis worksheet entry in TekMDS software for that sample.

16.3.8 For each sample, the sample ID and a dilution is entered into the TekMDS software. For water samples preserved to greater than 2% BrCl, a comment should be made stating the preservation percentage (and an appropriate preservation blank should be analyzed). Unless otherwise stated (e.g., all WI DNR samples, PRASA), all aqueous samples should be PB corrected. Note that all prep blank correction takes place after analysis in an Excel spreadsheet, not in the TekMDS software.

16.3.9 The analyst should continue preparing and adding samples to the run in the same fashion to maximize efficiency. Positions on the autosampler can be used more than one time throughout the analysis run by removing a previously analyzed sample vial and replacing it with a new sample.

16.4 Analysis of Digested Solids:

16.4.1 All analysts will show Initial Precision and Recovery (IPR) by analyzing four secondary spikes at 8.0ng/g. The spikes need to recover between 75-125% with an RSD < 20% for EFAFS-T-AFS-2795 and 2807. All other Frontier preps will be covered by the IPR performed for waters.

16.4.2 With this method it is possible to determine the concentration of total mercury in solid samples following proper digestion. The following highlight the majority of total mercury prep techniques for solids and their matrix specific SOPs.

16.4.2.1 For tissues, refer to *EFGS-T-AFS-SOP2795* "Digestion of Tissues for Total Mercury Analysis Using Nitric and Sulfuric Acids (70:30)" for the nitric acid/sulfuric acid digestion and *EFGS-T-TM-SOP2837* EFTM-T-TM-SOP2837 "Total Metals Digestion for Animal or Plant Tissues" for the concentrated nitric acid digest.

16.4.2.2 For soils/sediments, refer to *EFGS-T-AFS-SOP2807* "Preparation of Solid Samples for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion" for the cold aqua regia digestion, *EFGS-T-AFS-SOP2795* for the nitric acid/sulfuric acid digestion, and *EFGS-T-TM-SOP2821* "HF/HNO3/HCl Bomb Digestion of Sediments, Soils, Rocks, and Bayer Process Solids and Slurries for Mercury, followed by Repeated HNO3 Evaporation" for the hydrofluoric acid/nitric acid bomb digestion.

16.4.2.3 For coal and ash, refer to *EFGS-T-AFS-SOP2807* Preparation of Solid Samples for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion for the cold aqua regia digestion. For FSTM, refer to *EFGS-T-AFS-SOP2985* "Mercury Digest for Gas/Air Samples Collected on KCl/Quartz or KCl/Lime trap" for the digestion of traps.

16.4.3 After the instrument calibration sequence, preparation blanks, digested CRM(s), and LCS samples should be analyzed. For solid batches, the analyst should use the minimum dilution allowed for each preparation blank and diluting to 50mL with reagent water preserved to 2% BrCl. Analysts are to calculate the appropriate dilution for digested CRMs and LCS samples, ensuring that the sample concentration stays within the calibration curve. Analysts should also ensure that the recoveries for CRMs and LCS samples are within control limits before analyzing the associated batch samples.

16.4.4 Begin analyzing samples by the order of the digestion sheet, with the exception of the sample that has separate QC digested for MD/MS/MSD. It is appropriate to analyze this sample, and any associated QC, out of bench sheet order. The analyst should review any relevant project notes, historical data, or information given by client to the PM to help determine proper dilutions that will allow samples to recover within calibration curve. Note that the analyst may choose a smaller final volume (no less than 30 mL) so long as the ratio of sample to 25% NH2OH-HCl is preserved (e.g. 40 µL of 25% NH2OH-HCl for a 40 mL final volume). Note that volumetric verification at each final volume must be performed for every lot of tube received.

16.4.5 The procedure for analysis is similar to that of the calibration:

16.4.5.1 Selected digest samples are pipetted into a 50mL vial (one sample per vial) and diluted to 50mL with reagent water preserved to 2% BrCl. Ensure that appropriate dilutions are selected by consulting the minimum dilutions for the associated digests.

16.4.5.2 For each sample, the sample ID and dilution based on 50mL is entered into the TekMDS software. The dilution should also be noted on the digestion bench sheet for cross referencing in peer review. Unless otherwise stated, all solid samples should be PB corrected. Note: Prep blank correction takes place after analysis in the Excel spreadsheet, not in the TekMDS software.

16.4.5.3 After loading one set of samples, the analyst should begin preparing the next round of digested solid samples in the same fashion to maximize efficiency.

16.4.6 Quality Control Procedures for Digested Solid Samples:

16.4.6.1 Please refer to the appropriate SOP for each matrix's corresponding quality control samples. All quality control samples prepared for the batch should be run with its analysis unless stated otherwise by the project manager. Please see Table 1 for acceptance criteria.

16.4.6.2 Spiking standard LIMS ID and the amount used for the MS/MSD must be noted on the digestion bench sheet for cross referencing in peer review.

16.4.6.3 The analytical day must close with a CCV(OPR) /CCB.

16.5 Analysis of Fluegas Sorbent for Total Mercury (FSTM)/KCl Traps and Particulate Filter:

16.5.1 The IPR for waters will also cover *EFGS-T-AFS-SOP2985* and *EFGS-T-AFS-SOP2800* digestions.

16.5.2 With a few exceptions, FSTM traps and particulate filters are digested and analyzed as if they were solids.

16.5.3 FSTM traps or particulate filters should be digested according to *EFGS-T-AFS-SOP2985* "Digestion for Gas/Air Samples Collected on Fluegas Sorbent for Total Mercury TM Traps."

16.5.4 KCl traps should be digested according to *EFGS-T-AFS-SOP2800* "Mercury Digest for Gas/Air Samples Collected on KCl/Quartz or KCl/Lime trap."

16.5.5 The minimum dilution currently used for analysis should be 100x for FSTM and 20x for KCl diluted in 2% BrCl . Smaller dilution factors than these may be used at PM request, but is not recommended. To avoid any potential matrix interference it is recommended that the smallest reasonable aliquot sizes be used for this matrix. All blanks and low level/non-detect samples must be analyzed at the same dilution. Dilution should also be noted on the digestion bench sheet for cross referencing in peer review.

16.5.6 Quality Control Requirements for FSTM Traps and Particulate Filters:

16.5.6.1 Please refer to the appropriate SOP for each matrix's corresponding quality control samples. All quality control samples prepared for the batch should be run with its analysis unless stated otherwise by the project manager. Please see Table 1 for acceptance criteria.

16.5.6.2 The amount of spiking standard used, it's LIMS ID and dilution used for the MS/MSD as well the sample(s) used for MS/MSD/MD, must be noted on the digestion bench sheet for cross referencing in peer review.

16.6 End of analysis close-down procedure:

16.6.1 The gas flow to the phase separator automatically shuts off.

16.6.2 Move reagent lines to rinse carboy.

16.6.3 With pump set to "Local", rinse system for 5-minutes.

16.6.4 Release pump tubing for all but the "Sample" and "Waste" lines. Allow lines to drain.

16.6.5 Set pump to "Off".

16.6.6 Slowly release the "Sample" and" Waste" line. Carefully monitor the Wash station over the next 5 minutes, making sure it is not siphoning, or overflows.

16.6.7 Carryout all end of day cleaning and restocking tasks.

16.7 Analytical data is exported from the TekMDS software to an Excel file. The data is then copied and pasted into an Excel template that is LIMS compatible.

16.8 Tekran 2600 Mercury Analysis System Troubleshooting
The following is a summary of common troubleshooting techniques. This is not an all-inclusive list of what may be done to deal with analytical issues. Consultation with the group leader is preferred when performing these corrective actions. Analysts are encouraged not to rely on this guideline. Instead, this document should be used as a learning tool. Analysts should be actively striving to learn about troubleshooting as well as

creative, productive ways of dealing with analytical issues.

16.8.1 ISSUE: No peaks at all

16.8.1.1 Ensure that the system is powered.

16.8.1.2 Make sure that the base line is approximately 0.1 V.

16.8.1.3 Make sure that you are running the right event table file (ETF).

16.8.1.4 Ensure that the carrier gas fitting is properly connected to the Argon source. (See System components, User guides, Section 2-3 for details).

16.8.1.5 Ensure that the phase separator gas fitting is properly connected to the Argon/Nitrogen source. (See System components, User guides, Section 2-3 for details)

16.8.1.6 Check operation of heater B. (Refer to Heater B Test)

16.8.1.7 Check operation of heater A. (Refer to Heater A Test)

16.8.1.8 Check that V2 is working properly. (Refer to V2 Test)

16.8.1.9 Check that V1 is switching properly. (Refer to V1 Tests)

16.8.2 ISSUE: Low sensitivity

16.8.2.1 Make sure that all "No peaks detected" samples are checked.

16.8.2.2 Check all connections to V2 and V1 and tighten all friction fittings up and downstream the Cartridges A and B.

16.8.2.3 Make sure that you have freshly changed soda lime in the soda lime trap, and that it is from a good source.

16.8.2.4 Check and tighten all gas Teflon lines up and downstream of the soda lime trap and P/S.

16.8.2.5 Check the sample tubing following introduction of SnCl2 at the "Y" fitting for clogs. This line should also be the proper length.

16.8.2.6 Check that the frosted P/S rod is evenly wet. (Refer to P/S glass rod test).

16.8.2.7 Check that the tubing sizes in the main pump are correct. Also make sure that the tubing occlusion is set at the 12 o'clock position. Check the sample uptake (should be between 12 and 16 mL/min) and the SnCl2 uptake (should be between 3 and 5 mL/min).

16.8.2.8 Do not use old calibration standards to calibrate the system.

16.8.2.9 Make sure you are running fresh $SnCl_2$ solution.

16.8.2.10 Make sure that your stock Hg standard has not expired and is from a reliable source and that it is not compromised.

16.8.2.11 Check and tighten both sides of the ¼" straight Teflon union on the cuvette.

16.8.2.12 Check the cuvette (Refer to the System Component, User Guides Cuvette Removal and Cleaning, Section 4-3 and Cuvette cleaning procedure).

16.8.2.13 Check the lamp voltage. If the voltage is low, increase to required values (refer to System Component, User Guides Lamp voltage adjustment, Note 4-7).

16.8.2.14 Check both cartridges for failures

16.8.2.14.1 Check if Cartridge A is having problems. (Refer to Cartridge A test procedure).

16.8.2.14.2 Check if Cartridge B is having problems. (Refer to Cartridge B test procedure

16.8.3 ISSUE: HighBlanks

High blanks could be due to:
- Contamination in the system (liquid and/or gas lines)
- Water high in Hg
- Ambient Hg (in lab air)
- Poor quality of the reagents (KBr, $KBrO_3$, $SnCl_2$, Hydroxylamine, HCl etc).

16.8.3.1 Contamination in the system (liquid and/or gas lines), caused by:

16.8.3.1.1 System left without operating for an extended period of time (e.g. a month) and not shut down properly.

16.8.3.1.2 System not flushed and cleaned after running samples (especially high level samples). Note: Any sample over 200 ng/L requires a blank be ran after to check for carryover.

16.8.3.1.3 Following analysis of samples high in organics and not flushing properly after the run**.**
Sudden contamination when an extremely high in Hg concentration sample is run through the system: From past experience this type of contamination is very dependent on the type of samples the analyst was running in the system more so than the exact concentration of Hg within the sample. There are cases when even after analysis of a very high sample (~1.0 ppb) the blanks will come back to normal very quickly. In other cases, effort will need to be made to lower the blanks. Basically the methods of cleaning are the same as those described below.

16.8.3.1.4 Not following normal and necessary maintenance procedures.

16.8.3.1.4.1 Addressing contamination in gas lines:

16.8.3.1.4.1.1 Bypass the P/S. (Refer to P/S bypassing procedure).

16.8.3.1.4.1.2 Continue by running some CLEAN cycles. If high peaks result, clean Cartridge B. (Refer to Cleaning the Cartridge B procedure).

16.8.3.1.4.1.3 Continue running dry (Sample cycle). If at this point you still get high peak areas, clean Cartridge A (Refer to Cleaning the Cartridge A procedure).

16.8.3.1.3.1.5 Once again continue running dry. If you still get high peak areas, clean V2. (Refer to cleaning V2 procedure).

16.8.3.1.4.1.5 If high blank are still present, clean/replace the gas phase Teflon lines. (Refer to cleaning of the gas phase Teflon lines).

16.8.3.1.4.2 Addressing contamination in liquid lines:

16.8.3.1.4.2.1 Check/replace the silicone sample line.

16.8.3.1.4.2.2 Check/replace the sample/SnCl2 line to the P/S.

16.8.3.1.4.2.3 Check/clean the P/S. (Refer to Analytical Methods, Tekran Guide, Method 1631, section 5-1).

16.8.3.1.4.2.4 Clean system while running (Refer to clean while running procedure).

16.8.3.2 Poor water Quality

16.8.3.2.1 Refer to Analytical Methods, Tekran Guide, Method 1631, section 3-4

16.8.3.3 Poor quality of the reagents (KBr, KBrO3, SnCl2, Hydroxylamine, HCl etc)

16.8.3.3.1 Refer to Analytical Methods, Tekran Guide, Method 1631, section 3-4, 3-5.

16.8.4 ISSUE: Nonlinearity of the calibration curve

There are a few different types of non-linearity and factors causing them:

16.8.4.1 Cal. Factors which are very low for the low calibration points (0.5 and 1 ng/L) but better for the higher standards.

This is probably due to high Calblank values that cause lowest points of calibration to be affected during blank correction. Stop the run and go through the procedure for investigating High Blanks.

16.8.4.2 Cal. Factors are very erratic (no clear increasing or decreasing tendency

16.8.4.2.1 Dry spots on the glass rod of the P/S. (Refer to P/S glass rod test).

16.8.4.2.2 Check that you are running with fresh soda lime.

16.8.4.2.3 Check the heaters (Refer to Heater B test and Heater A test).

16.8.4.2.4 Check the silicone sample tubing for any twisting, pinching, or bubbles.

16.8.4.2.5 Check and tighten all liquid and gas phase connections.

16.8.4.2.6 Make sure your calibration standards are fresh and properly prepared.

16.8.4.3 Poor results for high calibration standards

16.8.4.3.1 Previously run samples with difficult matrixes or high acid vapor content could be a potential cause for this. Such matrixes, in very rare cases, could cause temporary passivation of Cartridge A, as well as temporarily poison the liquid lines. After running such difficult samples, the system needs a very thorough cleaning (see at the procedures High blanks). Running overnight in "dry" mode with the P/S flow between 50-100mL/min can also help.

16.8.4.4 Cal. Factors decrease moving up in concentration through the calibration curve

16.8.4.4.1 Improper preparation of the standards. Check and prepare fresh calibration standards.

16.8.4.4.2 Contaminated and expired soda lime. Change soda lime.

16.8.4.4.3 Loose P/S friction fittings: tighten them.

16.8.4.4.4 Loose Soda lime trap fittings: tighten them.

16.8.4.4.5 Loose gold trap friction fittings: tighten/replace them.

16.8.4.4.6 Loose connection of the ¼" nuts on V1 and V2. Tighten them.

16.8.4.4.7 Loose connection on both sides of ¼" straight Teflon union to the cuvette. Tighten both sides.

16.8.4.4.8 Open and examine the cuvette (Refer to the System Component, User Guides Cuvette Removal and Cleaning, Section 4-3 and Cuvette cleaning procedure)

17) Calculations:

17.1 Average all instrument blanks (PHX) using the peak area values from the TekMDS software. Subtract the average (IB) from the peak area for each standard and sample.

17.2 Calculate the calibration factor (CFx) for mercury in each of the five standards using the mean instrument-blank-subtracted peak area and the following equation:

$$CF_x = PA_x - IB / C_x$$

Where:

17.2.1 PA_x=peak area for mercury in standard

17.2.2 IB=mean peak area for mercury in instrument blank

17.2.3 C_x=mass in standard analyzed (ng/L)

17.2.4 CF_x=Response Factor of each concentration

17.2.4.1 Average the five response factors to establish mean value: CF(Avg) (units/ng/L).

17.3 Sample results are then corrected for the average peak area values of at least three preparation blanks (PBs), unless otherwise requested or for samples originating from Wisconsin *(*Wisconsin does not permit method blank subtraction*)*. This result is shown as the Initial Result on the Excel spreadsheet and in LIMS.

17.4 Total Mercury in Water:

$$Hg / Initial Result (ng/L) = ((((Peak Area - IB) / CF_{(Avg)}) \times D_s) - (PB_x \times D_b)) / D_s$$

$$THg Final Result (ng/L) = (THg / Initial Result) \times (D_s \times V_f) / V_i$$

Where:

17.4.1 $CF_{(avg)}$ = average response factor (in units/ng/L).

17.4.2 IB = average instrument blank peak area (in units)

17.4.3 V_f = final volume of sample analyzed in mL. The final volume should account for the added volume of BrCl needed for preservation. For instance, 100 mL of sample is preserved with 3% (v/v) BrCl. The final volume should be 103 mL.

17.4.4 V_i = initial volume of sample analyzed in mL prior to addition of BrCl.

17.4.5 D_s = final dilution factor of sample.

17.4.6 D_b = final dilution factor of corresponding blank results. All preparation blanks at the same preservation level must be analyzed at the same dilution.

17.4.7 PB_X= initial average (on instrument) of the preparation blanks in ng/L related to the preservation level of the samples (i.e., X=2 for a sample which is preserved at 2% BrCl), thus accounting for the extra contribution of mercury from the BrCl. Sample results are corrected for the average blank concentration of only the corresponding blanks preserved at the same BrCl preservation level. For example, if a sample is preserved at 2% and one PB was run at 2%, the sample is corrected using the results from that blank.

17.5 Total Mercury in Solids:

$$THg / Initial Result (ng/L) = ((((Peak Area - IB) / CF_{(Avg)}) \times D_s) - (PB \times D_b)) / D_s$$

THg Final Result (ng/g) = (THg / Initial Result) x (D_s x V_f) / (m x 1000)

Where:

17.5.1 $CF_{(avg)}$ = average response factor (in units/ng/L).

17.5.2 IB = average instrument blank peak area (in units)

17.5.3 V_f = final volume of the digested sample in mL.

17.5.4 m = initial mass of the digested sample in g.

17.5.5 D_s = final dilution factor of sample.

17.5.6 D_b = final dilution factor of corresponding blank results. All preparation blanks must be analyzed at the same dilution.

17.5.7 PB = initial average (on instrument) of the preparation blanks found in the digest in ng/L. The initial mass of the digestion blanks must be the default mass specific to the preparation.

18) Statistical Information/Method Performance:

18.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and and CA-Q-S-006.

18.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3). The PQL is determined by running ten samples with a concentration that will produce a recovery of 70-130 % for most analytes, but the recovery requirements are analyte dependent. The PQL is referred to as the Method Reporting Limit (MRL) in LIMS.

18.3 Current LODs, LOQs, MDLs and PQLs are stored at: \\tacorp\Corp\QA\QA_Facilities\Seattle-QA\Method-Limits-MDLs-IDLs\MDLs

19) Quality Assurance/Quality Control:

19.1 A minimum of three preparation blanks and one LCS/LCSD (preferably NIST 1641e), must be analyzed per preparation batch. The upper control limit for each preparation blank is equal to the LOQ (½ LOQ for DOD samples).

19.2 Initial Precision and Recovery test for water must be four spikes (at 5.0 ng/L) recovering between 79-121% with an RSD < 21%; the IPR for soil must be four spikes (at 8.0 ng/g) recovering between 75-125% with an RSD < 20%.

19.3 Matrix Spikes: One Matrix Spike/Matrix Spike Duplicate (MS/MSD) must be performed for every 10 samples. The recovery of the MS/MSD must be between 71%-125% recovery, and the Relative Percent Difference (RPD) below 24%. If an MS/MSD is out of control, the analyst should investigate to identify the source of the failure. The MS and MSD may be used as duplicates. Some failures may be qualified using QA Qualification Flow Charts (Appendix A).

19.3.1 For aqueous samples, the MS/MSD is spiked at 1 to 5 times the ambient concentration, with 0.25 ng being the minimum spiking level. Sample dilutions for the MS/MSD should be the same as the ambient sample dilution, if sufficient sample volume exists. NEVER ADD SPIKE DIRECTLY TO THE ORIGINAL SAMPLE CONTAINER UNLESS OTHERWISE INSTRUCTED.

19.4 Matrix Duplicates – Not required. A Matrix Duplicate (MD) or Matrix Triplicate (MT) may be analyzed for every batch of 20 samples upon client request. The MSD may serve as the MD if necessary. The Relative Percent Difference (RPD) and the Relative Standard Deviation (RSD) of duplicate samples must be less than 24%. Some failures may be qualified using QA Qualification Flow Charts.

19.4.1 For aqueous samples, analyze the parent, duplicate and triplicate at the same dilution.

19.5 Laboratory Control Standard (LCS) or Quality Control Sample (QCS): For every batch of samples, at least one LCS is processed and analyzed. The recovery of the LCS must be within 80-120% for the aqueous NIST 1641e. An LCS Duplicate (LCSD) should accompany the LCS.

19.5.1 For solid digestions, a Certified Reference Material (CRM) is the preferred LCS, but a blank spike may serve as an LCS if an appropriate CRM does not exist. The spiking level is based on client request, historical data, or a default of mid-curve. A duplicate blank spike must also be prepared as an LCSD. Recoveries need to be 75-125% with an RPD < 24%.

19.5.2 For water batches, the LCS and LCSD are prepared by spiking 2% BrCl with an appropriate amount of primary calibration standard to a concentration of 5.0 ppt.

19.6 Ongoing Precision and Recovery (OPR): An OPR must be analyzed at the beginning and end of each analytical batch, or at the end of each 12-hour shift. The recovery of the OPR must be within 77-123% to be considered in control.

19.7 All calibration standards must be traceable to the original standard source. The calibration curve must be established at the beginning of the analytical run. It must include at least five different concentrations, with the lowest concentration equal to the PQL. The average response factor of each calibration standard is used to calculate the sample values. The RSD of the response factors must be less than 15% of the mean or the calibration fails.

19.8 ICV control limit is 79-121%, while the CCV control limit is 77-123%. The CCV is analyzed every 10 sample injections and at the end of an analytical run. CCBs are always analyzed after the CCVs.

19.9 Field Blanks: To be compliant with EPA 1631, clients must submit a field blank for each set of samples (samples collected from the same site at the same time, to a maximum of 10 samples).

19.9.1 If no field blanks are submitted by the client, their data will be flagged with "FB-1631." "Required equipment/field/filter blank not submitted by the client. The sample has been analyzed according to 1631E, but does not meet 1631E criteria."

19.10 Method or Preparation Blanks (BLK): Method blanks are used to demonstrate that the analytical system is free from contamination that could otherwise compromise sample results. Method blanks are prepared and analyzed using sample containers, labware, reagents, and analytical procedures identical to those used to prepare and analyze the samples.

19.10.1 A minimum of three method blanks per analytical batch are required.

19.10.1.1 For solid digests, these blanks are created by using trace-metal grade boiling chips or blank FSTM material in lieu of sample and taking it through the digestion process.

19.10.1.1 For aqueous samples, these three blanks are simply 2% BrCl neutralized with 50 µL of NH_2OH-HCl (identical to IBLs). If samples are preserved to higher than 2% BrCl, then a single blank at that BrCl percentage must be added to the batch (that sample's blank correction should come from this higher percentage blank).

19.10.2 If analyzed preparation blanks are higher than the LOQ associated with the preparation method (or ½ LOQ for DOD samples or 2.2 times the LOD for WI-DNR samples), then it is necessary to carefully assess the results.

19.10.2.1 If the blanks for water batches are outside of control limits, then the system is deemed out of control. These blanks may be rerun to confirm this, but if they confirm then analysis should be halted and the system investigated.

19.10.2.1.1 Our current reporting limits for water samples are based off 1% BrCl preservation. These reporting limits should be used for our current 2% preserved samples. However, in the case that a sample is preserved to 5% or higher, the reporting limits should be multiplied by the preservation percentage.

19.10.2.1 For blanks associated with solid digestion batches, the system is not necessarily out of control if a preparation blank comes back above the LOQ (watch the CCBs to assess whether or not the system blank level is in control as well). If sample results are 10x higher than the blank result, then the data can be qualified. Otherwise, the samples associated with the high blank must be re-digested.

19.11 Instrument Blanks (IBL): A minimum of three instrument blanks must be analyzed with each analytical batch (before the first calibration standard). To analyze an instrument blank, analyze a sample of reagent water preserved to 2% BrCl.

19.11.1 If the instrument blank is found to contain more than 0.50 ng/L (or the standard deviation of the three blanks is greater than 0.10 ng/L), the system is out of control. The problem must be investigated and remedied before proceeding, and any samples run must be reanalyzed.

19.11.1.1 The result for all instrument blanks must be ≤ 0.50ng/L with a standard deviation of 0.10 ng/L.

19.12 Initial Calibration Blanks (ICBs) and Continuing Calibration Blanks (CCBs): These blanks are identical to IBLs (2% BrCl neutralized with NH_2OH-HCl) and are used to assess the blank level of the system throughout the analytical run. To report data without qualification, these must all be below the LOQ for the associated preparation method.

19.12.1 For DOD samples to be reported without qualification, the ICB and all CCBs must be below ½ the LOQ for the preparation method.

19.12.2 For WI-DNR samples to be reported without qualification, the ICB and CCBs must be below 2.2 times the LOD for the preparation method.

19.13 The analytical day must close with a CCV/OPR/CCB.

19.14 Since the method is done in real-time, it is EFGS' position that a single non-compliant QC sample result does not automatically invalidate a data set. All data points that can be explained and rerun with a passing result can be qualified. If the source of error cannot be corrected for a QC standard that day, none of the data can be validated. In the event that the system becomes out of control during the analysis day, all results bracketed between valid QC data points shall still be considered valid (CCV, OPR, CCB, etc).

19.15 The Control Limits are established from EPA 1631E.

19.16 Carryover: In 2020 a carryover study was completed monitoring Hg levels up to five times the top calibration point (200 ng/L). No carryover was detected during this study. Any sample ran with a concentration of Hg over 200 ng/L requires a blank be ran directly after to ensure there is no carryover. Additional samples may only be ran after the blank shows a concentration below the LOQ.

20) Corrective Action

20.1 The data is reviewed as in the QC section (or matrix specific QC section) for all parameters that pass specific requirements. If the data does not meet QC requirements for waters, it is reanalyzed for confirmation; if the failing MD/MS/MSD results confirm, another sample is used for the batch. For all digestions, it is qualified or submitted for reruns. Data may be qualified (based on scientific peer review) by the Group Supervisor, Project Manager, Lab Manager, or QA Officer.

20.1.1 Continuing Calibration Verification (CCV): If a recovery falls outside acceptance criteria, recalibrate the instrument and reanalyze all affected samples since the last acceptable CCV or immediately analyze two additional CCVs. If both CCVs are within acceptance criteria, the samples may be reported without reanalysis and the analysis of the next bracket may continue beginning with a CCB.

20.1.1.1 If either of the two CCVs fails, the analysis must be terminated, the problem resolved, the instrument recalibrated and then all of the affected samples since the last acceptable CCV reanalyzed.

20.2 Control Chart data is generated through LIMS to monitor the performance of the CCV, LCS, MS, and MSD. This is done by the QA department.

20.3 Due to the real-time nature of the CVAFS method, failures must be investigated as they happen. If the source of the problem can be identified, and corrected, the samples may be rerun. If source of problem cannot be isolated, see the Senior Analyst, Group Supervisor, or Laboratory Manager for instructions.

20.4 The Senior Analyst, Group Supervisor, Laboratory Manager, or QA Officer must be informed if QC fails. It is also advisable to always alert the Project Managers.

21) List of Attachments

Appendix 1: Hg Spill 3-Prep Contingency Plan
Table 1: QC Requirements for Total Mercury
Table 2: Troubleshooting Flow Chart

Appendix 1: Hg Spill 3-Prep Contingency Plan

Elemental Hg is sometimes used to remove sulfur post solvent extraction. In the case of a spill please follow the instructions below before analyzing.

On first attempt at analysis post spill, rinse or replace containers for working solutions and reagents. Prepare new working solutions from existing parent reagents. Avoid using CPI centrifuge tubes for reagent storage as contamination from the atmosphere has been found to occur in even capped tubes.

Attempt a calibration under normal conditions to test necessity of contingency. If the recoveries and/or blanks are high, proceed to prepare samples three at a time.

Start the calibration with a clean and washstations as normal. When washstations stabilize (two comparable results in a row) prepare the three IBLs and load immediately. Wait until the end of the second IBL to prepare the next three vials (CAL 1-3). Tubes can be labeled ahead of time, but do not pour BrCl until the instrument is finishing up the second IBL. Proceed through the rest of the calibration in this fashion, prepping the next three samples/QC for injection after the second injection of the previous three and loading immediately onto the instrument. If the IBLs and/or other blanks have results around or above the MRL, consider restricting analysis to samples likely to be qualifiable with regards to failing blanks. If the calibration continues to fail, remake reagents and parent reagents until source of contamination has been cleared.

Do not prepare and cap samples more than three in advance. The tubes can be contaminated through the caps, even when contained in the hood. Similarly, avoid making working reagents until they need to be replaced in order to minimize potential exposure. Run the instrument with only sealable reagent containers.

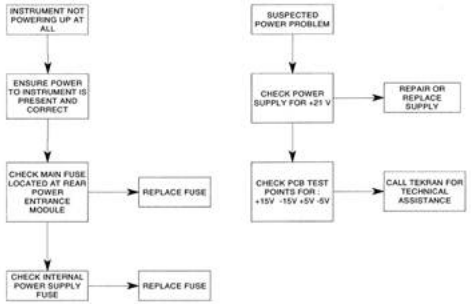
Continue analyzing one calibration under normal preparation conditions. If the calibration, including the ICB, is within control, expand preparation to one bracket at a time. Prep test blanks with increasing amounts of time prior to injection to determine further extensions to the amount which can be safely loaded onto the instrument without risk of significant contamination.

Table 1: QC Requirements for Total Mercury

QC Parameter	Acceptance Criteria
Initial Calibration Verification (ICV)	79-121% Recovery
Continuing Calibration Verification (CCV)	77-123% Recovery
Ongoing Precision and Recovery (OPR)	77-123% Recovery
Initial Calibration Blank (ICB)/ Continuing Calibration Blank (CCB)	Individually, IBL and CCB ≤ 0.50ng/L, but the mean of all the IBLs shall be ≤ 0.25ng/L with a standard deviation of ≤ 0.10ng/L. For WI DN
Laboratory Control Standard (LCS) or Quality Control Standard (QCS)	80-120% Recovery RSD ≤ 24%
Certified Reference Material	75-125% Recovery RPD ≤ 24%
Calibration Curve RSD (Referred to as "Corr. RSD CF" in Excel spreadsheet).	RSD of Calibration Response Factor ≤ 15%
Lowest Calibration Point	75-125%
1% BrCl Method Blank (BLK)	≤ 0.50ng/L (≤ 0.25ng/L for DOD/DOE projects, ≤ 0.15 ng/L for WI DNR) (individually)
Matrix Duplicate (MD) and Analytical Duplicate (AD)	≤ 24% RPD
Matrix Spike and Matrix Spike Duplicate (MS/MSD) ; Analytical Spike (AS) and Analytical Spike Duplicate (ASD)	71-125% Recovery ≤ 24% RPD

Table 2: Troubleshooting Flow Chart

INSTPOW.ABC\TopChart



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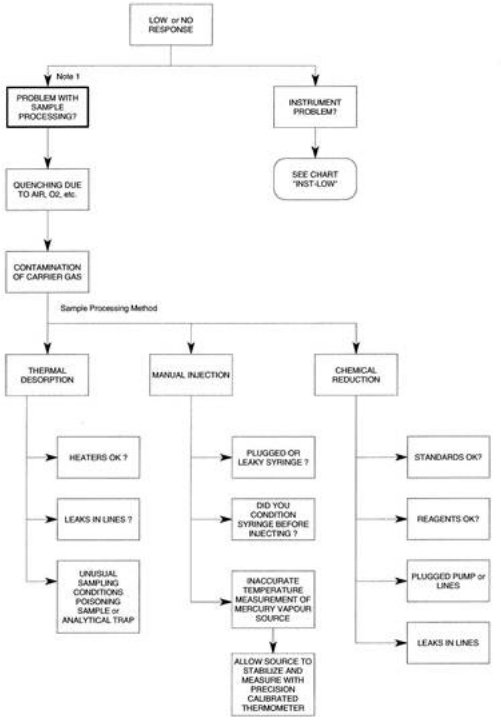

NOTES: 1) Most problems with low responses can be traced to chemical/physical problems with auxiliary equipment.

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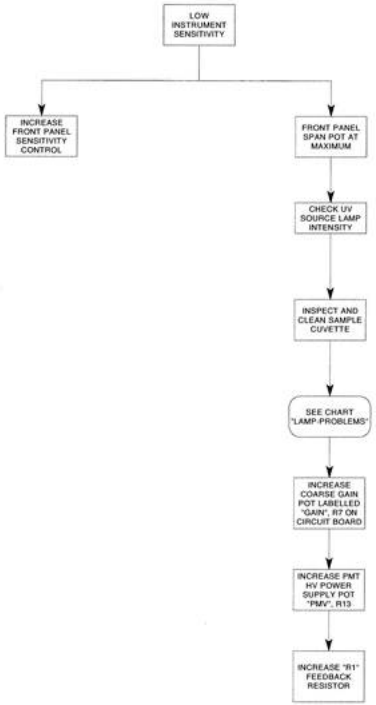

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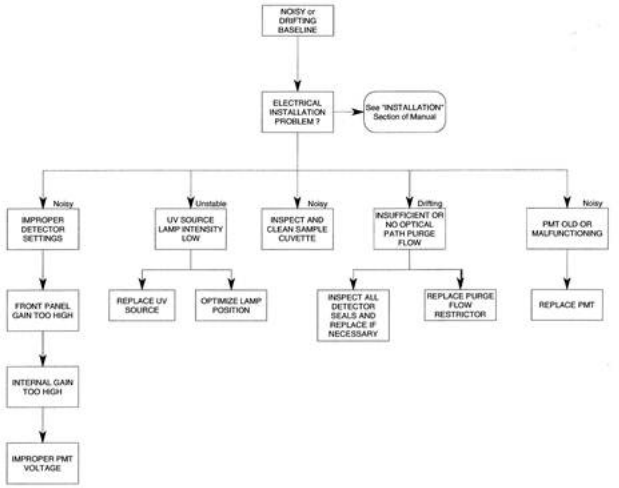

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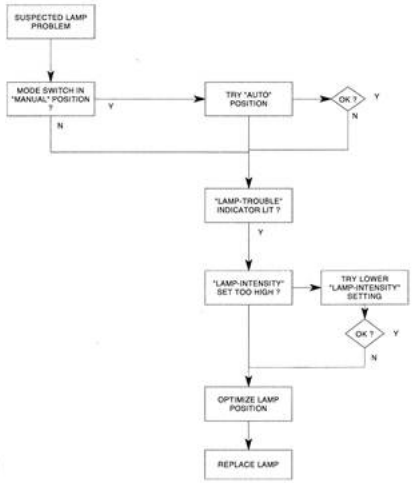
LAMPPROB.ABC\TopChart



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EFGS-P-DR-SOP2801 Data Review and Validation and Monthly Logbook Reviews
EFGS-Q-QD-SOP2710 Class 1 Weight Calibration, Balance Verification, Calibration & Maintenance
EFGS-Q-QD-SOP41510 Volumetric Verification and Pipette and Dispenser Operation & Maintenance
EFGS-Q-QM-QM5805 Quality Assurance Manual
EFGS-S-CS-SOP2794 Ultra-Clean Aqueous Sample Collection
EFGS-S-HS-QP12066.0004 Chemical Hygiene Plan
EFGS-S-HS-SOP2991 Waste Disposal Procedures for Client Sample Waste
EFGS-S-IT-WI7061 Eurofins Frontier Global Sciences - Instrument and Instrument Software Inventory
EFGS-S-SB-SOP5139 Cleaning of Sampling Equipment and Bottles for Trace Metals Analysis
EFGS-T-AFS-SOP2795 Digestion of Tissues for Total Mercury Analysis Using Nitric Acid and Sulfuric Acids (70:30)
EFGS-T-AFS-SOP2800 Digestion of KCl Traps for Total Mercury
EFGS-T-AFS-SOP2807 Preparation of Solids Samples for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion
EFGS-T-AFS-SOP2985 Digestion for Gas/Air Samples Collected on Fluegas Sorbent for Total Mercury™ Traps

EFGS-T-AFS-SOP2992 Mercury in Water by Oxidation, Purge & Trap and CV-AFS (EPA Method 1631, Rev E)
EFGS-T-TM-SOP2821 HF/HNO3/HCl Microwave Digestion of Solids for Total Mercury Followed by Repeated HNO3 Evaporation for Other Metals
EFGS-T-TM-SOP2837 Total Recoverable Metals Digestion for Solid, Animal or Plant Materials
EFGS-T-TM-SOP2839 Stock and Prepared Standards

End of document

Version history

Version	Approval	Revision information	
7.1	15.SEP.2021		
7.2	06.JAN.2023		
7.3	11.MAY.2023		

STANDARD OPERATING PROCEDURE L-2D: PREPARATION OF SOLIDS SAMPLES FOR TOTAL MERCURY ANALYSIS BY MODIFIED COLD AQUA-REGIA DIGESTION

eurofins | Frontier Global Sciences	**Document Title:** Preparation of Solids Samples for Total Mercury Analysis by Modified Cold Aqua-Regia Digestion	**Eurofins Document Reference:** EFAFS-T-AFS-SOP2807

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Prepared by	David Wunderlich
Reviewed and Approved by	David Wunderlich and Patrick Garcia-Strickland

Table of Contents

1 Revision Log:

Revision: 12	**Effective Date:** This version	
Section	**Justification**	**Changes**
2.4	Required	Updated reference
3	Required	Added link to SOP5133
14.6	Required	Corrected the recipe for the preparation of 0.2N BrCl

2 Reference:

2.1 EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, 2002.

2.2 Appendix to Method 1631 - Total Mercury in Tissue, Sludge, Sediment and Soil by Acid Digestion and BrCl Oxidation, 2001.

2.3 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.4 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019.

3 Cross Reference:

Document	Document Title
EFQA-Q-QM-QM5805	Quality Manual
EFHS-S-HS-12066	Chemical Hygiene Plan
EFAFS-T-AFS-SOP5133	Total Solids and Density Determination
EFQA-Q-QD-SOP10098	Procedures for Determining IDLs, MDLs, LODs, LOQs, OPRs, IQs, OQs, and PQs
EFQA-R-EQ-SOP2711	Pipette and volumetric dispenser Verification, Calibration and Maintenance
EFSR-S-CS-SOP2794	Ultra Clean Aqueous Sample Collection
EFQA-P-DR-SOP2801	Data Review and Validation
EFHS-S-HS-SOP2991	Waste Disposal Procedure for Client Sample Waste
EFAFS-T-AFS-SOP2821	HF/HNO_3 /HCl Bomb Digestion of Sediments, Soils, Rocks, and Other Solids for Mercury, followed by Repeated HNO_3 Evaporation for other Metals
EFAFS-T-AFS-SOP2822	Determination of Total Mercury in Various Matrices by Flow Injection Atomic Fluorescence Spectrometry (EPA Method 1631E)

4 Purpose:

4.1 The purpose of this Standard Operating Procedure (SOP) is to describe the method for digesting geological samples (sediments and soils) and carbon (coal) samples prior to analysis for total mercury.

5 Scope:

5.1 This is a strong acid digestion procedure for the preparation of sediments, soils, and other

types of solid materials prior to analysis for total mercury. If other metals besides Hg are to be analyzed as well, the preferred digestion is the HF/HNO_3 bomb digestion method (SOP *EFAFS-T-AFS-SOP2821*, "HF/HNO_3 /HCl Bomb Digestion of Sediments, Soils, Rocks, and Other Solids for Mercury, followed by Repeated HNO_3 Evaporation for other Metals"). Modified aqua regia is particularly capable of solubilizing cinnabar (HgS).

6 Basic Principles:

6.1 Modified aqua regia is not simply a mixture of the two acids. Rather, the oxidizing action of concentrated HNO_3 on HCl results in the formation of nitrosyl chloride (NOCl) and free Cl_2, which are particularly strong oxidizers for noble metals and metal-sulfide minerals. Modified aqua regia only exists as a concentrated acid species—dilution of modified aqua regia with water destroys its unique oxidizing capability, rendering it a simple mixture of HNO_3 and HCl. Furthermore, modified aqua regia loses its strength rapidly after preparation because of the loss of Cl_2 to the atmosphere. Modified aqua regia must therefore always be prepared fresh at the time of use.

6.2 This method involves leaching the sample overnight with modified aqua regia (4:1 HCl/HNO_3) at room temperature.

6.3 This procedure must be performed in a fume hood due to the copious quantities of noxious fumes, including, but not limited to, Cl_2, which are generated during this process.

6.4 Prior to digestion, samples must be homogenized as thoroughly as possible.

6.5 If dry weight correction is required, a separate aliquot of the samples are accurately weighed into small aluminum foil weighing dishes, dried for at least 12 hours at 103-105℃, and then weighed again according to *EFAFS-T-AFS-SOP5133*.

7 Reference Modifications:

7.1 No significant modifications were made to this method.

8 Definitions:

8.1 Batch – no more than 20 client samples grouped for preparation. 3 Preparation Blanks, 1 CRM or 1 LCS/LCSD (or BS/BSD) set are prepared per every 20 samples; 1 MS/MSD set is prepared for every 10 samples.

8.2 Celsius (C), conversion of Celsius to Fahrenheit: (C * 1.8) + 32.

8.3 Fahrenheit (F), conversion of Fahrenheit to Celsius: (F - 32) * 5/9

8.4 Method Detection Limit (MDL) – the limit derived from an exercise as described in 40 CFR, Part 136, Appendix B. The exercise produces a defined value that is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.5 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.6 Blank Spike (BS) and Blank Spike Duplicate (BSD), is a QC sample containing known concentrations of the analytes of interest that is taken through the entire preparation and analysis process in the same manner as the samples to monitor complete method performance.

8.7 Method or Preparation Blank (BLK) – Method blanks consist of the same reagents used to digest the samples, in the same volume or proportion, and are carried through the complete sample preparation and analytical procedure.

8.8 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – a representative sample is selected and should be spiked with a secondary source at *two* to five times the ambient concentration or at five times the MRL, whichever is greater These QC samples will indicate sample matrix effects on the analytes of interest.

8.9 May: This action, activity, or procedural step is optional.

8.10 May Not: This action, activity, or procedural step is prohibited.

8.11 Shall: This action, activity, or procedure is required.

8.12 Should: This action, activity, or procedure is suggested, but not required.

9 Interferences:

9.1 All free halogens in a sample must be reduced prior to purging onto gold traps, or the traps will be destroyed. For small aliquots of digest, this is accomplished by adding $SnCl_2$.

9.2 Low recoveries will result for carbon materials such as coal and iodated carbon traps unless the final solution contains > 40% acid, it remains oxidizing, and all carbon particles are settled out of the aliquot to be analyzed. Low recoveries result from re-adsorption of metals to the carbon particles, which can occur in the digest, after dilution. Following this SOP accurately will avoid this source of error.

9.3 Modified aqua regia is a leaching method and as such does not dissolve silicate minerals. Thus, crustal elements such as Fe, Al, Cr, Ba, and Si will not be quantitatively recovered in most media using this procedure.

10 Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to the Chemical Hygiene Plan (*EFHS-S-HS-12066*). This includes, but is not limited to, laboratory coat, eye protection, and protective gloves.

10.2 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Chemists should refer to the SDS (Safety Data Sheets) for each chemical they are working with.

10.2.1 Note: Use particular caution when preparing and using BrCl, as it releases extremely irritating, corrosive fumes similar in effect to free chlorine. Always handle this reagent in an approved fume hood.

10.2.2 Note: Modified aqua regia is very hazardous! Always work in fume hood wearing safety goggles and gloves while using this chemical.

CAUTION: THIS MIXTURE GETS HOT AND EMITS CAUSTIC FUMES.

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Frontier will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 Hydrochloric acid: Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer). Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering. For more information see SDS.

10.5 Nitric acid (HNO_3): Corrosive. Strong oxidizer. Contact with other material may cause a fire. Causes eye and skin burns. May cause severe respiratory tract irritation with possible burns. For more information see SDS.

10.6 See Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.7 Pollution prevention information can be found in the current Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.8 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to SOP *EFHS-S-HS-SOP2991* "Waste Disposal Procedures for Client Sample Waste," which provides instruction on dealing with laboratory and client waste.

11 Personnel Training and Qualifications:

11.1 An analyst and technician must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source spiked at 8 ng/g before being qualified to analyze samples without supervision. Recoveries for the IDOC need to be 79-121% with an RSD of < 20%. Continuing DOC will be maintained and monitored via performance on CRMs and other QC samples, as well as obtaining acceptable results on proficiency testing exercises.

11.2 The analyst/laboratory technician must have read this SOP and other relevant SOPs and have the training documented on the applicable form(s). The analyst may be questioned on SOP by supervisor(s) and/or trainers.

11.3 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.4 All employees must read the Quality Manual (QM) and complete annual Ethics training.

11.5 All training documents including IDOCs, CDOCs, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employees training file for ten years after the employee is no longer working for Frontier Global Sciences.

11.6 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous goods training, are stored by the Health and

Safety Officer for ten years after the employee is no longer working for Frontier Global Sciences.

12 Sample Collection, Preservation, and Handling:

12.1 Sediment, soil, and other geological samples must be collected in accordance with established ultraclean sampling techniques (see e.g. *EFSR-S-CS-SOP2794* "Ultra Clean Aqueous Sample Collection"). Samples may be placed in commercially available clean glass containers with Teflon-lined caps (i.e., I-Chem glass jars), or 125-mL or 250-mL HDPE jars.

12.2 Soil and sediment samples must be frozen at < □11 □C. Maximum holding time is 180 days at < □11 □C.

12.3 For Wisconsin, sediment samples will be refrigerated upon receipt and then homogenized, prepared and analyzed within 28 days of collection.

13 Apparatus and Equipment:

13.1 Digestion Vials: In most cases, this digestion is performed in tested-cleaned (i.e., I-Chem series 300 or equivalent) 40.0-mL borosilicate glass vials with Teflon lined caps.

13.2 Pipettors: Hydrochloric and nitric acids are conveniently dispensed separately from all glass or glass and Teflon bottle-top repetitive pipettors (10-mL size Re-Pipette or equivalent). Pipettes are to be calibrated according to SOPs *EFQA-R-EQ-SOP2711*.

13.3 Clean hood.

13.4 Analytical Balance: A laboratory analytical balance capable of weighing to ± 1 mg, with documented calibration.

13.5 Sample Digestion Log (LOG-HG-013) logbook.

13.6 Plastic or glass tools for homogenization.

13.7 Tongue Depressors and/or paper scoops.

13.8 Teflon boiling chips.

13.9 Centrifuge operating at 2000 RPM.

13.10 0.45-□m disposable filters.

14 Reagents and Standards:

14.1 Reagent Water: 18 M□ ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. As a final mercury and organic removal step, the activated carbon cartridge on the 18-M□ system is placed between the final ion exchange bed and the 0.2 µm filter.

14.2 Nitric Acid (HNO3): Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent should be from a lot number that has been previously tested to be low for the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to the same as the manufacturer's expiration date.

14.3 Hydrochloric Acid (HCl): Trace metal purified reagent-grade HCl is pre-analyzed to < 50

ng/L Hg and lot sequestered and before purchase. This solution shall be entered into LIMS and is considered stable until the expiration date on the bottle, 6 months from receipt.

14.4 Potassium Bromide (KBr), neat: This reagent is pre-certified by the vendor to be low in mercury. Reagent shall be entered into LIMS with a five year expiration date.

14.5 Potassium Bromate ($KBrO_3$), neat:

This reagent is pre-certified by the vendor to be low in mercury. Reagent shall be entered into LIMS with a five year expiration date**.**

14.6 0.2N Bromine Monochloride (BrCl):

14.6.1 27 g of KBr is added to a 2.5 L bottle of concentrated HCl (pre-analyzed and below 5 ng/L Hg). The bottle is inverted in a fume hood to mix the acid and KBr. The solution sits overnight, allowing the KBr to dissolve.

14.6.2 38 g of KBrO3 (certified to be low in Hg) is slowly added to the acid. As the KBrO3 is added, the solution should go from yellow to red to orange.

CAUTION: This process generates copious quantities of free halogens (Cl_2, Br_2, BrCl) which are released from the bottle. Add the $KBrO_3$ SLOWLY in a well operating fume hood.

14.6.3 Loosely cap the bottle and allow to sit for at least 1 hour in a fume hood before tightening. Once tightly capped, invert bottle to make sure all of the solids go into solution.

14.6.4 The BrCL solution must be tested by analyzing a prepared 0.5% solution. The result must be < 0.20ng/L.

14.6.5 The expiration time for this reagent is set by default to six months in LIMS. There is no suggested expiration date in EPA method 1631E, therefore it can be extended, as long as the primary reagent has not expired. The mercury concentration of the BrCl is monitored through the preparation of water preparation blanks.

14.7 0.07 N (35%) Bromine Monochloride. Dilute 330 ± 40 mL of the 0.2 N BrCl solution to 1.0 L with reagent water in a 1000-mL Teflon bottle.

14.7.1 Reagent shall be entered into LIMS with a six months expiration date.

14.8 5% (v/v) of 0.2N BrCl: 125 ± 40 mL of 0.2N BrCl is diluted up to 2.5 L with reagent water in a clean, empty HCl bottle. This bottle is fitted with a 50 mL repipettor.

14.8.1 Reagent shall be entered into LIMS with a six months expiration date.

15 Procedures:

15.1 Obtain samples from the designated refrigerator or freezer. All samples must be completely thawed before homogenizing and weighing out. All tools used for homogenization and weighing must be new, unused disposable tools or cleaned thoroughly between samples with one 10% HCl acid bath and one reagent bath.

15.2 Weigh a 0.5g to 1.0g aliquot for common, low-level or large-grain samples. Place the aliquot directly into a 40-mL digestion vial.

15.2.1 Batch requirements for this digestion limit the number of samples to 20. In each batch, there must be three method blanks (BLKs), a Blank Spike and Blank Spike Duplicate (BS/BSD, liquid spike, prepared at 8 ng/g), and a Matrix Spike and Matrix Spike Duplicate (MS/MSD). The customary spiking volume used for the MS is 200 uL of 1000 ng/mL. A certified reference material should also be added to the batch if available and representative of the sample matrix.

15.3 Add 8 mL of concentrated HCl and swirl the sample to wet all particles. Next, add 2 mL of concentrated HNO_3, swirl, and LOOSELY cap the vials.

15.4 Allow the loosely capped samples to digest in the fume hood at room temperature for at least 4 hours, or preferably overnight. Tightening the caps or heating the samples can cause the vials to explode. At temperatures cooler than 18 □C the reaction is less vigorous so there may be a longer digestion time. At temperatures higher than 25℃, the reaction can generate much free chlorine, causing some samples to foam over.

15.5 After digestion is complete, dilute soil or sediment digestions by adding 30 mL of 5% solution of 0.2 N BrCl. Shake vigorously and allow settling until the supernatant is clear prior to analysis.

15.6 For coal and other carbon materials, dilute the samples with 0.07 N BrCl solution (35% v/v). This ensures that of Hg will not re-adsorb to the carbon particles, producing low recoveries. Be sure that all finely grained particles are completely settled prior to analysis. This settling can be hastened by centrifuging for 20 minutes at 2000 RPM or by pre-filtering the sample through 0.45-□m disposable filters.

Caution: when adding BrCl to modified aqua regia, be aware of possible rapid bubble formation and foaming out of the vial. This is particularly a problem with carbon media, warm digests, and samples that have only been digested for a few hours

15.7 Analysis for total mercury is according to Eurofins Frontier SOP *EFAFS-T-AFS-SOP2822*.

16 Calculations:

16.1 This preparation procedure does not involve calculations.

17 Statistical Information/Method Performance

17.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and and *EFQA-Q-QD-SOP10098*.

17.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3). The PQL is determined by running ten replicate samples with a concentration the will produce a recovery of 70-130% for most analytes, but the recovery requirements are analyte dependent. The PQL is referred to as the Method Reporting Limit (MRL) in LIMS.

17.3 The current values for THg in sediments prepared by a Cold Modified Aqua Regia Digestion are 0.11 ng/g for the MDL and 1.00 ng/g for the PQL.

17.4 Current MDLs and PQLs are stored at: \General and Admin\Quality Assurance\MDLs & PQLs.

18 Quality Assurance/Quality Control:

18.1 Maximum Sample Batch Size: 20 samples.

18.2 Preparation Blanks: Minimum of three per batch. The preparation blanks are prepared with a similar mass of Teflon boiling chips as the samples, with the same reagents, and put through the same preparation process as the samples. The LIMS ID or lot # of the Teflon boiling chips is documented in the digestion logbook. Each preparation blank must be less than one-half the PQL for the method.

18.3 Certified Reference Material (CRM, representing the sample matrix when commercially available); One per batch if available.

18.4 Blank Spike (BS) and Blank Spike Duplicate (BSD): For every set of 20 samples or less, a blank spike and blank spike duplicate (BS1/BSD1) - made from spiking a liquid standard onto Teflon boiling chips - are digested. The LIMS ID or lot # of the Teflon boiling chips is documented in the digestion logbook.

18.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples: One set per 10 samples.

18.6 Follow the flow charts in SOP *EFQA-P-DR-SOP2801* "Data Review and Validation" to determine if any QC falling outside the established control limits can be qualified.

18.7 All of the quality control limits for the analysis method are included on the "Data Review Checklist."

18.7.1 The data review checklists are located at: \\cuprum\General and Admin\Quality Assurance\Data Review\Current Data Review Checklists.

19 Corrective Action:

19.1 A failing QC point does not necessary fail the entire dataset. If upon analysis a QC sample is out of control, some investigation must be performed to assess if the difficulties are related to matrix effects. The cause and method of determining the set's failure must be documented on the checklist and in the MMO notes, and the Group Supervisor shall be informed. See SOP *EFQA-P-DR-SOP2801* "Data Review and Validation" for flow charts regarding analytical issues.

19.2 If there is any question as to the completeness of the digestion procedure, the samples must be allowed to react for an additional amount of time. If there is no change in the sample, the digestion is considered complete and can be diluted.

EFAFS-T-AFS-SOP2822 Determination of Total Mercury in Various Matrices by FI-AFS
EFAFS-T-AFS-SOP5133 Total Solids and Density Determination
EFHS-S-HS-12066.0004 Chemical Hygiene Plan
EFHS-S-HS-SOP2991 Waste Disposal Procedures for Client Sample Waste
EFQA-P-DR-SOP2801 Data Review and Validation and Monthly Logbook Reviews
EFQA-Q-QD-SOP10098 Procedures for Determining IDLs, MDLs, LODs, PQLs, LOQs, OPRs, IQs, OQs and PQs
EFQA-Q-QM-QM5805 Quality Manual
EFQA-R-EQ-SOP2711 Pipette and Dispenser: Operation, Calibration & Maintenance
EFSR-S-CS-SOP2794 Ultra-Clean Aqueous Sample Collection
EFTM-T-TM-SOP2821 HF/HNO3/ HCl Bomb Digestion of Solids for Total Mercury Followed by Repeated HNO3 Evaporation for Other Metals

End of document

Version history

Version	Approval	Revision information
10	09.NOV.2016	
11	08.MAR.2018	
12	21.FEB.2020	

STANDARD OPERATING PROCEDURE L-2E: KOH/METHANOL DIGESTION OF TISSUES FOR METHYL MERCURY ANALYSIS

eurofins | Frontier Global Sciences	**Document Title:** KOH/Methanol Digestion of Tissues for Methyl Mercury Analysis	**Eurofins Document Reference:** EFAFS-T-AFS-SOP2986

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Prepared by	Terri Torres
Reviewed and Approved by	Terri Torres and Patrick Garcia-Strickland

Table of Contents

1 Revision Log:

Revision: 10	**Effective Date:** This version	
Section	**Justification**	**Changes**
2.5	Required	Updated reference
3	Required	Added CHP/QM
10.1/10.2	Required	Updated
11.4	Required	Added link to QM
13.1	Required	Removed Windows XP from apparatus
14.1.2	Required	Added pipette rinse
15.1	Updated	Changed acid cleaned to 409 cleaned, removed instruction to create equipment blanks for homogenization
17.1	Required	Updated definition
18.4/15.2	Required	Removed requirement for MD

2 Reference:

2.1 Chemical Hygiene Plan, Eurofins Frontier Global Sciences, current version.

2.2 Bloom, N. S. (1989) "Determination of Picogram Levels of Methyl Mercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapor Atomic Fluorescence Detection," *Can. J. Fish. Aq. Sci.*, 46: 1131.

2.3 Bloom, N. S. and Crecelius, E. A. (1983) "Determination of Mercury in Seawater at Subnanogram per Litre Levels," *Mar. Chem.* 14: 49

2.4 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.5 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019.

3 Cross Reference:

Document	Document Title
EFQA-Q-QM-QM5805	Quality Manual
EFHS-S-HS-12066	Chemical Hygiene Plan
EFQA-R-EQ-SOP2711	Pipette and Dispenser Operation, Calibration and Maintenance
EFSR-S-CS-SOP2794	Ultra Clean Aqueous Sample Collection
EFQA-P-DR-SOP2801	Data Review and Validation
EFAFS-T-AFS-SOP2808	Determination of Methyl Mercury in Various Matrices by CV–GC–AFS
EFAFS-T-AFS-SOP2808	Determination of Methyl Mercury in Various Matrices by Cold Vapor - Gas Chromatography - Atomic Fluorescence Spectrometry (CV-GC-AFS)
EFHS-S-HS-SOP2991	Waste Disposal Procedure for Client Sample Waste

4 Purpose:.

4.1 The purpose of this Standard Operating Procedure (SOP) is to describe the method for digesting biological tissue samples using a Potassium Hydroxide/Methanol solution for analysis of monomethyl mercury.

5 Scope:

5.1 This method is for the determination of monomethyl mercury (MMHg) in tissue samples that are expected to contain 'high' levels of MMHg. Such samples include tissues from all fish and animals from higher trophic levels. Although this method may also be used for the preparation of contaminated ('high') sediments and soils for MMHg analysis, this is rarely used for that application. Samples that are digested with potassium hydroxide (KOH) and methanol are analyzed using aqueous phase ethylation coupled with cold vapor – gas chromatography – atomic fluorescence spectroscopy (CV-GC-AFS), as described in Frontier SOP *EFAFS-T-AFS-SOP2808*, “Methyl Mercury Calibration and Analysis".

5.2 Monomethyl mercury, as defined by this method, means all MMHg forms and species found in the digestate. This includes, but is not limited to, CH_3Hg^+, CH_3HgCl, CH_3HgOH, and CH_3HgS-R.

6 Basic Principles:

6.1 Samples are collected using clean sample handling protocols into commercially available clean glass containers with Teflon-lined caps (i.e., I-Chem glass jars) or 125 mL or 250 mL HDPE jars. Freezing (< 18℃) preserves tissue s amples until sample preparation is performed.

6.2 Tissues samples are weighed out in glass vials and digested using heated 25% KOH in methanol.

7 Reference Modifications:

7.1 No significant modifications were made to this method.

8 Definitions:

8.1 Batch - 20 client samples grouped for preparation. See Quality Assurance section for batch requirements.

8.2 Method Detection Limit (MDL) – the limit derived from an exercise as described in 40 CFR, Part 136, Appendix B. The exercise produces a defined value that is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.3 Limit of Detection (LOD) – equal to MDL and verified on an annual basis by spiking within three times the established LOD and showing a positive result on the instrument.

8.4 Limit of Quantitation (LOQ) – equal to PQL and verified on an annual basis by spiking within 2 times the LOQ and showing a recovery between 70 – 130%.

8.5 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.6 Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD), is a sample containing known concentrations of the analytes of interest that is taken through the entire preparation and analysis process in the same manner as the samples to monitor complete method performance. A Certified Reference Material (CRM) is preferred as the LCS, but a blank spiked sample also meets the requirement.

8.7 Preparation Blank (BLK) – Method blanks consist of the same reagents used to digest the samples, in the same volume or proportion, and are carried through the complete sample preparation and analytical procedure. Teflon boiling chips are added to the preparation blanks.

8.8 Matrix Duplicate (MD) – a representative sample is selected and digested in the same manner. This QC sample will indicate sample homogeneity on the analytes of interest.

8.9 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) - a representative sample is selected and spiked with a secondary source at 1-5 times the ambient concentration or 1-5 times the MRL, whichever is greater. These QC samples will show sample matrix effects on the analytes of interest.

8.10 May: This action, activity or procedure is optional.

8.11 May Not: This action, activity or procedure is prohibited.

8.12 Shall: This action, activity or procedure is required.

8.13 Should: This action, activity or procedure is suggested, but is not required.

9 Interferences:

9.1 The tissue digestate itself causes an interference with the ethylation reaction during analysis. The use of uniform sample weights and the use of the smallest sample aliquot necessary for accurate quantification can overcome this.

9.2 No HNO_3 or other oxidizing agents (Cl_2, BrCl, CrO_4^{2-}, etc.) should be present in the sample, or MMHg compounds may be destroyed. In addition, chlorine present in dilution or reagent water destroys both MMHg and the reagent, rendering the method useless. As a precaution, a carbon column is placed on the output side of the 18 MO water purification systems to remove any traces of chlorine and deionizing resins.

10 Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to Chemical Hygiene Plan (CHP) *EFHS-S-HS-QP12066*. This may include, but is not limited to: laboratory coat, apron, eye protection, face shield and protective gloves.

10.2 The toxicity or carcinogenicity of each laboratory reagent has not been fully established. Therefore, every chemical must be treated as a potential health hazard. Exposures shall be reduced as much as possible. Analysts and technicians are expected to familiarize themselves with the characteristics and risks of each chemical they work with by referring to the SDS located at

https://msdsmanagement.msdsonline.com/company/5c1df5b3-747d-4789-8104-42457dc3a3e5/

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Eurofins Frontier will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 Methanol (CH_3OH, MeOH): May be fatal or cause blindness if swallowed. Flammable liquid and vapor. Harmful if swallowed, inhaled, or absorbed through the skin. Causes eye, skin, and respiratory tract irritation. May cause central nervous system depression. Cannot be made non-poisonous. See SDS for more details.

10.5 Potassium Hydroxide (KOH): very hazardous in case of skin or eye contact (corrosive, irritant) or ingestion, or inhalation. The amount of tissue damage depends on the length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering. See SDS for more details.

10.5.1 Eye Contact: Check for and remove any contact lenses. Immediately flush eyes with water for at least 15 minutes. Get medical attention immediately.

10.5.2 Skin Contact: Immediately flush skin with water for 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with emollient. Get medical attention immediately. Wash clothing and clean shoes before re-use.

10.6 See Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.7 Pollution prevention information can be found in the current Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.8 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to SOP *EFHS-S-HS-SOP2991* "Waste Disposal Procedure for Client Sample Waste," which provides instruction on dealing with laboratory and client waste.

11 Personnel Training and Qualifications:

11.1 A lab technician/analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source before being qualified to prepare samples without supervision. Continuing DOC will be maintained and monitored via performance on CRMs and other QC samples.

11.2 The analyst/laboratory technician must have read this SOP and other relevant SOPs and have the training documented on the applicable form(s). The analyst may be questioned on SOP by supervisor(s) and/or trainers.

11.3 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related

to this method.

11.4 All employees must read the *Quality Manual (QM)* and complete annual Ethics training.

11.5 All training documents, including demonstrations of capability, SOP reading, QA and ethics training, and safety training, are stored by QA in the employees training file for ten years after the employee is no longer working for EFGS.

12 Sample Collection, Preservation, and Handling:

12.1 Samples must be collected in accordance with established ultraclean sampling techniques (see *EFSR-S-CS-SOP2794* "Ultra Clean Aqueous Sample Collection").

12.2 Tissue sample preservation - The tissue sample must be frozen in the sampling container at less than -18℃ or freeze-dried and stored at ro om temperature. The holding time for tissue samples is 2 years.

12.3 Just prior to digestion, samples are thawed and if necessary homogenized. The sample is well mixed to ensure the most representative sample possible.

13 Apparatus and Equipment:

13.1 LIMS – Element, version 6.11 or higher; Computer – Windows 7 or 8.

13.2 20 mL I-Chem Vials: Borosilicate glass, series 300 vials with Teflon-lined septa in lids. The size used depends on the amount of sample available.

13.3 Hot plate: A hot plate with the ability to achieve and maintain a temperature of 75 ± 5℃ ℃.

13.4 Pipettors: All-plastic, pneumatic, fixed volume and variable pipettes in the range of 20 µL to 5 mL. Pipettes are to be calibrated weekly according to SOP *EFQA-R-EQ-SOP2711*.

13.5 Dispenser: Organic dispenser with digital readings able to dispense methanol.

13.6 Clean hood.

13.7 Analytical Balance: A laboratory analytical balance capable of weighing to ± 1 mg, with documented calibration.

13.8 Calibrated thermometer: Submerged in water in a 20 mL I-Chem vial. This vial is placed on the hotplate during the digestion process. The cell selected for temperature monitoring must be different than cells selected for the previous ten batches at a minimum. The analyst must record the cell position (designated as position A1, B6, C7, etc., from the diagram in the logbook), raw and corrected initial and final digestion temperatures and the serial number of the thermometer used in the digestion logbook.

13.9 Sample Digestion Log.

13.10 Stainless steel tools for homogenization

13.11 Tissue Homogenization Log.

13.12 Disposable spatula.

13.13 Teflon boiling chips.

13.14 Teflon reflux cap to fit the 40 mL and 20 mL I-Chem vials.

14 Reagents and Standards:

14.1 Reagent Water: 18 MW ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. As a final mercury and organic removal step, the activated carbon cartridge on the 18-MW system is placed between the final ion exchange bed and the 0.2 µm filter.

14.1.1 Methyl mercury is not analyzed on the monthly water samples, but is monitored through the preparation blanks.

14.1.2 Pipette tip rinse bottle labeled:

Speciation Rinse, MQ only

To be used for all speciation analysis: As, DMHg, CrVI, HgO, MMHg, Se and any other type of speciation analysis. Anything that requires us to evaluate an oxidation state of any metal.

14.2 Potassium Hydroxide (KOH): Reagent shall be entered into the LIMS with a five year expiration date.

14.3 Methanol (CH_3OH): Reagent shall be entered into the LIMS and is considered stable until the expiration date on the bottle, set by the manufacturer.

14.4 25% Potassium Hydroxide/Methanol: 250 g of reagent grade KOH is dissolved in methanol to make a final volume of 1.0 L. This solution has a 6 month shelf life when stored in a Teflon bottle at room temperature. CAUTION: THIS MIXTURE BECOMES VERY HOT - POTENTIALLY BRINGING THE METHANOL TO THE BOILING POINT.

15 Procedures:

15.1 If needed, the sample is dissected and homogenized with 409 cleaned stainless steel tools or a food processor. Note: Equipment blanks are not required for MHg analysis.

15.1.1 The process used for homogenization, number of samples, work order number, client name, and initials of the technician are entered into the Tissue Homogenization Log.

15.2 Approximately 0.25 g of the homogenate is transferred to a 20 mL I-Chem vial. All samples should be weighed to the nearest milligram and, if possible, within 10% of each other in mass.

15.2.1 It is imperative that all biological tissue samples are thoroughly homogenized. The importance of representativeness cannot be understated.

15.2.2 Batch requirements for this digestion limit the number of samples to 20. In each batch, there must be three method blanks (BLKs), a Blank Spike and Blank Spike Duplicate (BS/BSD) that is preferably a Certified Reference Material (CRM) or a Laboratory Control Spike (LCS), and a Matrix Spike and Matrix Spike Duplicate (MS/MSD).

15.3 Unused homogenate is returned to the freezer.

15.4 5 mL of the 25% KOH/methanol reagent is added to each sample.

15.5 The sample is capped, shaken, and placed on a hot plate at 75 ± 5℃ for 2-4 hours, or until all soft tissue is visibly made soluble. It is not unusual to have particulate matter (usually cartilage, shells, and/or fatty material) in the digestion vial. Care must be taken

not to overheat the vials, as the methanol may evaporate.

15.5.1 A calibrated thermometer submerged in water is placed in a 20 mL I-Chem vial. This I-Chem vial with a calibrated thermometer is placed on the hot plate during the digestion process. The cell selected for temperature monitoring must be different than cells selected for the previous ten batches at a minimum. The analyst must record the cell position (designated as position A1, B6, C7, etc., from the diagram in the logbook), raw and corrected initial and final digestion temperatures and the serial number of the thermometer used in the digestion logbook.

15.6 The samples are allowed to cool to room temperature and diluted with 15mL of methanol using the calibrated methanol dispenser. After dilution, samples are capped and agitated again.

15.7 Samples with un-dissolved solids are allowed to settle thoroughly prior to analysis.

15.8 Analysis for methyl mercury is according to Eurofins Frontier SOP *EFAFS-T-AFS-SOP2808*.

16 Calculations:

16.1 This preparation procedure does not involve calculations.

17 Statistical Information/Method Performance

17.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and *EFQA-Q-QD-SOP10098*.

17.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3). The PQL is determined by running ten replicate samples with a concentration that will produce a recovery of 70-130% for most analytes, but the recovery requirements are analyte dependent. The PQL is referred to as the Method Reporting Limit (MRL) in LIMS.

17.3 Current LODs and LOQs are stored at: General and Admin\Quality Assurance\MDLs & PQLs.

18 Quality Assurance/Quality Control:

18.1 Maximum Sample Batch Size: 20 samples.

18.2 Preparation Blanks: Minimum of three per batch. Each preparation blank must be less than one-half the PQL for the method.

18.2.1 The preparation blanks are prepared with a similar mass of Teflon boiling chips as the samples, with the same reagents, and put through the same preparation process as the samples. The LIMS ID or lot # of the Teflon boiling chips is documented in the digestion logbook.

18.3 Certified Reference Material (CRM, representing the sample matrix when commercially available); a Laboratory Control Spike (LCS) and Laboratory Control Spike Duplicate (LCSD) is used when a suitable CRM is not available: One per batch in duplicate. The control limits are 70-130% recovery.

18.4 Matrix Duplicate (MD): Not required. A Matrix Duplicate (MD) may be analyzed for every batch of 20 samples upon client request. The control limit for the RPD is = 35%.

18.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples: One set per 10 samples. The control limits are 65-130% recoveries and an RPD of = 35%.

18.6 Follow the flow charts in SOP *EFQA-P-DR-SOP2801* "Data Review and Validation" to determine if any QC falling outside the established control limits can be qualified.

18.7 All of the quality control limits for the analysis method are included on the "Data Review Checklist.

18.7.1 The data review checklists are located at: \\US34fila\General and Admin\Quality Assurance\Data Review\Current Data Review Checklists.

19 Corrective Action:

19.1 If CRM recovery is not within 70-130%, reanalyze to verify result. If CRM recovery is still outside of the control limits, consult with the group leader, QA Officer and the project manager. Under most circumstances, re-digest will be required.

19.2 If MD or MS/MSD RPD exceeds 35%, then reanalyze to verify results. If re-digestion is required, ensure that all samples are homogenized well.

19.3 If MS/MSD recoveries are not within 65-130%, reanalyze to verify result. If recoveries are still outside of the control limits, attempt to analyze a smaller aliquot size, if this is possible without compromising quality. Perform analytical spike and analytical spike duplicate (AS/ASD) to determine if matrix interference is an issue.

19.4 A failing QC point does not necessary fail the entire dataset. If upon analysis a QC sample is out of control, some investigation must be performed to assess if the difficulties are related to matrix effects. The cause and method of determining the set's failure must be documented on the checklist and in the MMO notes, and the Group Supervisor shall be informed. See SOP *EFQA-P-DR-SOP2801* "Data Review and Validation" for flow charts regarding analytical issues.

19.5 Additional corrective actions are listed in the SOP for methyl mercury analysis (Eurofins Frontier SOP *EFAFS-T-AFS-SOP2808*).

EFAFS-T-AFS-SOP2808 Determination of Methyl Mercury in Various Matrices by CV–GC–AFS
EFHS-S-HS-12066.0004 Chemical Hygiene Plan
EFHS-S-HS-SOP2991 Waste Disposal Procedures for Client Sample Waste
EFQA-P-DR-SOP2801 Data Review and Validation and Monthly Logbook Reviews
EFQA-Q-QD-SOP10098 Procedures for Determining IDLs, MDLs, LODs, PQLs, LOQs, OPRs, IQs, OQs and PQs
EFQA-Q-QM-QM5805 Quality Manual
EFQA-R-EQ-SOP2711 Pipette and Dispenser: Operation, Calibration & Maintenance
EFSR-S-CS-SOP2794 Ultra-Clean Aqueous Sample Collection

End of document

Version history

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8	21.MAY.2016	
9	09.MAY.2017	
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STANDARD OPERATING PROCEDURE L-2F: MERCURY IN WATER BY OXIDATION, PURGE & TRAP AND CV-AFS (EPA METHOD 1631, REV E)

eurofins | Frontier Global Sciences	**Document Title:** Mercury in Water by Oxidation, Purge & Trap and CV-AFS (EPA Method 1631, Rev E)	**Eurofins Document Reference:** EFAFS-T-AFS-SOP2992

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Prepared by	Bryn Fada
Reviewed and Approved by	Terri Torres and Patrick Garcia-Strickland

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1 Revision Log:

Revision: 06	**Effective Date:** This version	
Section	**Justification**	**Changes**
2.15	Required	Updated reference
3	Required	Added link to CHP/QM/standard SOP
6	Required	Delete references to the bubbler system
6	Required	Added description of the 2600 system
8.17	Required	Updated LOD definition
10.1/10.2	Required	Updated and added links to SDS/CHP
11.4	Required	Added link to QM
14.3	Required	Corrected the recipe for the preparation of 0.2N BrCl
14.8	Required	Updated NIST 1641 Standard (d to e).
14.8/9	Updated	Removed info regarding the receipt, prep, and storage of standards and added link to new standard SOP. Renumbered sections.
14.9	Required	Added HNO3 and RINSE
17	Required	Replaced algorithms with reference to SOP2822
19.3	Required	Reworded to clarify MD's aren't required
19.14	Required	Added carryover section. Blank now required after samples over 200 ng/L only.

2 Reference:

2.1 EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, 2002.

2.2 Method 1669, "Method for Sampling Ambient Water for Determination of Metals at EPA Ambient Criteria Levels," U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303), 401 M Street SW, Washington, DC 20460, April 1995 with January 1996 revisions.

2.3 Bloom, N.S.; and Tsalkitzis, E. Standard Operating Procedure FGS-012 Determination of Total Mercury in Aqueous Media (Modified EPA Method1631). Frontier GeoSciences Inc., Quality Assurance Manual 1995.

2.4 Bloom, N.S.; Ultra-Clean Sample Handling, Environmental Lab 1995, March/April, 20.

2.5 Bloom, N.S.; Horvat M., and Watras C.J. Results of the International Mercury Speciation Intercomparison Exercise. Wat. Air Soil Pollut. 1995, 80, 1257.

2.6 Bloom, N.S.; Crecelius, E.A. Determination of Mercury in Seawater at Sub-nanogram per Liter Levels.Mar.Chem.1983, 14, 49.

2.7 Bloom, N.S.; Crecelius, E.A. Distribution of Silver, Lead, Mercury, Copper, and Cadmium in Central Puget Sound Sediments Mar. Chem 1987, 21, 377-390.

2.8 Bloom, N.S.; Fitzgerald, W.F. Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection. Anal. Chem. Acta. 1988, 208, 151.

2.9 Cossa, D.; Couran, P. An International Intercomparison Exercise for Total Mercury in Seawater. App.Organomet. Chem.1990, 4, 49.

2.10 Fitzgerald, W.F.; Gill, G.A. Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis. Anal. Chem. 1979, 15, 1714.

2.11 Gill, G.A.; Fitzgerald, W.F. Mercury Sampling of Open Ocean Waters at the Picogram Level Deep Sea Res.1985, 32, 287.

2.12 EPA Method 30.B, Determination of total vapor phase mercury emissions from coal-fired combustion sources using carbon sorbent traps.

2.13 Chemical Hygiene Plan, Eurofins Frontier Global Sciences, current version.

2.14 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.15 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019.

3 Cross Reference:

Document	Document Title
EFQA-Q-QM-QM5805	*Quality Manual*
EFHS-S-HS-12066	*Chemical Hygiene Plan*
EFQA-R-EQ-SOP2711	*Pipette and Dispenser Operation, Calibration and Maintenance*
EFAFS-S-SB-SOP5132	*Cleaning of Sampling Equipment and Bottles for Mercury Analysis*
EFSR-S-CS-SOP2794	*Ultra Clean Aqueous Sample Collection*
EFSR-P-SP-SOP2796	*Oxidation of Aqueous Samples for Total Mercury Analysis*
EFAFS-S-T-SOP5138	*Gold Trap Construction*
EFHS-S-HS-SOP2991	*Waste Disposal Procedures for Client Sample Waste*
EFAFS-T-AFS-SOP2822	*Determination of Total Mercury by Flow Injection AFS (Mod 1631E)*
EFTM-T-TM-SOP2839	*Stock and Prepared Standards*

4 Purpose:

4.1 This SOP is designed to ensure that all reproducible traceable procedures in EPA 1631 are followed in the standardization of the total mercury analyzers and in the analysis of samples for total mercury, as well as to establish the limits wherein data will be considered acceptable.

5 Scope:

5.1 This Standard Operating Procedure (SOP) describes a method for the determination of total mercury (Hg) in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold vapor atomic fluorescence spectrometry (CVAFS).

5.2 This method is designed for the determination of mercury in the range of 0.5-40 ng/L (ppt). Application may be extended to higher levels by selection of a smaller sample size, as long as the instrument value (intensity) remains within the calibration curve.

5.3 The control limits used in this procedure are from EPA 1631E.

6 Basic Principles:

6.1 Total mercury analyses are split into two categories: waters and solids. For analysis of aqueous samples, a dilution (up to 1x) of oxidized sample is added to a 50mL vial. If less than 30mL of sample is used, the sample is diluted to a final volume of at least 30mL with 1% BrCl. The final volume is neutralized with 25uL of 25% hydroxylamine-hydrochloride (NH2OH-HCl). Approximately 25mL of sample is drawn into the system by an auto sampler. (Please refer to Figure 1. for a detailed system flow diagram of the Tekran 2600 analysis system.) Sample is then mixed with 3% stannous chloride (SnCl2) reducing Hg2+ to Hg0 before entering the phase separator.

6.2 As sample travels down the phase separator Hg0 is liberated by a counter flow of ultra pure argon (or nitrogen). Mercury then travels through a soda-lime acid vapor trap, a switching valve (V2), and amalgamates onto the fixed “sample trap”. Following primary amalgamation V2 is triggered, switching on the flow of pure argon through the sample trap. At the same time the sample trap is heated, and mercury is released into the pure argon gas stream, passing through a second switching valve (V1) and amalgamating onto the “analytical trap”. The analytical trap is then heated releasing mercury into the AFS detector. All event timing and peak integration is carried out via a PC running TekMDS-2 software running the EPA 1631 event timing file (ETF). NOTE: This method may also be run using 15ml vials and selecting the appropriate ETF with in the TekMDS-2 software. Sample must fill the vial up to the 15ml mark. All other procedures, reagent concentrations, and dilutions should be kept the same.

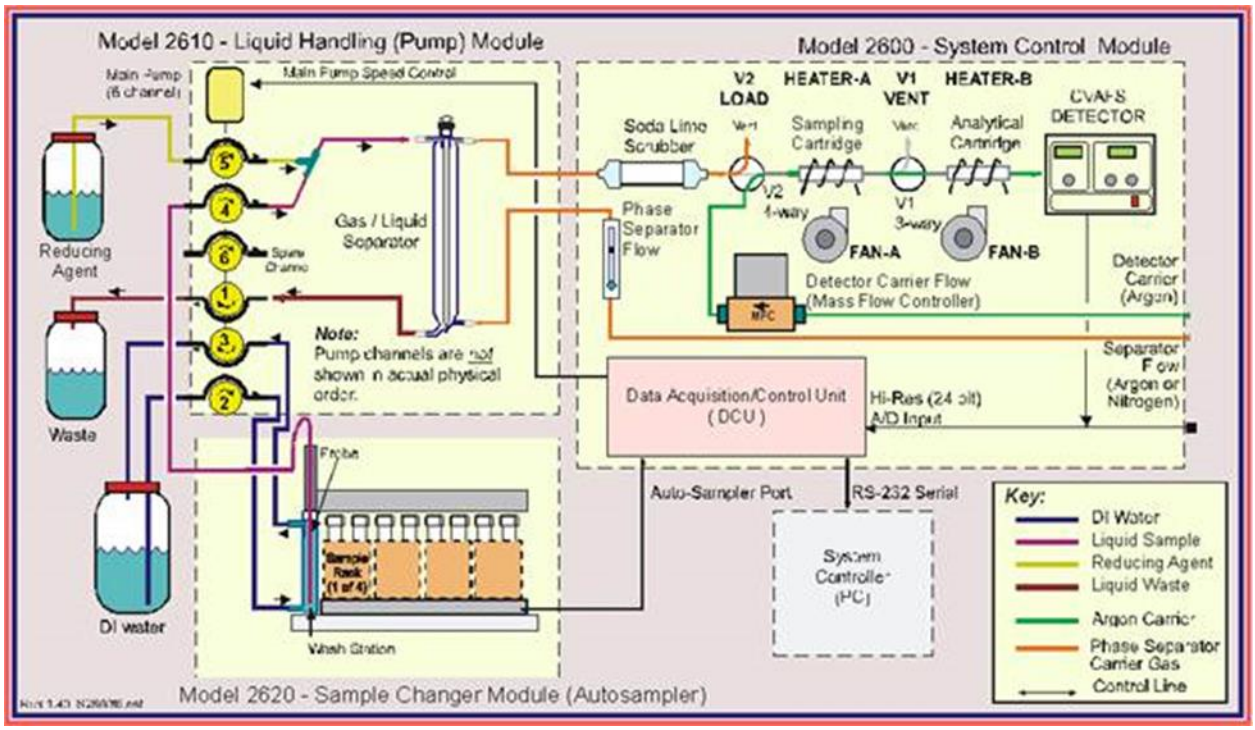

Figure 1 - Tekran 2600 Flow Diagram

7 Reference Modifications:

7.1 There were no significant modifications to this method.

8 Definitions:

8.1 Analytical Duplicate (AD): A representative sample (that yielded a result within the calibration curve) is analyzed a second time during the analytical run. The second analysis should be at the same aliquot as the original.

8.2 Analytical Run –The continuous analysis of one or more batches during the same 12 hour-shift. Each analytical day requires a minimum five-point calibration curve, ICV, at least 3 IBLs, and CCV/CCB every ten runs. An analytical day must conclude with a CCV/CCB.

8.3 Analytical Spike and Analytical Spike Duplicate (AS/ASD): A representative sample is selected and spiked, with a dilution of the primary source, during the analytical run, at a target concentration of 1-5X the ambient concentration of the sample. These QC samples are used to indicate sample matrix effects on the analyte of interest. Non-detectable samples are spiked at 1 – 5 x of the MRL/PQL.

8.4 Batch: 20 client samples or less grouped for preparation. See Quality Assurance Section for batch requirements.

8.5 Calibration Standards (CAL) – a series of standards that will be used to calibrate the instrument, made from a primary source stock standard. Three calibration blanks plus at least five different concentrations are required, beginning with one at PQL concentration.

8.6 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.7 Continuing Calibration Blank (CCB): An instrument blank that is used to monitor the ambient blank concentration after the Continuing Calibration Verification (CCV).

8.8 Continuing Calibration Verification (CCV): An aliquot of standard from a secondary source as the calibration standard, at a value of 5ng/L (0.5ng in ~100mL bubbler water). This standard is analyzed after every 10 analytical runs, and determines whether the instrument is maintaining calibration.

8.9 Continuing Demonstration of Capability (CDOC)

8.10 Control Limit (CL) – the limit of the range of acceptability for the quality control samples

8.11 Equipment Blank (EB): Reagent water processed through the sampling devices and placed in a sample container prior to using the equipment to collect samples and used to demonstrate that the sampling equipment is free from contamination.

8.12 Field Blanks (FB): A sample of reagent water placed in a sample container in the field and used to demonstrate that samples have not been contaminated by sample collection or transport activities. EPA-1631E recommends the analysis of at least one field blank per 10 samples collected at the same site at the same time. Analyze the blank immediately before analyzing the samples in the batch.

8.13 Initial Calibration Verification (ICV): A standard that is prepared from a secondary source stock standard with a value of 5ng/L (0.5ng in ~100mL bubbler). This standard is run immediately following the calibration curve and verifies instrument calibration.

8.14 Initial Blank Level (IBL): An instrument blank that is used to demonstrate the ambient blank concentration of the instrument. One per bubbler is needed at the beginning of the analytical run.

8.15 Initial Demonstration of Capability (IDOC).

8.16 Laboratory Control Sample (LCS and LCSD) or Quality Control Sample (QCS): A sample (and duplicate) containing a known concentration of mercury that is used to monitor complete method performance. The preferred LCS is a matrix matched Certified Reference Material (CRM), but a blank spike meets the requirement also. In LIMS, the LCS is always referred to as a Blank Spike (BS), whether it is matrix matched or not.

8.17 Limit of Detection (LOD) – The smallest concentration of a substance that must be present in a sample in order to be detected at the DL with 99% confidence. At the LOD, the false negative rate (Type II error) is 1%. The LOD shall be at least 2 times but no greater than 4 times the DL for multiple analyte methods or 2 times but no greater than 3 times the DL for single analyte methods.

8.18 Limit of Quantitation (LOQ) – equal to PQL and verified on a quarterly/annual basis, depending on the preparation, by spiking within 2 times the LOQ and showing a recovery between 70 – 130%.

8.19 LIMS: Laboratory Information Management System. Computer software used for managing samples, standards, and other laboratory functions.

8.20 May: This action, activity, or procedural step is optional.

8.21 May Not: This action, activity, or procedural step is prohibited.

8.22 Matrix Spike (MS) and Matrix Spike Duplicate (MSD): A representative sample is selected and spiked with a dilution of the primary source at a known concentration. The MS and MSD are run through the entire analytical process just as the samples are. These QC samples will indicate sample matrix effects on the analyte of interest.

8.23 Method Blank (MBLK) or Preparation Blank (PB): For waters, reagent water that is prepared and analyzed in a manner identical to that of samples. For digested solids, preparations blanks consist of the same reagents used to digest the samples, in the same volume or proportion and are carried through the complete sample preparation and analytical procedure. Boiling chips are used as a blank matrix for solids. Preparation blanks are referred to as BLK in LIMS.

8.24 Method Detection Limit (MDL): A limit derived from 40 CFR, Part 136, Appendix B. This method produces a defined value that is the minimum concentration that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.25 Method Duplicates/Method Triplicates (MD/MT): A second or third separate sample dilution, taken from the same source sample, prepared and analyzed in the laboratory separately. A MSD may be used as a duplicate.

8.26 Reagent water: 18 MO minimum, reagent water starting from a pre-purified (distilled, Reverse Osmosis, etc.) source.

8.27 Must: This action, activity, or procedural step is required.

8.28 Ongoing Precision and Recovery (OPR): A dilution of a secondary source resulting in an instrumental concentration of 5.0 ng/L mercury.

8.29 PM: Project Manager.

8.30 Practical Quantitation Limit (PQL), Method Reporting Limit (MRL): The minimum concentration that can be reported quantitatively. The PQL is often described as 1-10 times higher than MDL. Eurofins Frontier defines the PQL as the lowest concentration that can achieve 70-130% recovery for 10 replicate sample preparations. In LIMS, the PQL is referred to as the MRL.

8.31 Primary Source: The stock standard used to make the calibration standard. Procedural Method: A method where standards and samples are run through the analytical procedure exactly the same. By NELAC definition, this SOP is a procedural method.

8.32 Secondary Source: The stock standard used to make the OPR/ICV/CCV standard.

8.33 Shall: This action, activity, or procedure is required.

8.34 Should: This action, activity, or procedure is suggested, but not required.

8.35 Stock Standard Solution (SSS) – a standard of analyte that is purchased from a certified source for the preparation of working standards.

8.36 Total mercury: As defined by this method, all bromine monochloride-oxidizable mercury forms and species found in aqueous solutions. This includes, but is not limited to, Hg(II), Hg(0), strongly organo-complexed Hg(II) compounds, adsorbed particulate Hg(P), and several tested covalently bound organomercurials (i.e. CH_3HgCl, $(CH_3)_2Hg$, and $C_6H_5HgOOCCH_3$). The recovery of mercury bound within microbial cells may require additional preparation steps (i.e. UV oxidation, or oven digestion).

8.37 Travel or Trip Blank (TB): A sample of reagent water placed in a sample container in the laboratory and used to demonstrate that samples have not been contaminated by transport activities.

9 Interferences:

9.1 Gold and iodide are known interferences. At a mercury concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced from 100 to 0 percent. At iodide concentrations greater than 3 mg/L, the sample should be pre-reduced with $SnCl_2$ (to remove brown color immediately prior to analysis) and additional or more concentrated $SnCl_2$ should be added to the bubbler containing sample. If samples containing iodide concentrations greater than 30 mg/L are analyzed, it may be necessary to clean the analytical system with 4N HCl after the analysis.

9.2 Water vapor has the potential to create recovery interferences. To prevent interference from water, ensure that soda-lime pre-traps and gold traps remain dry.

9.3 The presence of high concentrations of silver and/or gold can cause $SnCl_2$ to precipitate out of solution and adhere to the bubbler walls. High concentrations of these metals can sometimes be found in the matrix spike samples from the digestion sets that are shared with the trace metals group. When analyzing digestates where the matrix spike samples have been spiked with silver or gold, the matrix-spiked samples must not be used for mercury analysis. Instead, an alternate matrix spike and matrix spike duplicate (MS/MSD) should be prepared and analyzed. If this is not possible, an Analytical Spike/Analytical Spike Duplicate (AS/ASD) must be analyzed on the ambient sample.

10 Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to the Chemical Hygiene Plan. This includes, but is not limited to, laboratory coat, safety goggles and nitrile gloves under clean gloves.

10.2 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Chemists should refer to the SDS (Safety Data Sheets) for each chemical they are working with.

10.2.1 Note: Use particular caution when preparing and using BrCl, as it releases extremely irritating, corrosive fumes similar in effect to free chlorine. Always handle this reagent in an approved fume hood

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Eurofins Frontier will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 Hydrochloric acid: Very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive), of ingestion. Slightly hazardous in case of inhalation (lung sensitizer).Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering. For more information see SDS.

10.5 See Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.6 Pollution prevention information can be found in the current Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.7 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to SOP *EFHS-S-HS-SOP2991* "Waste Disposal Procedure for Client Sample Waste," which provides instruction on dealing with laboratory and client waste.

11 Personnel Training and Qualifications:

11.1 An analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a primary or secondary source and a preparation blank before being qualified to analyze samples without supervision. Continuing DOC will be maintained and monitored via performance on CRMs and other QC samples.

11.2 The analyst/laboratory technician must have read this SOP and other relevant SOPs and have the training documented on the applicable form(s). The analyst may be questioned on the SOP by supervisor(s) and/or trainers.

11.3 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.4 All employees must read the Quality Manual (QM) and complete annual Ethics training.

11.5 All training documents including IDOCs, CDOCs, SOP reading, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employee's training file for ten years after the employee is no longer working for Eurofins Frontier Global Sciences.

11.6 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous goods, are stored by the Health and Safety

Officer for ten years after the employee is no longer working for Eurofins Frontier Global Sciences.

12 Sample Collection, Preservation, and Handling:

12.1 Aqueous samples are collected in rigorously cleaned fluoropolymer (e.g. Teflon) or PETG bottles and caps (as described in *EFAFS-S-SB-SOP5132* "Cleaning of Sampling Equipment and Bottles for Mercury Analysis"). Certified clean glass bottles with fluoropolymer lids may be used if mercury is the only analyte of interest.

12.1.1 Aqueous samples are preserved upon receipt with 0.2N BrCl that has tested low in mercury. Samples are typically preserved to 1% BrCl v/v, but may require further oxidation due to high levels of organic matter or mercury. Refer to *EFSR-P-SP-SOP2796* "Oxidation of Aqueous Samples for Total Mercury Analysis" for oxidation of aqueous samples.

12.2 All samples should be collected utilizing clean techniques, so as not to cross-contaminate samples with mercury. See *EFSR-S-CS-SOP2794* "Ultra Clean Aqueous Sample Collection" and EPA Method 1669 for aqueous sample techniques.

13 Apparatus and Equipment:

13.1 LIMS – Element, version 6.11 or higher; Computer – Windows XP, 7 or 8

13.2 Tekran Operating System – see Instrument Software Inventory *EFQA-S-IT-WI7061*

13.3 Model 2600 System Control Module – manufactured by Tekran, this module contains dual stage pre-concentration/desorption units, a high resolution analogue to digital converter, and a high sensitivity AFS Detector (IDL<1pg).

13.4 Model 2610 Pump Unit – manufactured by Tekran, this module contains a precision 6 channel peristaltic pump with optical speed feedback. Speed may be varied manually or under computer control. The pump head has three four-roller channels to providing high pumping rates for wash station circulation and waste removal, and three eight-roller channels to providing slower/low pulse delivery of $SnCl_2$ and sample (one extra channel).

13.5 Model 2620 Auto-Sampler – a specially modified Gilson Model 223 auto-sampler, includes reticulating wash station and allows for automatic sample handling with the 2600 analysis system.

13.6 50mL Polypropylene Vials with screw caps, manufactured by Environmental Express (Item No: SC475), or equivalent pre-cleaned and/or tested vials, graduated to 50mL.

13.7 Three-stop tubing, various inner diameters of Marprene for $SnCl_2$ (1.02mm), for wash station fill (2.38mm), wash station drain (2.79mm), and phase separator drain (2.79mm) Three stop silicone tubing (2.05mm) is used for sample feed.

13.8 Teflon Fittings and FEP tubing – of various sizes and lengths. Tubing from sample probe, $SnCl_2$, rinse water, phase separator, to and from wash station, and between gold traps is 1/16 inch (inner diameter) FEP.

13.9 Soda-Lime trap – a 14cm x 1.1cm diameter glass tube containing 12-14g of reagent grade, non-indicating 8-14 mesh soda-lime ($Ca(OH)_2$+NaOH) aggregates, packed between portions of silanized glass wool. This trap is purged of mercury by placing it on

the output of the phase separator and purging it to air with a 0.5% BrCl rinse solution and 3% $SnCl_2$ for approximately 20 minutes with Ar (or N_2)at 400 mL/min.

13.10 Phase separator – manufactured by Tekran, the phase separator utilizes laminar fluid flow of sample over a frosted rod counter current to a stream of argon gas at 400mL/min.

13.11 Gold Coated Quartz Sand Trap ("sample trap") – manufactured by Tekran or made in house, heated from 0% to 100%, 8 Amp maximum.

13.12 Pure Gold Bead Trap ("analytical trap") – manufactured by Tekran, heated from 0% to 100%, 8 Amp maximum.

13.13 Tekran 2500 Atomic Fluorescence Spectrophotometer (AFS) or equivalent: A high sensitivity AFS Detector (IDL<1pg) with a required wavelength of 253.7 nm and associated software.

13.14 Flow meter/needle valve: A unit capable of controlling and measuring gas flow to the cold vapor generator at 200-500 mL/min.

13.15 Teflon Fittings: Connections between components and columns are made using Teflon FEP tubing and Teflon friction fit tubing connectors.

13.16 Soda-Lime pre-trap: A 10cm x 0.9cm diameter Teflon tube containing 2-3 g of reagent grade, non-indicating 8-14 mesh soda-lime ($Ca(OH)_2$+NaOH) aggregates, packed between portions of silanized glass wool. This trap is purged of mercury by placing it on the output of a clean cold vapor generator and purging it with ~3-5% HCl and ~600 µL of $SnCl_2$ for approximately 20 minutes with N_2 at 40 mL/min.

13.17 Gold Traps: Made from 12 cm lengths of 6 mm OD quartz tubing, with a 4-way crimp 3.0 cm from one end. The tube is filled with approximately 2.5 cm of 20/40 mesh gold-coated quartz sand, the end of which is then plugged with quartz wool. Gold-coated sand traps are heated to 450-500°C (the coil should have a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24-gauge nichrome wire at a potential of 10 VAC. Potential is applied and finely adjusted with an auto-transformer. Refer to SOP *EFAFS-S-T-SOP5138* regarding the construction of gold traps used for total mercury analysis.

13.18 Agilent Integrator Recorder or equivalent: Any multi-range chart recorder or integrator with 0.1-5.0 mV input and variable speeds is acceptable. Data capture software may also be used.

13.19 Pipettes: Calibrated variable pipettes with a range of 20 µL – 10 mL. Used to make solutions and sample dilutions. Pipettes are to be calibrated weekly according to SOP *EFQA-R-EQ-SOP2711*.

13.20 Analytical Balance – capable of accurately weighing to the nearest 0.1mg, and able to tare at least one gram. The analytical balances are verified for accuracy on a daily basis according to EFQA-R-MT-SOP2710, "Balance Verification, Calibration and Maintenance."

14 Reagents and Standards:

14.1 Reagent Water: 18-MO ultra pure deionized water starting from a pre-purified (distilled, R.O., etc.) source is used. To remove any remaining trace metals and organics, an activated carbon cartridge is placed between the final ion exchange bed and the 0.2-µm

filter. Reagent water used in the mercury lab is checked monthly for total mercury concentrations, and must test below 0.25ng/L.

14.2 Hydrochloric Acid (HCl): Concentrated (36-38% weight basis). Must be trace-metal purified and reagent grade. HCl is typically monitored through performance of the BrCl. Sometimes it will be necessary to test the HCl directly. Do not prep blank correct. This reagent should test below 5.0 ng/L. This solution is considered stable until the expiration date on the bottle, set by the manufacturer.

14.3 0.2N Bromine Monochloride (BrCl):

14.4 27 g of KBr is added to a 2.5 L bottle of concentrated HCl (pre-analyzed and below 5 ng/L Hg). The bottle is inverted in a fume hood to mix the acid and KBr. The solution sits overnight, allowing the KBr to dissolve.

14.5 38 g of KBrO3 (certified to be low in Hg) is slowly added to the acid. As the KBrO3 is added, the solution should go from yellow to red to orange.

CAUTION: This process generates copious quantities of free halogens (Cl2, Br2, BrCl) which are released from the bottle. Add the KBrO3 SLOWLY in a well operating fume hood.

14.3.3 Loosely cap the bottle and allow to sit for at least 1 hour in a fume hood before tightening. Once tightly capped, invert bottle to make sure all of the solids go into solution.

14.6 The expiration time for this reagent is set by default to six months in LIMS. There is no suggested expiration date in EPA method 1631E, therefore it can be extended, as long as the primary reagent has not expired. The mercury concentration of the BrCl is monitored through the preparation of water preparation blanks.

14.7 This reagent must test below 0.20ng/L. Do not prep blank correct. Analyze one replicate per bottle.

14.8 Hydroxylamine hydrochloride: Dissolve 300g of NH2OH-HCl in reagent water and bring the volume up to 1L. This solution may be purified by the addition of 1mL SnCl2 solution and purging overnight at 500mL/min with mercury-free N2. The working reagent is a 25% solution that is made by adding one part reagent water to one part 50% hydroxylamine hydrochloride. This reagent must test below 0.25ng/L.

14.9 The expiration time for this reagent is set by default to six months in LIMS. There is no suggested holding time in EPA method 1631E; therefore the holding time can be extended, as long as the primary reagent has not expired (the stannous chloride that's added for purification is not considered a primary reagent).

14.10 Stannous Chloride (SnCl2): Weigh out 500 g SnCl2 using a calibrated balance that also has been verified for the day. Dissolve with three 100 mL aliquots of concentrated HCl and transfer to a 1L I-CHEM glass bottle, which contains approximately 300 mL of reagent water. Bring this solution up to approximately 1 L of volume and purge overnight with mercury-free N2 at 500 mL/min to remove all traces of mercury. Store tightly capped. The working reagent is a 25 % solution that is made by adding one part reagent water to one part 50 % stannous chloride.

14.11 This reagent must test below 0.20 ng/L. Do not prep blank correct. Analyze one replicate per bottle.

14.12 The expiration time for this reagent by default is set to six months in LIMS. There is no suggested holding time in EPA method 1631E; therefore the holding time can be extended, as long as the primary reagent has not expired.

14.13 Argon Grade 4.7 or better (ultra high-purity grade): Argon that has been further purified by the removal of mercury using a gold trap that is located in line between the gas output and the analyzer gas input.

14.14 Nitrogen Grade 4.5 (standard laboratory grade): Nitrogen that can be further purified of mercury using a gold trap that is located in-line.

14.15 Total Mercury Stock and Prepared Standards:

14.16 See SOP EFTM-T-TM-SOP2839 for information regarding the receipt, documentation, preparation, and storage of purchased and prepared standards used by EFGS.

14.17 Total Mercury Stock Standard Solution (Stock): Certified mercury standard purchased from High Purity Standards (1000 µg/mL (1 000 000 ng/mL) primary source) or Absolute Standards (100 µg/mL (100 000 ng/mL) secondary source), or any equivalent standard.

14.18 100,000 ng/mL Spiking Standard: Made from the Primary Stock Standard (High Purity, or equivalent vendor). Dilute 10 mL of the stock standard to 100 mL of reagent water containing 2 % BrCl. (Can also be made by preserving Secondary Stock Standard to 2% BrCl).

14.19 10,000 ng/mL Spiking Standard: If made from the Primary Stock Standard (High Purity, or equivalent vendor). Dilute 1.0 mL of the stock standard to 100 mL of reagent water containing 2 % BrCl. If made from Secondary Stock Standard, dilute 10mL of stock standard to 100mL with reagent water containing 2% BrCl.

14.20 1,000 ng/mL Spiking Standard: If made from the Primary Stock Standard (High Purity, or equivalent vendor). Dilute 0.250 mL of the stock standard to 250 mL RO water containing 2% BrCl. If made from Secondary Stock Standard dilute 2.5mL of stock standard to 250mL with RO water containing 2% BrCl.

14.21 100 ng/mL Spiking Standard: Made from a stock standard or dilution of a stock standard with a concentration of 100,000 ng/mL. Dilute 0.100 mL of the 100,000 ng/mL dilution to 100 mL of reagent water containing 2 % BrCl. Expiration date is currently set at 3 months or when the stock standard expires, whichever is shorter.

14.22 Calibration Standard (10 ng/mL): Must be made from a dilution of the Primary Stock Standard (High Purity, or equivalent vendor). Typically made by diluting 0.5mL of a 10,000 ng/mL Primary Spiking Standard to 500 mL of reagent water containing 2 % BrCl. Transfer to glass or Teflon bottle. The calibration standard is considered stable for three months or until the stock standard expires.

14.23 Calibration Standard (1 ng/mL): Must be made from a dilution of a Primary Stock Standard. Typically made by diluting 1.0mL of a 100 ng/mL Primary Spiking Standard to 100mL with Reagent water containing 2% BrCl.

14.24 Initial Calibration Verification (ICV): A 10 ng/mL ICV solution is prepared using the Secondary Stock Standard (Absolute Standards, or equivalent vendor). Use 0.100 mL (100 µL) of the Secondary Stock Standard to 1000 mL Milli-Q containing 2 % BrCl. Transfer to one 1000 mL glass or Teflon bottle. The ICV standard is considered stable for

three months or until the stock standard expires. It is recommended to alternate expiration date with the CAL standard.

14.25 Continuing Calibration Verification (CCV): For CCV analysis, use 200 µL of the 10 ng/mL CAL standard (documented in LIMS as SEQ-CAL3). The True Value is 20 ng/L.

14.26 Certified Reference Material (CRM) for Total Mercury in Water: A 1.5679 mg/L solution (1.557 mg/kg at a density of 1.007 g/mL) is prepared by adding a 5.0 mL of CRM NIST 1641e (from ampoule) into a 1000 mL flask containing of reagent water. This solution is diluted to 1000 mL, and an additional 10 mL of 0.2N BrCl is added, resulting in a final volume of 1010 mL. Preparing the solution in this manner makes a 1:200 dilution of the stock CRM. This solution is considered stable for one year, or until the stock standard expires. Results are corrected for the additional 1 % BrCl in the analysis Excel spreadsheet and in LIMS.

14.27 Ongoing Precision and Recovery (OPR) for “Strict” 1631E: A 5.0 ng/L solution is prepared by adding 100 µL of the 100 ng/mL secondary spiking standard into 2000 mL reagent water. An additional 1 % BrCl (20 mL) of BrCl is added, so that the final volume is 2020 mL. This standard is analyzed at 100 mL at the instrument, and preparation blank corrected exactly in the same manner as samples.

14.28 Nitric Acid (HNO3): concentrated (69%-70% weight basis). Trace metal purified reagent-grade HNO3 is pre-analyzed and lot sequestered. Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent should be from a lot number that has been previously tested to be low for the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to the same as the manufacturer’s expiration date.

14.28.1 Nitric Acid, 5%

14.28.1.1 Rinse bottle labeled:

14.28.2 Metals Rinse, 5% HNO3

14.28.2.1 To be used for CV-AFS (THg only) and ICPMS preps/analysis.

15 Calibration:

15.1 Follow the calibration in *EFAFS-T-AFS-SOP2822* while still adhering to the QA/QC criteria of this method.

16 Procedure:

16.1 Follow the procedure in *EFAFS-T-AFS-SOP2822* while still adhering to the QA/QC criteria of this method.

17 Calculations:

17.1 The Tekran 2500 is no longer operated by the laboratory. For the calculations that are based on data generated from a Tekran 2600, see EFAFS-T-AFS-SOP2822.

18 Statistical Information/Method Performance

18.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and and EFQA-Q-QD-SOP10098.

18.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3). The PQL is determined by running ten samples with a concentration that will produce a recovery of 70-130 %. The PQL is referred to as the Method Reporting Limit (MRL) in LIMS.

18.3 Using clean handling techniques and reagents tested low for Hg content, the LOD value for Total Hg in water is typically less than 0.2 ng/L, while the PQL is 0.50 ng/L.

18.4 Current LODs, LOQs, MDLs, and PQLs are stored at: \\us34fivp002\General and Admin\Quality Assurance\Method-Limits-MDLs-IDLs\MDLs & PQLs.

19 Quality Assurance/Quality Control:

19.1 A minimum of three preparation blanks and one LCS/LCSD (preferably NIST *1641e* or equilivalent), must be analyzed per preparation batch. The upper control limit for each preparation blank is equal to the PQL.

19.2 Matrix Spikes: One Matrix Spike/Matrix Spike Duplicate (MS/MSD) must be performed for every 10 samples. The recovery of the MS/MSD must be between 71%-125% recovery, and the Relative Percent Difference (RPD) below 24%. If an MS/MSD is out of control, the analyst should investigate to identify the source of the failure. The MS and MSD may be used as duplicates. Some failures may be qualified using QA Qualification Flow Charts.

19.2.1 For aqueous samples, the MS/MSD is spiked at 1 to 5 times the ambient concentration, with 0.25 ng, being the minimum spiking level. Sample *dilutions* for the MS/MSD should be the same as the ambient sample *dilution*, if sufficient sample volume exists. NEVER ADD SPIKE DIRECTLY TO THE ORIGINAL SAMPLE *CONTAINER* UNLESS OTHERWISE STATED.

19.3 Matrix Duplicates – Not required. A Matrix Duplicate (MD) or Matrix Triplicate (MT) may be analyzed for every batch of 20 samples upon client request. The MSD may serve as the MD if necessary. The Relative Percent Difference (RPD) and the Relative Standard Deviation (RSD) of duplicate samples must be less than 24%. Some failures may be qualified using QA Qualification Flow Charts.

19.3.1 For aqueous samples, analyze the parent, duplicate and triplicate at the same dilution.

19.4 Laboratory Control Standard (LCS) or Quality Control Sample (QCS): For every batch of samples, at least one LCS is processed and analyzed. The recovery of the LCS must be within 80-120% for the aqueous NIST *1641e* or equivalent. An LCS Duplicate (LCSD) should accompany the LCS.

19.4.1 A Certified Reference Material (CRM) is the preferred LCS, but a Blank Spike may serve as an LCS if an appropriate CRM does not exist. The spiking level is based on client request, historical data, or a default of mid-curve. A duplicate blank spike must also be prepared as an LCSD.

19.5 Ongoing Precision and Recovery (OPR): An OPR must be analyzed at the beginning and end of each analytical batch, or at the end of each 12-hour shift. The recovery of the OPR must be within 77-123% to be considered in control.

19.6 All calibration standards must be traceable to the original standard source. The calibration curve must be established at the beginning of the analytical run. It must include at least five different concentrations, with the lowest concentration equal to the PQL. The average response factor of each calibration standard is used to calculate the sample values. The RSD of the response factors must be less than 15% of the mean or the calibration fails.

19.7 ICV and CCV control limit is 77-123%. The CCV is analyzed every 10 analyses, and at the end of an analytical run. CCBs are always analyzed after the CCVs.

19.8 Field Blanks: To be compliant with EPA 1631, clients must submit a field blank for each set of samples (samples collected from the same site at the same time, to a maximum of 10 samples).

19.8.1 If no field blanks are submitted by the client, their data will be flagged with “FB-1631.” “Required equipment/field/filter blank not submitted by the client. The sample has been analyzed according to 1631E, but does not meet 1631E criteria.”

19.9 Method or Preparation Blanks (BLK): Method blanks are used to demonstrate that the analytical system is free from contamination that could otherwise compromise sample results. Method blanks are prepared and analyzed using sample containers, labware, reagents, and analytical procedures identical to those used to prepare and analyze the samples.

19.9.1 A minimum of three 1 % BrCl method blanks per analytical batch are required. Any sample requiring an increased amount of reagent must be accompanied by at least one method blank that includes an identical amount of reagent.

19.9.2 If the result for any 1 % BrCl method blank is found to contain =0.50 ng/L Hg (0.25 ng/L for DOD, 0.1835 for WI-DNR), the system is out of control. Mercury in the analytical system must be reduced until a method blank is free of contamination at the 0.50 ng/L level.

19.9.3 For method blanks containing more than 1% BrCl, the control limit is equal to 0.50 ng/L multiplied by the final preservation percentage of BrCl. For example, for a method blank preserved to 2 % BrCl, the control limit for the blank is 0.50 ng/L * (102/101), or 0.50 ng/L. For 3% BrCl the control limit is (103/101)*0.50ng/L, or 0.51ng/L.

19.10 Instrument Blanks (IBL): A minimum of three instrument blanks must be analyzed with each analytical batch.

19.10.1 If the instrument blank is found to contain more than 0.50ng/L, (0.25 ng/L for DOD, 0.15 for WI-DNR), the system is out of control. The problem must be investigated and remedied and the samples must be reanalysed.

19.10.1.1 The mean result for all instrument blanks must be <0.25ng/L with a standard deviation of 0.10 ng/L.

19.11 The analytical day must close with a CCV(OPR)/CCB.

19.12 Since the method is done in real-time, it is EFGS’ position that a single non-compliant QC sample result does not automatically invalidate a data set. All data points that can be

explained and rerun with a passing result can be qualified. If the source of error cannot be corrected for a QC standard that day, none of the data can be validated. In the event that the system becomes out of control during the analysis day, all results bracketed between valid QC data points shall still be considered valid (CCV, OPR, CCB, etc.).

19.13 The Control Limits are established from EPA 1631E.

19.14 Carryover: In 2020 a carryover study was completed monitoring Hg levels up to five times the top calibration point (200 ng/L). No carryover was detected during this study. Any sample ran with a concentration of Hg over 200 ng/L requires a blank be ran directly after to ensure there is no carryover. Additional samples may only be ran after the blank shows a concentration below 0.50 ng/L.

20 Corrective Action:

20.1 The data is reviewed as in the QC section (or matrix specific QC section) for all parameters that pass specific requirements. If the data does not meet QC requirements, it is qualified or submitted for reruns. Data may be qualified (based on scientific peer review) by the Group Supervisor, Project Manager, Lab Manager, or QA Officer.

20.1.1 Continuing Calibration Verification (CCV): If a recovery falls outside acceptance criteria, recalibrate the instrument and reanalyze all affected samples since the last acceptable CCV or immediately analyze two additional CCVs. If both CCVs are within acceptance criteria, the samples may be reported without reanalysis and the analysis of the next bracket may continue beginning with a CCB.

20.1.1.1 If either of the two CCVs fails, the analysis must be terminated, the problem resolved, the instrument recalibrated and then all of the affected samples since the last acceptable CCV reanalyzed.

20.2 Control Chart data is generated through LIMS to monitor the performance of the CCV, LCS, MS, and MSD. This is done by the QA department.

20.3 Due to the real-time nature of the CVAFS method, failures must be investigated as they happen. If the source of the problem can be identified, and corrected, the samples may be rerun. If source of problem cannot be isolated, see the Senior Analyst, Group Supervisor, or Laboratory Manager for instructions.

20.4 The Senior Analyst, Group Supervisor, Laboratory Manager, or QA Officer must be informed if QC fails. It is also advisable to always alert the Project Managers.

21 List of Attachments:

Table 1: QC Requirements for Total Mercury

Table 1: QC Requirements for Total Mercury

QC Parameter	Acceptance Criteria
Initial Calibration Verification (ICV)	79-121% Recovery
Continuing Calibration Verification (CCV)	77-123% Recovery
Ongoing Precision and Recovery (OPR)	77-123% Recovery
Initial Calibration Blank (ICB)/ Continuing Calibration Blank (CCB)	Individually, IBL and CCB ≤0.50ng/L, (≤0.25 ng/L for DOD, ≤0.15 for WI-DNR), but the mean of all the IBLs shall be ≤0.25ng/L with a standard deviation of ≤0.10ng/L.
Laboratory Control Standard (LCS) or Quality Control Standard (QCS)	80-120% Recovery for *NIST1641e*; 75-125% for all other CRMs. RPD≤24%
Calibration Curve RSD (Referred to as "Corr. RSD CF" in Excel spreadsheet).	RSD of Calibration Response Factor ≤15%
Lowest Calibration Point	70-130%
1% BrCl Method Blank (BLK)	≤0.50ng/L, (≤0.25 ng/L for DOD, ≤0.15 for WI-DNR)
Matrix Duplicate (MD) and Analytical Duplicate (AD)	≤ 24% RPD
Matrix Spike and Matrix Spike Duplicate (MS/MSD); Analytical Spike (AS) and Analytical Spike Duplicate (ASD)	71-125% Recovery ≤ 24% RPD

Version history

Version	Approval	Revision information
3	03.NOV.2015	
4	19.MAY.2016	
5	09.MAY.2017	
6	03.NOV.2020	

STANDARD OPERATING PROCEDURE L-2G: DIGESTION OF TISSUES FOR TOTAL MERCURY ANALYSIS USING NITRIC ACID AND SULFURIC ACIDS (70:30)

eurofins | Frontier Global Sciences	**Document Title:** Digestion of Tissues for Total Mercury Analysis Using Nitric Acid and Sulfuric Acids (70:30)	**Eurofins Document Reference:** EFAFS-T-AFS-SOP2795

Eurofins Document Reference	EFAFS-T-AFS-SOP2795	**Revision**	11
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Prepared by	David Wunderlich
Reviewed and Approved by	David Wunderlich and Patrick Garcia-Strickland

Table of Contents

1 Revision Log:

Revision: 11	**Effective Date:** This version	
Section	**Justification**	**Changes**
2.4, 2.5	Required	Updated references
9	Updating	No more than 2.5mL instead of 5.0mL
13.1	Updating	Removed Windows XP as an OS option
14.7	Required	Corrected the recipe for the preparation of 0.2N BrCl
15.5.1	Required	A section was added to instruct technicians to use a timer.
17.1	Required	Referenced new MDL requirements

2 Reference:

2.1 Chemical Hygiene Plan, Eurofins Frontier Global Sciences, current version.

2.2 EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, 2002.

2.3 Appendix to Method 1631 -Total Mercury in Tissue, Sludge, Sediment and Soil by Acid Digestion and BrCl Oxidation, 2001.

2.4 TNI Environmental Laboratory Sector, Vol 1,Management and Technical Requirements, ELV1-2016.

2.5 Department of Defence / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019.

3 Cross Reference:

Document	Document Title
EFQA-Q-QM-QM5805	QA Manual
EFQA-Q-QD-SOP10098	Procedures for Determining IDLs, MDLs, LODs, LOQs, OPRs, IQs, OQs, and PQs
EFQA-R-EQ-SOP2711	Pipette and Volumetric Dispenser Verification, Calibration and Maintenance
EFSR-S-CS-SOP2794	Ultra Clean Aqueous Sample Collection
EFQA-P-DR-SOP2801	Data Review and Validation
EFHS-S-HS-SOP2991	Waste Disposal Procedure for Client Sample Waste
EFAFS-T-AFS-SOP2822	Determination of Total Mercury in Various Matrices by Flow Injection Atomic Fluorescence Spectrometry (EPA Method 1631E)

4 Purpose:

4.1 The purpose of this Standard Operating Procedure (SOP) is to describe the method for digesting biological tissue samples prior to analysis by CV-AFS for total mercury.

5 Scope:

5.1 This method is for the preparation of biological tissue samples for the determination of total mercury at concentrations less than 1 ng/g. Through the analysis of smaller

digestate aliquots, contaminated tissues of up to 10,000 ng/g can be directly measured. Using clean handling techniques and low-level reagents, the typical detection limit for samples prepared by this method is less than 1 ng/g.

5.2 Total mercury, as defined by this method, is all HNO3/H2SO4/BrCl-oxidizable mercury forms and species found in tissue matrices. This includes, but is not limited to, Hg(II), Hg(O), HgS, strongly organo-complexed Hg(II) compounds, adsorbed particulate Hg, and several covalently bound organo-mercurials (i.e., CH_3HgCl, $(CH_3)_2Hg$, and $C_6H_5HgOOCCH_3$).

6 Basic Principles:

6.1 Samples are collected using clean sample handling protocols into commercially available clean glass containers with Teflon-lined caps (i.e., I-Chem glass jars) or 125 mL or 250 mL HDPE jars. Freezing (< -15℃) preserves tissue samples until sample preparation is performed.

6.2 A subsample of homogenized sample is digested with 10 mL of 70:30 HNO_3/H_2SO_4.

6.3 The digested sample is diluted up to 40 mL with 5% (v/v) BrCl.

7 Reference Modifications:

7.1 No significant modifications were made to this method.

8 Definitions:

8.1 Batch – no more than 20 client samples grouped for preparation. 3 Preparation Blanks, 1 CRM when available, and 1 LCS/LCSD (or BS/BSD) set and 1 MD are prepared per every 20 samples; 1 MS/MSD set is prepared for every 10 samples.

8.2 Celsius (C), conversion of Celsius to Fahrenheit: (C * 1.8) + 32.

8.3 Fahrenheit (F), conversion of Fahrenheit to Celsius: (F - 32) * 5/9.

8.4 Method Detection Limit (MDL) – the limit derived from an exercise as described in 40 CFR, Part 136, Appendix B. The exercise produces a defined value that is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.5 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.6 Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD), is a sample containing known concentrations of the analytes of interest that is taken through the entire preparation and analysis process in the same manner as the samples to monitor complete method performance. A Certified Reference Material (CRM) is preferred as the LCS, but a blank spiked sample also meets the requirement.

8.7 Preparation Blank (BLK) – Method blanks consist of the same reagents used to digest the samples, in the same volume or proportion, and are carried through the complete sample preparation and analytical procedure. Teflon boiling chips are added to the preparation blanks.

8.8 Matrix Duplicate (MD) – a representative sample is selected and digested in the same

manner. This QC sample will indicate sample homogeneity on the analytes of interest

8.9 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – a representative sample is selected and spiked with a secondary source at two to five times the ambient concentration or at two to five times the MRL, whichever is greater. These QC samples will indicate sample matrix effects on the analytes of interest.

8.10 May: This action, activity or procedure is optional.

8.11 May Not: This action, activity or procedure is prohibited.

8.12 Shall: This action, activity or procedure is required.

8.13 Should: This action, activity or procedure is suggested, but is not required.

9 Interferences:

9.1 Due to the high levels of halogens (i.e., iodine) typically found in tissue digestates, it is recommended that aliquots of no more than 2.5 mL of the digestate be analyzed. Otherwise, soda-lime traps may be overloaded and the gold traps may lose the ability to amalgamate and retain mercury Safety Precautions, Pollution Prevention and Waste Handling:

10 Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to the Chemical Hygiene Plan (*EFHS-S-HS-QP12066*). This includes, but is not limited to laboratory coat, eye protection and protective gloves.

10.2 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Chemists should refer to the SDS (Safety Data Sheets) located at https://msdsmanagement.msdsonline.com/company/5c1df5b3-747d-4789-8104-42457dc3a3e5/ for each chemical they are working with.

10.2.1 Note: Use particular caution when preparing and using BrCl, as it releases extremely irritating, corrosive fumes similar in effect to free chlorine. Always handle this reagent in an approved fume hood.

10.2.2 Note: Use particular caution when preparing and using the Nitric/Sulfuric Mixture. Always handle this reagent in an approved fume hood.

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Eurofins Frontier will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 Nitric acid (HNO_3): Corrosive. Strong oxidizer. Contact with other material may cause a fire. Causes eye and skin burns. May cause severe respiratory tract irritation with possible burns. May cause severe digestive tract irritation with possible burns. For more information see SDS.

10.5 Sulfuric acid (H_2SO_4): Corrosive. Causes eye and skin burns. May cause severe eye irritation with possible burns. May cause severe respiratory tract irritation with possible burns. May cause severe digestive tract irritation with possible burns. Cancer

hazard. Animal studies suggest this acid may cause fatal effects. May cause kidney damage. May cause lung damage. May be fatal if inhaled. Hygroscopic, Strong oxidizer. Contact with other material may cause a fire. For more information see SDS.

10.5.1 Eyes: Get medical aid immediately. Do NOT allow victim to rub or keep eyes closed. Extensive irrigation with water is required (at least 30 minutes).

10.5.2 Skin: Get medical aid immediately. Flush skin with soap and water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Destroy contaminated shoes.

10.6 See Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.7 Pollution prevention information can be found in the current Eurofins Frontier Global Sciences Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.8 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to SOP *EFHS-S-HS-SOP2991* "Waste Disposal Procedure for Client Sample Waste," which provides instruction on dealing with laboratory and client waste.

11 Personnel Training and Qualifications:

11.1 An analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source spiked at 8 ng/g before being qualified to analyze samples without supervision. Recoveries for the IDOC need to be 75-125% with an RSD of < 20%. Continuing DOC will be maintained and monitored via performance on CRMs and other QC samples, as well as obtaining acceptable results on proficiency testing exercises.

11.2 The analyst/laboratory technician must have read this SOP and other relevant SOPs and have the training documented on the applicable form(s). The analyst may be questioned on SOP by supervisor(s) and/or trainers.

11.3 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.4 All employees must read the Quality Manual (*EFQA-Q-QM-QM5805*) and complete annual Ethics training.

11.5 All training documents including IDOCs, CDOCs, SOP reading, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employees training file for ten years after the employee is no longer working for Eurofins Frontier Global Sciences.

11.6 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous goods, are stored by the Health and Safety Officer for ten years after the employee is no longer working for Eurofins Frontier Global Sciences.

12 Sample Collection, Preservation, and Handling:

12.1 Samples must be collected in accordance with established ultraclean sampling techniques (see *EFSR-S-CS-SOP2794* "Ultra Clean Aqueous Sample Collection"). Samples may be in commercially available clean glass containers with Teflon-lined caps (i.e., I-Chem glass jars), or 125 mL or 250 mL HDPE jars.

12.2 Tissue sample preservation - The tissue sample must be frozen in the sampling container at less than -15℃ or freeze-dried and stored at ro om temperature (Wisconsin only permits the freezing option). The holding time for tissue samples is 1 year.

12.3 Just prior to digestion, frozen samples are thawed and if necessary homogenized. The sample is well mixed to ensure the most representative sample possible.

13 Apparatus and Equipment:

13.1 LIMS – Element, version 6.0 or higher; Computer – Windows 7, 8 or 10

13.2 40 mL or 20 mL I-Chem Vials: Borosilicate glass, series 300 vials with Teflon-lined septa in lids. The size used depends on the amount of sample available.

13.3 Hot plate: A hot plate with the ability to achieve and maintain a temperature of 75 ℃.

13.4 Pipettors: All-plastic, pneumatic, fixed volume and variable pipettes in the range of 5 µL to 10 mL. Pipettes are to be calibrated weekly according to SOP *EFQA-R-EQ-SOP2711*.

13.5 Clean hood.

13.6 Analytical Balance: A laboratory analytical balance capable of weighing to ± 1 mg, with documented calibration.

13.7 Calibrated thermometer: Submerged in water in a 20 mL I-Chem vial. This vial is placed on the hotplate during the digestion process. The analysts must record the actual digestion temperature and the serial number of the thermometer used in the digestion logbook.

13.8 Sample Digestion Log.

13.9 Stainless steel tools for homogenization

13.10 Tissue Homogenization Log.

13.11 Disposable spatula.

13.12 Teflon boiling chips.

13.13 Teflon reflux cap to fit the 40 mL and 20 mL I-Chem vials.

14 Reagents and Standards:

14.1 Reagent Water: 18 MW ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. As a final mercury and organic removal step, the activated carbon cartridge on the 18-MW system is placed between the final ion exchange bed and the 0.2 µm filter.

14.2 Nitric Acid (HNO3): Trace metal purified reagent-grade HNO3 is pre-analyzed and lot sequestered. Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent should be from a lot number that

has been previously tested to be low for the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to the same as the manufacturer's expiration date.

14.3 Sulfuric acid (H_2SO_4) - Trace metal purified reagent-grade H_2SO_4 is pre-analyzed to < 50 ng/L Hg and lot sequestered before purchase. This reagent shall be entered into the LIMS and is considered stable until the expiration date on the bottle (set by the manufacturer.

14.4 Nitric/Sulfuric Acid Mixture: Carefully add 750 ± 50 mL of pre-analyzed, low mercury (< 50 ng/L) concentrated sulfuric acid to 1750 ± 50 mL of pre-analyzed, low mercury concentrated nitric acid to a pre-marked glass bottle. Cap the bottle and invert the solution 10 times to ensure mixture is complete. This reagent shall be entered into the LIMS with an expiration date of six months. CAUTION: THIS MIXTURE BECOMES VERY HOT AND EMITS CAUSTIC FUMES.

14.5 Potassium Bromide (KBr), neat: this reagent is pre-certified by the vendor to be low in mercury and is entered into the LIMS with a three year expiration date.

14.6 Potassium Bromate ($KBrO_3$), neat: this reagent is pre-certified by the vendor to be low in mercury and is entered into the LIMS with a three year expiration date.

14.7 0.2N Bromine Monochloride (BrCl):

14.7.1 27 g of KBr is added to a 2.5 L bottle of concentrated HCl (pre-analyzed and below 5 ng/L Hg). The bottle is inverted in a fume hood to mix the acid and KBr. The solution sits overnight, allowing the KBr to dissolve.

14.7.2 38 g of KBrO3 (certified to be low in Hg) is slowly added to the acid. As the KBrO3 is added, the solution should go from yellow to red to orange.

CAUTION: This process generates copious quantities of free halogens (Cl_2, Br_2, BrCl) which are released from the bottle. Add the $KBrO_3$ SLOWLY in a well operating fume hood.

14.7.3 Loosely cap the bottle and allow to sit for 30 minutes (in a fume hood) before tightening. Once tightly capped, invert bottle to make sure all of the solids go into solution.

14.7.4 This reagent shall be entered into the LIMS with a six month expiration date.

14.8 5% (v/v) of 0.2N BrCl: 125 ± 40 mL of 0.2N BrCl is diluted up to 2.5 L with reagent water in a clean, empty HCl bottle. This bottle is fitted with a 50 mL repipettor. The expiration time for this reagent is set by default to six months in the LIMS.

15 Procedures:

15.1 If needed, the sample is dissected and homogenized with acid-washed stainless steel tools.

15.1.1 The process used for homogenization, number of samples, work order number, client name, and initials of the technician are entered into the Tissue Homogenization Log.

15.2 Weigh at least a 0.5 g aliquot (but not more than 0.65 g) for common and unknown samples, and up to 1.0 g ± 0.025 g for low-level or large-grain samples. This aliquot is placed into a 40 mL I-Chem glass vial.

15.2.1 If limited sample is available, use 20 mL glass vials and drop the initial mass of the samples to 0.25g.

15.2.2 It is imperative that all biological tissue samples are thoroughly homogenized. The importance of representativeness cannot be understated.

15.2.3 Batch requirements for this digestion limit the number of samples to 20. In each batch, there must be three method blanks (BLKs), a Blank Spike and Blank Spike Duplicate (BS/BSD) that is preferably a Certified Reference Material (CRM) or a Laboratory Control Spike (LCS, prepared at 8 ng/g), a Matrix Duplicate (MD), and a Matrix Spike and Matrix Spike Duplicate (MS/MSD). The customary spiking volume used for the MS is 200 uL of 1000 ng/mL.

15.3 10.0 mL of 70:30 (v/v) HNO_3/H_2SO_4 solution is pipetted in and the sample is swirled. Note: 5.0 mL of 70:30 (v/v) HNO_3/H_2SO_4 solution is used for limited samples prepared in 20 mL vials (15.2.1).

15.4 The vial is placed on a hot plate operating at 75±5℃ with a Teflon reflux cone in place instead of the vial's lid. An aluminum rack is often used to keep the vials from tipping over while on the hot plate.

15.4.1 A calibrated thermometer, submerged in water, is placed in a 20 mL I-Chem vial. The vial containing the thermometer is placed in a cell on the hot plate during the digestion process. The cell selected for temperature monitoring must be different than cells selected for the previous ten batches at a minimum. The analyst must record the cell position (designated as position A1, B6, C7, etc., from the diagram in the logbook), raw and corrected initial and final digestion temperatures and the serial number of the thermometer used in the digestion logbook.

15.5 After the samples start to reflux, the samples are heated at 75±5℃ for an additional 2 hours or until all organic matter is dissolved.

15.5.1 During the two hour digestion, a timer should be used if leaving the hotplate on without supervision. Hotplate should not be left unattended.

15.6 The samples are allowed to cool and are diluted to 40 mL (or to 20 mLs for limited sample digestions as described in 15.2.1) by using a repipettor to add 30 mL for 40 mL final volume or 15 mL for 20 mL final volume with a 5% (v/v) solution of 0.2N BrCl. Cap with their respective lids, shake vigorously and allow settling until the supernatant is clear prior to analysis.

15.7 Analysis for total mercury is according to Eurofins Frontier SOP *EFAFS-T-AFS-SOP2822*.

16 Calculations:

16.1 This preparation procedure does not involve calculations.

17 Statistical Information/Method Performance

17.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and and *EFQA-Q-QD-SOP10098*.

17.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3). The PQL is

determined by running ten replicate samples with a concentration that will produce a recovery of 70-130% for most analytes, but the recovery requirements are analyte dependent. The PQL is referred to as the Method Reporting Limit (MRL) in LIMS.

17.3 The current LOD value for Total Hg in tissue prepared by the Nitric and Sulfuric Acids (70:30) Digestion is 0.16 ng/g, while the PQL is 0.8 ng/g.

17.4 Current LODs and PQLs are stored at: \General and Admin\Quality Assurance\MDLs & PQLs.

18 Quality Assurance/Quality Control:

18.1 Maximum Sample Batch Size: 20 samples.

18.2 Preparation Blanks: Minimum of three per batch. Each preparation blank must be less than one-half the PQL for the method.

18.2.1 The preparation blanks are prepared with a similar mass of Teflon boiling chips as the samples, with the same reagents, and put through the same preparation process as the samples. The LIMS ID or lot # of the Teflon boiling chips is documented in the digestion logbook.

18.3 Certified Reference Material (CRM, representing the sample matrix when commercially available); a Laboratory Control Spike (LCS) and Laboratory Control Spike Duplicate (LCSD) prepared at 8 ng/g is used when a suitable CRM is not available: One per batch in duplicate. The control limits are 75-125% recovery.

18.4 Matrix Duplicate (MD) Sample: One per batch. The control limit for the RPD is = 24%.

18.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples: One set per 10 samples. The control limits are 71-125% recoveries and an RPD of = 24%.

18.6 Follow the flow charts in SOP *EFQA-P-DR-SOP2801* “Data Review and Validation” to determine if any QC falling outside the established control limits can be qualified.

18.7 All of the quality control limits for the analysis method are included on the “Data Review Checklist.

18.7.1 The data review checklists are located at: \\cuprum\General and Admin\Quality Assurance\Data Review\Current Data Review Checklists.

19 Corrective Action:

19.1 Limiting the source of contamination/error in the preparatory stage can decrease QC problems during analysis. Limiting such contamination/error sources may include: cleaning all digestion tools in a 10% HCl solution, ensuring all samples are thoroughly homogenized, changing gloves whenever appropriate, flushing repipettors at least three times before dispensing into vials and, in general, following ultra-clean procedures.

19.2 A failing QC point does not necessary fail the entire dataset. If upon analysis a QC sample is out of control, some investigation must be performed to assess if the difficulties are related to matrix effects. The cause and method of determining the set's failure must be documented on the checklist and in the MMO notes, and the Group Supervisor shall be informed. See SOP *EFQA-P-DR-SOP2801* “Data Review and Validation” for flow charts regarding analytical issues.

19.3 Additional corrective actions are listed in the SOP for total mercury analysis (Eurofins Frontier SOP *EFAFS-T-AFS-SOP2822*).

EFAFS-T-AFS-SOP2822 Determination of Total Mercury in Various Matrices by FI-AFS
EFHS-S-HS-12066.0004 Chemical Hygiene Plan
EFHS-S-HS-SOP2991 Waste Disposal Procedures for Client Sample Waste
EFQA-P-DR-SOP2801 Data Review and Validation and Monthly Logbook Reviews
EFQA-Q-QD-SOP10098 Procedures for Determining IDLs, MDLs, LODs, PQLs, LOQs, OPRs, IQs, OQs and PQs
EFQA-Q-QM-QM5805 Quality Manual
EFQA-R-EQ-SOP2711 Pipette and Dispenser: Operation, Calibration & Maintenance
EFSR-S-CS-SOP2794 Ultra-Clean Aqueous Sample Collection

End of document

Version history

Version	Approval	Revision information
9	19.MAY.2016	
10	09.NOV.2016	
11	18.OCT.2019	

STANDARD OPERATING PROCEDURE L-2H: DISTILLATION OF AQUEOUS SAMPLES FOR METHYL MERCURY ANALYSIS

eurofins | Frontier Global Sciences	**Document Title:** Distillation of Aqueous Samples for Methyl Mercury Analysis	**Eurofins Document Reference:** EFAFS-T-AFS-SOP2797

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Prepared by	Bryn Fada
Reviewed and Approved by	Terri Torres and Patrick Garcia-Strickland

Table of Contents

eurofins | Frontier Global Sciences	**Document Title:** Distillation of Aqueous Samples for Methyl Mercury Analysis	**Eurofins Document Reference:** EFAFS-T-AFS-SOP2797

1 Revision Log:

Revision: 12	**Effective Date:** This version	
Section	**Justification**	**Changes**
8	Required	Removed duplicate entries
13.3	Required	Removed MDN instructions
14.1.1	Required	Added pipette rinse
15.1.1, 15.4.1	Required	Removed MDN instructions
15.9	Required	Changed spike level to suggested vs set amount
18.4	Required	Removed requirement for MD

2 Reference:

2.1 Bloom, N.S. Determination of Picogram Levels of Methyl Mercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapour Atomic Fluorescence Detection. Can. J.Fish.Aq. Sci.1989,46, 1131.

2.2 Bloom, N.S.;Fitzgerald, W.F. Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection. Anal.Chem.Acta.1988,208,151.

2.3 Horvat,M.;Bloom,N.S: Liang, L. A Comparison of Distillation with Other Current Isolation Methods for the Determination of Methyl Mercury Compounds in Low Level Environmental Samples Part 2, Water. Anal.Chem.Acta.1993, 282, 153.

2.4 Chemical Hygiene Plan, Eurofins Frontier Global Sciences (EFGS), current version.

2.5 EPA Method 1630 Draft Method:, Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap and CVAFS, January 2001.

2.6 TNI Environmental Laboratory Sector, Vol 1, Management and Technical Requirements, ELV1-2016.

2.7 Department of Defense / Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, prepared by DoD Environmental Data Quality Workgroup (EDQW) and DOE Consolidate Audit Program (DOECAP) Data Quality Workgroup (DOE-DQW), Version 5.3, May 2019

3 Cross Reference:

Document	Document Title
EFQA-Q-QM-QM5805	Quality Manual
EFHS-S-HS-12066	Chemical Hygiene Plan
EFQA-Q-QD-SOP10098	Procedure for Determining IDLs, MDLs, LODs, PQLs, LOQs, OPRs, IQs, OQs and PQs
EFQA-R-EQ-SOP2711	Pipette and Volumetric Dispenser Verification, Calibration and Maintenance
EFSR-S-CS-SOP2794	Ultra Clean Aqueous Sample Collection
EFQA-P-DR-SOP2801	Data Review and Validation
EFHS-S-HS-SOP2991	Waste Disposal Procedure for Client Sample Waste

Document	Document Title
EFAFS-T-AFS-SOP2808	Determination of Methyl Mercury in Various Matrices by Cold Vapor-Gas Chromatography- Atomic Fluorescence Spectrometry (EPA Method 1630)

4 Purpose:

4.1 The purpose of this Standard Operating Procedure (SOP) is to describe the method for the distillation of aqueous samples prior to analysis by CV-GC-AFS for methyl mercury.

5 Scope:

5.1 This method is for the distillation of aqueous samples (natural waters, precipitation, pore water, industrial and municipal effluents) for the analysis of monomethyl mercury (MMHg) at concentrations as low as 0.05 ng/L. In general, using clean handling and reagents, method detection limits (MDLs) in the range of 0.005 - 0.030 ng/L are routinely attainable.

5.2 Methyl mercury as defined by this method means all chloride-distillable methyl mercury forms and species found in aqueous solution and on aqueous suspended matter. This includes, but is not limited to, CH_3Hg^+, CH_3HgCl, CH_3HgOH, and CH_3HgS-R.

6 Basic Principles:

6.1 Samples are collected using ultra-clean sample handling protocols into rigorously cleaned or tested clean glass bottles or disposable PETG bottles.

6.2 The samples must be acid-preserved within 48 hrs of sampling. Acid-preserved samples are stable for at least six months, if kept dark and cool (EPA 1630). Samples are preserved with 0.4% hydrochloric acid (HCl) and stored dark, in a refrigerator at a temperature between 0-4°C until distillation.

6.3 Before analysis, the MMHg in an aliquot of the sample is co-distilled into pure water. The distillates are then analyzed for MMHg by aqueous phase ethylation and Cold Vapor-Gas Chromatography-Atomic Fluorescence Spectroscopy (CV-GC-AFS) as described in SOP EFAFS-T-AFS-SOP2808 “Methyl Mercury Calibration and Analysis.”

7 Reference Modifications:

7.1 No significant modifications were made to this method.

8 Definitions:

8.1 Batch – no more than 20 client samples grouped for preparation. 3 Preparation Blanks, 1 CRM or 1 LCS/LCSD (or BS/BSD) set and 1 MD are prepared per every 20 samples; 1 MS/MSD set is prepared for every 10 samples.

8.2 CDOC - Continuing Demonstration of Capability.

8.3 Certified Reference Material (CRM) – a standard of known composition that is certified by a recognized authority and representing a sample matrix. It is used to verify the accuracy of a method.

8.4 IDOC - Initial Demonstration of Capability.

8.5 Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD), reagent water is spiked with a secondary source at 1.0 ng/L and is taken through the entire preparation and analysis process in the same manner as the samples to monitor

complete method performance. A Certified Reference Material (CRM) is preferred as the LCS, but a blank spiked sample also meets the requirement.

8.6 LIMS: Laboratory Information Management System. Computer software used for managing samples, standards, and other laboratory functions.

8.7 May: This action, activity or procedure is optional

8.8 May Not: This action, activity or procedure is prohibited

8.9 Method or Preparation Blank (BLK) – Method blanks consist of the same reagents used to digest the samples, in the same volume or proportion, and are carried through the complete sample preparation and analytical procedure.

8.10 Matrix Duplicate (MD) – a representative sample is selected and digested in the same manner. This QC sample will indicate sample homogeneity on the analytes of interest.

8.11 Matrix Spike (MS) and Matrix Spike Duplicate (MSD) – a representative sample is selected and spiked with a secondary source at 1.0 ng/L. These QC samples will indicate sample matrix effects on the analytes of interest.

8.12 Method Detection Limit (MDL) – the limit derived from an exercise as described in 40 CFR, Part 136, Appendix B. The exercise produces a defined value that is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero from a given matrix.

8.13 MMHg - monomethyl mercury

8.14 Shall: This action, activity or procedure is required.

8.15 Should This action, activity or procedure is suggested, but is not required.

9 Interferences:

9.1 The use of the distillation procedure eliminates most method interferences from organic matter, particulate, and sulfides, all of which can affect the recovery of methyl mercury.

9.2 Under no circumstances should ordinary plastic (i.e., polyethylene, polypropylene, polycarbonate, or vinyl) containers be used with the exception of PETG containers, as they are very diffusive to Hg^o gas from the air. Containers should be made of acid-cleaned Teflon with Teflon caps, borosilicate (or quartz) glass bottles with Teflon-lined caps, or PETG bottles. It is critical that the bottles have very tightly sealing caps to avoid diffusion of atmospheric Hg through the threads.

9.3 The low detection limit of this method depends on the stringent cleaning of equipment used for sample collection and storage.

9.4 It is important that the HCl concentration in the sample be between 0.2% and 0.6% (v/v) for effective distillation of the CH_3HgCl. If the chloride concentration present in the sample is too high (resulting from the addition of too much HCl upon preservation), HCl will co-distill with the sample during distillation, which lowers the pH of the distillate. If the low pH of the samples is not compensated for by adding additional acetate buffer, the sample will not be at the optimal pH for the ethylation reaction, resulting in low recoveries. The problems associated with the distillation of samples high in chloride can also be avoided by distilling smaller aliquots of the sample; however, this results in higher detection limits. Typically, samples known to be high in chlorides (i.e., salinity) are preserved with 0.2%

sulfuric acid. This minimizes the addition of chlorides to the sample, yet creates the appropriate sample pH for proper distillation.

9.5 No HNO_3 or other oxidizing agents (i.e., Cl_2, BrCl, CrO_4^{2-}, etc.) can be present in the sample, or CH_3Hg may be destroyed. Particular care must be taken to eliminate the chlorine present in the municipal water that feeds the deionized water system by passing it through an activated carbon bed.

10 Safety Precautions, Pollution Prevention and Waste Handling:

10.1 Personnel will don appropriate laboratory attire according to Chemical Hygiene Plan (CHP) EFHS-S-HS-QP12066. This may include, but is not limited to: laboratory coat, apron, eye protection, face shield and protective gloves.

10.2 The toxicity or carcinogenicity of each laboratory reagent has not been fully established. Therefore, every chemical must be treated as a potential health hazard. Exposures shall be reduced as much as possible. Analysts and technicians are expected to familiarize themselves with the characteristics and risks of each chemical they work with by referring to the SDS located at https://msdsmanagement.msdsonline.com/company/5c1df5b3-747d-4789-8104-42457dc3a3e5/

10.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease-causative agents. Eurofins Frontier will reimburse the expense of Hepatitis A and B immunizations for any laboratory staff member who desires this protection.

10.4 Hydrochloric Acid (HCl) is hazardous. Always work in fume hood wearing safety glasses and gloves while using this chemical. In case of skin contact (corrosive, irritant, permeator), of eye contact (irritant, corrosive),of ingestion. Slightly hazardous in case of inhalation (lung sensitizer).Non-corrosive for lungs. Liquid or spray mist may produce tissue damage particularly on mucous membranes of eyes, mouth and respiratory tract. Skin contact may produce burns. Inhalation of the spray mist may produce severe irritation of respiratory tract, characterized by coughing, choking, or shortness of breath. Severe over-exposure can result in death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

10.4.1 Eye Contact: Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

10.4.2 Skin Contact: In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

10.4.3 Serious Skin Contact: Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

10.4.4 Inhalation: If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

10.4.5 Serious Inhalation: Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING:

It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

10.4.6 Ingestion: If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

10.5 See EFGS Chemical Hygiene Plan (CHP) for general information regarding employee safety, waste management, and pollution prevention.

10.6 Pollution prevention information can be found in the current EFGS Chemical Hygiene Plan (CHP), which details and tracks various waste streams and disposal procedures.

10.7 All laboratory waste is accumulated, managed, and disposed of in accordance with all federal, state, and local laws and regulations. Any waste generated by this procedure should be disposed of according to SOP EFHS-S-HS-SOP2991 "Waste Disposal Procedure for Client Sample Waste," which provides instruction on dealing with laboratory and client waste.

11 Personnel Training and Qualifications:

11.1 An analyst must perform an initial demonstration of capability (IDOC) that includes four replicates of a secondary source before being qualified to analyze samples without supervision. Continuing DOC will be maintained and monitored via performance on CRMs and other QC samples, as well as obtaining acceptable results on proficiency testing exercises.

11.2 The analyst/laboratory technician must have read this SOP and other relevant SOPs and have the training documented on the applicable form(s). The analyst may be questioned on SOP by supervisor(s) and/or trainers.

11.3 Training is documented by the employee and supervisor, and is kept on file in the QA Office. The employee must read, understand, and by signing the training document, agree to perform the procedures as stated in all Standard Operating Procedures (SOPs) related to this method.

11.4 All employees must read the Quality Manual (EFQA-Q-QM-QM5805) and complete annual Ethics training.

11.5 All training documents including IDOCs, CDOCs, SOP reading, Initial QA orientation, and Ethics training are stored by the Quality Assurance Manager in the employees training file for ten years after the employee is no longer working for Eurofins Frontier Global Sciences.

11.6 Chemical Safety Training, Compressed Gas Training, Chemical Hygiene Plan documentation, and Shipping of Hazardous goods training, are stored by the Health and Safety Officer for ten years after the employee is no longer working for Eurofins Frontier Global Sciences.

12 Sample Collection, Preservation, and Handling:

12.1 Samples are collected using ultra-clean sample handling protocols into rigorously cleaned or tested clean glass bottles.

12.2 Aqueous sample preservation - The samples must be acid-preserved within 48 hrs of

sampling. Samples are preserved with 0.4% hydrochloric acid (HCl) and stored dark, in a refrigerator at a temperature between 0-5°C until distillation.

12.3 Acid-preserved samples are stable for at least six months, if kept dark and cool (EPA 1630).

13 Apparatus and Equipment:

13.1 LIMS – Element, version 6 or higher; Computer – Windows 7 or 8

13.2 Teflon Still: The still is constructed of 60 mL heavy wall Teflon vials (Savillex). The vial is fitted with a special cap, allowing insertion of 1/8" Teflon tubing. Each vial should be engraved with a line at the 40.0 mL mark, determined by weighing 40.0 g of reagent water into the vial. One length of tubing goes from the purged nitrogen source into the distillation vessel (or sample vessel), so that it reaches the bottom of the vial. The second length of tubing goes from the headspace of the sample vial into the bottom of the receiving vial. The sample vial is heated to approximately 120□C in a temperature-controlled aluminum block, while the receiving vial is maintained in an ice-water bath. The rate of distillation will be between 2.5 to 4 hours.

13.3 Sampling Bottles: It is imperative for accurate sub-ng/L MMHg measurements that PETG bottles or appropriately cleaned Teflon bottles or glass bottles, with Teflon-lined, tight-fitting lids are used for all steps contacting the sample. These bottles are washed according to SOP EFGS-007, “Cleaning of Sampling Equipment and Bottles for Mercury Analysis.” Bottles used for Mercury Deposition Network (MDN) samples are washed according to SOP MDN-009, “Cleaning of MDN Sampling Glassware.

13.4 Pipettors: All-plastic, pneumatic, fixed volume and variable pipettes in the range of 20 µL to 10 mL. Pipettes are to be calibrated weekly according to SOP EFQA-R-EQ-SOP2711.

13.5 pH paper: paper with the range appropriate to evaluating the pre and post distillation pH checks. Ideally 0 to 7.

13.6 Clean hood.

13.7 Analytical Balance: A laboratory analytical balance that measures accurately to 0.01mg, with documented calibration.

14 Reagents and Standards:

14.1 Reagent Water: 18 MΩ ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. As a final mercury and organic removal step, the activated carbon cartridge on the 18-MΩ system is placed between the final ion exchange bed and the 0.2 µm filter.

14.1.1 Pipette tip rinse bottle labelled:

Speciation Rinse, MQ only

To be used for all speciation analysis: As, DMHg, CrVI, HgO, MMHg, Se and any other type of speciation analysis. Anything that requires us to evaluate an oxidation state of any metal.

14.2 Hydrochloric Acid: Trace metal purified reagent-grade HCl is pre-analyzed and lot sequestered. Several brands (Baker, Fisher, Omnitrace) have been found to have lots with acceptably low levels of trace metals. This reagent should be from a lot number that

has been previously tested to be low for the analytes of interest. This reagent shall be entered into LIMS and the expiration date is set to the same as the manufacturer's expiration date.

14.2.1 0.4% Hydrochloric Acid: In a designated Teflon bottle, 995 ± 25mL reagent water is weighed out and 4 mL of HCl is measured out with a pipette or re-pipettor. Solution must be made fresh prior to each distillation. The LIMS ID of the HCl used must be entered to the LIMS bench sheet.

14.3 1% APDC Solution: To 100 mL of reagent water, add 1.0 g of reagent-grade ammonium pyrrolidine dithiocarbamate (APDC), and shake to dissolve. Add 10 mL of methylene chloride, and shake for two minutes. Let stand for 15 minutes and then decant the top layer into the APDC bottle. The solution is then stored in refrigerator A. The solution is entered into LIMS with a holding time of 1 week.

14.4 Nitrogen: Grade 4.5 (standard laboratory grade)

15 Procedures:

15.1 Samples are collected and handled according to SOP EFSR-S-CS-SOP2794, "Ultra Clean Aqueous Sample Collection."

15.2 Obtain pairs of clean sample and receiving distillation vials. Empty the contents of the vials into a large beaker with sodium bicarbonate. Rinse each vial three times with reagent water, making sure to rinse the lids and tubes thoroughly.

15.3 Tape the receiving vials, distinguished by a black line on the caps, so that the bottom of the tape is just touching the top of the 40.0-mL engraved mark. Pipette 5 mL of reagent water into each of the receiving vials, so that the bottom of the tubing is covered.

15.4 Retrieve the samples to be distilled from the walk-in refrigerator. Organize the samples in the same order as they are listed on the LIMs bench sheet, and make sure that all samples are accounted for.

15.5 Check the pH of each sample by removing a small aliquot with a clean pipet and dispensing the aliquot on pH paper. The samples should be acidic (< pH 2). If the pH is greater than or equal to 2, add concentrated hydrochloric acid (HCl) dropwise until the pH is less than 2. Document the pH and note any adjustments in the sample distillation logbook.

15.6 Each sample vial is placed on the balance and tared before adding up to 45.0 ± 0.2 g of sample. A smaller aliquot volume may be used if samples are suspected to be high in MMHg, or if there is a limited amount of sample available. These smaller aliquots are diluted to 45 mL with the 0.4% HCl.

Note: For samples that are suspected to have densities that are not 1.00 ± 0.02 g/mL, the density must be determined and the aliquot size must be adjusted to accommodate this difference between mass and volume.

15.7 Prepare three blanks, one blank spike, and one blank spike duplicate at 45.0 mL using 0.4% HCl as the diluent.

15.8 Using a pipette add 200 µL of 1% APDC to each vial (sample and QC) before capping the vial. The sample vial is then placed next to its corresponding receiving vial in a holding rack. Record the LIMS ID of the APDC solution in the logbook.

15.9 After all samples are prepared, spike *50* µL of 1.0 ng/mL standard into the blank spike and matrix spike samples for a true value of 1.0 ng/L. The LIMS ID of the standard used for spiking must be added to LIMS bench sheet.

15.9.1 Due to the lack of a CRM for methyl mercury in water, at least one blank spike/blank spike duplicate must be analyzed per analytical batch.

15.10 Turn on the heating blocks in the distillation area after verifying to make sure that they are set at 120°C. Fill the ice-water bath container with half water and half ice. Turn on the nitrogen gas lines, assuring the flow rates are equivalent. The flow rate is normally between 300-400cm^3/min and is indicated by a gentle, steady flow of bubbles.

15.11 Place the receiving vessel into the ice-water bath and its sample vial counterpart into the corresponding heating block hole. The tubing from the receiving vial is placed into the hole in the cap of the sample vial, and the tubing from the sample vial is plugged into the airflow bank. Teflon tape is used to ensure a snug fit on the tubing. After all vials are in a block, the aluminium cover piece is placed over the sample vials.

15.12 A distillation rate of 10-15 mL per hour should be maintained, until a total volume of 40 □ 1 mL is achieved in a receiving vial. The distillation is complete when the water line in the receiving vial reaches the bottom of the tape. The receiving vial is then disconnected from the sample vial. The distillation for a water sample of 40 mL should take approximately 2.5-4 hours.

15.13 The pH is measured for all samples and is recorded on the logbook.

15.14 The optimum pH for the distillate is 3.5-7. For pH <3.0, the sample will be analyzed, but should be re-distilled if sufficient sample volume remains. This shall be entered as a comment in the MMO notes in LIMS.

15.15 The distillate may then be analyzed using aqueous phase ethylation, GC separation, and CVAFS detection. For water samples, the entire sample will usually be analyzed. Calculation of MMHg content is based upon the actual volume of sample distilled corrected by the empirically derived distillation efficiency factor. For samples determined to be possibly high in MMHg, a fraction of the total distillate may be analyzed.

16 Calculations:

16.1 This preparation procedure does not involve calculations.

17 Statistical Information/Method Performance

17.1 Method Detections Limits (MDL) are determined during method development and then annually thereafter according to 40 CFR Part 136, Section B and and EFQA-Q-QD-SOP10098.

17.2 The Practical Quantitation Limit (PQL) is the reporting limit for this method and is included as the lowest calibration point (2003 NELAC regulation 5.5.5.2.2.1.h.3). The PQL is determined by running ten replicate samples with a concentration that will produce a recovery of 70-130% for most analytes, but the recovery requirements are analyte dependent. The PQL is referred to as the Method Reporting Limit (MRL) in LIMS.

17.3 The current values for MMHg in aqueous samples are 0.05 ng/L for the LOD and 0.05 ng/L for the PQL.

17.4 Current LODs and PQLs are stored at: \\us34fivp002\General and Admin\Quality Assurance\Method-Limits-MDLs-IDLs\MDLs & PQLs.

18 Quality Assurance/Quality Control:

18.1 Maximum Sample Batch Size: 20 samples.

18.2 Preparation Blanks: Minimum of three per batch. Each preparation blank must be less than the PQL for the method.

18.2.1 The preparation blanks are prepared using the 0.4% HCl diluent; these are put through the same preparation process as the samples.

18.3 Certified Reference Material (CRM, representing the sample matrix when commercially available); or a Laboratory Control Spike (LCS) and Laboratory Control Spike Duplicate (LCSD) is used when a suitable CRM is not available: One per batch in duplicate. The control limits are 70-130% recovery.

18.4 *Matrix Duplicate (MD): Not required. A Matrix Duplicate (MD) may be analyzed for every batch of 20 samples upon client request. The control limit for the RPD is <=35%.*

18.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples: One set per 10 samples. The control limits are 65-130% recoveries and an RPD of <= 35%.

18.6 Follow the flow charts in SOP EFQA-P-DR-SOP2801 “Data Review and Validation” to determine if any QC falling outside the established control limits can be qualified.

18.7 All of the quality control limits for the analysis method are included on the “Data Review Checklist.

18.8 The data review checklists are located at:

\\cuprum\GeneralandAdmin\QualityAssurance\DataReview\CurrentDataReviewChecklists.

19 Corrective Action:

19.1 Limiting the source of contamination/error in the preparatory stage can decrease QC problems during analysis. Limiting such contamination/error sources may include: cleaning all digestion tools in a 10% HCl solution, ensuring all samples are thoroughly homogenized, changing gloves whenever appropriate, flushing repipettors at least three times before dispensing into vials and, in general, following ultra-clean procedures.

19.2 A failing QC point does not necessary fail the entire dataset. If upon analysis a QC sample is out of control, some investigation must be performed to assess if the difficulties are related to matrix effects. The cause and method of determining the set's failure must be documented on the checklist and in the MMO notes, and the Group Supervisor shall be informed. See SOP EFQA-P-DR-SOP2801 “Data Review and Validation” for flow charts regarding analytical issues.

19.3 If a matrix spike sample does not show recovery within the control limits, it is possible that the sample was not spiked properly. The analyst preparing the samples should review the spiking level for accuracy. Spikes are always witnessed by a peer who then initials/dates the logbook.

19.4 If contamination is suspected to be a problem, the vials may need to be deep cleaned using BrCl. Additionally, reagents should be checked for contamination or remade in clean bottles.

19.5 If samples render abnormal results, several other variables should be investigated to discover the source of error. The Senior Analyst, and/or the Group Supervisor should be consulted to discuss possible areas for trouble-shooting.

19.5.1 Check for a loose connection or air leak in the tubing connecting the vials, and check to ensure that all vial caps were screwed on tightly during the distillation process.

19.5.2 The temperature of the heating blocks should be checked and, if necessary, adjusted within the range of 120°C and 125°C.

19.5.3 Airflow should also be checked to ensure that it is functioning within between 300-400cm^3/min.

19.6 If the distillation process is determined to be the cause of the analytical problems, then all samples with sufficient volume must be re-distilled. Samples without sufficient volume will be flagged during the review process and then narrated in the case narrative by the Project Manager.

Version history

Version	Approval	Revision information
9	30.NOV.2016	
10	04.APR.2018	
11	22.JUL.2019	
12	3.NOV.2020	

Standard Operating Procedure for the Determination of Lipids in Tissue

Issue date: 6/14/2023
Revision: 2

SGS North America Inc.
5500 Business Drive
Wilmington, North Carolina 28405

Approved by:

J. Harrison Land, Last Revised by — Date: 6/14/2023

Greg Dickinson, Technical Director — Date: 6-14-2023

Jeannie Milholland, Quality Assurance Director — Date: 6-14-2023

(Official copies of final documents will contain all three signatures.)

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Revision History

- The following changes were made effective on June 7, 2023:
  - Updated TOC
  - Section 2.0 revised equation
  - Section 7.7 updated reference for NYSDEC
  - Section 7.9 added details
  - Section 7.10 added details
- The following changes were made effective on April 5, 2023:
  - Section 2 added equation
  - Section 4 added information about holding times
  - Section 5 added desiccator, fritted funnel, rotary evaporator and TurboVap, update weight of Al weigh boats
  - Section 7 added desiccator and drying times to procedure, reference to DC_560 and other details
  - Section 8 added approximate weight of aluminum pans and revised equation
  - Section 9 – new section for definitions
  - Section 10 added reference to DC_560 and 3550C.
- The following changes were made effective on February 2, 2022:
  - Section 2.1 Added reporting limit information
  - Section 5.0 Added balance details
  - Section 7.0 updated procedure with additional details
- The following changes were made effective on February 2, 2022:
  - Added Sections 5.6 – 5.8 to Equipment and Supplies
  - Added Section 6 (Reagents and Standards)
  - Replaced "MC" with methylene chloride throughout the SOP
- SOP has been reviewed by Amber Nunalee, on 7/2/2020 and no revisions are necessary
- Review was completed on March 21, 2020, by Ricky Ballard and no updates needed
- The following changes were made effective on August 12, 2015:
  - New SOP converted to SGS format from AP-SP-C3

1.0 Scope and Application

1.1 To describe the procedures followed for the determination of lipids in tissue samples

1.2 See Document DC_139 Appendix D for a full list of definitions.

2.0 Summary of Method

2.1 An aliquot of the homogenized samples is weighed out separately and sonicated. Reporting Limit of 0.05% is achieved using 8 grams of sample on a balance capable of 0.00001 g resolution per the following calculation.

*Wt. diff =0.1% margin=> Uncertainty = 0.001*2(Uncertainty of W_1 and W_2) => 0.002g/8g (sample wt.) = 0.00025g*100 = 0.025% * (2 crit wt.) = 0.05% accuracy with certainty*

3.0 Safety Precautions

3.1 Gloves must be worn when handling samples, standards, and reagents.

3.2 Safety glasses must be always worn when working in the laboratory.

3.3 A lab coat must be worn while dealing with samples, standards, and reagents.

3.4 In the interest of safety and pollution prevention, all spills must be cleaned up immediately.

4.0 Sample Collection, Preservation and Storage

4.1 Tissue samples are kept frozen until thawed for extraction.

4.2 Holding times begin and are calculated when the fish is fully thawed.

4.3 Waste is disposed of in appropriate waste containers in accordance with the local, state, and federal regulations. No sample or reagent is ever disposed of down a drain or in the trash. See document MI_278 for waste disposal, pollution prevention and spill cleanup.

5.0 Equipment and Supplies

5.1 Meat grinder/Blender

5.2 Freezer

5.3 Glass container (40 mL vials, 60mL vials or 4 oz jars)

5.4 Balance capable of Resolution to 0.00001 grams

5.5 Aluminum foil

5.6 Forceps

5.7 Sonicator

5.8 ~ 1 gram Aluminum weigh boats

5.9 Desiccator

5.10 Fritted funnel

5.11 Rotary Evaporator

5.12 Turbovap

6.0 Standards and Reagents

6.1 Acetone

6.2 Methylene Chloride

6.3 Sodium Sulfate

7.0 Procedure

7.1 Weigh and record approximately 8 g of the ground and homogenized tissue sample into a tarred container appropriate for sonication extraction on a balance capable of resolving weight to 0.00001g.

7.2 Add 20 mL of 1:1 methylene chloride: acetone and sonicate for 15 minutes. Let sit in hood overnight with cap on. Tissue must be completely submerged in the solvent.

7.3 Transfer solvent to appropriate glass container carefully so as not to transfer any tissue, add 20 ml of methylene chloride to the original extraction container, and shake for 1 minute.

7.4 Repeat step 7.3., for a total of 60mL of extraction solvent.

7.5 Pass solvent through a Na2SO4 plug into a 4-oz jar or other appropriate container (round bottom flask for Roto-vap/ Glass borosilicate vial for TurboVap.)

7.6 Make sure that all water has been removed and no Na2SO4 crystals are present. If crystals are present repeat step 7.5

7.7 Concentrate the extracted sample using the rotary evaporator, TurboVap, or ambiently in a clean hood. (For NYSDEC samples TurboVap will be the primary form of sample concentration, with Roto-vap as a backup if

significant amounts of solvent are required)

7.8 Pre-weigh an aluminum boat on the analytical balance to the nearest 0.00001 g. Use forceps when handling the aluminum boat and do not touch the boat with fingers.

7.9 Transfer the lipids from the extraction vessel to the aluminum boat using a small amount of DCM (~3-4mL) to ensure quantitative transfer of lipids, allow the transfer solvent to evaporate in the fume hood (minimum time of 30 minutes), and place the sample inside the desiccator for thirty minutes to ensure dryness. Weigh to the nearest 0.00001 g.

7.10 Repeat cycle of evaporation to dryness for an additional 30 minutes until the mass change of the residue is less than 1.0 % of the previous weight to ensure the solvent has been completely removed.

7.11 Record weight on SGS % Lipids Determination worksheet DC_560

8.0 Details of Calculations

8.1 As per the method, calculate the lipids content to the nearest three significant figures using the formulae:

8.2 Lipid/Oil residue weight

Residue wt. = (Tare wt. with dried sample) – Tare wt.

8.3 Oil/Lipid Content:

$$\%Oil/Lipid = \left(\frac{Residue\ Weight}{Sample\ Weight}\right) \times 100$$

where,

Residue wt. = final weight after drying
Sample wt. = initial weight of sample
tare = weight of pan (should be approximately 0.8 grams)

9.0 Definitions

9.1 Desiccator – an apparatus that hold a drying agent for removing moisture from specimens and protecting specimens from water vapor in the air.

9.2 NYSDEC – New York State Department of Environmental Conservation

10.0 References

10.1 SGS document DC_139, Appendix D Definitions.

10.2 SGS document MI_278, Waste Disposal, Pollution Prevention and Spill Clean up.

10.3 SGS document DC_560, % Lipid Determination Worksheet

10.4 SW-846 Method 3550C : Ultrasonic Extraction Revision 3 February 2007

10.5 SGS document DC_560, Bench Sheet (Including % Lipid)

% Lipid Determination WorkSheet

SGS

Batch: _____ Date and Time in Desiccator:

Balance ID: _____ Date and Time out of Desiccator:

Lab Sample ID	Sample Wt. (g)	Boat Wt. (g)	Boat and Residue Wt. 1 (g) *(After 30minutes of evaporation)*	Lipid Wt. 1 (g) *(After 30minutes of evaporation)*	Boat and Residue Wt. 2 (g) *(After dessication)*	Lipid Wt. 2 (g) *(After dessication)*	Percent Difference *((W2-W1)/W1 x 100))*	% Lipid	Comments
Date/Initials:									

STANDARD OPERATING PROCEDURE L-3B: % MOISTURE CALCULATION AND % SOLIDS CALCULATION (GRAVIMETRIC) BY SM 2540 G 1997 AND SM G-2011

Standard Operating Procedure for the Determination of Percent Moisture in Solid Samples

Issue date: 10/12/2017
Revision: 14

SGS North America Inc.
5500 Business Drive
Wilmington, North Carolina 28405

Approved by:

Jeannie Milholland, Last Revised By — Date: 10-12-16

Greg Dickinson, Technical Director — Date: 10-12-2017

Jeannie Milholland, Quality Assurance Director — Date: 10-12-16

(Official copies of final documents will contain all three signatures.)

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Revision History

- The following changes were made effective on October 12, 2017:
  - Section 9.1; defined the Horizon LIMS procedure
  - Section 9.2: added section to include AP LIMS procedure
  - Section 10.1; defined the Horizon LIMS procedure
  - Section 10.2; added section to include AP LIMS procedure
  - Section 14.0; added preventative maintenance
- The following changes were made effective on July 20, 2016:
  - Sections 1.2 & 17.1: changed D2216-98 to D2216-10
  - Sections 6.6, 8.2, 10.11-10.13: new sections added
  - Sections 9.1, 9.2, 9.4, 10.1, 10.3, 10.9: new sections inserted, renumbering rest of sections
  - Sections 9.5, 9.6, 9.8, 10.4, 10.6-10.8, 10.10: updated to reflect current practices
  - Section 16.2: section deleted, renumbering rest of section
- The following changes were made effective on February 16, 2016:
  - Sections 5.4 & 17.3: updated MI_278 name
  - Section 12.1: changed to say that temp accuracy is checked prior to samples entering the drying oven
- Updated summary of method for correct display of temperature ranges
- Updated references for new Waste Disposal and Pollution Prevention SOP, MI_278

1.0 Scope and application

1.1 This method details the determination of percent moisture in soils and other solid and semi-solid samples.

1.2 This SOP is based on ASTM D2216-10.

1.3 See Document DC_139 Appendix D for a full list of definitions.

2.0 Summary of method

2.1 A 5-20 gram aliquot of sample is weighed into a drying pan. The sample is placed in a drying oven at 110 ± 5°C. The sample is allowed to go to complete dryness and is then weighed again. The percent moisture (or solids) can then be determined.

3.0 Safety precautions

3.1 Gloves must be worn when handling samples, standards, and reagents.

3.2 Safety glasses must be worn at all times when working in the laboratory.

3.3 A lab coat must be worn while dealing with samples, standards, and reagents.

3.4 In the interest of safety and pollution prevention, all spills must be cleaned up immediately.

4.0 Interferences and preventative measures

4.1 Rocks, sticks and debris are removed from the sample. Removal must be documented.

5.0 Sample collection, preservation and storage

5.1 SGS will provide certified pre-cleaned polyethylene sample bottles or amber glass soil jars upon request.

5.2 All samples should be shipped and stored at 4(±2) °C.

5.3 Analyze as soon as practical after sampling.

5.4 Waste is disposed of in appropriate waste containers in accordance with the local, state and federal regulations. No sample or reagent is ever disposed of down a drain. See document MI_278 for waste disposal, pollution prevention and spill cleanup.

6.0 Equipment and supplies

6.1 Drying Oven- Fisher Scientific

6.2 Mettler-Toledo PB3002-S balance- capable of weighing to the one-hundredth of one gram.

6.3 Aluminum drying pans from Fisher Scientific or VWR.

6.4 Tongue Depressors

6.5 Desiccator

6.6 Glass beads

7.0 Standards and reagents

7.1 Not applicable to this SOP.

8.0 Calibration

8.1 The balance is calibrated daily using 3 class "S" weights of varying mass according to the SOP MI_1.

8.2 The thermometer in the drying oven is calibrated annually or quarterly depending on type of thermometer according to SOP MI_1.

9.0 Sample preparation

9.1 Horizon LIMS Procedure

9.1.1 Create batch in Horizon.

9.1.2 Pull batch into SGS Solids Control Program.

9.1.3 Label aluminum drying pans with the appropriate laboratory sample ID number.

9.1.4 Record the balance ID into SGS Solids Control Program

9.1.5 Place the pan on the balance and upload tare weight in the SGS Solids Control Program.

9.1.6 Homogenize each sample. Stirring the entire sample in its container is sufficient for wet samples.

9.1.7 Document and remove any sticks, rocks or debris.

9.1.8 Weigh a 5-20 g aliquot of the sample and upload the total weight of the sample and pan in the "Wet Wt" field SGS Solids Control Program.

9.2 AP LIMS Procedure

9.2.1 Load Excel Workbook from network: //amr/wilmington/groupdata/software/excelreports/prep/UT_solids_calc_v0.x.xlsm

9.2.2 Create solids batch in the following format: YYYYMMDDX (X=any character A-Z starting with A)

9.2.3 Enter the APLIMS LabIDs(B####_###) and the client IDs(from COCs) with their collection dates and times. (date/time format is MM/DD/YY HH :MM).

9.2.4 Label aluminum drying pans with the appropriate laboratory sample ID number.

9.2.5 Record the balance ID, Date started, analyst and oven ID.

9.2.6 Place the pan on the balance and upload tare weight in the UT_Solids_Calc Program.

9.2.7 Homogenize each sample. Stirring the entire sample in its container is sufficient for wet samples.

9.2.8 Document and remove any sticks, rocks or debris.

9.2.9 Weigh a 5-20 g aliquot of the sample and upload the total weight of the sample and pan in the "Wet Wt" field UT_Solids_Calc Program.

10.0 Analytical procedure

10.1 HORIZON LIMS PROCEDURE

10.1.1 Select the OVEN ID from the dropdown box in the Solids Control Program.

10.1.2 Place the sample into the drying oven with the temperature set at 110 ± 5°C.

10.1.3 Click on the Oven Temp Start and the Solids Control Program will enter the current oven temperature.

10.1.4 Heat the sample a minimum of two hours, until dry.

10.1.5 Once the sample has dried, remove it from the oven and allow it to cool covered or in a desiccator.

10.1.6 Place the sample on the balance and upload the weight of the dried sample and pan in the "Dry Wt 1" field of the SGS Solids Control Program.

10.1.7 Place the sample and pan back in oven for a minimum of one hour. Once cooled Place the sample on the balance and upload the weight of the dried sample and pan in the "Dry Wt 2" field of the SGS Solids Control Program

10.1.8 Repeat cycle of drying and cooling or desiccating until the mass change is less than 1% of the previous weight.

10.1.9 Click on the Oven Temp End in the Solids Control Program to enter the final weight.

10.1.10 The "Dry Wt Final" will provide the result to use for the final calculation of %solids. When the final drying cycle passes the one percent, the Solids Control program will calculate the final %solids.

10.1.11 Do a final commit to save the data to the raw data tables.

10.1.12 Upload data to the Horizon LIMS.

10.1.13 When data is uploaded to the LIMS, a copy of the data grid will be saved to the SCANs folder on the file server in Excel format as a copy of the raw data. The data in this spreadsheet is locked so no changes can be made.

10.2 APLIMS PROCEDURE

10.2.1 Place the samples into the drying oven with the temperature set at 110 ± 5°C.

10.2.2 Record the oven start temperature.

10.2.3 Heat the sample a minimum of two hours, until dry.

10.2.4 Once the sample has dried, remove it from the oven and allow it to cool covered or in a desiccators.

10.2.5 Place the sample on the balance and upload the weight of the dried sample and pan in the "Dry Wt 1" field of the UT_Solids_Calc Program.

10.2.6 Place the sample and pan back in oven for a minimum of one hour. Once cooled Place the sample on the balance and upload the weight of the dried sample and pan in the "Dry Wt 2" field of the UT_Solids_Calc Program.

10.2.7 Repeat cycle of drying and cooling or desiccating until the mass change is less than 1% of the previous weight.

10.2.8 Record the oven end temperature.

10.2.9 The "Dry Wt Final" will provide the result to use for the final

calculation of %solids. When the final drying cycle passes the one percent, the UT_Solids_Calc Program will calculate the final %Moisture, %Solids and Dry Wt EQUIV.

10.2.10 When complete save to //amr/wilmington/groupdata/SCANS/DRY as Batch.xls (YYYYMMDDX) and submit for data review.

11.0 Details of calculations

11.1 Percent solids,

$$\%Solids = \left(\frac{dry - tare}{wet - tare} \right) \times 100$$

where,

dry = weight after drying
wet = wet weight of sample
tare = weight of pan

11.2 Relative Percent Difference (RPD): To compare the precision of duplicate analysis. Precision expressed as RPD is calculated for laboratory sample duplicates, laboratory control sample duplicates, matrix spike duplicates, etc., as follows:

$$RPD = \frac{(C_1 - C_2)}{\left(\frac{(C_1 + C_2)}{2} \right)} \times 100$$

where,

C_1 = larger of the two values
C_2 = smaller of the two values

12.0 Quality control requirements

12.1 The drying oven's temperature accuracy is checked prior to samples entering the drying oven.

12.2 One Method Blank per daily batch. Use glass beads for the method blank. Criteria of 99.0 – 101.0%.

12.3 A Duplicate will be analyzed with each daily batch of samples. If the RPD between the duplicate and the parent sample is > 7.8%, then the batch will be rerun.

12.4 Data outside of QC limits may be addressed by one or more of the following options:

12.4.1 Re-preparation and re-analysis of sample

12.4.2 Client notification

12.4.3 Discussion and qualification of data by case narrative

12.4.4 Re-sampling and reanalysis (client decision)

12.5 Data outside of QC limits may be reported if directed by the client. It must be qualified by a case narrative detailing the QC problems with advice on the usability of the data.

13.0 Data review and reporting requirements

13.1 Please see SGS document MI_141 for data review SOP.

14.0 Preventative maintenance

14.1 Replace desiccant when needed.

14.2 Keep balance clean and free of debris.

15.0 Definitions

15.1 ASTM – American Society for Testing and Materials

15.2 RPD – Relative Percent Difference

15.3 QC – Quality Control

16.0 References

16.1 ASTM Standard D 2216-10 Laboratory Determination of Water. (Moisture) Content of Soil and Rock by Mass.

16.2 SGS document DC_139, Appendix D Definitions.

16.3 SGS document MI_278, Waste Disposal, Pollution Prevention and Spill Cleanup.

16.4 SGS document MI_1, Daily Monitoring of Support Equipment.

16.5 SGS document MI_141, Review of Analytical Data.

STANDARD OPERATING PROCEDURE L-3C: SW846 8082A DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY

AND

SULFURIC ACID/PERMANGANATE CLEANUP

LAB SUPERVISOR: Co-

QA OFFICER: Olga Y. Agrinier

EFFECTIVE DATE: 3-12-2021

TITLE: SW846 8082A: DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY
REFERENCES: SW846 8082A (Revision 1, February 2007)
REVISED SECTIONS: reference

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by SGS-Dayton to acquire samples for analysis of polychlorinated biphenyls (PCBs) as Aroclors, using dual open-tubular, capillary columns with electron capture detectors (ECD).

1.2 This gas chromatographic (GC) method applicable to the determination of the PCB Aroclors listed in Table 1 in extracts from solid and aqueous matrices.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (from 250 mL to 1 L for liquids, 15 g for solids) is extracted using the appropriate matrix-specific sample extraction technique. Petroleum Products and organic wastes are diluted with an organic solvent and follow SW 846 Method 3580A. Aqueous samples are extracted at neutral pH with methylene chloride using Method 3510 (separatory funnel). Solid samples are extracted with using Method 3546, Microwave Extraction. Wipes are extracted using Method 3550C, Sonication.

2.2 Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for these analytes. This cleanup technique will remove (destroy) many single components organochlorine or organophosphorus pesticides.

2.3 After cleanup, the extract is analyzed by injecting a 1 or 2-µL aliquot into a gas chromatograph with dual narrow bore fused silica capillary columns and electron capture detectors (GC/ECD). The chromatographic data may be used to determine the seven Aroclors in Table 1.

2.4 The peaks detected are qualitatively identified by comparison to retention times specific to the known target list of PCBs on two different column types (primary and confirmation).

2.5 Once identified, the Aroclor is quantitated by external standard techniques with an average calibration factor generated from a calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. RL's may vary depending on matrix difficulties and sample volumes or weight and percent moisture. Refer to Table 1 for current reporting limits.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B, Revision 2, and SOP EQA075.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. The types of blanks are Method Blank; Instrument Blank, Storage Blank, and Sulfur Blank.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours and at the end of analytical sequence to verify the initial calibration of the system.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the electron capture detector to the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is <u>not</u> synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards (or SMCs for VOA), that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is distinguishable from method blanks results. MDLs must be determined according to the procedure detailed in SOP EQA075.

PERCENT DIFFERENCE (%D) - As used in this SOP and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105^{o}C. The percent moisture determined in this manner also includes

contributions from all compounds that may volatilize at or below 105° C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

REAGENT WATER - water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest.

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the instrument response of an analyte. Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RETENTION TIME (RT) - the time required (in minutes) for a standard compound to elute from a chromatographic column.

SURROGATES - for semivolatiles and pesticides/Aroclors, compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recoveries. Surrogate are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

INSTRUMENT BLANK - a system evaluation sample containing solvent and surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the SGS Health and Safety Plan and Personal Protection Policy, which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 Polychlorinated biphenyls have been classified as known or suspected human or mammalian carcinogens. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator must be worn when the analyst handles high concentrations of these toxic compounds.

6.0 SAMPLE PRESERVATION AND HOLDING TIME

6.1 PRESERVATION

6.1.1 Water Samples

6.1.1.1 Samples are collected in 300mL or 1000mL glass amber bottles without preservatives.

6.1.1.2 A minimum of 250mL of an unpreserved sample is required for extraction. Additional sample volume is necessary for any samples used for matrix spike and matrix spike duplicates. Therefore, 1 liter of at least one sample in every group of 20 field samples are required for analysis to accommodate all quality control requirements.

6.1.2 Soil Samples

6.1.2.1 Samples are collected in a glass containers. No preservative is required.

6.1.3 Sample must be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing possible phthalate contamination.

6.1.4 The samples must be protected from light and refrigerated at $\leq$ 6 °C from the time of receipt until extraction and analysis.

6.2 HOLDING TIME

6.2.1 Aqueous sample must be extracted within 1 year of sampling.

6.2.2 Soil sample must be extracted within 1 year of sampling.

6.2.3 Extracts must be analyzed within 40 days following extraction.

7.0 APPARATUS AND MATERIALS

7.1 GAS CHROMATOGRAPH SYSTEM

7.1.1 Gas Chromatograph-Agilent or Hewlett Packard Model 5890, 6890, and/or 7890. The analytical system comes complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port is designed for split or splitless injection with capillary columns. The capillary columns are directly coupled to the detectors.

7.1.2 Columns

7.1.2.1 Column pair 1

7.1.2.1.1 30 m x 0.32 mm fused silica (0.32 μm film thickness) ZBCLP-1 narrow-bore capillary column or equivalent.

7.1.2.1.2 30 m x 0.32 mm fused silica (0.25μm film thickness) ZBCLP-2 narrow-bore capillary column or equivalent.

7.1.2.2 Column pair 2

7.1.2.2.1 30 m x 0.32 mm fused silica (0.5 μm film thickness) RTX CLPI narrow-bore capillary column or equivalent.

7.1.2.2.2 30 m x 0.32 mm fused silica (0.25 μm film thickness) RTX CLPII narrow-bore capillary column or equivalent.

7.1.3 Detectors

7.1.3.1 Electron Capture Detectors (HP).

7.1.3.2 Micro Electron Capture Detectors (HP).

7.2 AUTOSAMPLER

7.2.1 Agilent or Hewlett Packard Model 7673A, 7683, 7643A capable of holding 100 of 2-ml crimp vials.

7.3 DATA SYSTEM

7.3.1 MSD interfaced to the gas chromatograph which allows the continuous acquisition and storage on machine readable media (disc) of all chromatographic data obtained throughout the duration of the analysis.

7.3.2 The ENVIROQUANT data system is capable of quantitation using multi-point calibration.

7.3.3 Lagato Networker with lookup database on 4mm DAT tape for long term, offline magnetic storage of data.

7.4 SYRINGE

7.4.1 Manually held ul-syringes, various volumes (Hamilton or equiv.).

7.4.2 10 μl graduated, auto sampler (Hamilton or equiv.).

8.0 REAGENTS AND STANDARDS

8.1 Refer to SGS Sample Preparation SOPs EOP001 and EOP3546 for reagents and standards used for sample extraction.

8.2 Solvents - Ultra pure, chromatography grade Hexane.

8.3 Stock standard solutions.

8.3.1 Two separate sources of commercially prepared standards with traceability documentation are used. The standards contain Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260. Separate calibrations are prepared and performed for Aroclors 1262 and 1268 when needed for identification of the compounds in client samples.

8.4 Working Solutions

8.4.1 Prepare working solutions, using stock solution, in hexane, as needed, that contain the compounds of interest, either singly or mixed together. Refer to Table 3A, 3B for details.

8.5 Calibration Standards

8.5.1 Initial Calibration Standards

8.5.1.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks in the other five Aroclor mixtures. As a result, a multi-point calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibration for each of the seven Aroclors. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260, including surrogates, by dilution of the above working solutions (Section 9.4) with hexane. Suggested levels and preparations are shown in Table 4A.

8.5.1.2 Separate calibration standards are required for the other five Aroclors. Unless otherwise necessary for a specific project, a single calibration standard near the mid-point of the expected calibration range of each remaining Aroclor is employed to determine its calibration factor and for pattern recognition. Refer to Table 4B for preparation scheme. Optional curves as shown on Table 4C may also be used for a multi-point calibration per project's specification.

8.5.2 Continuing Calibration Verification (CCV)

8.5.2.1 For Aroclor analyses, the continuing calibration checks must be a mixture of Aroclor 1016 and Aroclor 1260. Two standards at 500 μg/l and 1,000 μg/l are prepared as described in Table 5A. During the analysis, these two solutions are alternated to check the initial calibration.

8.5.2.2 In situations where only a few Aroclors are of interest for a specific project, the calibration checks of each Aroclor of interest may be prepared (Table 5B) and analyzed as the 1016/1260 mixture throughout the analytical sequence.

8.6 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

8.6.1 Prepare the ICV check standards from separate sources of stock standards from the calibration curve following the procedures in Table 6A, and 6B.

8.6.2 The ICV is prepared at 1,000 μg/l for each Aroclor and is analyzed immediately after the initial calibration.

8.7 Surrogates

8.7.1 Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) are used as surrogate standards for this method.

8.7.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

8.7.3 Surrogate compounds are also contained in continuing calibration checks, and second source calibration check standard.

8.7.4 Spike each sample, QC sample and blank with an appropriate amount of corresponding surrogate spiking solution, prior to extraction, for a final concentration in the extract of 40 µg/l of each surrogate compound.

8.8 Instrument Blank

8.8.1 An instrument blank is run after each Continuing Calibration Check. Spike hexane with an appropriate amount of surrogate spiking solution for a final concentration of 20 µg/l of each surrogate compound.

8.9 Storage of Standards

8.9.1 Store unopened stock standard solutions according to the manufacturer's documented holding time and storage temperature recommendations. Protect from light.

8.9.2 Store all other working standard solutions in glass vials with Teflon lined screw caps at ≤ 6°C in the dark.

8.9.3 Opened stock standard solutions must be replaced after 6 months or sooner if manufacturer's expiration date comes first or comparison with quality control check samples indicates a problem.

8.9.4 All other standards must be replaced after six months or sooner if routine QC indicates a problem or manufacturer's expiration date comes first.

9.0 INTERFERENCES

9.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

9.2 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Glassware must be scrupulously cleaned. Refer to "The Preparation of Glassware for Extraction of organic contaminants" SOP for practices utilized in the extraction department.

9.3 Interferences may be caused by contaminants that are co-extracted from the sample. The extent of the interferences will vary from source to source, which can be grouped into three broad categories.

9.3.1 Contaminated solvents, reagents, or sample processing hardware.

9.3.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

9.3.3 Compounds extracted from the sample matrix to which the detector will respond**.**

9.4 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determination.

9.4.1 Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. Avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination can best minimize interference from phthalate esters.

9.4.2 Exhaustive cleanup of solvents, reagent and glassware may be required to eliminate background phthalate ester contamination.

9.4.3 These materials can be removed through the use of Method 3665 (sulfuric acid/permanganate cleanup).

9.5 Elemental sulfur is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Method 3660 is suggested for removal of sulfur.

9.6 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of an instrument blank to check for cross contamination.

10.0 Procedure

10.1 INITIAL CALIBRATION

10.1.1 The method reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Lower concentration standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentration standard.

10.1.2 The initial calibration for this method consists of two parts, described below.

10.1.2.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detectors and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. The calibration range covered for Aroclor 1016 and Aroclor 1260 employs standards of 50, 250, 500, 1,000, 2,000, and 3,000 μg/l.

10.1.2.2 Standards of the other five Aroclors are necessary for pattern recognition. These standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture in Section 10.1.2.1 has been used to describe the detector response. The concentration of each Aroclor standard is near the mid-point of the linear range of the detector, usually at 1,000 μg/l. The standards for these five Aroclors must be analyzed before the analysis of any samples and may be analyzed before or after the analysis of those 1016/1260 standards.

10.1.2.3 In situations where only a few Aroclors are of interest for a specific project, an initial calibration of a minimum of five standards of each Aroclors of interest instead of the 1016/1260 mixture may be performed.

10.1.3 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of each surrogate compound to the calibration solution to define a range similar to the target compounds.

10.1.4 Aliquot proper amount of each calibration standard into a 2 ml crimp top vial.

10.1.5 PCBs are quantitatively determined as Aroclors by the external standard technique. The Calibration Factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards is calculated using the equation in Section 14.1.

10.1.5.1 Use at least five peaks for the Aroclor 1016/1260 mixture, none of which are found in both of these Aroclors. At least five sets of calibration factors will be generated, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture.

10.1.5.2 A minimum of 3 characteristic peaks must be chosen for each of the other Aroclors, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Thus, each single standard will generate at least three calibration factors, one for each selected peak.

10.1.5.3 Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 6 peaks must include at least one peak that is unique to that Aroclor.

10.1.5.4 The calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the calibration model chosen for this mixture must be applied to the other five Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors, use the calibration factors from those standards to evaluate linearity.

10.1.6 For the initial calibration to be valid, the percent relative standard deviation (% RSD) (see Section 14.2) must be less than 20 % for each Aroclor of interest on each column. If any analyte exceeds the 20% acceptance limit for a given calibration, corrective action must be taken.

10.1.6.1 If the problem is associated with specific standards, reanalyze the standard and recalculate the RSD.

10.1.6.2 Alternately, the laboratory may remove individual analyte calibration levels from the lowest and/or highest levels of the curve. Multiple levels may be removed, but removal of interior levels is not permitted.

10.1.6.2.1 The laboratory may remove an entire single standard calibration level from the interior of the calibration curve when the instrument response demonstrates that the standard was not properly introduced to the instrument, or an incorrect standard was analyzed. If a calibration standard was removed from the interior of the calibration, this particular standard calibration level must be removed for all analytes.

Removal of calibration points from the interior of the curve is not to be used to compensate for lack of maintenance or repair to the instrument.

10.1.6.2.2 The laboratory must adjust the LOQ/reporting limit and quantitation range of the calibration based on the concentration of the remaining high and low calibration standards.

10.1.6.2.3 The laboratory must ensure that the remaining initial calibration standards are sufficient to meet the minimum requirements for number of initial calibration points as mandated by the method, or regulatory requirements.

10.1.6.2.4 The laboratory may replace a calibration standard provided

10.1.6.2.4.1 the laboratory analyzes the replacement standard within twenty-four (24) hours of the original calibration standard analysis for that particular calibration level;

10.1.6.2.4.2 the laboratory replaces all analytes of the replacement calibration standard if a standard within the interior of the calibration is replaced; and

10.1.6.2.4.3 the laboratory limits the replacement of calibration standards to one calibration standard concentration.

10.1.6.2.5 The laboratory must document a technically valid reason for either removal or replacement of any interior calibration point.

10.2 INITIAL CALIBRATION VERIFICATION (ICV) - SECOND SOURCE CALIBRATION CHECK STANDARD

10.2.1 The initial calibration is verified with an ICV, a second source calibration check standard from an external source (Section 9.6). It must be performed right after the initial calibration.

10.2.2 The percent difference (%D) (Section 14.3) for this standard must meet the %D criteria of 20% used for calibration verification on each column.

10.2.2.1 If %D is greater than 20%, reanalyze the second source check. If the limit cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.2.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that match each other.

10.3 CONTINUING CALIBRATION VERIFICATION (CCV)

10.3.1 Continuing calibration verification (CCV) standards (Section 9.5.2) must be acquired at the beginning of each 12-hour shift, after every 10 injections not to exceed 12 hours and at the end of the analysis sequence. The 500 μg/l check standard is alternated with 1,000 μg/l standard for calibration verification.

10.3.2 For Aroclor analyses, the calibration verification standard must be a mixture of Aroclor 1016 and Aroclor 1260. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclors after the 1016/1260 mixture used for calibration verification throughout the analytical sequence.

10.3.3 The percent difference (%D) (see section 14.3) must be less than 20**%** for each Aroclor of interest on each column.

10.3.4 Each sample analysis must be bracketed by periodic analyses of acceptable calibration verification standards every 10 injections not to exceed 12 hours. If %D criteria fails during a mid-sequence calibration check or at the end of the analysis sequence, a continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. In situations where the first check fails to meet the criteria, the instrument logbook must have clearly documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.5 A continuing calibration standard is analyzed whenever the analyst suspects that the analytical system is out of calibration. If the calibration cannot be verified, corrective action is performed to bring the system into control. Analysis may not continue until the system is under control.

10.3.6 When a calibration verification standard fails to meet the QC criteria at the end of the analysis sequence, all samples injected after the last standard that met the QC criteria must be evaluated to prevent mis-quantitation, and re-injection of the sample extracts may be required.

10.3.6.1 If the analyte was not detected in the specific samples analyzed during the analytical shift or sequence, the extracts for those samples do not need to be reanalyzed when the calibration standard response is above the initial calibration response.

10.3.6.2 If the analyte was detected in the specific samples analyzed during the analytical shift or sequence, or the calibration standard response is below the initial calibration response, then the extracts for those samples need to be reanalyzed.

10.3.7 Each subsequent injection of a continuing calibration standard during the 12-hour analytical shift must be checked against the retention time windows established in Section 11.0. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

10.4 RETENTION TIME WINDOWS

10.4.1 Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows must be calculated for each surrogate and at least 3 to 5 characteristic peaks of each Aroclor on each GC column, when a new initial calibration is run and whenever a new chromatographic column is installed, or when there are significant

changes in the operating conditions. The retention time windows must be reported with the analysis results in support of the identifications made.

10.4.2 Employ the following approach to establish retention time windows:

10.4.2.1 Make three injections of each Aroclor at approximately equal intervals during the 72-hr period.

10.4.2.2 For each Aroclor, choose three or five major peaks and calculate the mean and standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in the samples. Record the retention time to three decimal places (e.g. 10.015 min) for each Aroclor.

10.4.2.3 In those cases where the standard deviations of the retention time window for a particular Aroclor is 0.01 minutes or less, the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

10.4.2.4 Apply plus or minus three times the standard deviations to retention time of each Aroclor standard (continuing calibration or middle level of initial calibration). This will be used to define the retention time window for the sample.

10.4.2.4.1 If default standard deviation of 0.01 minutes is employed, the width of the window will be 0.03 minutes.

10.4.2.5 Establish the center of the retention time window for each Aroclor and surrogate by using the absolute retention time for each Aroclor and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

10.4.2.6 When retention time windows are to be determined, analyze a standard containing DDT analogs to ensure that they do not elute at the same retention time as the last major Aroclor 1254 peak. The analyst must either adjust the GC conditions for better resolution or choose another peak that is characteristic of the Aroclor and which does not elute at the same time as of the DDT analogs.

10.5 SAMPLE EXTRACTION

10.5.1 In general, water samples are extracted at a neutral pH with methylene chloride using a separate funnel (Method 3510) (Refer to SOP: EOP001 and EOP004). Solid samples are extracted using Method 3546, Microwave Extraction (Refer to SOP: EOP3546).

10.6 SAMPLE CLEANUP

10.6.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. Refer to appropriate SOPs for details.

10.6.1.1 Interferences by phthalate esters can be removed through the use of a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for PCBs. This method must be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs.

10.6.1.2 Element sulfur, which may be present in certain sediments and industrial wastes, interfere with the electron capture gas chromatography of certain Aroclors. Sulfur must be removed by the technique described in Method 3660.

10.7 INSTRUMENT CONDITIONS.

10.7.1 Recommended instrument conditions are listed in Table 2. Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification must be approved by team leader/manager.

10.8 Initial calibration

10.8.1 Refer to Section 10.1.

10.9 Initial calibration Verification (ICV) -Second source calibration check standard

10.9.1 Refer to Section 10.2.

10.10 Continuing calibration Verifications (CCV)

10.10.1 Refer to Section 10.3.

10.11 Sample analysis (Primary)

10.11.1 All samples and quality control samples are injected into the Gas Chromatograph using the autosampler. Program the sampler for an appropriate number of syringe rinses and a 1ul or 2 μl injection size. A split or splitless injection technology is used.

10.11.2 Sample concentrations are calculated by comparing sample responses with the initial calibration of the system (Section 14.4). If sample response exceeds the limits of the initial calibration range, dilute the extract and reanalyze. Extracts must be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale.

10.11.3 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the sample meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

10.11.4 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst must consult with the source of the sample to determine whether further concentration of the sample is warranted.

10.11.5 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract or replacement

of the capillary column or detector is warranted. Rerun the sample on another instrument to determine if the problem results from analytical hardware or the sample matrix.

10.12 Confirmation analysis.

10.12.1 Confirmation analysis is to confirm the presence of Aroclors tentatively identified in the primary analysis.

10.12.1.1 All instrument performance quality control criteria for calibration and retention time must be satisfied on the confirmation analysis.

10.12.2 Each tentative identification must be confirmed: using a second GC column of dissimilar stationary phase (as in the dual-column analysis), based on a clearly identifiable Aroclor pattern, or using another technique such as GC/MS.

10.12.2.1 The primary and secondary analysis is conducted simultaneously in the dual-column analysis.

10.12.2.2 GC/MS confirmation may be used in conjunction with dual-column analysis if the concentration is sufficient for detection in GC/MS, normally a concentration of approximately 10 ng/μl in the final extract for each Aroclor is required. Method 8270 is recommended as a confirmation technique when sensitivity permits.

10.12.3 Once the identification has been confirmed, the agreement between the quantitative results on both columns must be checked.

10.13 Sample Dilution

10.13.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

- Utilize screen data (specific project only).
- Utilize acquired sample data.
- Utilize the history program or approval from client/project.
- Sample characteristics (appearance, odor).

10.13.2 If no lower dilution has been reported, the dilution factor chosen must keep the response of the largest peak for a target analyte in the upper half of the initial calibration range of the instrument.

10.13.3 Preparing Dilutions.

10.13.3.1 Prepare sample dilutions quantitatively. Dilute the stored sample extract if available with hexane using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc.

10.13.3.2 Syringe Dilutions - A calibrated 1ml syringe must be used to prepare dilutions. Gently shake to disperse the extract throughout the solvent prior to loading on the auto-sampler tray for further analysis.

10.13.3.3 Volumetric Flask Dilutions – Dilutions can also be made with a Class A volumetric flask. Measure appropriate sample extract volume in a calibrated syringe and bring to a final volume with dilution solvent in a Class A volumetric flask. Gently shake to disperse the extract throughout the solvent prior to loading on the auto-sampler tray for further analysis.

10.14 Data interpretation

10.14.1 Qualitative identification

10.14.1.1 Analyst shall identify the target analytes with competent knowledge interpreting retention time and/or chromatographic pattern by comparison of the sample to the standard of the suspected Aroclor. The criteria required for a positive identification are:

10.14.1.1.1 The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

10.14.1.1.2 The target analytes must elute within the daily absolute retention time window on both primary and confirmation column.

10.14.1.1.3 For PCBs, at least five major peaks are selected. The retention time window for each peak is determined from the initial calibration analysis. This identification of PCBs as Aroclors is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of multi-component target analytes. Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte.

10.14.1.1.4 Be aware of matrix interfering effects on peak shape and relative peak ratios which could distort the pattern. Interpretation of this phenomenon may require a highly experienced chromatographer or at least a second opinion.

10.14.2 Quantitative analysis

10.14.2.1 Once the Aroclor pattern has been identified, compare the responses of at least 3 major peaks in the single-point calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each corresponding peak and the linear calibration established from the multi-point calibration of the 1016/1260 mixture. A concentration (see section 14.4) based on the integrated area/or height of each of the characteristic peaks is determined and then those resulting concentrations are averaged to provide the final result for the sample.

10.14.2.2 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific

Aroclor is no longer recognizable. The quantitation may then be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs on the basis of retention times must be subtracted from the total area. When quantitation is performed in this manner, the problems must be fully described for the data user and the specific procedures employed by the analyst must be thoroughly documented.

10.14.2.3 When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results must be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula in Section 14.6. The lower result is reported.

10.14.2.3.1 If 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.

10.14.2.3.2 If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the lower result with the footnote (remark) indicating “More than 40% RPD for detected concentrations between two GC columns”.

11.0 QUALITY CONTROL

11.1 QC Requirements Summary

Initial Calibration	Whenever needed
Initial Calibration Verification (ICV)	Following initial calibration
Continuing Calibration Verifications (CCV)	Every 12-hour shift, after every 10 samples and at the end of analysis sequence
Instrument Blank	After each CCV
Method blank	One per extraction batch*
Blank Spike	one per extraction batch*
Matrix Spike	one per extraction batch*
Matrix Spike Duplicate	one per extraction batch*
Surrogates	every sample and standard

*The maximum number of samples per batch is twenty or per project specification.

11.2 Initial Calibration.

11.2.1 Refer to Section 10.1.

11.3 Initial Calibration Verification (ICV) -Second Source Calibration Check.

11.3.1 Refer to Section 10.2.

11.4 Continuing Calibration Verifications (CCV)

11.4.1 Refer to Section 10.3.

11.5 Instrument Blank

11.5.1 If the instrument blank contains a target analyte above its MDL, the source of the contamination must be identified and corrected before proceeding with the analysis.

11.6 Method Blank.

11.6.1 The method blank is either DI water or ottawa sand (depending upon the sample matrix) which must be extracted with each set of 20 or less samples. For a running batch, a new method blank is required for each different extraction day. The method blank must be carried through all stages of the sample preparation and measurement.

11.6.2 If the method blank contains a target analyte above its MDL established by the laboratory, the entire batch must be re-extracted and reanalyzed.

11.6.3 Surrogate compounds are added to the method blank prior to extraction and analysis. If the surrogate accuracy in the blank does not meet criteria established by the laboratory, the entire batch must be re-extracted and reanalyzed.

11.7 Blank Spike (Laboratory Control Sample)

11.7.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. It is spiked with the same analyte at the same concentration as matrix spike. When the presence of specific Aroclors is not anticipated, the Aroclor 1016/1260 mixture may be appropriate choice for spiking. In situations where the other Aroclors are of interest for a specific project, the analyst may employ different spiking mixtures. The blank spike is prepared at a concentration of 2 μg/l or 133.3 μg/kg (on a dry weight basis) for each Aroclor.

11.7.2 The blank spike recoveries must be assessed using in house limits established by the laboratory.

11.7.3 If a blank spike is out of control, the following corrective actions must be taken. In the case where the blank spike recovery is high, and no hits reported in associated samples and QC batch the sample results can be reported with footnote (remark) and no further action is required.

11.7.3.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

11.7.3.2 Check the instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the batch.

11.7.3.3 If no problem is found, re-extract and reanalyze the batch.

11.8 Matrix Spike (MS) / Matrix Spike Duplicate (MSD).

11.8.1 One sample is randomly selected from each extraction batch and spiked in duplicate with select Aroclors to assess the performance of the method as applied to a particular matrix and to provide information on the homogeneity of the matrix. Both the MS and MSD are carried through the complete sample preparation, cleanup, and determinative procedures.

11.8.2 The MS and MSD must be spiked with the Aroclors of interest. If samples are not expected to contain target analytes, a matrix spike and matrix spike duplicate pair must be spiked with Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclor must be used for spiking.

11.8.3 Matrix spikes are prepared by spiking an actual sample at a concentration 2 μg/l or 133.3μg/kg on a dry weight basis.

11.8.4 Assess the matrix spike recoveries and relative percent difference (RPD) against the control limits established by the laboratory.

11.8.5 If the matrix spike accuracy of any individual Aroclor is out of control, the accuracy for that Aroclor in the blank spike must be within control. Matrix interference is assumed, and the data is reportable. No further corrective action is required.

11.9 Surrogates.

11.9.1 Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB) are used as surrogate standards. All blanks, samples, matrix spikes, and calibration standards contain surrogate compounds which are used to monitor performance of the extraction, cleanup (when used), and analytical system.

11.9.2 The recoveries (Section 14.5) of the surrogates must be evaluated versus the surrogate control limits developed by the laboratory annually.

11.9.3 If surrogate recoveries are not within established control limits, corrective action must be performed if surrogate recoveries indicate that a procedural error may have occurred during the analysis of the sample.

11.9.3.1 Check the surrogate calculations for calculation or integration errors and perform corrections if detected.

11.9.3.2 Reanalyze the extract if no calculation errors are detected. If the surrogate recoveries for the reanalyzed extract are in control, report the data from the reanalysis only.

11.9.3.3 If the data from the reanalysis is also out of control, re-extract and reanalyze the samples

11.9.3.4 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and the reanalysis results and note the holding time problem.

11.9.3.5 If recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

11.9.4 The retention time shift for surrogate must be evaluated after the analysis of each sample. The sample must be reanalyzed when the retention times for both surrogates are outside the retention time window.

11.9.4.1 Reanalyses are not required for samples having visible matrix interference, defined as excessive signal levels from target or non-target interfering peaks. This judgment must be approved by a team leader or a supervisor.

11.10 Refer to Project Specific Bench Notes (GC8082) for additional program or client specific QC requirements.

11.11 Calculations

11.11.1 Calibration Factor (CF).

$$CF = \frac{A_s}{C_s}$$

where:
A_s = Area of the peak for the compound being measured.
C_s = Concentration of the compound being measured (µg/l).

11.11.2 Percent Relative Standard Deviation (% RSD).

$$\%RSD = \frac{SD}{CF_{av}} \times 100$$

where:
SD = Standard Deviation.
CF_{av} = Average calibration factor from initial calibration.

11.11.3 Percent Difference (% D).

$$\% D = \frac{|CF_{av} - CF_c|}{CF_{av}} X\ 100$$

where:
CF_c = CF from continuing calibration (CBCHK).

11.11.4 Concentration (Conc.).

For water:

$$\text{Conc. } (\mu g/l) = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{}$$

$$\frac{}{V_i}$$

For soil/sediment (on a dry weight basis, see SOP EGN007):

$$\text{Conc. } (\mu g/kg) = \frac{A_c \times M}{CF_{av}}$$

$$M = \frac{V_f \times D}{W_s \times S}$$

where:
A_c = Area of peak for compound being measured.
V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).
W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100 or % solid/100.
M = Multiplier.

11.11.5 Percent Recovery (% R).

$$\%\ R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

11.11.6 Relative Percent Difference (RPD).

$$RPD = \frac{|C_1 - C_2|}{(1/2)(C_1 + C_2)} \times 100$$

where:
C_1 = Matrix Spike Concentration or the result on column 1.
C_2 = Matrix Spike Duplicate Concentration or the result on column 2.

12.0 DOCUMENTATION

12.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

12.1.2 If samples require reanalysis, a brief explanation of the reason must be documented in this log. For consistency, if surrogates are high or low indicate it as (↑) for high and (↓) for low.

12.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed, the page must be signed and dated by the respective person.

12.2.2 The SGS Lot Number must be cross-reference on the standard vial.

12.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

12.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

12.5 Unused blocks of any form must be X'ed and Z'ed by the analyst before submitting the data for review.

12.6 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information must also be verified during this review.

13.0 DATA REVIEW AND REPORTING

13.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

13.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

13.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

13.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

13.3 Chromatogram Review. The chromatogram of each sample is evaluated for target analytes.

13.3.1 Check specific retention time windows for each target compound for the presence of the target compound in each chromatogram.

13.3.1.1 Each sample may require the reporting of different target analytes. Review the login to assure that the correct target compounds are identified.

13.3.2 The Aroclor must be identified on the primary and confirmatory column before assigning a qualitative identification.

13.3.3 Manual integration of chromatographic peaks must be identified by the analysts. An electronic signature is applied upon data review.

13.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

14.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices

designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 17.2.

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non-hazardous aqueous wastes.

14.2.2 Hazardous aqueous wastes

14.2.3 Chlorinated organic solvents

14.2.4 Non-chlorinated organic solvents

14.2.5 Hazardous solid wastes

14.2.6 Non-hazardous solid wastes

Table 1. PCB Aroclors and Reporting Limits				
Compound	**CAS Number**	**Water (µg/l)**	**Soil (µg/kg)**	**Oil (µg/kg)**
Arochlor – 1016	12674-11-2	0.5	33.5	500
Arochlor – 1221	11104-28-2	0.5	33.5	500
Arochlor – 1232	11141-16-5	0.5	33.5	500
Arochlor – 1242	53469-21-9	0.5	33.5	500
Arochlor – 1248	12672-29-6	0.5	33.5	500
Arochlor – 1254	11097-69-1	0.5	33.5	500
Arochlor – 1260	11096-82-5	0.5	33.5	500
Arochlor – 1262	37324-23-5	0.5	33.5	500
Arochlor – 1268	11100-14-4	0.5	33.5	500

Table 2. RECOMMENDED OPERATING CONDITION	
Gas Chromatograph/Electron Capture Detectors	
Carrier Gas	Helium
Make-up gas	5 % Methane/ 95 % Argon
Make-up gas flow	*30 ml/min
Injection port temperature	*235 °C
Injection type	Split / Splitless
Detector temperature	*320 °C
Column flow	*5 ml/min
Gas Chromatograph Temperature Program*	
Initial temperature	*170 °C
Time 1	*2 min
Column temperature rate 1	*30 degrees/min
Temperature 1	*180 °C
Column temperature rate 2	*3.5 degrees/min
Temperature 2	*240 °C
Column temperature rate 3	*10 degrees/min
Final temperature	*280 °C
Time 3	*5 min
Total run time	30-40 min

* Parameter modification allowed for performance optimization as long as QC criteria are achieved.

Table 3A. Aroclors 1016/1260 Mixture and Surrogates Working Solution	
Stock Solution	**Volume Added**
Aroclor 1016/1260 (1,000 µg/ml)	500 µl
Pesticides Surrogate Std Spiking Solution (200 µg/ml)	100 µl
Hexane	fill to volume
Total	25.0 ml

- Aroclors 1016/1260 (20 µg/ml) and Surrogates (0.8 µg/ml) Working Solution: Prepared by measuring 500 µl of 1,000 µg/ml Aroclor 101/1260 and 100µ of 200 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 3B. Individual Aroclor* and Surrogates Working Solution	
Stock Solution	**Volume Added**
Individual Aroclor* (1,000 µg/ml)	500 µl
Pesticides Surrogate Std Spiking Solution (200 µg/ml)	100 µl
Hexane	24.4 ml
Total	25 ml

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262 & 1268

- Individual Aroclor (20 µg/ml) and Surrogates (0.8 µg/ml) Working Solution: Prepared by measuring 500 µl of 1,000 µg/ml each individual Aroclor, 100 µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4A. Aroclors 1016/1260 Calibration Standard Solutions					
Standard	**Working Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration (µg/l)**
Standard A	Aroclors 1016/1260	20	62.5	25	50
	Surrogates	0.8			2
Standard B	Aroclors 1016/1260	20	312.5	25	250
	Surrogates	0.8			10
Standard C	Aroclors 1016/1260	20	625	25	500
	Surrogates	0.8			20
Standard D	Aroclors 1016/1260	20	1250	25	1,000
	Surrogates	0.8			40
Standard E	Aroclors 1016/1260	20	2,500	25	2,000
	Surrogates	0.8			80
Standard F	Aroclors 1016/1260	20	3,750	25	3,000
	Surrogates	0.8			120

- Standard A: Prepared by measuring 62.5 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A) and bringing to 25 ml with hexane.

- Standard B: Prepared by measuring 312.5 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A) and bringing to 25 ml with hexane.

- Standard C: Prepared by measuring 625 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A) and bringing to 25 ml with hexane.

- Standard D: Prepared by measuring 1,250 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A) and bringing to 25 ml with hexane.

- Standard E: Prepared by measuring 2,500 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A) and bringing to 25 ml with hexane.

- Standard F: Prepared by measuring 3,750 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A) and bringing to 25 ml with hexane.

Table 4B. Single-Point Calibration Standard (1,000 µg/l) for Individual Aroclor*	
Stock Solution	**Volume Added**
Individual Aroclor*/Surrogate Working Solution (20 µg/ml/0.80µg/ml) (Table 3B)	1,250 µl
Hexane	23.75 ml
Total	25 ml

* Aroclor: 1221, 1232, 1242, 1248, 1254, 1262, & 1268.

- Individual Aroclor Calibration Standard (1,000 µg/l) and Surrogates (40 µg/l) Solution: Prepared by measuring 1,250 µl of individual Aroclor and surrogates working solution, containing 20 µg/ml of each corresponding Aroclor and 0.80 µg/ml of both surrogate compounds, and bringing to 25 ml with hexane.

Table 4C. Multi-point Calibration Standards for Individual Aroclor* (optional)					
Standard	**Stock Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration(µg/l)**
Standard A	Aroclor*	20	62.5	25	50
	Surrogates	0.8			2
Standard B	Aroclor*	20	312.5	25	250
	Surrogates	0.8			10
Standard C	Aroclor*	20	625	25	500
	Surrogates	0.8			20
Standard D	Aroclor*	20	1250	25	1,000
	Surrogates	0.8			40
Standard E	Aroclor*	20	2,500	25	2,000
	Surrogates	0.8			80
Standard F	Aroclor*	20	3,750	25	3,000
	Surrogates	0.8			120

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262, & 1268.

- Standard A: Prepared by measuring 62.5 µl of Individual Aroclor and Surrogates Working Solution (Table 3B) and bringing to 25 ml with hexane.

- Standard B: Prepared by measuring 312.5 µl of Individual Aroclor and Surrogates Working Solution (Table 3B) and bringing to 25 ml with hexane.

- Standard C: Prepared by measuring 625 µl of Individual Aroclor and Surrogates Working Solution (Table 3B) and bringing to 25 ml with hexane.

- Standard D: Prepared by measuring 1,250 µl of Individual Aroclor and Surrogates Working Solution (Table 3B) and bringing to 25 ml with hexane.

- Standard E: Prepared by measuring 2,500 µl of Individual Aroclor and Surrogates Working Solution (Table 3B) and bringing to 25 ml with hexane.

- Standard F: Prepared by measuring 3,750 µl of Individual Aroclor and Surrogates Working Solution (Table 3B) and bringing to 25 ml with hexane.

Table 5A. Continuing Calibration Check Solutions for Aroclors 1016/1260					
Checks	**Working Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration (µg/l)**
Solution 1	Aroclors 1016/1260	20	625	25	500
	Surrogates	0.8			20
Solution 2	Aroclors 1016/1260	20	1250	25	1,000
	Surrogates	0.8			40

- Solution 1: Prepared by measuring 625 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A) and bringing to 25 ml with hexane.

- Solution 2: Prepared by measuring 1,250 µl of Aroclors 1016/1260 Mixture and Surrogates Working Solution (Table 3A) and bringing to 25 ml with hexane.

Table 5B. Continuing Calibration Check Solutions for Individual Aroclor*					
Checks	**Working Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration (µg/l)**
Solution 1	Aroclor*	20	625	25	500
	Surrogates	0.8			20
Solution 2	Aroclor*	20	1250	25	1,000
	Surrogates	0.8			40

* Aroclor: 1221, 1232, 1242, 1248, 12541262, & 1268

- Solution 1: Prepared by measuring 625 µl of Individual Aroclor and Surrogates Working Solution (Table 3B) and bringing to 25 ml with hexane.

- Solution 2: Prepared by measuring 1,250 µl of Individual Aroclor and Surrogates Working Solution (Table 3B) and bringing to 25 ml with hexane.

Table 6A. Second Source Calibration Check Standard for Aroclors 1016/1260 (1,000 µg/l)	
Stock Solution	**Volume Added**
Aroclors 1016/1260 (25 µg/ml) and Surrogates (2.5 µg/ml) Working Solution	1,000 µl
Hexane	24 ml
Total	25 ml

- Aroclors 1016/1260 (25 µg/ml) and Surrogates (2.5 µg/ml) Working Solution: Prepared by measuring 250 µl of 1,000 µg/ml Aroclors 1016/1260 mix solution (2nd source), 125 µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 10 ml with hexane.

- Aroclors 1016/1260 (1,000 µg/l) and Surrogates (100 µg/l) Solution: Prepared by measuring 1,000 µl of Aroclors 1016/1260 (25 µg/ml) and surrogates (2.5 µg/ml) working solution and bringing to 25 ml with hexane.

Table 6B. Second Source Calibration Check Standard for Individual Aroclor* (1,000 µg/l)	
Stock Solution	**Volume Added**
Individual Aroclor* (100µg/ml)	250uL
Surrogates (200 µg/ml)	5uL
Hexane	Add to bring to 25mL volume
Total	25 ml

*Aroclor: 1221, 1232, 1242, 1248, 1254, 1262 & 1268

- ICV preparation: Using Individual Aroclor (100 µg/ml) and Surrogates (200 µg/ml) Stock Solutions : Measure 250 µl of 1,00 µg/ml each individual Aroclor stock solution 2nd source and 5µl of 200 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Current Version Revision Information

Changes / Edits made (this should include added or deleted information within a sentence or paragraph only):

Section / Subsection	Detailed description of what was revised
reference	Changed revision 2 to rev. 1, which is the correct revision

Sections or Subsections deleted:

Section / Subsection	Reason section or subsection was removed

Sections or Subsections added:

Section / Subsection	Reason section or subsection was added

History of Revisions

Version #	Date of Revision	Revised By
09	10/04/2018	Wahied Bayoumi
10	10/27/2020	Wahied Bayoumi
11	11/06/2020	Olga Azarian
12	03/12/2021	Olga Azarian

END OF DOCUMENT

LAB MANAGER: _____

QA MANAGER: _____

EFFECTIVE DATE: 11-19-21

TITLE: SULFURIC ACID/PERMANGANATE CLEANUP
REFERENCES: SW846 3665A (12/96)
REVISED SECTIONS: SGS FORMAT

1.0 SCOPE AND APPLICATION

1.1 This method is suitable for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls. This method should be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

1.2 This method can be utilized for aqueous, soil, and waste dilution samples.

2.0 SUMMARY

2.1 An extract is solvent exchanged to hexane, then the hexane is sequentially treated with (1) concentrated sulfuric acid and, if necessary, (2) 5% aqueous potassium permanganate. Appropriate caution must be taken with these corrosive reagents.

2.2 Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.

2.3 It is important that all the extracts be exchanged to hexane before initiating the following treatments.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 See determinative method.

4.0 DEFINITIONS

BLANK. An analytical sample designed to assess specific sources of laboratory contamination

EXTRACTION. The process of removing a desired compound from a matrix using chemical or mechanical procedures. The process is used to isolate and concentrate targeted constituents for instrumental analysis

MATRIX. The predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid)

MATRIX SPIKE. Aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery

MATRIX SPIKE DUPLICATE. A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method

METHOD BLANK. An analytical control consisting of all reagents, internal standards and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination

PERCENT MOISTURE. An approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105oC. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 oC, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted

REAGENT WATER. Water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the lab safety SOPs which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets is available to all personnel involved in these analyses.

6.0 COLLECTION, PRESERVATION, & HOLDING TIMES

6.1 Sample Collection

6.1.1 Water samples are collected in glass amber bottles. Certain aqueous methods require samples to be tested for residual chlorine using test paper for free and total chlorine. If the sample tests positive for residual chlorine, add 80 mg of sodium thiosulfate to each liter of sample and mix well.

6.1.2 Soil samples are collected in widemouth glass with Teflon-lined lid.

6.2 The samples must be protected from light and refrigerated at 0 to <6° C from the time of receipt until extraction and analysis.

6.3 Holding Times

6.3.1 Aqueous samples must be extracted within 7 days of sampling.

6.3.2 Soil, sediments and concentrated waste samples must be extracted within 14 days of sampling.

6.4 Prepare samples within 14 days of sampling and analyze the extract within 40 days of the extraction.

7.0 APPARATUS & MATERIALS

7.1 One (1) ml volumetric pipettes or pre-calibrated 1ml syringes.

7.2 Vials - 2, 4 and 10 mL, glass with Teflon lined screw caps or crimp tops.

7.3 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent).

7.4 Vortex mixer.

8.0 STANDARDS & REAGENTS

8.1 Solvents - reagent grade for trace organic analysis. Each solvent lot must be checked for interferences prior to use. Refer to SOP EOP013 for the procedure regarding solvent lot approval.

8.1.1 Hexane

8.2 Reagent water- deionized and carbon filtered water prepared to ASTM Type II specification.

8.3 Sulfuric acid/Water, H2SO4/H2O, (1:1, v/v).

8.4 Potassium permanganate, KMnO4, 5 percent aqueous solution (w/v). Add 5.0g of potassium permanganate to 100mL of water and mix well.

Caution – Potassium permanganate is a strong oxidizing agent. Handle with care. Do not allow potassium permanganate in its powder form to come in contact with glycol- spontaneous combustion may result.

8.5 Sodium Chloride-Hydroxylamine solution. Add 2.4g of sodium chloride and 2.4g of hydroxylamine hydrochloride to 20mL of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

9.0 INTERFERENCES

9.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. Blanks must be analyzed to demonstrate that these materials are free from interferences under the conditions of the analysis.

9.2 Interferences co-extracted from the samples will vary considerably from source to source. If interferences prevent the analysis of an extracted sample, further cleanup of the sample extract may be employed if necessary. Refer to SW-846 Method 3600 for cleanup procedures.

9.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Avoid plastics in particular because they contain phthalates, used as plasticizers, which can leach from these materials. Practice sound, consistent materials control to avoid phthalate contamination, which may occur at any time.

9.4 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, Aldrin, Heptachlor, and most organophosphorus pesticides will degrade in this situation. This occurs in glassware that is difficult to rinse (e.g., 500-mL K-D flask). Carefully hand-rinse these items to avoid this problem.

9.5 This technique will not destroy chlorinated benzenes, chlorinated naphthalenes (Halowaxes), and a number of chlorinated pesticides.

10.0 PROCEDURE

10.1 Sulfuric acid cleanup

10.1.1 Using a syringe or a volumetric pipet, transfer 2mL of the hexane extract to a 4mL vial. In a fume hood, carefully add 2mL of the 1:1 sulfuric acid/water solution.

10.1.2 The volume of hexane extract used depends on the requirements of the GC autosampler used by the laboratory. If the autosampler functions reliably with 1mL of sample volume, 1mL of extract should be used. If the autosampler requires more than 1mL of sample volume, 2mL of extract should be used.

CAUTION: Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.

10.1.3 Cap the vial tightly and shake or vortex for one minute.

CAUTION: Stop the shaking/vortexing immediately if the vial leaks. AVOID SKIN CONTACT, SULFURIC ACID BURNS.

10.1.4 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer; it should not be highly colored nor should it have a visible emulsion or cloudiness.

10.1.5 If the hexane layer is highly colored or the emulsion persists for several minutes, transfer the hexane layer to a new 4mL vial and repeat the sulfuric acid cleanup with another 2mL of clean 1:1 sulfuric acid/water.

Note: If the hexane layer remains highly colored or the emulsion persists after the second sulfuric acid cleanup, permanganate cleanup may be needed (10.3)- seek assistance from a team lead, supervisor, or manager.

10.1.6 If a clean phase separation is achieved and the extract is no longer highly colored, proceed to final preparation (10.3).

10.2 Permanganate cleanup

10.2.1 Transfer the hexane layer to a clean 10mL vial.

10.2.2 Add an additional 1mL of hexane to the sulfuric acid layer, cap and shake. This second extraction is done to ensure quantitative transfer of the PCBs and Toxaphene.

10.2.3 Remove the second hexane layer and combine with the hexane from Sec. 10.2.1.

CAUTION: Do not transfer any of the sulfuric acid layer- may react with potassium permanganate solution.

10.2.4 Add 5mL of the 5 percent aqueous potassium permanganate solution to the combined hexane fractions.

CAUTION: Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.

10.2.5 Cap the vial tightly and shake/vortex for 1 minute. A vortex must be visible in the vial.

CAUTION: Stop the shaking/vortexing immediately if the vial leaks. AVOID SKIN CONTACT, POTASSIUM PERMANGANATE BURNS.

10.2.6 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer, it should not be highly colored nor should it have a visible emulsion or cloudiness.

10.2.7 If the hexane layer is colored or the emulsion persists for several minutes, transfer the hexane layer to a new 10mL vial and repeat the permanganate cleanup with another 5mL of clean aqueous permanganate solution. Perform the permanaganate cleanup a maximum of two times.

10.2.8 If a clean phase separation is achieved and the extract is no longer highly colored, transfer the hexane layer to a clean concentrator tube.

10.2.9 Add an additional 1mL of hexane to the permanganate layer, cap the vial securely and shake. This second extraction is done to ensure quantitative transfer of the PCBs and Toxaphene.

10.2.10 Remove the second hexane layer, combine with the hexane from Sec. 10.2.7, and proceed with final preparation (10.3).

10.2.11 Disposal of potassium permanganate solution. Used permanganate must be neutralized prior to disposal.

10.2.11.1 Add Sodium Chloride-Hydroxylamine solution dropwise into used permanganate solution. Reaction will result in a vigorous bubbling action.

10.2.11.2 Continue dropwise addition until bubbling reaction ceases and solution turns clear. This indicates the permanganate solution has been neutralized.

10.2.11.3 Dispose of neutralized permanganate solution in appropriate waste stream.

10.3 Final preparation

10.3.1 If needed, reduce the volume of the hexane to the original starting volume (2mL) using the Nitrogen Blowdown Technique.

10.3.2 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

10.3.3 Rinse the internal wall of the tube with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

10.4 Cleanup. Remove any remaining organochlorine pesticides from the extracts using Florisil Column Cleanup (EOP3620C) or Silica Gel Cleanup (EOP3630).

10.5 Vialing. Refer to Microwave (EOP3546) or Sonication (EOP003) SOP for proper vialing instructions.

11.0 QUALITY CONTROL

11.1 A method blank and blank spike is required on each day of extraction or every 20 samples, whichever is more frequent.

11.2 A matrix spike/ matrix spike duplicate is required per 20 samples.

11.3 Perform solvent checks for each new solvent lot to verify the absence of interferences. See SOP EOP013.

11.4 Sulfur/Permanganate cleanup is treated as an inclusive step of the soil/sediment extraction procedure. Accordingly, all field and QC samples (blanks, spiked blanks/LCS, and matrix spikes) must be treated.

12.0 DOCUMENTATION

12.1 All sample preparation activities and related information must be documented in the respective extraction logbook. Complete all information required for the extraction summary logbook.

12.1.1 If sulfur and/or permanganate cleanup is performed, their use must be documented on the extraction log.

13.0 DATA REPORTING

13.1 Not Applicable

14.0 POLLUTION PREVENTATION & WASTE MANAGEMENT

14.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 14.2.

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non hazardous aqueous wastes.

14.2.2 Hazardous aqueous wastes

14.2.3 Chlorinated organic solvents

14.2.4 Non-chlorinated organic solvents

14.2.5 Hazardous solid wastes

14.2.6 Non-hazardous solid wastes

15.0 REFERENCES

15.1 Not Applicable

Current Version Revision Information

Changes / Edits made (this should include added or deleted information within a sentence or paragraph only):

Section / Subsection	Detailed description of what was revised
	SGS format

Sections or Subsections deleted:

Section / Subsection	Reason section or subsection was removed

Sections or Subsections added:

Section / Subsection	Reason section or subsection was added

History of Revisions

Version #	Date of Revision	Revised By
07	11/19/2021	Maria Ruschke

END OF DOCUMENT

STANDARD OPERATING PROCEDURE L-3D: DETERMINATION OF ORGANOCHLORINE PESTICIDES USING GC SYSTEM BY SW846 8081B1B

AND

FLORISIL COLUMN CLEANUP

LAB SUPERVISOR: _____

QA OFFICER: Olga Y. Gaidan

EFFECTIVE DATE: 4-16-2020

TITLE: DETERMINATION OF ORGANOCHLORINE PESTICIDES USING GC SYSTEM
REFERENCES: SW846 8081B (Revision 2, February 2007)
REVISED SECTIONS: 4.0 (MDL),10.1.6.2
DELETED SECTIONS: 3.2.1, 3.2.2, 10.1.6.2.1
ADDED SECTIONS: 10.1.6.3, 10.1.6.4, 10.1.6.5, 10.1.6.6, 10.1.6.7

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by SGS to acquire samples for analysis of organochlorine pesticides and screening of polychlorinated biphenyls (PCBs) by gas chromatography with Electron Capture Detectors (ECD).

1.2 The method is applicable to extracts from solid and liquid matrices. The compounds listed in Table 1 are determined by a dual-column analysis system.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (from 250 mL to 1 L for liquids, 15 g for solids) is extracted using the appropriate matrix-specific sample extraction technique. Liquid samples are extracted at neutral pH with methylene chloride using Method 3510 (separatory funnel). Solid samples are extracted using Method 3546 Microwave Extraction or Method 3550C, Sonication. A variety of cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes. Cleanups include Florisil (Method 3620), silica gel (Method 3630), gel permeation chromatography (Method 3640), and sulfur (Method 3660).

2.2 After cleanup, the extract is analyzed by injecting1-µL of sample **into a gas chromatograph.** The sample is split between two different narrow-bore fused silica capillary columns and run through two electron capture detectors (GC/ECD).

2.3 The peaks detected are qualitatively identified by comparison to retention times specific to the known target list of compounds on two different column types (primary and confirmation).

2.4 If sensitivity permits, the positive hit must be confirmed by GC/MS method 8270D.

2.5 Once identified the compound is quantitated by internal standard techniques with an average response factor generated from a calibration curve.

3.0 REPORTING LIMIT & METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. RL's may vary depending on matrix and sample volumes or weight and percent moisture. Refer to Table 1 for current reporting limits.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B, Revision 2. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. The different types of blanks are Method Blank, Instrument Blank, Storage Blank, and Sulfur Blank.

FIELD BLANK – an analytical sample prepared from organic-free water and carried through the sampling handling protocol serves as a check for contamination.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours and at the end of analytical sequence to verify the initial calibration of the system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the term's continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the electron capture detector to the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. A sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) – The minimum concentration of a substance that can be measured and reported with 99% confidence that the measured concentration is distinguishable from method blank results.

PERCENT DIFFERENCE (%D) - to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 °C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

REAGENT WATER - water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest.

RELATIVE PERCENT DIFFERENCE (RPD) - to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the instrument response of an analyte. Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RETENTION TIME (RT) - the time required (in minutes) for a standard compound to elute from a chromatographic column.

SURROGATES - for semivolatiles and pesticides/Aroclors, compounds added to every blank, sample, matrix spike, matrix spike duplicate, and standard; used to evaluate analytical efficiency by measuring recoveries. Surrogate are brominated, fluorinated, or isotopically labeled compounds not expected to be detected in environmental media.

INSTRUMENT BLANK - a system evaluation sample containing lab reagent grade water with internal standards and/or surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the SGS Health and Safety Plan and Personal Protection Policy, which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, and the BHCs. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator must be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other stages of sample processing. Refer to "The Preparation of Glassware for Extraction of Organic Contaminants" SOP for practices utilized in the extraction department.

6.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary from source to source. Interferences such as sulfur and phthalate are treated with copper and alumina by organics preparation respectively.

6.3.1 The presence of elemental sulfur will result in broad peaks that interfere with detection of early-eluting organochlorine pesticides. Method 3660 is suggested for removal of sulfur.

6.3.2 Avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination can best minimize interference from phthalate esters.

6.4 Waxes, lipids, and other high molecular weight materials can be removed by method-3640 (Gel Permeation Chromatography-GPC column cleanup).

6.5 To reduce carryover when high-concentration samples are sequentially analyzed, the syringe must be rinsed out between samples with solvent.

6.6 In the case where an unusually concentrated sample is encountered, it must be followed by the analysis of an instrument blank. An instrument blank is a sample containing hexane with surrogate standards added at 20 ppb. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

7.0 SAMPLE PRESERVATION AND HOLDING TIME

7.1 PRESERVATION

7.1.1 Water Samples

7.1.1.1 Collect samples in 300 mL glass amber bottles without preservatives.

7.1.1.2 A minimum of 250 mL of an unpreserved sample is required for extraction. Additional sample volume is necessary for any samples used for matrix spike and matrix spike duplicates. Therefore, 1 liter of at least one sample in every group of 20 field samples is required for analysis to accommodate all quality control requirements.

7.1.2 Soil Samples

7.1.2.1 Samples are collected in a 300-ml amber glass sample bottle. No preservative is required.

7.1.3 Sample must be taken with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing possible phthalate contamination.

7.1.4 The samples must be protected from light and refrigerated at $\leq 6\ ^{0}C$ from the time of receipt until extraction and analysis.

7.2 HOLDING TIME

7.2.1 Aqueous sample must be extracted within 7 days of sampling.

7.2.2 Soil sample must be extracted within 14 days of sampling.

7.2.3 Extracts must be analyzed within 40 days following extraction.

8.0 APPARATUS AND MATERIALS

8.1 GAS CHROMATOGRAPH SYSTEM

8.1.1 Gas Chromatograph – Agilent or Hewlett Packard Models 7890, 6890 and 5890. The analytical system is completed with a temperature programmable gas chromatograph and all required accessories including syringes, capillary chromatographic columns, and gases. The capillary column is directly coupled to the source. The injection port is designed for splitless injection with capillary columns.

8.1.2 Columns

8.1.2.1 Column pair 1

8.1.2.1.1 30 m x 0.32 mm ID, 0.5 μm film thickness fused silica, DB-1701 narrow-bore capillary column or equivalent.

8.1.2.1.2 30 m x 0.32 mm ID, 0.5 μm film thickness fused silica, DB-5 narrow-bore capillary column.

8.1.2.2 Column pair 2

8.1.2.2.1 30 m x 0.32 mm ID, 0.5 μm film thickness fused silica, RTX CLPI narrow-bore capillary column or equivalent.

8.1.2.2.2 30 m x 0.32 mm ID, 0.25 μm film thickness fused silica, RTX CLPII narrow-bore capillary column or equivalent.

8.1.3 Detectors

8.1.3.1 Electron Capture Detectors (HP).

8.1.3.2 Micro Electron Capture Detectors (HP).

8.2 AUTOSAMPLER

8.2.1 Agilent or Hewlett Packard Model 7673A, 7683, 7643A capable of holding 100 of 2-ml crimp vials.

8.3 DATA SYSTEM

8.3.1 MSD interfaced to the gas chromatograph which allows the continuous acquisition and storage on machine-readable media (disc) of all chromatographic data obtained throughout the duration of the analysis.

8.3.2 The ENVIROQUANT (PC) data system is capable of quantitation using multipoint calibration.

8.3.3 Legato Networker with lookup database on 4mm DAT tape for long term, off line magnetic storage of data.

8.4 SYRINGES

8.4.1 Manually held ul graduated syringes, various volumes (Hamilton or equiv.).

8.4.2 10 µl graduated, auto sampler (Hamilton or equiv.).

8.5 VOLUMETRIC FLASKS, Class A.

9.0 REAGENTS AND STANDARDS

9.1 Refer to SGS Sample Preparation SOPs EOP001 and EOP040A for reagents and standards used for sample extraction.

9.2 Solvents - Ultra pure, chromatography graded Hexane.

9.3 Stock Standard Solutions

9.3.1 Two separate sources of commercially prepared standards with traceability documentation are used.

9.3.1.1 Pesticides Mixtures containing one or more of the following compounds: alpha-BHC, beta-BHC, delta-BHC, gamma-BHC(Lindane), Heptachlor, Aldrin, Heptachlor Epoxide, Endosulfan I, Dieldrin, 4,4'-DDE, Endrin, Endosulfan II, 4,4'-DDD, Endosulfan sulfate, 4,4—DDT, Methoxychlor, Endrin ketone, Endrin Aldehyde, alpha-Chlordane & gamma-chlordane, Alachlor and Hexachlorobenzene.

9.3.1.2 Individual standards containing Toxaphene, Chlordane, 2'4 DDT and Mirex.

9.4 Working Solutions

9.4.1 Prepare working solutions, using stock solution, in hexane, as needed, that contain the compounds of interest, either singly or mixed together. Refer to Table 3 for details.

9.5 Calibration Standards

9.5.1 Initial Calibration Standards

9.5.1.1 Calibration standards are prepared at a minimum of five concentrations, including surrogates, from the above working solutions. Suggested levels and preparations are shown in Table 4A.

9.5.1.2 Separate calibration standards are required for each multi-component target analyte (i.e., Toxaphene and Chlordane). Unless otherwise necessary for a specific project, such as Ohio VAP or the Dept. of Defense (DoD), a single calibration standard near the mid-point of the expected calibration range of each multi-component analyte is employed. Refer to Table 4B and 4C for preparation scheme. Optional curves as shown on Table 4D and 4E may also be used for a multi-point calibration per project's specification.

9.5.2 Continuing Calibration Verification (CCV)

9.5.2.1 Continuing calibration checks containing all the single-component analytes are prepared at concentrations of 10 μg/l, 25 ug/l and 50 μg/l as described in Table 5. During analysis, these alternate concentrations are run to check the initial calibration.

9.5.2.2 In situations where only Toxaphene or Chlordane is of interest for a specific project and for Ohio VAP multi-level calibration checks of each multi-component analyte of interest may be prepared and analyzed throughout the analytical sequence.

9.6 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

9.6.1 Prepare the ICV standards from separate sources of stock standards from the calibration curve following the procedures in Tables 3 and 4.

9.6.2 The ICV must be analyzed immediately following the initial calibration.

9.7 Surrogates

9.7.1 Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) are used as surrogate standards for this method.

9.7.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.7.3 Surrogate compounds are also contained in continuing calibration checks, and second source calibration check standard.

9.7.4 Spike each sample, QC sample and blank with an appropriate amount of corresponding surrogate spiking solution, prior to extraction, for a final concentration in the extract of 40 μg/l of each surrogate compound.

9.8 Internal Standard Solution

9.8.1 1-Bromo-2-nitrobenzene (CAS #577-19-5) is the internal standard being used as recommended for dual column analysis by sw846. The standard is being made at 5 mg/L, and 10uL is being added to all standards and samples for a final concentration of 50ug/L.

9.9 Breakdown Evaluation Solution

9.9.1 The DDT and Endrin breakdown evaluation solution is prepared in hexane as outlined in Table 6.

9.10 Instrument Blank

9.10.1 An instrument blank is run after each Continuing Calibration Check. Spike hexane with an appropriate amount of surrogate spiking solution for a final concentration of 40 μg/l of each surrogate compound.

9.10 Storage of Standards

9.10.1 Store unopened stock standard solutions according to the manufacturer's documented holding time and storage temperature recommendations. Protect from light.

9.10.2 Store all other working standard solutions in glass vials with Teflon lined screw caps at $\leq$ 6°C in the dark.

9.10.3 Opened stock standard solutions must be replaced after 6 months or sooner if manufacturer's expiration date comes first or comparison with quality control check samples indicates a problem.

9.10.4 All other standards must be replaced after six months or sooner if routine QC indicates a problem or manufacturer's expiration date comes first.

10.0 CALIBRATION

10.1 Initial Calibration

10.1.1 The calibration range covered for all single-component analytes employs at least five of the following standards: 1, 2, 5, 10, 25, 50, 75 and 100* μg/l (*this point may be dropped if it exceeds the linear range of the instrument). The method reporting limit is established by the concentration of the lowest standard analyzed during the initial calibration. Lower concentration standard may be needed to meet the reporting limit requirements of state specific regulatory program. The linear range covered by this calibration is the highest concentration standard. Calibration is performed for both the primary and secondary columns.

10.1.2 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of each surrogate compound to the calibration solution to define a range similar to the target compounds.

10.1.3 Unless otherwise necessary for a specific project, the analysis of the multi-component analytes (such as: Toxaphene or Chlordane) employs a single-point calibration. This single calibration standard is included with the initial calibration of the single component analytes for pattern and retention time recognition. For Ohio VAP and Dept. of Defense (DoD) projects an initial 5-point calibration is required for these analytes if there are positive hits.

10.1.4 Aliquot proper amount of each calibration standard into a 2-ml crimp top vial.

10.1.5 Prior to analysis, add 10 µl of the applicable internal standard solution (Section 9.8.1) to each standard. This results in a concentration of 50 µg/ml. Each analyte is quantitatively determined by internal standard technique.

10.1.6 For the initial calibration to be valid, the percent relative standard deviation (% RSD) (see Section 14.2) must be less than 20 % for each analyte of interest on each column. If any analyte exceeds the 20% RSD acceptance limit for a given calibration other calibration options, such as linear regression or quadratic regression not through the origin may be used or corrective action must be taken.

10.1.6.1 If the problem is associated with a standard, reanalyze the standard and recalculate the RSD.

10.1.6.2 Alternatively, the laboratory may remove individual analyte calibration levels from the lowest and/or highest levels of the curve. Multiple levels may be removed, but removal of interior levels is not permitted.

10.1.6.3 The laboratory may remove an entire single standard calibration level from the interior of the calibration curve when the instrument response demonstrates that the standard was not properly introduced to the instrument, or an incorrect standard was analyzed. If a calibration standard was removed from the interior of the calibration, this particular standard calibration level must be removed for all analytes. Removal of calibration points from the interior of the curve is not to be used to compensate for lack of maintenance or repair to the instrument.

10.1.6.4 The laboratory must adjust the LOQ/reporting limit and quantitation range of the calibration based on the concentration of the remaining high and low calibration standards.

10.1.6.5 The laboratory must ensure that the remaining initial calibration standards are sufficient to meet the minimum requirements for number of initial calibration points as mandated by the method, or regulatory requirements.

10.1.6.6 The laboratory may replace a calibration provided that:

10.1.6.6.1 the laboratory analyzes the replacement standard within twenty-four (24) hours of the original calibration standard analysis for that particular calibration level;

10.1.6.6.2 the laboratory replaces all analytes of the replacement calibration standard if a standard within the interior of the calibration is replaced; and

10.1.6.6.3 the laboratory limits the replacement of calibration standards to one calibration standard concentration.

10.1.6.7 The laboratory must document a technically valid reason for either removal or replacement of any interior calibration point.

10.1.7 If the 20% criterion is not met for average response factor, employ a linear (5 point minimum) or quadratic (6 point minimum) model. Do not force the regression line through the origin and do not employ 0,0 as a sixth calibration standard. The correlation coefficient (r value) must be ≥0.99 for each compound to be acceptable. Additionally, the measurement of the Relative Error (%RE) must be calculated using the following equation:

$$\% \text{ Relative Error} = \frac{x'_i - x_i}{x_i} \times 100$$

x_i = true value for the calibration standard
x'_i = measured concentration of the calibration standard

This calculation shall be performed for two (2) calibration levels: the standard at or near the mid-point of the initial calibration and the standard at the lowest level. The Relative Error at both of these levels must be within 30%.

10.2 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

10.2.1 The initial calibration is verified with a second source calibration check standard from an external source (Section 9.6). At a minimum, it must be performed right after the initial calibration.

10.2.2 The percent difference (%D) (Section 14.3) for this standard must meet the %D criteria of 20% used for calibration verification on each column.

10.2.2.1 If %D is greater than 20%, reanalyze the ICV second source check or re-prepare using a fresh ampoule and reanalyze the ICV second source check standard.

10.2.2.2 If the %D criteria cannot be achieved after re-injection of the second source check standard. a new calibration curve must be prepared by making fresh calibration standards using one of the two standard sources that match each other.

10.3 Continuing Calibration Verification (CCV)

10.3.1 Continuing calibration check standards (Section 9.5.2) must be acquired at the beginning of each 12-hour shift prior to analyzing samples or after every 20 injections whichever comes first.

10.3.2 For the continuing calibration to be valid, the percent difference (%D) must be less than 20 % for each compound of interest on each column.

10.3.3 The use of an internal standard does not require all samples be bracketed with calibration verification standards. If the%D criteria fail, a continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. In situations where the first check fails to meet the criteria, the instrument logbook must have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.3.1 Retention times and area responses of internal standards must be checked in every analysis. Areas responses must be within -50% or +100% and the retention time shift cannot be > 30 seconds.

10.3.4 Ending CCVs are required for all analysis sequences. If an ending calibration verification standard fails to meet the QC criteria all samples injected after the last standard that met the QC criteria must be evaluated to prevent mis-quantitations and possible false negative results. Re-injection of the sample extracts may be required.

10.3.4.1 If the analyte was not detected in the specific samples analyzed during the analytical shift or sequence, the extracts for those samples do not need to be reanalyzed when the calibration standard response is above the initial calibration response, i.e. >20%.

Note: For DoD projects, check the bench notes for additional QC requirements.

10.3.4.2 If the analyte was detected in the specific samples analyzed during the analytical shift, or the calibration standard response is below the initial calibration response, then the extracts for those samples need to be reanalyzed.

10.3.4.3 If after rerun the ending CCV fails again, report the original run and use the second run for confirmation. Flag the compounds that were out in the first CCV in LIMS.

10.3.5 Each subsequent injection of a continuing calibration standard must be checked against the retention time windows established in Section 11.0. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is not in control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

11.0 RETENTION TIME WINDOWS

11.1 Retention time windows must be calculated for each analyte and surrogate on each GC column and whenever a new chromatographic column is installed, when a new initial calibration is analyzed or when there are significant changes in the operating conditions. The retention time windows must be reported with the analysis results in support of the identifications made.

11.2 Employ the following approach to establish retention time windows.

11.2.1 Make three injections of all single component standard mixture and multi-response products at approximately equal intervals during the 72-hr period.

11.2.2 Calculate the mean and standard deviation of the three absolute retention times-recording the retention time to three decimal places (e.g. 10.015 min) - for each single component pesticide.

11.2.3 For multi-response pesticides, choose five major peaks and calculate the mean and standard deviation of the three retention times for those peaks. The peak chosen must be fairly immune to losses due to degradation and weathering in the samples.

11.2.4 In those cases where the standard deviations of the retention time window for a particular pesticide is <0.01 minutes, the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

11.2.5 The width of the retention time window for each analyte and surrogate is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period. If the default standard deviation is employed, the width of the window will be 0.03 minutes.

11.2.6 Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

12.0 PROCEDURE

12.1 Sample Extraction

12.1.1 In general, water samples are extracted at a neutral pH with methylene chloride using a separate funnel (Method 3510) (Refer to SOP: EOP001 and EOP004-01). Solid samples are extracted using Method 3546 Microwave Extraction (Refer to SOP: EOP3546) or Method 3550C, Sonication (Refer to SOP: EOP003).

12.2 Sample Cleanup

12.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. Refer to the appropriate SOPs for details.

12.2.1.1 If a sample is of biological origin, or contains high molecular weight materials, the use of Method 3640 (GPC cleanup - pesticide option) is recommended. Frequently, one of the adsorption chromatographic cleanups (alumina, silica gel, or florisil) may also be required following the GPC cleanup.

12.2.1.2 Method 3610 (alumina) may be used to remove phthalate esters.

12.2.1.3 Method 3620 (florisil) may be used to separate organochlorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds.

12.2.1.4 Method 3630 (silica gel) may be used to separate single component organochlorine pesticides from some interferants.

12.2.1.5 Elemental sulfur, which may be present in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur must be removed by the technique described in Method 3660.

12.3 Instrument Conditions

12.3.1 Recommended instrument conditions are listed in Table 2. Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification must be approved by team leader/manager.

12.4 DDT and Endrin Breakdown Evaluation

12.4.1 DDT and Endrin are easily degraded in the injection port. Breakdown occurs when the injection port liner is contaminated high boiling residue from sample injection or when the injector contains metal fittings. Check for degradation problems by injecting a standard containing only 4,4'-DDT and Endrin. Presence of 4,4'-DDE, 4,4'-DDD, Endrin ketone or Endrin aldehyde indicates breakdown.

12.4.2 Before the initial calibration and at the beginning of each 12-hour shift, inject 1 μl of an evaluation standard directly on column. (Refer to Section 9.8).

12.4.3 The percent breakdown for Endrin and DDT (Section 14.7) is calculated and the breakdown report is saved in the LIMS system.

12.4.4 If degradation of either DDT or Endrin exceeds 15**%**, injector maintenance must be completed before proceeding with calibration. Refer to EQA036-01 for GC system maintenance utilized in the lab.

12.5 Initial Calibration

12.5.1 See Section 10.1.

12.6 Initial Calibration Verification (ICV)

12.6.1 Refer to Section 10.2.

12.7 Continuing Calibration Verification (CCV)

12.7.1 Refer to Section 10.3.

12.8 Sample Analysis (Primary)

12.8.1 All samples and quality control samples are injected into the Gas Chromatograph using the autosampler. Program the sampler for an appropriate number of syringe rinses and a 1ul or 2 μl injection size. A splitless injection technology is used.

12.8.2 Sample concentrations are calculated by comparing sample responses with the initial calibration of the system (Section 14.4). If sample response exceeds the limits of the

initial calibration range, dilute the extract and reanalyze. Extracts must be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale.

12.8.3 Sample injections may continue for as long as the calibration verification standards meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

12.8.4 If chromatographic peaks are masked by the presence of interferences, further sample cleanup is necessary. Refer to Section 12.2 for extract cleanup alternatives.

12.8.4.1 If extract cleanup is required, all QC samples must also be processed through the cleanup method.

12.9 Confirmation Analysis

12.9.1 Confirmation analysis is to confirm the presence of all compounds tentatively identified in the primary analysis.

12.9.1.1 All instrument performance quality control criteria for calibration and retention times must be satisfied on the confirmation analysis.

12.9.2 Each tentative identification must be confirmed using either a second GC column of dissimilar stationary phase or using another technique such as GC/MS.

12.9.2.1 The primary and secondary analysis is conducted simultaneously in the dual-column analysis.

12.9.2.2 GC/MS confirmation may be used in conjunction with dual-column analysis if the concentration is sufficient for detection in GC/MS**,** normally a concentration of approximately 10 ng/μl in the final extract for each single component compound is required. Method 8270 is recommended as a confirmation technique when sensitivity permits.

12.9.3 Once the identification has been confirmed, the agreement between the quantitative results on both columns must be checked.

12.10 Sample Dilution

12.10.1 Establish dilution of sample in order to fall within calibration range or to minimize the matrix interference.

* Utilize screen data (specific project only).
* Utilize acquired sample data.
* Utilize the history program or approval from client/project.
* Sample characteristics (appearance).

12.10.2 If no lower dilution has been reported, the dilution factor chosen must keep the response of the largest peak for a target analyte in the upper half of the initial calibration range of the instrument.

12.10.3 Preparing Dilutions.

12.10.3.1 Prepare sample dilutions quantitatively. Dilute a stored sample extract, if available with hexane using logical volume to volume ratios, i.e., 1:5, 1:10, 1:50, etc.

12.10.3.2 Syringe dilutions. – Refer to Table 8 for dilutions. A calibrated 1ml syringe must be used to prepare dilutions. Gently shake to disperse the extract throughout the solvent prior to loading on the auto-sampler tray for further analysis.

12.10.3.3 Volumetric Flask Dilutions - Dilutions can also be made with a Class A volumetric flask. Measure the appropriate sample extract volume in a calibrated syringe and bring to final volume with dilution solvent in a Class A volumetric flask. Gently shake to disperse the extract throughout the solvent and transfer to auto-sampler vial for analysis.

12.11 Data interpretation

12.11.1 Qualitative identification

12.11.1.1 Analyst shall identify the targeted compounds with competent knowledge interpreting retention time and/or chromatographic pattern by comparison of the sample to the standard of the suspected compound. The criteria required for a positive identification are:

12.11.1.1.1 The sample component must elute at the absolute retention time window (Refer to Section 11.0) for both primary and confirmation run.

12.11.1.1.2 For the multi-response pesticides 5 major peaks are selected. The retention time window for each peak is determined from the initial calibration analysis. Identification of a multi-component analyte in the sample is based on pattern recognition in conjunction with the elution of these 5 peaks within the retention time windows of the corresponding peaks of the standard on both GC columns.

12.11.1.1.3 Be aware of matrix interfering effects on peak shape and relative peak ratios that could distort the pattern. Interpretation of these phenomena may require a highly experienced chromatographer or at least a second opinion.

12.11.2 Quantitative analysis

12.11.2.1 When a target compound has been identified, concentration (see section 14.4) will be based on the integrated area/or height of the peak and calculated by an internal standard technique. Proper quantitation requires the appropriate selection of a baseline from which the peak area or height can be determined. Report all concentrations down to the MDL.

12.11.2.2 For multi-response pesticides, a minimum of 3 peaks are used for quantitation to calculate the calibration factors for those peaks, but 5 may be used depending on the extent of matrix interferences. These calibration factors are then used to

calculate the concentration of each corresponding peak in the sample chromatogram and the resulting concentrations are averaged to provide the final result for the sample.

12.11.2.3 When sample results are confirmed using two dissimilar columns or with two dissimilar detectors, the agreement between the quantitative results must be evaluated after the identification has been confirmed. Calculate the relative percent difference (RPD) between the two results using the formula in Section 14.6. Report the lower result.

12.11.2.3.1 A program to perform the RPD calculation had been developed and incorporated into ENVIROQUANT software.

12.11.2.3.2 If 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.

12.11.2.3.3 If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the lower result with the footnote (remark) indicating “More than 40% RPD for detected concentrations between two GC columns”.

12.11.2.3.4 If %RPD>100%, then perform additional cleanup or analyze the sample at a secondary dilution. Qualify the data as necessary, indicating potential matrix interference on the higher signal.

13.0 QUALITY CONTROL

13.1 QC Requirements Summary

DDT and Endrin Breakdown Evaluation	Every 12-hour shift
ICV -Second Source Calibration	Following initial calibration
Continuing Calibration Checks	Every 20 injections or 12 hours (whichever comes first)
Instrument Blank	After DDT/Endrin Breakdown check, and after each subsequent CCV
Method Blank	One per extraction batch* or per day for a running batch
Blank Spike	One per extraction batch* or per day for a running batch
Matrix Spike	One per extraction batch*
Matrix Spike Duplicate	One per extraction batch*
Surrogate	Every sample and standard

*The maximum number of samples per batch is twenty or per project specification.

13.2 DDT and Endrin Breakdown Evaluation

13.2.1 Refer to Section 12.4.

13.3 Initial Calibration Verification (ICV) - Second Source Calibration Check

13.3.1 Refer to Section 10.2.

13.4 Continuing Calibration Verification (CCV)

13.4.1 Refer to Section 10.3.

13.5 Instrument Blank

13.5.1 If the instrument blank contains a target analyte above its MDL, the source of the contamination must be identified and corrected before proceeding with the analysis.

13.6 Method Blank

13.6.1 The method blank is either DI water or sodium sulfate (depending upon the sample matrix) which must be extracted with each set of 20 or less samples. For a running batch, a new method blank is required for each different extraction day. The method blank are then extracted and run through any clean-up procedures along with the other samples in that batch.

13.6.2 If the method blank contains a target analyte above its MDL, the entire batch must be re-extracted and re-analyzed.

13.6.3 Surrogate compounds are added to the method blank prior to extraction and analysis. If the surrogate accuracy in the blank does not meet criteria, the entire batch must be re-extracted and re-analyzed.

13.7 Blank Spike

13.7.1 A blank spike must be extracted with each set of 20 or less samples. For a running batch, a new blank spike is required for each different extraction day. The blank spike consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. A separate blank spike may be needed if the sample requires Chlordane and/or Toxaphene. It is spiked with the same analytes at the same concentrations as the matrix spike/matrix spike duplicate.

13.7.1.1 For single-component analytes, the blank spike is prepared at 0.25 μg/l or 8.33 μg/kg on a dry weight basis.

13.7.1.2 For Toxaphene only analysis or per project specification, the blank spike is prepared at 5 μg/l or 167 μg/kg on a dry weight basis.

13.7.1.3 For Chlordane only analysis or per project specification, the blank spike is prepared at 5 μg/l or 133 μg/kg on a dry weight basis.

13.7.2 The blank spike recoveries must be assessed using in house limits.

13.7.3 If a blank spike is out of control, the following corrective actions must be taken. In the case where the blank spike recovery is high and no hits reported in associated samples and QC batch the sample results can be reported with footnote (remark) and no further action is required.

Note: For DoD projects, check the bench notes for additional QC requirements.

13.7.3.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

13.7.3.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample batch.

13.7.3.3 If no problem is found, re-extract and reanalyze the sample batch.

13.8 Matrix Spike (MS)/Matrix Spike Duplicate (MSD)

13.8.1 One sample is randomly selected from each extraction batch of similar matrix types and spiked in duplicate to determine whether the sample matrix contributes bias to the analytical results.

13.8.2 A separate matrix spike and matrix spike duplicate set may be needed if the sample requires Chlordane and/or Toxaphene. Matrix spikes are prepared by spiking an actual sample for a concentration of 0.25 μg/l or 8.33 μg/kg on a dry weight basis for pesticides, 5 μg/l or 167 μg/kg for Toxaphene, 5 μg/l or 133 μg/kg for Chlordane.

13.8.3 Assess the matrix spike recoveries and relative percent difference (RPD) against the in house control limits.

13.8.4 If the matrix spike accuracy of any individual compound is out of control, the accuracy for the compound in the blank spike must be within control. Matrix interference is assumed and the data is reportable. No further corrective action is required.

13.9 Surrogates

13.9.1 Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB) are used as surrogate standards. All blanks, samples, QC samples, and calibration standards contain surrogate compounds which are used to monitor performance of the extraction, cleanup (when used), and analytical system.

13.9.2 The recoveries (refer to Section 14.5) of the surrogates must be evaluated versus the surrogate control limits developed by the laboratory.

13.9.3 If surrogate recovery is not within established control limits, corrective action must be performed if surrogate recoveries indicate that a procedural error may have occurred during the analysis of the sample.

13.9.3.1 Check the surrogate calculations for calculation or integration errors and perform corrections if detected.

13.9.3.2 Re-analyze the extract if calculation errors are not detected. If the surrogate recoveries for the re-analyzed extract are in control, report data from the re-analysis only.

13.9.3.3 If data from the reanalysis is also out of control, re-extract and reanalyze the sample.

13.9.3.4 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and reanalysis results and note the holding time problem.

13.9.3.5 If the recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

13.9.4 The retention time shift for surrogate must be evaluated after the analysis of each sample. The sample must be reanalyzed when the retention time of any surrogate compound is outside the retention window.

13.9.4.1 Reanalysis may not be required for samples having visible matrix interference, defined as excessive signal levels from target or non-target interfering peaks. This judgment must be approved by team leader or supervisor.

13.10 Internal Standards.

13.10.1 The use of internal standard calibration techniques does not require that all sample results be bracketed with calibration verification standards. However, when internal standard calibration is used, the retention times of the internal standards and the area responses of the internal standards must be checked for each analysis. Retention time shifts of >30 sec from the retention time of the most recent calibration standard and/or changes in internal standard areas of more than -50 to +100% are cause for concern and must be investigated.

13.11 Refer to Project Specific Bench Notes (GC8081) for additional program or client specific QC requirements.

14.0 CALCULATION

14.1 Response Factor (RF).

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:
A_s = Area of the compound being measured.
A_{is} = Area of the specific internal standard.
C_s = Concentration of the compound being measured (μg/L).
C_{is} = Concentration of the specific internal standard (μg/L).

14.2 Percent Relative Standard Deviation (% RSD).

$$\%RSD = \frac{SD}{CF_{av}} \times 100$$

Where:
SD = Standard Deviation.
CF_{av} = Average calibration factor from initial calibration.

14.3 Percent Difference (% D).

$$\% D = \frac{CF_{av} - CF_c}{CF_{av}} X\ 100$$

Where:
CF_c = CF from continuing calibration (CBCHK).

14.4 Concentration (Conc.).

14.4.1 <u>For water:</u>

$$\text{Conc. } (\mu g/l) = \frac{A_c \times M \times C_{is}}{RF_{av} \times A_{is}}$$

$$M = \frac{V_f \times D}{V_i}$$

14.4.2 <u>For soil/sediment</u> (on a dry weight basis, see EGN007):

$$\text{Conc. } (\mu g/kg) = \frac{A_c \times M \times C_{is}}{RF_{av} \times A_{is}}$$

$$M = \frac{V_f \times D}{W_s \times S}$$

Where:
A_c = Area of peak for compound being measured.
V_f = Final Volume of total extract (ml).
D = Secondary dilution factor.
V_i = Initial volume of water extracted (ml).
W_s = Weight of sample extracted (g).
S = (100 - % moisture in sample) / 100 or % solid/100.
M = Multiplier.
C_{is} = Concentration of the specific internal standard (µg/L).

14.5 Percent Recovery (% R).

$$\% R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

14.6 Relative Percent Difference (RPD).

$$RPD = \frac{|C_1 - C_2|}{(1/2)(C_1+C_2)} \times 100$$

Where:
C_1 = Matrix Spike Concentration or the result on column 1.
C_2 = Matrix Spike Duplicate Concentration or the result on column 2.

14.7 Percent Breakdown.

$$\%\ \text{Breakdown for DDT} = \frac{\text{Total DDT degradation peak area}}{\text{Total DDT peak area}} \times 100$$

Where:
Total DDT degradation peak area = DDE + DDD
Total DDT peak area = DDT + DDE + DDD

$$\%\ \text{Breakdown for Endrin} = \frac{\text{Total Endrin degradation peak area}}{\text{Total Endrin peak area}} \times 100$$

Where:
Total Endrin degradation peak area = Endrin aldehyde + Endrin ketone.
Total Endrin peak area = Endrin + Endrin aldehyde + Endrin ketone.

14.8 Linear regression by the internal standard technique.

$$C_s = \left(\frac{\frac{A_s}{A_{is}} - b}{a} \right) \times C_{is}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard
b = Intercept
a = slope of the line

$$a = \frac{N \Sigma xy - \Sigma x \Sigma y}{N \Sigma x^2 - (\Sigma x)^2}$$

$$b = \frac{\Sigma y - a \Sigma x}{N}$$

N = number of points
x = amount of analyte
y = response of instrument

14.9 Quadratic curve with internal standard technique

$$Cs = \frac{-b \pm \sqrt{b^2 - 4a\left(c - \frac{A_s \times C_{is}}{A_{is}}\right)}}{2a}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard
b = Intercept
a = slope of the line

14.10 Correlation Coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where:
r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

15.0 DOCUMENTATION

15.1 The Analytical Logbook is a record of the analysis sequence; the logbook must be completed by the analyst daily. Each instrument will have a separate logbook. The daily sequence must be recorded in the logbook by giving a file number to every instrument standard, QC, and samples in appropriate spaces. The files must be never overwritten or skipped intentionally. In case where the file is skipped or overwritten, a thorough explanation must be documented in the notes section. Upon completion, every analytical batch must be reviewed and signed by a supervisor/team lead. Supervisor signature indicates all documentation was performed correctly.

15.1.1 If samples or blank spike require reanalysis, a brief explanation of the reason and corrective action must be documented in the Comments section. For consistency, if surrogates are high or low indicate it as (↑) for high and (↓) for low.

15.1.2 If maintenance was done on the instrument in order to pass the CCV or any other reason, the analyst must document it in the logbook.

15.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed; the page must be signed and dated by the respective person.

15.2.1 The SGS Lot Number must be cross-referenced on the standard vial.

15.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

15.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

15.5 Unused blocks of any form must be x'ed or z'ed by the analyst before submitting the data for review.

15.6 Supervisory personnel must review and sign all laboratory logbooks monthly to ensure that information is being recorded properly. Additionally, the instrument maintenance logbooks and the accuracy of the recorded information must also be verified and signed off on the first page of the logbook quarterly by a supervisor/team lead.

16.0 DATA REVIEW AND REPORTING

16.1 Initial and continuing calibration check. Verify that all calibration and continuing calibration criteria have been achieved. If the criteria had not been achieved, corrective action must be performed to bring the system in control before analyzing any samples.

16.1.1 If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

16.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

16.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and re-analyzed before processing data.

16.3 Chromatogram Review. The chromatogram of each sample is evaluated for target compounds.

16.3.1 Check specific retention time windows for each target compound for the presence of the target compound in each chromatogram.

16.3.1.1 Each sample may require the reporting of different target compounds. Review the login to assure that the correct target compounds are identified.

16.3.2 The compound must be identified on the primary and confirmatory column before assigning a qualitative identification.

16.3.3 Manual integration of chromatographic peaks must be identified by the analysts by initialing and dating the changes made to the report.

16.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

17.0 POLLUTION PREVENTION & WASTE MANAGEMENT

17.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment

must be followed. All method users must be familiar with the waste management practices described in section 17.2.

17.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

17.2.1 Non hazardous aqueous wastes.
17.2.2 Hazardous aqueous wastes
17.2.3 Chlorinated organic solvents
17.2.4 Non-chlorinated organic solvents
17.2.5 Hazardous solid wastes
17.2.6 Non-hazardous solid wastes

Table 1 Target Compound List and Reporting Limits

Compound	CAS No.	Water (µg/l)	Soil (µg/kg)
alpha-BHC	319-84-6	0.01	0.67
beta-BHC	319-85-7	0.01	0.67
delta-BHC	319-86-8	0.01	0.67
Gamma-BHC (Lindane)	58-89-9	0.01	0.67
Heptachlor	76-44-8	0.01	0.67
Aldrin	309-00-2	0.01	0.67
Heptachlor epoxide	1024-57-3	0.01	0.67
Endosu1fan I	959-98-8	0.01	0.67
Dieldrin	60-57-1	0.01	0.67
4,4'-DDE	72-55-9	0.01	0.67
Endrin	72-20-8	0.01	0.67
Endosulfan II	33213-65-9	0.01	0.67
4,4'-DDD	72-54-8	0.01	0.67
Endosulfan sulfate	1031-07-8	0.01	0.67
4,4'-DDT	50-29-3	0.01	0.67
Methoxychlor	72-43-5	0.02	1.3
Endrin ketone	53494-70-5	0.01	0.67
Endrin aldehyde	7421-93-4	0.01	0.67
α-Chlordane	5103-71-9	0.01	0.67
γ-Chlordane	5103-74-2	0.01	0.67
Mirex	2385-85-5	0.02	1.3
Alachlor	15972-60-8	0.10	6.67
Hexachlorobenzene	118-74-1	0.01	0.67
2'4 DDT	789-02-6	0.01	0.67
Chlordane (technical)	12789-03-6	0.50	34
Toxaphene	8001-35-2	0.25	17

Table 2 RECOMMENDED OPERATING CONDITION	
Gas Chromatograph/Electron Capture Detectors	
Carrier Gas	Helium
Make-up gas	5 % Methane/ 95 % Argon
Make-up gas flow	*40 ml/min
Injection port temperature	*280°C
Injection type	Splitless
Detector temperature	*320°C
Column flow	2 ml/min
Gas Chromatograph Temperature Program*	
Initial temperature	*160°C
Time 1	*2 minutes
Column temperature rate 1	*45 degrees/min
Temperature 1	*200°C
Column temperature rate 2	*7 degrees/min
Temperature 2	*260°C
Column temperature rate 3	*50 degrees/min
Final temperature	*305°C
Time 3	*0.8 minutes
Total run time	10-20 minutes

*Parameter modification allowed for performance optimization as long as QC criteria are achieved.

Table 3a Pesticides and Surrogates Working Solution	
Stock Solution	**Volume Added**
Pesticides Mixture (1,000 μg/ml)	0.1 ml
Pesticides Surrogate Std Spiking Solution (200 μg/ml)	0.5ml
Mirex (1000ug/ml) (optional)	0.1ml
Hexane	9.4 ml (or 9.3 ml with Mirex)
Total	10.0 ml

Pesticides Mixture (10 μg/ml) and Surrogates (10 μg/ml) Working Solution: Prepared by measuring 0.1 ml of 1,000 μg/ml of pesticides mixture, 0.5ml of 200 μg/ml pesticides surrogate std spiking solution and bringing to 10 ml with hexane. Note larger or smaller volumes of standards may be prepared, as needed using the same ratios. ICV is prepared in the same way, but a second source is used.

Table 3b Internal Standard Working Solution	
Stock Solution	**Volume Added**
1-Bromo-2-nitrobenzene (1,000 μg/ml)	0.25 ml
Hexane	49.75 ml
Total	50.0 ml

Table 4A Pesticides Calibration Standard Solutions					
Solution	**Working Solution**	**Concentration (μg/ml)**	**Volume Added (μl)**	**Final Volume in Hexane (ml)**	**Final Concentration(μg /l)**
Standard	Pesticides Mixture	10	500	50	100

A	Surrogates	10			100
Standard	Pesticides Mixture	10	250	50	50
B	Surrogates	10			50
Standard	Pesticides Mixture	10	125	50	25
C	Surrogates	10			25
Standard	Pesticides Mixture	10	50	50	10
D	Surrogates	10			10
Standard	Pesticides Mixture	10	25	50	5
E	Surrogates	10			5
Standard	Pesticides Mixture	10	10	50	2
F	Surrogates	10			2
Standard	Pesticides Mixture	10	5	50	1
G	Surrogates	10			1
Standard	Pesticides Mixture	10	375	50	75
H	Surrogates	10			75

Standard A: Prepared by measuring 500 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard B: Prepared by measuring 250 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard C: Prepared by measuring 125 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard D: Prepared by measuring 50 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard E: Prepared by measuring 25 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard F: Prepared by measuring 10 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard G: Prepared by measuring 5 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Standard H: Prepared by measuring 375 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Table 4B Toxaphene Calibration Standard Solution (20ug/ml)	
Stock Solution	**Volume Added (µl)**
Toxaphene stock (4000 µg/ml)	125
Pesticides Surrogate Std Spiking Solution (200 µg/ml)	100
Hexane	24775
Total	25000

Toxaphene (20 μg/ml) and Surrogates (0.80 μg/l) Calibration Solution: Prepared by measuring 125 μl of 4000 μg/ml of Toxaphene stock solution, 100 μl of 200 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4C Chlordane Calibration Standard Solution (20 μg/ml)	
Stock Solution	**Volume Added (μl)**
Chlordane stock (2000 μg/ml)	250
Pesticides Surrogate Std Spiking Solution (200 μg/ml)	100
Hexane	24650
Total	25000

Chlordane (20 μg/ml) and Surrogates (0.80 μg/ml) Calibration Solution: Prepared by measuring 250 μl of 2000 μg/ml of Chlordane stock solution, 100 μl of 200 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4D Multi-point Toxaphene Calibration Standards (optional)					
Solution	**Stock Solution**	**Concentration (μg/ml)**	**Volume Added (μl)**	**Final Volume in Hexane (ml)**	**Final Concentration(μg/l)**
Standard A	Toxaphene	20	3750	25	3000
	Surrogate Spiking	0.8	3750		120
Standard B	Toxaphene	20	2500	25	2000
	Surrogate Spiking	0.8	2500		80
Standard C	Toxaphene	20	1250	25	1000
	Surrogate Spiking	0.8	1250		40
Standard D	Toxaphene	20	625	25	500
	Surrogate Spiking	0.8	625		20
Standard E	Toxaphene	20	312.5	25	250
	Surrogate Spiking	0.8	312.5		10
Standard F	Toxaphene	20	62.5	25	50
	Surrogate Spiking	0.8	62.5		2

Standard A: Prepared by measuring 3750 μl of 20 μg/ml of Toxaphene stock solution, 3750 μl of 0.8 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard B: Prepared by measuring 2500 μl of 20 μg/ml of Toxaphene stock solution, 2500 μl of 0.8 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard C: Prepared by measuring 1000 μl of 20 μg/ml of Toxaphene stock solution, 1000 μl of 0.8 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard D: Prepared by measuring 625 μl of 20 μg/ml of Toxaphene stock solution, 625 μl of 0.8 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard E: Prepared by measuring 312.5 μl of 20 μg/ml of Toxaphene stock solution, 312.5 μl of 0.8 μg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard F: Prepared by measuring 62.5 µl of 20 µg/ml of Toxaphene stock solution, 32.5 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 4E Multi-point Chlordane Calibration Standards (optional)					
Solution	**Stock Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration(µg/l)**
Standard A	Chlordane	20	3750	25	3000
	Surrogate Spiking	0.8	3750		120
Standard B	Chlordane	20	2500	25	2000
	Surrogate Spiking	0.8	2500		80
Standard C	Chlordane	20	1250	25	1000
	Surrogate Spiking	0.8	1250		40
Standard D	Chlordane	20	625	25	500
	Surrogate Spiking	0.8	625		20
Standard E	Chlordane	20	312.5	25	250
	Surrogate Spiking	0.8	312.5		10
Standard F	Chlordane	20	62.5	25	50
	Surrogate Spiking	0.8	62.5		2

Standard A: Prepared by measuring 3750 µl of 20 µg/ml of Chlordane stock solution, 3750 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard B: Prepared by measuring 2500 µl of 20 µg/ml of Chlordane stock solution, 2500 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard C: Prepared by measuring 1000 µl of 20 µg/ml of Chlordane stock solution, 1000 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard D: Prepared by measuring 625 µl of 20 µg/ml of Chlordane stock solution, 625 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard E: Prepared by measuring 312.5 µl of 20 µg/ml of Chlordane stock solution, 312.5 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Standard F: Prepared by measuring 62.5 µl of 20 µg/ml of Chlordane stock solution, 32.5 µl of 0.8 µg/ml pesticides surrogate std spiking solution and bringing to 25 ml with hexane.

Table 5 Continuing Calibration Check Solutions					
Checks	**Working Solution**	**Concentration (µg/ml)**	**Volume Added (µl)**	**Final Volume in Hexane (ml)**	**Final Concentration(µg/l)**
Solution 1	Pesticides Mixture	10	250	50	50
	Surrogates	10			50
Solution 2	Pesticides Mixture	10	50	50	10
	Surrogates	10			10
Solution 3	Pesticides Mixture	10	125	50	25
	Surrogates	10			25

Solution 1: Prepared by measuring 250 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Solution 2: Prepared by measuring 50 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Solution 3: Prepared by measuring 125 µl of Pesticides Mixture (10 µg/ml) and Surrogates (10 µg/ml) Working Solution and bringing to 50 ml with hexane.

Table 6 DDT and Endrin Breakdown Evaluation Standard	
Stock Solution	**Volume Added (µl)**
Pesticides Performance Evaluation Mixture (10-250 µg/ml)	50
Hexane	4995 0
Total	5000 0

DDT and Endrin Breakdown Evaluation Standard (10-250 µg/l): Prepared by measuring 50 µl of Pesticides Performance Evaluation Mixture (10-250 µg/ml) and diluting to 50 ml with hexane.

Table 7
Sample Dilution Table

All dilutions must be made using a 1ml calibrated syringe.

Dilution	*Intact Sample*	*Solvent*
1:2	500ul	500ul
1:5	200ul	800ul
1:10	100ul	900ul
1:20	50ul	950ul
1:25	40ul	960ul
1:50	20ul	980ul

Two Step dilution				
Dilution	**Step 1**		**Step 2**	
	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*
1:100	100ul	900ul	100ul	900ul
1:200	100ul	900ul	50ul	950ul
1:250	100ul	900ul	40ul	960ul
1:500	100ul	900ul	20ul	980ul

Three Step Dilution			
Dilution	**Step 1**	**Step 2**	**Step 3**

	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*	*Sample Aliquot from Step 2*	*Solvent*
1:1000	100ul	900ul	100ul	900ul	100ul	900ul
1:2000	100ul	900ul	100ul	900ul	50ul	950ul
1:2500	100ul	900ul	100ul	900ul	40ul	960ul
1:5000	100ul	900ul	100ul	900ul	20ul	980ul

Four Step Dilution

Dilution	**Step 1**		**Step 2**		**Step 3**		**Step 4**	
	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*	*Sample Aliquot from Step 2*	*Solvent*	*Sample Aliquot from Step 3*	*Solvent*
1:10,000	100ul	900ul	100ul	900ul	100ul	900ul	100ul	900ul
1:20,000	100ul	900ul	100ul	900ul	100ul	900ul	50ul	950ul
1:25,000	100ul	900ul	100ul	900ul	100ul	900ul	40ul	960ul
1:50,000	100ul	900ul	100ul	900ul	100ul	900ul	20ul	980ul

Changes / Edits made (this should include added or deleted information within a sentence or paragraph only):

Section / Subsection	Detailed description of what was revised
10.1.6.2	Added TNI acceptable procedure to delete points from an ICAL
4.0	MDL definition revised

Sections or Subsections deleted:

Section / Subsection	Reason section or subsection was removed
3.2.1; 3.2.2	MDL procedure
10.1.6.2.1	See sections 10.1.6.3-10.1.6.7

Sections or Subsections added:

Section / Subsection	Reason section or subsection was added
10.1.6.3-10.1.6.7	TNI procedure for removing calibration points

History of Revisions

Version #	Date of Revision	Revised By
13	09/28/2018	Wahied Bayoumi
14	02/17/2020	Olga Azarian
15	03/24/2020	Maria Ruschke

END OF DOCUMENT

LAB MANAGER: _____

QA MANAGER: _____

EFFECTIVE DATE: 8/11/2017

TITLE: FLORISIL COLUMN CLEANUP
REFERENCES: SW846 3620C (JULY 2014)
REVISED SECTIONS: 10.1.2

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered trade name of the Floridin Co., is a magnesium silicate with acidic properties. It is used for general column chromatography as a cleanup procedure prior to sample analysis by gas chromatography.

1.2 General applications: Cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes (Floridin). Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates (Gordon and Ford).

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing the following analyte groups: phthalate esters; organochlorine pesticides; and chlorinated hydrocarbons; however only organochlorine pesticides / PCB's are cleaned up using this method.

1.4 This method is utilized for aqueous, soil, and TCLP waste dilution samples.

2.0 SUMMARY

2.1 The sample to be analyzed is loaded onto a prepacked florisil cartridge. Elution is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated to final volume.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 See determinative method.

4.0 DEFINITIONS

BLANK. An analytical sample designed to assess specific sources of laboratory contamination. Types of Blanks may include: Method Blank, Instrument Blank, Storage Blank, and Leachate Blank.

BATCH. A group of samples and associated quality control samples which are similar with respect to matrix and the testing procedures being employed and which are processed as a unit. A sample batch is limited to a maximum of 20 samples.

BLANK SPIKE (BS). An analyte-free matrix spiked with a known amount of analyte(s), processed simultaneously with the samples through all the steps of the analytical procedure. Blank Spike Recoveries are used to document laboratory performance for a given method. This may also be called a Laboratory Control Sample (LCS).

CLASS A GLASSWARE. Volumetric laboratory glass that has been manufactured, calibrated and certified to established ASTM volume standards. Under normal laboratory conditions, Class A Glassware does not require volume calibration or verification.

EXTRACTION. The process of removing a desired compound from a matrix using chemical or mechanical procedures. The process is used to isolate and concentrate targeted constituents for instrumental analysis.

GAS LIQUID CHROMATOGRAPHY (GC). An instrumental procedure used to separate mixtures of organic compounds based on polarity or boiling point. The technique employs long capillary columns containing a high molecular weight organic polymer to effect the separation.

HOLDING TIME. The maximum time that samples may be held prior to preparation and/or analysis and still are considered valid.

MATRIX. The predominant material of which a sample is composed. For the purpose of this method, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

MATRIX SPIKE. Aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE. A second aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

METHOD BLANK. An analytical control consisting of all reagents, internal standards, and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

REAGENT WATER. Purified water in which an interferant is not observed at or above the minimum reporting limit of the parameters of interest.

SURROGATE. An organic compound which is similar to the target analyte(s) in chemical composition and behavior, but which is not normally found in environmental samples. Surrogates are used to measure the extraction efficiency.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the SGS Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets is available to all personnel involved in these analyses.

6.0 COLLECTION, PRESERVATION, & HOLDING TIMES

6.1 Sample Collection

6.1.1 Water samples are collected in 1 L glass amber bottles. Certain aqueous methods require samples to be tested for residual chlorine using test paper for free and total chlorine. If the sample tests positive for residual chlorine, add 80 mg of sodium thiosulfate to each liter of sample and mix well.

6.1.2 Soil samples are collected in 125-mL widemouth glass with Teflon-lined lid.

6.2 The samples must be protected from light and refrigerated at 0 to <6° C from the time of receipt until extraction and analysis.

6.3 Holding Times

6.3.1 Aqueous samples must be extracted within 7 days of sampling.

6.3.2 Soil, sediments and concentrated waste samples must be extracted within 14 days of sampling.

6.4 Prepare samples within 14 days of sampling and analyze the extract within 40 days of the extraction.

7.0 APPARATUS & MATERIALS

7.1 10mL Class A volumetric containers

7.2 2mL graduated amber glass vial and associated PTFE lined cap (screw top or crimp).

7.3 Top loading balance, capable of weighing to 0.01 grams

7.4 1mL volumetric pipettes or calibrated syringes

8.0 STANDARDS & REAGENTS

8.1 Solvents - reagent grade for trace organic analysis. Each solvent lot must be checked for interferences prior to use. Refer to SOP EOP013 for the procedure regarding solvent lot approval.

8.1.1 Acetone

8.1.2 Hexane

8.1.3 Methylene Chloride

8.2 Florisil cartridge phenol check solution (for organochlorine pesticide)- Prepare a solution of 2,4,5-trichlorophenol in acetone at a concentration of 0.1mg/L (0.1ug/mL).

8.3 Pesticide spike solution- Refer to the analytical SOP for target compound specifications. Refer to the most current version of Form OP026 for details on Standard and Spike preparation.

Note: Unopened stock solutions must be stored according to the manufacturers documented holding time and storage temperature recommendations. After opening, stock standards must be replaced after 6 months or sooner if manufacturer's expiration date comes first or comparison with quality control check samples indicate degradation.

9.0 INTERFERENCES

9.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. Blanks must be analyzed to demonstrate that these materials are free from interferences under the conditions of the analysis.

9.2 Interferences co-extracted from the samples will vary considerably from source to source. If interferences prevent the analysis of an extracted sample, further cleanup of the sample extract may be employed if necessary. Refer to SW-846 Method 3600 for cleanup procedures.

9.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Avoid plastics in particular because they contain phthalates, used as plasticizers, which can leach from these materials. Practice sound, consistent materials control to avoid phthalate contamination, which may occur at any time.

9.4 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, Aldrin, Heptachlor, and most organophosphorus pesticides will degrade in this situation. This occurs in glassware that is difficult to rinse (e.g., 500-mL K-D flask). Carefully hand-rinse these items to avoid this problem.

10.0 PROCEDURE

10.1 Procedure for Florisil Cartridge Performance check.

10.1.1 Each new lot of Florisil cartridges must have two cartridges (duplicate) tested prior to use. In addition, one additional cartridge must be tested for every 300 cartridges of a lot before they are used for cleanup.

10.1.2 Add 0.5 ml of 0.1ug/mL 2,4,5 trichlorophenol solution, 0.1 mL of pesticide spike solution, and 0.1 mL of pesticide surrogate to 1.3 mL of hexane. Concentrate using the nitrogen blowdown technique to a volume of 0.5 mL to drive off acetone present in spike solution.

10.1.3 Place the mixture on a pre-eluted organochlorine pesticide/PCB florisil cartridge (see 10.3.2) and elute with 9mL of 90/10 hexane/acetone.

10.1.4 Reduce the final volume to 1mL using the nitrogen blowdown technique, and analyze the solution by Method 8081.

10.1.5 The lot is acceptable if all of the pesticides are recovered at 80 to 110 percent, the recovery of 2,4,5 trichlorophenol is less than 5 percent, and there are no interfering peaks detected. Refer below to Section 12.0 Data Review & Documentation for proper documentation requirements for florisil cartridge checks. Any lot of Florisil cartridges that does not meet these criteria must be discarded and replaced by a new lot.

10.2 Phthalate esters.

10.2.1 Reduce the sample extract volume to 2mL prior to cleanup. The extract solvent must be hexane.

10.2.2 Pre-elute the cartridge with 4mL of hexane. If gravity filtration is sufficient to maintain a rate of about 2mL/min, no vacuum is required. Discard the eluate and, just prior to exposure to the air, quantitatively transfer the 2mL sample extract onto the column. Rinse the vial with an additional 0.5mL of hexane and add the rinse to the cartridge to complete the quantitative transfer.

10.2.3 Elute the cartridge with 10mL of methylene chloride in hexane (20/80 v/v). This fraction contains organochlorine pesticides and should be discarded.

10.2.4 Next elute the cartridge with 10mL of 90/10 acetone/hexane. Concentrate the collected fraction to the required volume, as needed. No solvent exchange is necessary. Compounds that elute in this fraction are:

- Bis(2-ethylhexyl) phthalate
- Butyl benzyl phthalate
- Di-n-butyl phthalate
- Diethyl phthalate
- Dimethyl phthalate
- Di-n-octyl phthalate

10.3 Organochlorine pesticides/PCBs.

10.3.1 Reduce the sample extract volume to 10mL prior to cleanup. The extract solvent must be hexane.

10.3.2 Pre-elute the cartridge with 5mL of 90/10 hexane/acetone. If gravity filtration is sufficient to maintain a rate of about 2mL/min, no vacuum is required. Discard the eluate and, just prior to exposure to the air, quantitatively transfer 1mL of sample extract onto the column.

10.3.3 Elute the cartridge with 9mL of 90/10 hexane/acetone into a 10mL volumetric flask.

10.3.4 Reduce the volume to 1 ml using the nitrogen blow down technique.

10.3.5 The eluate will contain all of the organochlorine pesticides/PCB's.

10.4 Chlorinated hydrocarbons.

10.4.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

10.4.2 Pre-elute the cartridge with 5 mL of 90/10 hexane/acetone. If gravity filtration is sufficient to maintain a rate of about 2ml/min, no vacuum is required. Discard the eluate and, just prior to exposure to the air, quantitatively transfer the 2 mL sample extract onto the column.

10.4.3 Rinse the vial with an additional 0.5ml of 90/10 hexane/acetone and add the rinse to the cartridge to complete the quantitative transfer.

10.4.4 Elute the column with 10 mL of 90/10 hexane/ acetone into a 10 mL concentrator tube.

10.4.5 Adjust the final volume to 2 ml using the nitrogen blowdown technique.

10.4.6 The eluate should contain all of the chlorinated hydrocarbons:

- 2-Chloronaphthalene
- 1,2-Dichlorobenzene
- 1,3-Dichlorobenzene
- 1,4-Dichlorobenzene
- Hexachlorobenzene
- Hexachlorobutadiene
- Hexachlorocyclopentadiene

- Hexachloroethane
- 1,2,4-Trichlorobenzene

11.0 QUALITY CONTROL

11.1 Perform solvent checks for each new solvent lot to verify the absence of interferences. See SOP EOP013.

11.2 Florisil cartridge check.

11.2.1 The data is analyzed by the Semi-volatile analytical department, reviewed and released by the Organic Prep supervisor, Team Leader, or scheduler.

11.2.2 The person releasing the solvent or standard for use must complete the Spike-Surr-Solvent Verification electronic tracking form located on the Extraction Drive (form OP031).

12.0 DOCUMENTATION

12.1 The organics management staff evaluates data from the analysis of the florisil cartridge check to determine acceptability for use.

12.1.1 Document all information on the “Active Spike-Surr-Solvent Verification” electronic log located on the N:Extraction Directory (form OP031).

12.1.2 If acceptable, it is released for use by the organics management staff. The solvent check data link is added to Active Spike- Surr-Solvent Verification Log (form OP031).

12.1.3 Case by case exceptions may be made with the concurrence of the Semi-Volatiles Managers and Org Prep Manager for failed compounds. Exceptions must be documented on the electronic log.

12.2 All sample preparation activities and related information must be documented in the respective extraction logbook. Complete all information required for the extraction summary logbook.

12.2.1 Errors must be stricken with a single line, initialed and dated. The correct information must be written adjacent to the erroneous information.

12.2.2 The individual with custody responsibility must sign the extraction log.

12.2.3 The individuals involved in the processing of the batch must initial in the appropriate respective locations.

12.2.4 All spikes, surrogates, reagents, solutions, and applicable manufacturer and lot information must be filled in the appropriate respective locations.

12.2.5 If Florisil column cleanup is performed, its use must be documented on the extraction log.

12.2.6 All equipment, equipment identifiers, and the operating parameters at time of use must be filled in the appropriate respective locations.

12.2.7 The logbooks and/or e-logs must be reviewed and initialed by a team leader or supervisor. The approved page is copied and given to the Report Generation Dept.

12.3 Sample custody transfers must be updated according to proper Chain of Custody protocols.

12.4 All standards preparation must be documented in the standards preparation logbook.

12.5 Equipment maintenance logs must be maintained

13.0 DATA REPORTING

13.1 Not Applicable

14.0 POLLUTION PREVENTATION & WASTE MANAGEMENT

14.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 14.2.

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non hazardous aqueous wastes.

14.2.2 Hazardous aqueous wastes

14.2.3 Chlorinated organic solvents

14.2.4 Non-chlorinated organic solvents

14.2.5 Hazardous solid wastes

14.2.6 Non-hazardous solid wastes

15.0 REFERENCES

15.1 Not Applicable

STANDARD OPERATING PROCEDURE L-3E: COLD WATER VAPOR ANALYSIS OF MERCURY FOR SOIL SAMPLES BY SW846 7471B846 7471B

LAB SUPERVISOR: Natasha Vera

QA OFFICER: Olga M. Agüero

EFFECTIVE DATE: 2-14-2022

TITLE: COLD VAPOR ANALYSIS OF MERCURY FOR SOIL SAMPLES
REFERENCES: SW846 7471B, revision 2, February 2007
REVISED SECTIONS: 12.2, 12.10

1.0 SCOPE AND APPLICATION

1.1 This method can be applied for the analysis of mercury in soils, sediments, bottom deposits, and sludge type materials. The reporting limit for mercury soil samples, based on a 0.6 g sample size, is 0.033 mg/kg.

2.0 SUMMARY

2.1 Cold vapor mercury is a flameless AA procedure based on the absorption of radiation at 253.7 by mercury vapor. Organic mercury compounds are oxidized, and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Results are quantitated by comparison to a daily calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B Revision 2, and SOP EQA075.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed, and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. Recovery requirements vary by method. For this method a recovery from 90 to 110% is required. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's)

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent must be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent must be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs must be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

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.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards must be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation.

LOWER LIMIT OF QUANTITATION CHECK (also referred to as CRI, CRA, or LLQC). For all runs, a low check at the level of the reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. A method criterion of 50 to 150% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the SGS-Dayton Chemical Hygiene Plan Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 After the mercury digestate is reduced to Hg vapor, it must be handled in a closed system or in a hood to prevent inhalation of the toxic vapor. Make sure that the Hg instrument is vented directly to a hood.

6.0 PRESERVATION AND HOLDING TIME

6.1 All solid samples must be stored at 4 $\pm$ 2ºC until the time of digestion.

6.2 All samples must be analyzed within 28 days of the date of sampling.

7.0 APPARATUS

7.1 Leeman Hydra II AA automated analyzers. Refer to the instrument manuals for further details on this instrumentation, including proper venting and safety requirements. Instrument maintenance is outlined below.

7.1.1 Change the sample tubing as needed.

7.1.2 Change the drying tubing as needed.

7.1.3 Clean the exterior of the instrument as needed.

7.1.4 Adjust the Hg lamp as needed. This can be done in the software on both instruments.

7.1.5 Complete any other maintenance required to maintain the instrument in good running order including, but not limited to, cleaning the cell, changing other tubing, changing the Hg lamp, etc.

7.2 Graphite heating block. Capable of heating at 95 ± 3 °C for 2 hours.

7.3 Digestion Bottles. Disposable plastic digestion tubes (65 ml volume) with tops for graphite heating block.

7.4 Calibrated glass tubes with verified 100.0 ml final volume calibration mark for bringing graphite heating block digestates to their final volume.

7.4.1 At a minimum of once per year, the calibration of these bottles must be verified and documented in the Hg Bottle calibration log following the procedure outlined below.

7.4.2 Carefully measure 100.0 ml of room temperature (20 to 25 deg. C) deionized water with a class A to deliver volumetric cylinder and pour into the calibrated Hg bottle.

7.4.3 If the bottom of the meniscus is on the calibration line, then the bottle passes calibration and can be used.

7.4.4 If the bottom of the meniscus is not on the line, then the bottle must be removed from service and replaced with a newly calibrated bottle. New bottles are calibrated following the same procedure as above, except that a line must be etched into the bottle at the bottom of the meniscus of the 60 ml of DI water.

7.5 Class A, to deliver, volumetric cylinders for measuring initial sample volumes and for calibrating glass tubes as outlined above.

7.6 Analytical Balance, 4 places. Calibration must be verified daily before use with NIST traceable weights.

7.7 Automatic pipettor bottles. The calibration on these bottles must be verified as outlined in EQA063.

7.8 Volumetric pipets, class A.

7.9 Glass digestion tubes. The purchased glass tubes have 50ml and 100 ml marks and are calibrated for these two volumes by the manufacturer. Calibration certificate is provided by manufacturer. This can be used for digestion instead of disposable digestion tubes.

7.10 Disposable Wood Spatulas

7.11 Ceramic Mixing Bowl

8.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required. All solutions listed below may be scaled up or down proportionally as needed. Different reagents are required for the different heating techniques.

8.1 Digestion Block Reagents.

8.1.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated nitric.

8.1.1.1 Make sure to only prepare the amount of acid that will be needed for the prep and analysis.

8.1.1.2 This preparation must be done in a hood.

8.1.2 Dilution Acid: To approximately 800 ml of DI water, add 37.5 ml of concentrated HCl and 12.5 ml of concentrated nitric acid. Dilute to 1000 ml with DI water and mix well. This dilution acid is used for making dilutions of digested samples from the digestion block digestion procedures.

8.1.3 Potassium permanganate, 5% solution: Dissolve 50 g of potassium permanganate in 1000 ml of DI water. **Caution** - Potassium permanganate is a strong oxidizing agent. Handle with care.

8.1.4 Stannous chloride. Add 7.5 ml of concentrated sulfuric acid to approximately 400 ml of DI water. Dilute to 500 ml with DI water and mix well. Add 50 g of stannous chloride di-hydrate or 42 g stannous chloride anhydrous and dissolve. Make sure that this solution is dissolved while in use.

8.1.4.1 Stannous sulfate may be used in place of stannous chloride.

8.1.4.2 If clogging occurs during analysis using the automated analyzer, then a less concentrated solution may be used.

8.1.5 Sodium chloride-Hydroxylamine hydrochloride or Sodium Chloride-Hydroxylamine hydrosulfate. Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to 2000 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

8.2 Mercury standard solutions.

8.2.1 10 ppm Hg solution. Using a 1.00 ml volumetric pipette, add 1.00 ml of 1000 ppm stock to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with water and mix well. This standard may be held for up to 28 days.
1000 ppm Stock can be purchased from the outside vendor such as Ultra and Inorganic ventures, they are light sensitive and must be kept away from the direct light.

8.2.1.1 The 10-ppm external source must be made up using a different mercury stock and following the directions in 8.2.1. External stock solution must be from different vendor than calibration source.

8.2.2 100 ppb Hg solution. Using a 1.00 ml volumetric pipette, add 1.00 ml of 10 ppm Hg solution to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

8.2.2.1 The 100-ppb external source must be made up following the directions in 8.2.2.

8.2.3 10 ppb Hg solution. Using a 10.0 ml volumetric pipette, add 10.0 ml of 100 ppb Hg solution to a 100 ml volumetric flask containing approximately 75 ml of DI water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

8.2.4 Teflon Chips

8.2.5 Solid Lab Control (Mixture of Metals analytes in Soil Matrix).This is commercially purchased.

9.0 INTERFERENCES

9.1 Potassium permanganate is added to eliminate possible sulfide interferences. Concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water. High copper concentrations (> 10 mg/kg) may also interfere with mercury recoveries.

9.2 Samples that are high in chlorides may require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 254 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and analyzed. This may be accomplished by using an excess of the hydroxylamine hydrosulfate.

9.3 Certain volatile organics may also absorb at this wavelength and can interfere.

10.0 GRAPHITE DIGESTION BLOCK PROCEDURE FOR SOIL DIGESTION

10.1 Make up a standard curve consisting of 5 standards and a blank. Suggested concentrations are shown below. Different concentrations may also be used, as long as all of the method requirements are met. Make sure to clearly label each digestion tube. Calibration standards must be prepared fresh each day. Add 5 ml of DI water to each standard before digestion. The final concentration of Hg is calculated in the final digestate.

Ml of 10 ppb Hg solution	ml of 100 ppb Hg solution	Total ug of Hg	ug/L of Hg
0.000	0.000	0.000	0.000
2.00	0.000	0.020	0.20
5.00	0.000	0.050	0.50
0.00	1.00	0.100	1.00
0.00	2.50	0.250	2.50
0.00	5.00	0.500	5.00

10.2 Samples. For each sample, homogenize the sample well, weigh out an amount of wet sample equivalent to 0.5-0.6 g of dry sample into a numbered digestion tubes, Label each digestion tube. The sample must be weighed out using an analytical balance and the weights must be recorded. Make sure that the sample identification is accurately recorded with the digestion tube numbers on the sample digestion log. A solid lab control must be prepared in the same manner.

10.2.1 Make sure that the sample has been thoroughly mixed before weighing out the representative sample. Discard rocks, sticks, etc. from the sample. (Refer to the SOP EQA042 for proper sample aliquot procedures). All homogenization and sample handling must be done with wooden spatulas and ceramic (or other non-metal) bowls.

10.2.2 If the sample is leachate oil, measure 0.6ml of the sample and follow the steps starting at section 10.7. Leachate oil samples are handled using soil procedure on a volume basis.

10.2.3 If the sample is a wipe, weighing is not necessary. Transfer the entire wipe into the labeled digestion tube and proceed with the digestion following steps 10.7. Extra wipes must be supplied by the client for the matrix spike or duplicate.

10.3 In addition to the samples, a spike blank and a method blank must be set up with each batch of 20 samples or less. A solid lab control sample is used in addition to the blank spike by client requirement. A matrix spike, a matrix spike duplicate or a duplicate must be set up with each batch of 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements.

10.3.1 For leachate oil QC samples use 0.6ml of leachate and proceed with section 10.7.

10.4 For the method blank and spike blank, instead of weighing out soil add approximately 0.6 g of Teflon chips to the digestion tube. Add the spiking solution to the blank spike after the chips are in the tube.

10.5 Solid lab control must be weighed out in the same manner as a sample, but weight can be adjusted based on the concentration. See area supervisor for the weight information.

10.6 Make up additional quality control samples as shown below. (Note: if a different standard curve is run, then the levels of the CCV and ICV standards must be adjusted accordingly in accordance with the requirements in the method.) Make sure to clearly label each digestion tube. Make sure to prepare enough CCV checks for the entire run. The ICV check must be from an alternate source of standards than the calibration curve and at a different level than the CCV or the calibration standards. A low check standard is also required. This 0.20 ug/l check can be made up as outlined for the standard curve.

Sample ID	ml of 100 ppb Hg solution	ml of DI water	µg/l of Hg
CCV Check(s)	2.5	7.5	2.5
MB	0.0	10.0	0.0
BS	2.0	0.0	2.0
MS	2.0	0.0	2.0
MSD	2.0	0.0	2.0
Spike blank	2.0	0.0	2.0
Duplicate*	0.0	0.0	0.0
ICV	3.0	7.0	3.0

*Per project specification.

10.7 To all samples, QC, and standards add 5 ml of DI water and 5 ml of aqua regia and then heat for 2 minutes in a digestion block set at 95 ± 3 °C. These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

10.8 Cool the samples and then add 25 ml of DI water and 15 ml of potassium permanganate solution to each sample and mix thoroughly. Allow the samples to stand for at least 15 minutes after the addition of the permanganate. If the sample decolorizes, add additional permanganate until the purple color persists. When additional potassium permanganate added to a sample, equal amounts must be added to the associated batch quality control samples such as Method blank, Blank spike, Matrix spike, Matrix duplicate, QC sample and Duplicate.

10.8.1 These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

10.8.2 For samples containing a mixture of solvent and water, take a sample aliquot of approximately 20 g (lower for higher solvent samples) of sample and add the reagents listed above. Pour the sample in a beaker and heat on a hot plate at 95 ± 3 °C until no solvent layer is visible. Then transfer the digestate to a digestion tube and proceed as outlined below. A method blank and spike blank must also be taken through this entire procedure.

10.9 Cap the samples and place them in the graphite digestion block for 30 minutes at 95 ± 3 °C. Record the temperature and time for each digestion batch on the analysis sheet. Remove and cool.

10.10 Enter the prep data into the LIMS system, double checking all weights and spike amounts. After the prep data is checked, it can be approved and is available for use in the final calculation.

11.0 MERCURY ANALYSIS PROCEDURE HYDRA AA II

11.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operator's manual.

11.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

11.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath must be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

11.1.3 Turn on the analyzer and allow it to warm up.

11.1.3.1 Open the Envoy software. Go to Method and click Instrument Control. On the Instrument Control page, click the startup icon. This will turn on the lamp, gas, and pump. You may also turn on/off the lamp, gas and pump individually on the Instrument Control Page.

11.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not over tighten.

11.1.5 Go to the Instrument control tab and pick the gas control test option. The input must be approximately 0.25 LPM. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.6 Start a batch to save your data.

11.1.6.1 Create a new chapter (Data File) by clicking Analysis. The batch must normally be named H5 followed by the month date and year, followed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument for 3/24/03 would be named H5032411w1. The realtime print option can also be turned on from this tab.

11.1.7 Set up autosampler racks containing the samples that are going to be run.

11.1.7.1 Create a new sequence by clicking sequence-new. Type the sequence name. After typing the samples in to sequence page make sure to click update and save. CCV and CCB checks can be entered in the macro column of the sequence page.

11.1.8 Set up the calibration.

11.1.8.1 For the Hydra AA II, go to the Method menu, enter or verify the standard concentration by clicking on the standard tab. Also select number of replicates to be run for each standard. Normally one replicate is run per standard. The check standard concentrations and acceptance ranges are also defined under this standard info tab. Make sure to always click apply when any changes are made in a tab.

11.2 Finish the preparation of the samples and standards as outlined below.

11.2.1 For samples that were digested in the water bath or the graphite digestion block, add 6 ml of hydroxylamine hydrochloride or hydroxylamine hydrosulfate to each sample and standard and mix well. Transfer the entire digestate to a calibrated glass tube. Rinse the digestion tube 3 times with approximately 10 ml aliquots of DI water and add them to the digestate in the calibrated glass tube. Then bring the sample to a final volume of 100 ml with DI water and mix well.

11.2.1.1 If calibrated glass tubes are used for digestion and the final volume of 100 ml is brought up in the same tube, be sure to mix well using parafilm.

11.2.1.2 Reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

11.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

11.4 Start the calibration.

11.4.1 Click run sequence. The instrument will run the calibration and then pause. Click stop. Go to the Calibration page. Accept the calibration and then print the calibration. Click the Document icon, then choose HG5-PDF. Rename the file as MA*****_cal.

11.5 After the calibration has been accepted, start to run the samples.

11.5.1 For the Hydra AA II, go to the Sequence page. Right click on the first sample (i.e. ICV) and click start from here.

11.5.2 Review the data. Any samples that are over the range of the curve must be diluted with the dilution acid (see 8.1.2) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

11.6 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports must be transferred into the LIMS system where the final calculations are done.

11.6.1 Go to analysis-Click result-Click chapter. Then go to report and select report spec. The normal report spec is "ACCUTEST". Click OK. Click on chapter in order to select all samples. Then click report output and then csv.file. Save as MA*****.csv. To print, select printer output and then type the report title (i.e. MA*****) and enter OK.

11.7 The calculations are done in the LIMS as described below. . For soils, the calculation shown below is used. A final volume of 100 ml is used for calculation purposes. (The final volume is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 100 ml.)

$$\text{Final sample concentration in mg/kg} = \frac{\text{concentration in the digestate in ug/l x final volume}}{\text{Initial weight in g x (\%solids/100)}}$$

11.8 Review the data in the LIMS, adding comments and accepting results as appropriate.

11.9 Shut down the instruments.

11.9.1 To shut down the Hydra AA II, move the stannous chloride line from the stannous chloride bottle to the 10% HNO3 rinse bottle. Let the system rinse with 10% HNO3 for several minutes. Then switch the line to DI water bottle and let rinse for several more minutes. Let the pump and gas run until the lines are completely dry. Then go to instrument control menu and click off icon for Lamp, Gas and Pump.

12.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

12.1 Instrument Detection Limits (IDLs). The instrument detection limits are determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of 7 consecutive replicates of a standard solution at a concentration from 3 to 5 times the estimated detection limit. IDLs must be done quarterly (every 3 months) for each instrument.

12.2 Method Detection Limits (MDLs). MDLs must be established using the lab's SOP EQA075.

12.3 Instrument Calibration. The instrument must be calibrated daily or at a minimum of once every 24 hours and each time the instrument is set up. Calibration standards must be digested using the same procedure as the samples. A minimum of a blank and 5 standards are required. The correlation coefficient of the curve must be a minimum of 0.995. No samples must be analyzed until all of the calibration criteria are met.

12.3.1 A linear calibration using the equation y = mx + b is applied where m is the slope and b is the intercept. The calibration is not forced through zero.

12.3.2 The correlation coefficient is calculated using the following equation:

$$Correl(X,Y) = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}}$$

where x is the measured absorbance and y is the standard concentration.

12.3.3 If the calibration curve does not meet criteria, and is redigestion, then any samples digested along with that calibration curve must also be redigested.

12.4 Initial Calibration Verification Standard (ICV). During each analysis, a standard from a different source than the calibration standard must be analyzed. This is analyzed at the beginning of the run. For this method, the ICV must be within 10 percent of the true value. When the measurements exceed these control limits, the analysis shall be terminated, and the problem corrected before proceeding. All reported results must be bracketed by compliant QC.

12.5 Continuing Calibration Verification. Analyze the continuing calibration verification solution and the continuing calibration blank at the beginning of each run and after every tenth sample and at the end of the sample run. If the CCV solution is not within 20 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) Relative Error(%RE) must be 20% for CCV (See section 12.12 for calculation)

12.6 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

12.7 CRA (Low) Check or LLQC (Lower Limit of Quantitation Check). For all runs, a low check at the level of the reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. A criterion +/- 30% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check. Relative Error (%RE) must be 30% for CRA (See section 12.12 for calculation)

12.7.1 A number of clients have specific program requirements for frequency and recovery ranges on CRA checks. Check with the metals supervisor for additional information on these programs.

12.7.2 If the CRA is biased high and there is no mercury found in the samples, then the sample results may be reported for mercury. If the CRA is biased high and there is mercury found in the samples, then the samples with Hg at levels ranging from the CCV to the high standard may be reported. Samples with levels of mercury between the CRA and the CCV standard may be biased high and cannot be reported.

12.8 Method Blank. The laboratory must digest and analyze a method blank with each batch of 20 samples. A minimum of one method blank is required for every 20 samples. A sample batch is defined as a maximum of 20 field samples in a preparation batch over a time period of 24 hours. A matrix spike/matrix spike duplicate, matrix spikes and/or duplicate is required every 20 samples. The method blank must contain mercury at less than ½ the reporting limit (< 1/2 RL). If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit. (Note: Not all program codes allow this. Verify prior to proceeding.)

12.9 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control or spike blank is required for every 20 samples. Note: For soils, if a lab control is not available, a spike blank can be used. For a running batch, a new lab control sample is required for each different digestion day. The laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120%. In house lab control limits may also be generated to support these default limits. For solid lab controls, the elements must be within the range of "QC Performance Acceptance Limits" given by the lab control supplier. If the lab control is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

12.10 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. The laboratory must assess the matrix spike recovery against control limits of 80 to 120. (In house control limits are generated annually for information purposes only.). If a matrix spike is out of control, then the sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. An analyte spike is added to a portion of a prepared sample, or its dilution, and must be recovered to within 80-120% of the known value. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result)/Amount Spiked) x 100 = matrix spike recovery

12.11 Matrix Spike Duplicate or Matrix Duplicate. The laboratory must digest a matrix spike duplicate or a duplicate sample for a minimum of 1 in 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. The relative percent difference (rpd) between the matrix spike duplicate and the matrix spike or between the duplicate and the original sample must be assessed. The rpds are calculated as shown below and must be assessed against a limit of 20% RPD. (In house control limits are generated annually for information purposes only.). If a matrix spike duplicate or a duplicate is out of control, then the results must be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

$$\frac{\text{(Sample Result - Duplicate Result) x 100}}{\text{(Sample Result + Duplicate Result) x 0.5}} = \text{\% RPD}$$

or

$$\frac{\text{(|MS Result - MSD Result|) x 100}}{\text{(MS Result + MSD Result)/2}} = \text{MSD RPD}$$

12.12 Measurement the Relative Error (%RE):
Relative error is calculated using the following equation:

$$\text{\% Relative Error} = \frac{x'i - xi}{xi} \times 100$$

xi = True value for the standard
x'i = Measured concentration of the standard
The Relative Error for the CCV is 20% and for LLCCV (CRI/CRA) is 30%

13.0 DOCUMENTATION REQUIREMENTS

Refer to the laboratory Quality Assurance Manual for additional documentation requirements.

13.1 Sample Worksheets. Digestion data sheets for the Hg soil samples must show all digestion information including the sample ID's, sample weights, bottle numbers, type of heating used, start times, end times, and pressure or temperature, as appropriate for all digestions. All sample information must be clearly entered on these sheets. In addition, any unusual characteristics of the samples or the digestion procedure must be noted in the comments sections. Make sure also that all dilutions are clearly documented.

13.2 Make sure to record thermometer ID, correction factor, and corrected and uncorrected temperatures for all temperature measurements.

13.3 Standards and Reagents. All stocks and reagents must be recorded in the reagent log book. All standards must be recorded on the digestion log with the samples.

13.4 Any run comments must be written on the raw data for the analysis and on the run log in the LIMS.

13.5 Annual bottle calibration verifications must be documented in the Mercury Bottle calibration log.

14.0 DATA REVIEW AND REPORTING

14.1 All samples must be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for making sure that the raw data is fully documented, and it is loaded into the LIMS system. They are responsible for submitting samples for redigestion and reanalysis, when appropriate.

14.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The reviewer is also responsible for making sure that the QC calculations are done correctly and that appropriate flags are added.

14.3 After the reviewer completes their review, the data is released for client access in the LIMS. The raw data and the run log are submitted to the area manager. The manager periodically does an additional review on data for technical completeness. Any hardcopy raw data is transferred to the report generation department for scanning and storage. Instrument data is transferred electronically.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non-hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes.

15.2.3 Chlorinated organic solvents.

15.2.4 Non-chlorinated organic solvents.

15.2.5 Hazardous solid wastes.

15.2.6 Non-hazardous aqueous wastes.

16.0 ADDITIONAL REFERENCES

16.1 Leeman Hydra AA instrument manual.

16.2 Leeman Hydra AA II instrument manual.

Current Version Revision Information

Changes / Edits made (this should include added or deleted information within a sentence or paragraph only):

Section / Subsection	Detailed description of what was revised
12.2	MDL reference added
12.10	Added post digestion spike procedure

Sections or Subsections deleted:

Section / Subsection	Reason section or subsection was removed

Sections or Subsections added:

Section / Subsection	Reason section or subsection was added

History of Revisions

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15	8/20/2019	Wei Zhou
16	1/22/20	Wei Zhou
17	2/14/22	Olga Azarian

END OF DOCUMENT

STANDARD OPERATING PROCEDURE L-3F: ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIENZOFURANS (PCDD/Fs)

Standard Operating Procedure for the Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans (PCDD/Fs)

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SGS North America Inc.
5500 Business Drive
Wilmington, North Carolina 28405

Approved by:

Paul Walton, Last Revised by — Date: 2/11/22

Greg Dickinson, Technical Director — Date: 02-11-2022

Jeannie Milholland, Quality Assurance Director — Date: 2/11/2022

(Official copies of final documents will contain all three signatures.)

TABLE OF CONTENTS

Revision History

- The following revisions were made on February 11, 2022:
  - WV requirements removed from SOP as we are no longer accredited by WV
  - Pagination formatting corrected
- The SOP was reviewed on 8/31/2021
- The following revisions were made on January 8, 2021:
  - Section 13.3.2; Added a note on method improvements
  - Section 13.4; new section on narration of method improvements
  - Section 13.5.7; added reference to removal or replacement of ICAL points
  - Section 17.6; added reference to confirm SOP
  - Section 17.7; added reference to SGS-ILM Quality Manual
  - Section 18.0; new section listing method improvements
- SOP has been reviewed by Amber Nunalee, on 9/8/2020 and no revisions are necessary
- The following revisions were made on June 1, 2020:
  - Section 5.3; added section on holding times and storage requirements
  - Section 7.3.1; referenced SOP DC_508
  - Section 12.3; reference EPA 1613B
  - Section 13.4.2 & 13.4.3; added S/N requirements
  - Section 13.6.7 & 13.7; added sections
  - Section 15.0; table 7- updated table
  - Section 17.6; added reference
- The following revisions were made on February 5, 2020:
  - Section 1.1, 1.3, 1.6, 10.1.2, 12.10; Changed wording for better understanding
  - Section 6.2; Updated instrument
  - Section 7.1, 7.2; Updated reagents and solvent list
  - Section 9.0, 9.1; Added clean-up in section and SOP reference
  - Section 16.0; updated definition list
  - Section 17.0; Added SOP references for DC_441 and DC_365
- The following revisions were made on April 9, 2018:
- For changes made on or before April 9, 2018, see previous versions of SOP

1.0 Scope and Application

1.1 This SOP covers all analyses of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in all matrices. It incorporates, standardizes, and expands on EPA Methods 8290, 1613, 23, 0023A, TO-9A. SGS provides two options for quality control. SGS offers an enhanced quality control option based on a document dubbed internally Method 8223, upon client request. We also use the traditional QC model, as detailed in published EPA methods unless otherwise requested by client. A unified approach is taken to all analyses using these methods, and procedural details vary only according to matrix**.**

1.2 The provisions of this SOP may be overridden by client request and represent the default instructions to follow. In all cases, SGS strives to provide advice to clients in the preparation of such documents. Such client-specific needs will be communicated to the laboratories through the use of special instructions entries in the LIMS or by use of paperwork developed specifically for the project in question.

1.3 This SOP is applicable to all matrices.

1.4 The limits of detection (LODs) and limits of quantitation (LOQs) in various matrices are available for analyses of samples for the Department of Defense (DOD).

1.5 This method is intended to apply to all PCDD/F extractions performed at SGS, regardless of matrix. It is consistent with the Final Rule on the Methods Innovation Rule 40 CFR Parts 63, 268, et al.; June 14th, 2005; pp. 34538-34592. The lists of target analytes can be found in Table 3.

1.6 Our Statement of Performance thoroughly documents the method's performance and includes the results of proficiency testing studies batch QC and instrument QC.

2.0 Summary of Method

2.1 This SOP details how to analyze and report samples by the methods referenced in Section 1. HRGC/HRMS is used to detect and quantify PCDD/Fs. Samples arrive at the Mass Spec lab having been extracted and fractionated. Analyses are grouped into 12-hour runs, which include analyses of samples and standards mixtures. Upon completion of the run, the analyst reviews the data associated with both standards and samples in order to confirm the validity of the run and to determine any potential need for re-analysis or re-extraction. The analyst generates quantitation reports and chromatograms using Ultra Trace Pro software. These reports are used to generate forms that summarize the results of the analysis.

3.0 Safety Precautions

3.1 Gloves must be worn when handling samples, standards, and reagents.

3.2 Safety glasses must be worn at all times when working in the laboratory.

3.3 A lab coat must be worn while dealing with samples, standards, and reagents.

3.4 In the interest of safety and pollution prevention, all spills must be cleaned up immediately.

4.0 Interferences and Preventive Measures

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. The use of high purity reagents and solvents helps minimize interference problems. All new materials used in the analysis shall be demonstrated to be free from interferences by running an initial reagent blank. Interferences co-extracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the analytes. The elimination of interferences is essential. Cleanup steps are used to reduce or eliminate these interferences and thereby permit reliable determination of the analyte as close as possible to the specified sensitivity.

5.0 Sample Collection, Preservation, Storage and Pollution Prevention

5.1 Sample holding times and other storage requirements by method for solid samples are as follows:

5.1.1 Method 1613: holding time is up to 1 year, store in the dark at 0-4°C until extracted then frozen (-10°C) until disposal

5.1.2 Method 8290: holding time is 30 days from collection to extraction, store in the dark at ≤ 6°C

5.1.3 CARB 429 (air sample XAD and filters): holding time for extraction is within 21 days from collection, store at 4°C

5.2 Sample holding times and other storage requirements by method for tissue samples are as follows:

5.2.1 Method 1613: holding time is up to 1 year, store in freezer at -10°C

5.2.2 Method 8290: holding time is 30 days from collection to extraction, store in freezer at -10°C

5.3 Sample holding times and other storage requirements by method for aqueous samples are as follows:

5.3.1 Method 1613: hold time is up to one year from collection to extraction, store in the dark at 0 – 4 °C until extracted, then frozen (-10°C) until disposal. NPDES permit compliance samples must have a pH <9.

5.3.2 Method 8290: hold time is 30 days from collection to extraction, store in the dark ≤ 6°C.

5.3.3 Refer to SOP DC_441 section 9.3 for residual chlorine requirement.

5.4 Extracts should be analyzed within 45 days for PCDDs and PCDFs.

5.5 Note: for PCDD/F analysis, exceedance of the stated extraction and analysis time frames does not necessarily indicate inferior data quality. Stability of these compounds in the received matrix, if in question and deemed critical to generation of valid results, should ideally be accessed through stability studies conducted over the time period necessary to establish valid data. SGS freezes non-tissue samples only upon client request and strongly recommends against the practice.

5.6 Minimize use of solvents as much as possible.

5.7 Waste is disposed of in appropriate waste containers in accordance with the local, state and federal regulations. No sample or reagent is ever disposed of down a drain or in the trash. See document MI_278 for waste disposal, pollution prevention and spill cleanup.

6.0 Equipment and Supplies

6.1 Autosampler

6.2 PC with UTP

6.3 Neslab Water Coolers or equivalent

6.4 Waters/Micromass Autospec Magnetic Sector High-Resolution Mass Spectrometer

6.5 Pipet, disposable, serological, 10mL

6.6 DB-5MS (Agilent J&W GC Column p/n 122-5562 or equivalent)

7.0 Standards and Reagents

7.1 Reagents

7.1.1 PFK; perfluorokerosene

7.2 Solvents

7.2.1 Methylene Chloride. Highest available purity.

7.2.2 Tetradecane. Highest available purity.

7.2.3 Toluene, Highest available purity.

7.3 Standards

7.3.1 Analytical standards (Cambridge Isotope Laboratory, Woodburn, MA, Wellington Laboratories, or other qualified vendor). See Table 3 for details on composition of standard solutions. See SOP DC_508 for standard management and preparation.

7.3.2 Cambridge Isotope laboratory standards are used as the primary source. The ICAL uses this source.

7.3.3 Wellington Laboratories standards are the second source and are used for all Lab QC and for the BCS3.

8.0 Calibration

8.1 Initial HRMS Calibration (ICAL)

8.1.1 The ICAL establishes reference relative response factors for continuing calibration and, secondarily, demonstrates linear response over a given detector response range at a single point in time. The components of the ICAL solutions are summarized in Table 3.

8.1.1.1 Supply the reference compound -- e.g., perfluorokerosene (PFK) -- to the HRMS system. The reference compound provides the required lock masses and is used for tuning the mass spectrometer.

8.1.1.2 The lock-mass ion from the reference compound depends on the masses of the ions monitored within each m/z descriptor. Monitor each m/z descriptor in succession as a function of GC retention time to ensure that all PCDD/PCDFs are detected.

8.1.1.3 Monitor an appropriate QC Check Ion for each mass descriptor and use it to monitor system performance throughout the respective retention time windows. Evaluate specific situations where "deflections" are detected on a case-by-case basis with emphasis on the impact on the reliability of the analyte data.

8.1.1.4 Inject all initial calibration solutions in a single analytical sequence. Due to special customer requirements, you may inject a truncated ICAL (e.g., dropping the highest and lowest calibration point) in addition to the full ICAL. In either case, proceed with processing and reporting of the ICAL in the same manner. The same acceptance criteria will apply regardless of the number of injections.

8.2 Initial Calibration Verification (ICV)

8.2.1 Analyze after the ICAL prior to analyzing any samples

8.2.2 The ICV is a second source from the ICAL

8.2.3 For unlabeled standards the RF must be within ± 20% D of RF established in the ICAL

8.2.4 The ICV concentration is at the midpoint of the calibration range. (CS3)

8.2.5 For labeled standards the RF must be within ±30% D of RF established in the ICAL.

8.2.6 No samples will be analyzed until ICAL has been verified with the ICV.

8.3 Continuing Calibration

8.3.1 Continuing calibration demonstrates the stability of the HRMS system in addition to the BCS_3 system – provides a means to correct systematic errors.

8.3.2 Unless the client specified the use of the BCS3(all air samples), use an OPR,

8.3.2.1 Start a (maximum) 12-hour sequence with a CS3 or BCS_3 and close with a BCS3 or CS3 (if required per method).

8.3.2.2 Using the same operating conditions used for the ICAL, inject 1 µL of the control spike (CS3 or BCS_3) to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, establish the PCDD/PCDF retention time windows and isomer-specificities, and to validate the standards used and the spiking technique.

8.3.2.3 For air samples returning with multiple trap preparations for a given project, select the BCS_3s representing the largest number of traps and use it for continuing calibration. However, use the ICAL RRFs to process all the samples associated with such a project if you determine that the data reliability is not adversely affected. The laboratory will make every effort to communicate to the stack-sampling firm the significance of the trap preparation considering the QA/QC.

9.0 Sample Preparation and clean-up

9.1 Please see SGS SOP Extraction of Various Matrices DC_441 for sample preparation and SGS SOP Fractionation DC_365 for sample clean up.

10.0 Analytical Procedure

10.1 Establish the necessary operating conditions. The following GC operating conditions are for guidance, and adjustments may be required.

10.1.1 The reference compound provides the required lock masses. Use it for tuning the mass spectrometer (see instrument manuals for details on tuning).

10.1.2 The instrument is tuned to the minimum required resolving power of 10,000 (10 percent valley or 5 percent crossing over) at an appropriate reference signal close to the mass-to-charge ratios of interest. Document the resolving power using the mass peak profile display. Obtain at the beginning and the end of each analytical sequence of 12 hours or less.

10.1.3 The QC Check Ion from the reference compound is dependent on the masses of the ions monitored within each descriptor. Each descriptor will be monitored in succession as a function of GC retention time to ensure that all PCDD/PCDFs are detected.

10.1.4 Set up the analytical run following this sequential injection pattern: CPSM (as necessary), BCS_3 (or CS_3, if an OPR was required), OPR (if required), Solvent Blank, Method Blank, Samples, BCS_3 or CS3 (if required).

10.1.5 If the analytical sequence will exceed 12 hours, ensure an ending calibration injection occurs before 12 hours from the sequence start expires.

10.1.6 Use the column performance standard mix (CPSM) to verify retention time windows and the retention times of individual congeners and co-eluting clusters of congeners.

10.2 Qualitative Determination

10.2.1 Identify a chromatographic peak as a PCDD or PCDF (either a native or a labeled compound) using the following criteria:

10.2.1.1 The signals for the two exact m/zs being monitored must be present and must maximize within ±2 seconds of one another.

10.2.1.2 The signal-to-noise ratio (S/N) of each of the two native exact m/zs must be greater than or equal to 2.5:1 for a sample extract, and greater than or equal to 10:1 for a calibration standard. The S/N for labeled compounds must always be at least 10:1. If an interference diminishes the signal for one native m/z to the point that it is not detected and all other criteria are met, the peak may be considered a PCDD/F and quantified using the one m/z available. The chromatographic peak will be annotated to indicate that this choice was made.

10.2.1.3 The ratio of ion abundances for the two m/zs must lie within the limits established for the homologous series. If the ratio for a native compound lies outside these limits while all other criteria are met, the peak is still considered to be a PCDD/F but will be reported as an Estimated Maximum Possible Concentration (EMPC).

10.2.1.4 In the absence of inferences, the absolute retention times for all congeners must be within 2 seconds of those obtained in the CPSM.

10.2.1.5 The absolute retention times for native (only) 2,3,7,8-substituted congeners must be within 0 to +2 seconds of the isotopically-labeled standard.

10.3 Quantitative Determination

10.3.1 For peaks that meet the criteria listed above, quantitate the PCDD and PCDF peaks from the mean BCS_3 (or ICAL when using CS_3) RRFs relative to the appropriate Extraction Standard established, unless they fail to meet acceptance criteria (see acceptance criteria below) and the appropriate corrective action involves using other RRFs. For peaks that meet all the criteria above except the ratio of ion abundances, report the peak as an EMPC.

10.3.2 For circumstances in which an EMPC cannot be reported, report any out-of-ratio peaks meeting all other identification criteria as a non-detect using the peak concentration as the detection limit.

10.3.3 Report results in picogram per gram, picogram per liter or picogram per sample.

10.3.4 A correction for the contribution at m/z 322 from the CS ($^{37}Cl_4$-2,3,7,8-TCDD) is applied automatically in our calculations. This correction subtracts 0.06% of the CS peak area from the m/z 322 ion for 2,3,7,8-TCDD (only).

10.3.5 Calculate a sample- and analyte-specific estimated detection limit for each congener.

10.3.6 Report the data.

10.4 External Dilutions

10.4.1 If a target compound is above the calibration range, a percentage of the sample that would be within the calibration range is removed, and diluted into the standard spiking profile to allow the compound to be quantitated within that calibration range. The result is then multiplied by the percentage removed to calculate the original sample concentration.

10.4.2 Determine the necessary dilution (ex. E flagged compound is between 2 and 10 times the high level in the calibration range, chose an External 10 dilution)

10.4.3 Assuming an External 10 dilution is to be performed. 10 percent of the remaining original sample extract is re-vialed in the new external dilution vial.

10.4.4 Account for any remaining standard in the sample (ex. 10 percent of the original sample will contain 10 percent of the original standard)

10.4.5 Add the extraction and injection standard, at their original spike volumes, minus the percentage of remaining standard to the new external dilution vial containing 10% of the original sample. (ex. For the same 10x dilution, assuming the extraction and injection standard were spiked at 10uL originally, 9uL of each would be added to the new external dilution vial.)

10.4.6 It is not our standard procedure to perform external dilutions and they will only be performed when specifically requested by the client

11.0 Details of Calculations

11.1 Calculate the concentrations for the PCDD or PCDF compounds using the formula:

$$C_X = \frac{A_X \times Q_{is}}{A_{is} \times W \times RRF}$$

Where

C_X = Concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within an homologous series) in pg/g.

A_X^{Is} = Sum of the integrated ion abundances of the quantitation ions for unlabeled PCDD/PCDFs.

Q_{is} = Quantity, in pg, of the Extraction Standard added to the sample before extraction.

A_{is} Sum of the integrated ion abundances of the quantitation ion (See Table 6 of EPA Method 8290) for the labeled Extraction Standards.

W = Weight of the sample (solid-corrected for percent solid as required or liquid).

RRF = Calculated relative response factor for the analyte.

11.2 The detection limits for each absent PCDD/PCDF can be calculated using the following formula:

$$DL = \frac{2.5 \times H_N \times Q_{is}}{H_{IS} \times W \times RRF}$$

DL = Estimated detection limit for PCDD/PCDFs.

H_N = Noise height (peak to peak).

H_{IS} = Peak height of the Extraction Standard.

Q_{is} = Quantity, in pg, of the Extraction Standard added to the sample before extraction.

W = Weight of the sample (solid or liquid).

RRF = Calculated relative response factor for the analyte.

11.3 Percent solids:

$$\%solids = \frac{(weight\ of\ residue + weight\ of\ boat) - weight\ of\ boat}{(weight\ of\ sample + weight\ of\ boat) - weight\ of\ boat} \times 100$$

11.4 Lipid content:

$$\%Lipids = \frac{Weight\ of\ \mathrm{Re}\ sidue\,(g)}{Weight\ of\ Wet\ Sample\,(g)} \times 100$$

11.5 EMPC Calculations

11.5.1 Where the isotope ratio of the two peaks (i.e. from the areas of the peaks of the primary and secondary ions; Ra = A_{pri} / A_{sec}) is within the acceptable range, the peak response used for concentration or recovery calculations is simply the sum of the two areas. For the EMPC calculation, it is assumed that one of the two peaks has an interference that has increased its area, and hence led to the ratio error. If the measured ratio is greater than the upper limit, the primary ion is assumed to be at fault and hence the peak response is determined from the secondary ion's area summed with a calculated (pseudo) area for the primary ion based on the secondary area and the theoretical isotope ratio; if the measured ratio is less than the lower limit, the opposite applies.

11.6 Relative Standard Error (RSE)

$$RSE = 100\ x\ \sqrt{\sum_{i=1}^{n} \left[\frac{x'_i - x_i}{x_i}\right]^2 \Big/ (n-p)}$$

x_i = True amount of analyte in calibration level
x'_i = Measured amount of analyte in calibration level i
p = Number of terms in fitting equation
(Use 1 for p as this method requires average RSD calculation for initial calibration curve)

12.0 Quality Control Requirements

12.1 A method detection limit (MDL) study determination is required by this method. This study need only be performed once unless changes are made to an instrument that would be expected to alter its detection limits.

12.2 LOD and LOQ verification studies are required quarterly for DoD. The LOQ is equivalent to the LLOQ. The verifications are performed on clean control material. The verifications are spiked at the LLOQ and are prepared, extracted and analyzed in the same manner as samples or any other QC would be. Please see section 9.0 for sample preparation reference. LLOQ acceptance criteria is 60% - 140%.

12.3 Initial Demonstration of Proficiency – New staff are required to demonstrate initial proficiency by generating data of acceptable accuracy and precision for target analytes in a clean matrix. Initial precision and

recovery criteria must be met for EPA 1613B.

12.4 (Laboratory) Method Blank (LMB): The method blank enables monitoring of lab processes to ensure that the laboratory introduces no target analytes or specific interferences during routine operations and to quantify them should they be found. The laboratory analyzes the method blank using the same procedures followed for the rest of the analytical batch.

12.4.1 Include a method blank with every analytical batch or 20 field samples (whichever is less) per matrix type.

12.4.2 The extraction standard recoveries of the method blank indicate extraction efficiency performance for a quality control sample.

12.4.3 Select the weight or volume of method blank matrix to approximately match that used in the samples, leaning towards the largest amount used in any sample.

12.4.4 For air samples, prepare the LMB at the same time as the air traps/PUFs and spike them with the same amount of sampling standard that is spiked into the traps/PUFs. When preparing a large number of traps/PUFs (e.g., 10+), consider preparing more than one LMB. Refrigerate these LMBs until the traps/PUFs return to the laboratory for analysis.

12.5 On-Going Precision & Accuracy (OPR = Laboratory Control Spike): The OPR assesses extraction efficiency performance for a quality control sample and, native analyte recovery.

12.5.1 Use a known amount of native PCDD/Fs for spiking.

12.5.2 Analyze an OPR with every analytical batch or 20 field samples (whichever is less) per matrix type.

12.5.3 Apply the same guidelines that apply to the method blank for choosing the matrix -- and the weight or volume thereof -- to make the same choices for the OPR.

12.5.4 Do not prepare a batch control spike (BCS_3) when an OPR is used.

12.6 Matrix Spike (MS/MSD): SGS considers MS/MSD samples to be billable samples.

12.6.1 Use known amount of native PCDD/Fs for spiking.

12.6.2 Unless specified by the customer, choose the sample to use for an MS/MSD at random from those samples being analyzed in the batch.

12.6.3 Analyze MS/MSDs at a frequency specified by the customer.

12.6.4 Apart from spiking native PCDD/Fs into the sample, analyze the sample in the same manner as all other samples.

12.7 Laboratory Duplicate Samples: Laboratory duplicate samples are two separate subsamples taken from a well-homogenized sample.

12.7.1 Analyze duplicate samples independently to assess laboratory precision.

12.7.2 Analyze the duplicate samples in the same manner as all other samples in the batch.

12.8 Data outside of QC limits referenced in section 13 may be addressed by one or more of the following options:

12.8.1 Re-preparation and re-analysis of sample

12.8.2 Client notification

12.8.3 Discussion and qualification of data by case narrative

12.8.4 Re-sampling and reanalysis (client decision)

12.9 Data outside of QC limits referenced in section 13 may be reported if directed by the client. It must be qualified by a case narrative detailing the QC problems with advice on the usability of the data.

12.10 Software audit trails are always in use.

13.0 Data Review and Reporting Requirements

13.1 This method is performance-based (see Federal Register: October 6, 1997 (Volume 62, Number 193), Page 52098-52100). Thus, the acceptance criteria (i.e., target objective guidelines) are ideally determined by the project needs through a process of negotiation with the client and any other ultimate end-user of the data. These criteria should ensure that the performance of the method is adequate for the purposes for which it is intended. The criteria will likely not resemble those used in the past. If negotiations with the client yield no criteria, statistically determined criteria or the default criteria below may be used.

13.2 A failure to meet all criteria does not necessarily result in a particular course of action (see section 13.11 for details). Data assessment includes

a thinking process that assesses the impact of a particular analytical problem and develops the most appropriate response, in the context of the data user's needs. Data that do not meet all criteria for all target analytes may still be reported with relevant qualifiers and notes in the case narrative, if appropriate.

13.3 GC/MS Analysis Performance Acceptance Criteria

13.3.1 The mass resolving power (10% valley or 5% crossing over definition) must be at least 10,000, over the full mass range used.

13.3.2 The valley between 2,3,7,8-TCDD and its close eluters must not exceed 25% and the valley between 2,3,7,8-TCDF and its close eluter must not exceed 40% . When a valley fails all samples with positive detection for a TCDD or TCDF isomer must be reinjected.

NOTE: Improved procedure uses separation criteria of 40% from a DB-5MS column. If prescriptive methodology is required or requested, SGS will follow the procedure outlined in SOP DC_90.7.

13.4 Any improvements to the method will be detailed in the case narrative of the level 2 and/or level 4 reports. Also see notes at end of this document.

13.5 ICAL Acceptance Criteria

13.5.1 The percent RSD for the mean response factors must be within method limits.

13.5.2 Method 1613B: ≤ 20% for the native standards and ≤ 35% for extraction standards. All S/N must be at least 10:1 for CS1 - CS6.

13.5.3 Method 8290A: 20% for the native standards and ≤ 30% for extraction standards. DoD requirements are ≤20% for both native and extraction standards. All S/N must be at least 10:1 for CS1 – CS-6.

13.5.4 Ion-abundance ratios must come to ±15% of the theoretical ratios.

13.5.5 Corrective action may be required if any %RSD does not meet criteria, including but not limited to instrument operating conditions, reanalysis of a single ICAL point and/or elimination of an ICAL

point.

13.5.6 To determine calibration function acceptability of the initial calibration, calculate Relative Standard Error (RSE). See section 13.4 for acceptance criteria for target analytes and ES standards.

In the rare circumstance that a calibration point is dropped please the MI_15, SGS Quality Manual for the procedure for the removal or replacement of calibration standards.

13.6 Batch Control Spike (BCS_3) Acceptance Criteria

13.6.1 In order to use the front- and back-end BCS_3s averaged RRFs to process the samples, the individual front- and back-end chromatographic peaks need to meet a number of requirements (independent verification, RPD, and PD or bias).

13.6.1.1 The first and last PCDD/F eluters are verified to be within the eight homologue retention time windows.

13.6.1.2 The signal to noise ratio (S/N) exceeds 10:1 for all compounds spiked and monitored,

13.6.1.3 The ion abundance ratio measurements are within ± 15 percent of the theoretical ratio,

13.6.1.4 The first and last eluters in each homolog group are verified to be within the eight homologue retention time windows.

13.6.1.5 The RRFs Percent Differences (PDs) relative to the ICAL should remain within established criteria. These criteria may be established statistically or on a per-project basis, according to the data user's needs. If no criteria are established through negotiation with the client or statistically, the following criteria are recommended.

13.6.1.5.1 ±20% for the unlabeled compounds

13.6.1.5.2 ±30% for the labeled ES compounds

13.6.1.5.3 ±20% for air's labeled SS, and

13.6.1.5.4 ±30% for non air's labeled CS compounds

13.6.1.6 Other requirements are shown in Tables 2, 3,4 and 5

13.6.2 The RRFs Relative Percent Differences (RPDs) between the front and back BCS_3 injections should

meet the following criteria established on 8290A.

13.6.2.1 ±20% for the unlabeled compounds

13.6.2.2 ±30% for the labeled compounds

13.7 CS_3 Acceptance Criteria

13.7.1 CS3 analyzed at the beginning and the end of each 12-hr operation period for method 8290 and all DoD work. CS3 analyzed at the beginning of each 12-hr operation period for method 1613.

13.7.2 The signal to noise ratio (S/N) exceeds 10:1 for all compounds spiked and monitored,

13.7.3 The ion abundance ratio measurements are within ± 15 percent of the theoretical ratio for all the compounds spiked and monitored.

13.7.4 The RRFs and any PD's must be within the criteria established in Method 1613B or Method 8290A.

13.7.5 Corrective action may be required if any %D does not meet criteria, including but not limited to instrument operating conditions or reanalysis of the CS3

13.7.6 For DoD projects CS3 criteria for unlabeled standards is ±20% D of the RF in the ICAL; for labeled standards RF within ±30% D of RF in the ICAL.

13.7.7 See section 10.1.2 of this SOP for resolution check requirements.

13.8 Criteria for labeled compounds

13.8.1 EPA 1613B – see table 5 of this SOP

13.8.2 EPA 8290A – 40 – 130%

13.9 Method Blank (LMB) Acceptance Criteria

13.9.1 Ideally, the LMB analysis will return only non-detects. Occasionally, an amount of OCDD just above the detection limit may be found.

13.9.2 Any hits in the LMB must be less than the lower limit of quantitation (LLOQ) for the analyte or less than the level specified in the approved QAPP or other planning document.

13.10 OPR Acceptance Criteria

13.10.1 The acceptance criteria for the OPR depend on the scope of target analytes, as detailed below

13.10.2 If only TCDD and/or TCDF is(are) analyzed, the acceptance criteria are given in Table 5.

13.10.3 The acceptance criteria are given in Table 4 if the analysis includes the full list of 17 2,3,7,8-PCDD/F containing analytes.

13.11 MS/MSD Acceptance Criteria

13.11.1 The laboratory considers MS/MSDs in which the recovery of the spike is within the range 80-120% acceptable, provided the matrix used does not contain PCDD/Fs at levels impairing the measurements.

13.11.2 If a customer requires relative percent difference criteria for acceptance of duplicate matrix spikes, RPDs between MS/MSD samples should be ≤20%, provided the matrix used does not contain PCDD/Fs at levels impairing the measurements and is not so non-homogenous as to make representative sub-sampling practically impossible.

13.12 Laboratory Duplicate Acceptance Criteria

13.12.1 If a customer requires relative percent difference criteria for acceptance of duplicate samples, RPDs between the duplicate sample should be ≤20%, provided the matrix used does not contain PCDD/Fs at levels impairing the measurements and is not so non-homogenous as to make representative sub-sampling practically impossible.

13.13 CORRECTIVE ACTIONS

13.13.1 Corrective actions are taken whenever needed, regardless of acceptance criteria. It is not always the case that data meeting all acceptance criteria should be accepted nor that data not meeting all criteria should be rejected. The end user data quality needs guide the determination of whether and what corrective action may be required in any given situation.

13.14 See Data review SOP (MI_141) for additional information.

14.0 Preventative Maintenance

14.1 Instrument Maintenance

14.1.1 All instrumentation is serviced by an external instrumentation service vendor or by SGS personnel trained in preventative maintenance. Preventative maintenance is performed at scheduled intervals on all equipment. All instrument preventative maintenance is performed according the manufacturer's recommended procedures. All maintenance shall be documented in the maintenance log.

14.1.2 Corrective maintenance is deemed necessary when the analytical system cannot meet calibration, or other protocol specific QC criteria. Corrective maintenance may include, but is not limited to, injector liner replacement, injector seal replacement, clipping of a small portion of the column from the injector side of column, decontamination of the system, source cleaning, column replacement, or filament replacement. All corrective maintenance is performed according the manufacturer's recommended procedures by trained personnel. All corrective maintenance shall be documented in the maintenance log.

15.0 Tables and Figures

Table 1

Column Flow Rate:	1.3 mL/min
Injector temperature:	280 °C
Interface temperature:	280 °C
Initial time:	2 minutes at 190°C
Temperature program:	190 to 220 ° C, at 5 °C/min
	220 °C for 14.5 minutes
	220 to 290 ° C, at 5 °C/min
	290 °C for 1 minute
	290 to 305 ° C, at 14 °C/min
	305°C for 10 min

Table 2: Theoretical Ion Abundance Ratios and Control Limits for PCDDs and PCDFs. (a) Used for 13C-HxCDF (IS) only. (b)Used for 13C-HpCDF (IS) only

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	$\frac{M}{M+2}$	0.77	0.65	0.89
5	$\frac{M+2}{M+4}$	1.55	1.32	1.78
6	$\frac{M+2}{M+4}$	1.24	1.05	1.43
6[a]	$\frac{M}{M+2}$	0.51	0.43	0.59
7[b]	$\frac{M}{M+2}$	0.44	0.37	0.51
7	$\frac{M+2}{M+4}$	1.04	0.88	1.20
8	$\frac{M+2}{M+4}$	0.89	0.76	1.02

Table 3: PRIMARY HIGH-RESOLUTION CONCENTRATION CALIBRATION SOLUTIONS (Regular Initial Calibration)

Concentrations in pg / µL	CS0	CS1	CS2	CS3	CS4	CS5	CS6
Unlabeled Analytes							
2,3,7,8-TCDD	0.25	0.5	2	10	40	200	500
2,3,7,8-TCDF	0.25	0.5	2	10	40	200	500
1,2,3,7,8-PeCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,7,8-PeCDF	1.25	2.5	10	50	200	1000	2500
2,3,4,7,8-PeCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,4,7,8-HxCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,6,7,8-HxCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,7,8,9-HxCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,4,7,8-HxCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,6,7,8-HxCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,7,8,9-HxCDF	1.25	2.5	10	50	200	1000	2500
2,3,4,6,7,8-HxCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,4,6,7,8-HpCDD	1.25	2.5	10	50	200	1000	2500
1,2,3,4,6,7,8-HpCDF	1.25	2.5	10	50	200	1000	2500
1,2,3,4,7,8,9-HpCDF	1.25	2.5	10	50	200	1000	2500
OCDD	2.5	5	20	100	400	2000	5000
OCDF	2.5	5	20	100	400	2000	5000
Extraction Standards							
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200	200	200
$^{13}C_{12}$-OCDF	200	200	200	200	200	200	200
Cleanup/Sampling Standards							
$^{37}Cl_4$-2,3,7,8-TCDD	-	0.5	2	10	40	200	-
$^{13}C_{12}$-1,2,3,4,7-PeCDD	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6-PeCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,9-HxCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,8,9-HpCDF	100	100	100	100	100	100	100
Injection Standards							
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4-TCDF	100	100	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7-HxCDD	100	100	100	100	100	100	100

Table 4: Acceptance Criteria for Method 1613

TABLE 6. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ALL CDDS/CDFS ARE TESTED[1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] 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
2,3,4,6,7,8-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	26–166	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.

Table 5: Additional 1613 Criteria

TABLE 6A. ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS WHEN ONLY TETRA COMPOUNDS ARE TESTED [1]

CDD/CDF	Test Conc. (ng/mL)	IPR [2,3] 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

[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.

TABLE 7. LABELED COMPOUND RECOVERY IN SAMPLES WHEN ALL CDDS/CDFS ARE TESTED

Compound	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] Specification given as concentration in the final extract, assuming a 20-µL volume.

Table 6: Reporting Limits

Analyte	Air RL pg per train	Solid RL pg/g	Tissue RL pg/g (25g)	Tissue RL pg/g (10g)	Water RL pg/L
2,3,7,8-TCDD	10	0.5	0.2	0.5	5
1,2,3,7,8-PeCDD	50	2.5	1	2.5	25
1,2,3,4,7,8-HxCDD	50	2.5	1	2.5	25
1,2,3,6,7,8-HxCDD	50	2.5	1	2.5	25
1,2,3,7,8,9-HxCDD	50	2.5	1	2.5	25
1,2,3,4,6,7,8-HpCDD	50	2.5	1	2.5	25
OCDD	100	5	2	5	50
2,3,7,8-TCDF	10	0.5	0.2	0.5	5
1,2,3,7,8-PeCDF	50	2.5	1	2.5	25
2,3,4,7,8-PeCDF	50	2.5	1	2.5	25
1,2,3,4,7,8-HxCDF	50	2.5	1	2.5	25
1,2,3,6,7,8-HxCDF	50	2.5	1	2.5	25
2,3,4,6,7,8-HxCDF	50	2.5	1	2.5	25
1,2,3,7,8,9-HxCDF	50	2.5	1	2.5	25
1,2,3,4,6,7,8-HpCDF	50	2.5	1	2.5	25
1,2,3,4,7,8,9-HpCDF	50	2.5	1	2.5	25
OCDF	100	5	2	5	50

Table 7: DoD LOD and LOQ Limits

Analyte	Solid MDL pg/g (10g)	Solid LOD pg/g (10g)	Solid LOQ pg/g (10g)	Aqueous MDL pg/L (1L)	Aqueous LOD pg/L (1L)	Aqueous LOQ pg/L (1L)
2,3,7,8-TCDD	0.500	1.0	1.0	2.5	5	10
1,2,3,7,8-PeCDD	1.25	2.5	2.5	10	20	25
1,2,3,4,7,8-HxCDD	1.25	2.5	2.5	10	20	25
1,2,3,6,7,8-HxCDD	2.50	5.0	5.0	10	20	25
1,2,3,7,8,9-HxCDD	1.25	2.5	2.5	10	20	25
1,2,3,4,6,7,8-HpCDD	1.25	2.5	2.5	10	20	25
OCDD	5.0	10	10	25	50	50
2,3,7,8-TCDF	0.250	0.5	1.0	2.5	5	10
1,2,3,7,8-PeCDF	1.25	2.5	2.5	6.25	12.5	25
2,3,4,7,8-PeCDF	2.5	5.0	5.0	10	20	25
1,2,3,4,7,8-HxCDF	1.25	2.5	2.5	10	20	25
1,2,3,6,7,8-HxCDF	1.25	2.5	2.5	6.5	12.5	25
2,3,4,6,7,8-HxCDF	1.25	2.5	2.5	10	20	25
1,2,3,7,8,9-HxCDF	1.25	2.5	2.5	10	20	25
1,2,3,4,6,7,8-HpCDF	1.25	2.5	2.5	25	50	50
1,2,3,4,7,8,9-HpCDF	1.25	2.5	2.5	10	20	25
OCDF	2.5	2.0	5.0	25	50	50

16.0 Definitions

16.1 See Document DC_139 Appendix D for a full list of definitions.

16.2 A_x = target analyte

16.3 BCS_3 = batch control spike

16.4 CPSM = column performance standard mixture

16.5 CS_3 = calibration solution corresponding to the middle point of the initial calibration curve

16.6 CS = cleanup standard

16.7 GC = gas chromatography

16.8 ICAL = initial calibration

16.9 LLOQ = lower limit of quantitation

16.10 LOD = limit of detection

16.11 LOQ = limit of quantitation

16.12 MB = lab method blank

16.13 MDL = method detection limit (not sample-specific)

16.14 MS/MSD = matrix spike/matrix spike duplicate

16.15 OPR = on-going precision & recovery (equivalent to LCS or Lab Control Spike)

16.16 PCDD/F = polychlorinated dibenzo-*p*-dioxin and dibenzofuran

16.17 PD = percent difference

16.18 RPD = relative percent difference

16.19 RRF = relative response factor

16.20 RSD = relative standard deviation

16.21 S/N = signal-to-noise ratio

17.0 References

17.1 SGS document DC_139: Appendix D Definitions.

17.2 SGS document MI_278: Waste Disposal, Pollution Prevention and Spill Cleanup.

17.3 SGS document MI_141: Review of Analytical Data.

17.4 SGS document DC_441: Extraction of Various Matrices

17.5 SGS document DC_365: Fractionation

17.6 SGS document DC_90: 2,3,7,8-TCDF Confirmations

17.7 SGS document MI_15: SGS-ILM Quality Manual

17.8 DC_508: Management and Preparation of Standards

17.9 USEPA Method 8290, Revision 0, Dated September 1994.

17.10 USEPA Method 8290B, Dated July 2002.

17.11 USEPA Method 1613, Revision B, Dated October 1994.

17.12 USEPA Method 8290A; Revision 1, Dated February 2007.

17.13 USEPA Method 8000D; Revision 4, Dated July 2014.

17.14 Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors

18.0 List of Improvements:

18.1 EPA Method 1613B is a performance-based method that allows for improvements, provided acceptance criteria are not altered. SGS-ILM uses a DB-5MS, not DB-5; industry accepts that this column provides adequate resolution. While the method states 25% resolution/valley check for 2,3,7,8-TCDF, that is with a DB-225 or SP-2330 column. There are no specifications for DB-5MS; resolution chromatograms are provided with every project. SGS-ILM maintains a letter of approval from EPA regarding Method 23 to perform analysis using the changes as stated- which is no different than how SGS-ILM analyzes M1613B or SW-846 M8290A (i.e. all dioxin methods are analyzed the same at SGS-ILM).

18.2 Solvent dilution will not alter results unless the failing standard was affected by a quantitative interference which SGS-ILM performs when deemed necessary. A typical external standard dilution could "bias" the results of the labeled standards-bringing the results near 100%, but that is not representative of the extraction efficiencies. If the original ICAL and CS3/calibration verification standard are already acceptable, there is no need to recalibrate and re-analyze the samples. The purpose of isotope dilution is to account for losses incurred during process through the lab. Any anomalies are noted in the case narrative.

18.3 Labeled OCDF was not readily available/accepted when the method was written. Using 13C-OCDF provides a more accurate quantitation as it is directly analogous isotopically to the unlabeled compound; thus, there is no need for a "correction" as indicated in the method. With the addition of a carbon labeled standard for each analogous unlabeled compound (all 17-2,3,7,8-substituted compounds), overall results are more accurate. SGS-ILM provides an ONGOING PRECISION AND RECOVERY (OPR) with every set of samples in order to demonstrate accuracy and precision. The OPR, as well as continuing calibrations (CS3) meet criteria before samples are analyzed. The standard association list for all labeled standards used at SGS-ILM is listed below:

Individual Native Standards	
2378-TCDD	ES 2378-TCDD
12378-PeCDD	ES 12378-PeCDD
123478-HxCDD	ES 123478-HxCDD
123678-HxCDD	ES 123678-HxCDD
123789-HxCDD	ES 123789-HxCDD
1234678-HpCDD	ES 1234678-HpCDD
OCDD	ES OCDD
2378-TCDF	ES 2378-TCDF
12378-PeCDF	ES 12378-PeCDF
23478-PeCDF	ES 23478-PeCDF
123478-HxCDF	ES 123478-HxCDF
123678-HxCDF	ES 123678-HxCDF
234678-HxCDF	ES 234678-HxCDF
123789-HxCDF	ES 123789-HxCDF
1234678-HpCDF	ES 1234678-HpCDF
1234789-HpCDF	ES 1234789-HpCDF
OCDF	ES OCDF

Extraction Standards

ES 2378-TCDD	1234 TCDD 13C12
ES 12378-PeCDD	1234 TCDD 13C12
ES 123478-HxCDD	123467 HxCDD 13C12
ES 123678-HxCDD	123467 HxCDD 13C12
ES 123789-HxCDD	123467 HxCDD 13C12
ES 1234678-HpCDD	123467 HxCDD 13C12
ES OCDD	123467 HxCDD 13C12
ES 2378-TCDF	1234 TCDF 13C12
ES 12378-PeCDF	1234 TCDF 13C12
ES 23478-PeCDF	1234 TCDF 13C12
ES 123478-HxCDF	123467 HxCDD 13C12
ES 123678-HxCDF	123467 HxCDD 13C12
ES 234678-HxCDF	123467 HxCDD 13C12
ES 123789-HxCDF	123467 HxCDD 13C12
ES 1234678-HpCDF	123467 HxCDD 13C12
ES 1234789-HpCDF	123467 HxCDD 13C12
ES OCDF	123467 HxCDD 13C12

Cleanup/Sampling Standards

CS 37Cl-2378-TCDD	1234 TCDD 13C12
CS 12347-PeCDD	1234 TCDD 13C12
CS 12346-PeCDF	1234 TCDF 13C12
CS 123469-HxCDF	123467 HxCDD 13C12
CS 1234689-HpCDF	123467 HxCDD 13C12

Alternate Standards

AS 1368-TCDD	1234 TCDD 13C12
AS 1368-TCDF	1234 TCDF 13C12

Injection Standards

1234 TCDD 13C12
1234 TCDF 13C12
123467 HxCDD 13C12

LAB SUPERVISOR: Natasha Verma

QA OFFICER: Olga A. Gonzalez

EFFECTIVE DATE: 2-14-2022

TITLE: COLD VAPOR ANALYSIS OF MERCURY FOR WATER SAMPLES
REFERENCES: EPA 245.1, revision 3.0 (1994) and SW846 7470A, revision 1 (1994).
REVISED SECTIONS: 12.8.2

1.0SCOPE AND APPLICATION

1.1 This method can be applied for the analysis of mercury for all potable and non-potable water samples. This SOP is based on the May 1994 revision of EPA method 245.1. The reporting limit for mercury water samples based on the procedures outlined in this SOP is 0.0002 mg/l.

1.2 Aqueous wastewater may also be analyzed following method 7470A. The modification to this method is a direct scale-down of the reagents and the use of an automated analyzer.

2.0 SUMMARY

2.1 Cold vapor mercury is a flameless AA procedure based on the absorption of radiation at 253.7 by mercury vapor. Organic mercury compounds are oxidized, and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Results are quantitated by comparison to a daily calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B, Revision 2 and lab SOP EQA075. This value represents the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed, and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD: The calibration check standard is a mid-range calibration standard. The calibration check standard must be run at a frequency of 10 percent or less. The mid-level calibration check standard criteria are either ± 10 percent of the true value.

EXTERNAL CHECK STANDARD: The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory must initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits must also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses).

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits must also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses).

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 per batch. For EPA 245.1 every 10 samples and for SW846 7470A one every 20 samples needed. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results must be flagged with the appropriate footnote.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

METHOD BLANK: The laboratory must digest and analyze a method blank with each set of

samples. A minimum of one method blank is required for every 20 samples. A new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDL): This value represents the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure.

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.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards must be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 After the mercury digestate is reduced to Hg vapor, it must be handled in a closed system or in a hood to prevent inhalation of the toxic vapor. Make sure that the Hg instrument is vented directly to a hood.

6.0 PRESERVATION AND HOLDING TIME

6.1 All water samples must be preserved by acidification with nitric acid to a pH of 2 or lower and stored in a polyethylene or glass container.

6.1.1 If samples cannot be preserved at collection, they may be acid preserved upon receipt in the laboratory. Following acidification, the sample needs to be mixed, held for 24 hours, and then verified to be pH <2 just prior withdrawing an aliquot for processing. If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added, and the sample held for additional 24 hours until verified to be pH <2.

6.2 All samples must be analyzed within 28 days of the date of collection.

7.0 INTERFERENCES

7.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations of sulfide (as sodium sulfide) as high as 20 mg/l do not interfere with mercury recoveries when following this method. High copper concentrations (> 10 mg/l) may also interfere with mercury recoveries.

7.2 Samples that are high in chloride such as seawater, brine, and industrial effluent may require as much as 25 ml of additional permanganate. NOTE: When chloride concentrations are high, hydroxylamine sulfate and stannous sulfate must be used in place of the corresponding chlorides.

7.3 Finally, certain volatile organic materials will also absorb at this wavelength and can interfere. It can be determined if this type of interference is present by doing a preliminary run without reagents.

8.0 APPARATUS

8.1 Three Leeman instruments are available for analysis. **They are Leeman Hydra II** automated analyzers. Refer to the instrument manuals for further details on this instrumentation, including proper venting and safety requirements. Instrument maintenance is outlined below.

8.1.1 Change the sample tubing as needed.

8.1.2 Change the drying tubing as needed.

8.1.3 Clean the exterior of the instrument as needed.

8.1.4 Adjust the Hg lamp as needed. This can be done in the software on both instruments.

8.1.5 Complete any other maintenance required to maintain the instrument in good running

order including, but not limited to, cleaning the cell, changing other tubing, changing the Hg lamp, etc.

8.2 Heating Equipment.

8.2.1 Graphite heating block capable of heating at 95 °C (90-95 °C) for 2 hours.

8.3 Digestion Bottles. Disposable plastic digestion tubes are used with the graphite heating block.

8.3.1 Disposable plastic digestion tubes (65 ml volume) with tops for graphite heating block.

8.4 Class A, to deliver, volumetric cylinders for measuring initial sample volumes and for calibrating glass tubes as outlined above.

8.5 Automatic pipettor bottles. Refer to EQA063 for calibration information.

9.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required. All solutions listed below may be scaled up or down proportionally as needed.

9.1 Sulfuric acid, concentrated.

9.2 Nitric acid, concentrated. This acid must have a low mercury content.

9.3 Dilution acid. To approximately 400 ml of DI water, add 33.4 ml of concentrated sulfuric and 16.6 ml of concentrated nitric. Dilute to a final volume of 1000 ml. This dilution acid is used for making dilutions of digested samples.

9.4 Stannous chloride. Add 25 ml of concentrated hydrochloric acid to approximately 400 ml of DI water. Dilute to 500 ml with DI water and mix well. Add 50 g of stannous chloride dihydrate or 42 g of stannous chloride anhydrous and dissolve. Make sure that this solution is dissolved while in use.

9.4.1 Stannous sulfate may be used in place of stannous chloride.

9.5 Sodium chloride-Hydroxylamine hydrochloride. Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to 2000 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

9.6 Potassium Permanganate, 5 percent solution, w/v. Add 50 g of potassium permanganate to 1000 ml of water and mix well. **Caution** - Potassium permanganate is a strong oxidizing agent. Handle with care.

9.7 Potassium Persulfate, 5 percent solution, w/v. Dissolve 50.0 g of potassium persulfate in 1000 ml of water and mix well. **Caution** - Potassium persulfate is a strong oxidizing agent. Handle with care.

9.8 Mercury standard solutions

9.8.1 10ppm Hg solution. Using a 1.00 ml volumetric pipet or autopipet, add 1.00 ml of 1000 ppm stock to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with water and mix well. This standard may be held for up to 28 days.
1000 ppm Stock can be purchased from the outside vendor such as Ultra and Inorganic ventures, they are light sensitive and must be kept away from the direct light.

9.8.1.1 The 10ppm external source must be made up following the directions in 9.8.1. External stock solution must be from different vendor than calibration source.

9.8.2 **30.0**ppb Hg solution. Using an autopipet, add **0.300** ml of 10 ppm Hg solution to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

9.8.2.1 The 30.0 ppb external source must be made up following the directions in 9.8.2.

9.8.3 **3**ppb Hg solution. Using volumetric pipets or autopipets, add 10.0 ml of **30.0** ppb Hg solution to a 100 ml volumetric flask containing approximately 75 ml of DI water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

10.0 WATER DIGESTION FOR GRAPHITE HEATING BLOCK

Below is a step-by-step procedure for the digestion and analysis of water samples for mercury.

10.1 If necessary, acid rinse disposable digestion tubes with 10% nitric acid and deionized water before use.

10.2 Make up a standard curve consisting of 5 standards and a blank. Suggested concentrations are shown below. All standards are made up to a final volume of **30** ml. Different concentrations may also be used, as long as all of the method requirements are met. Make sure to clearly label each bottle. Calibration standards must be prepared fresh with each digestion batch.

ml of 3 ppb Hg solution	ml of 30 ppb Hg solution	Ml of DI water	Total ug of Hg	ug/L of Hg
0.000	0.000	**30**	0.000	0.000
2.00	0.000	**28.0**	**0.006**	0.20
5.00	0.000	**25.0**	**0.015**	0.50
0.00	1.00	**29.0**	**0.030**	1.00
0.00	2.50	**27.5**	**0.075**	2.50
0.00	5.00	**25.0**	**0.150**	5.00

10.3 Before starting the analysis, check the initial pH of the sample with pH paper and verify that it is < 2. Below is procedure for the checking pH and preservation of metals samples when pH is NOT <2. Add a small amount of concentrated nitric acid (~2mls) dropwise to the sample and mix. Using a pipet tip, place a small amount of sample on a piece of pH paper or pour

directly on the pH paper at the sink to confirm that the pH is <2. Document the date and time of the pH adjustment and the lot number of the nitric acid used for the preservation on the preservation log. Mark the date and time of preservation on the bottle to ensure that the analysis is not started for 24 hours from the time of preservation.

10.3.1 For highly basic or buffered samples, where more than a few drops of acid are required, adjust an aliquot of the sample rather than the whole amount and record the amount of acid used for the adjustment

10.3.2 For each sample, homogenize the sample well and pour out a representative aliquot of the sample into the digestion tube to the 30 ml mark. A smaller volume may be used if there are matrix problems or known high levels of mercury in the sample. Smaller than 5 ml volume must be taken using calibrated auto pipet. Digestion tubes are calibrated at all graduation lines by the vendor, confirm the provided certificate of analysis.

10.3.3 Samples for TCLP matrix or leachate spikes will be received unpreserved from the TCLP leaching area. These must be aliquoted, spiked, and preserved on receipt in the metals prep area. For handling leachate oil samples refer to the SOP EMA228.

10.4 Make up additional quality control samples as shown below, using a final volume of **30** ml for each check standard. (Note: if a different standard curve is run, then the levels of the CCV and ICV standards must be adjusted accordingly in accordance with the requirements in the methods) Make sure to clearly label each bottle. Make sure to prepare enough CCV checks for the entire run. The ICV check must be from an alternate source of standards than the calibration curve. The CCV must be made from the same source as the calibration curve. A low check standard at the level of the CRDL (0.20 ug/l) is also required. This 0.20 ug/l check can be made up as outlined for the standard curve. Witness signature is required in the reagent sheet or prep log for pouring, aliquoting and spiking samples

Sample ID	**ml of** 30 **ppb Hg solution**	**ml of DI water**	**Total ug of Hg**
CCV Check(s)	2.5	27.5	**0.075**
MB	0.0	30	**0.0**
MS	2.0	(a)	**0.06 (b)**
MSD	2.0	(a)	**0.06 (b)**
ICV	3.0	**27.0**	**0.09**
LCS	2.0	**28.0**	**0.06**

(a) **30** ml of sample

(b) plus, the level of Hg in the sample.

10.5 To all samples, QC, and standards add the reagents listed below, swirling the samples well after each addition of reagent. Allow the samples to stand for at least 15 minutes after the addition of the permanganate. If the sample decolorizes, add additional permanganate until the purple color persists. When additional potassium permanganate added to a sample, equal amounts must be added to the associated batch quality control samples such as Method blank, Blank spike, Matrix spike, Matrix duplicate, QC sample and Duplicate

- **1.5** ml of conc. sulfuric acid.
- **0.75** ml of conc. nitric acid.

- **4.5** ml of 5% permanganate solution.

Wait 15 minutes, then

- **2.4** ml of potassium persulfate solution.

10.5.1 All of the additions shown can be done with a bottle pipettor which must be accurate to within a range of 90 to 110%.

10.6 Cap the samples and place them in the graphite heating block and heat for 2 hours at 90 to 95 °C. Record the digestion times and temperature.

Note: For method 245.1 Calibration standards, Continuing calibration standards, initial calibration verification and continuing calibration blanks are not digested.

10.7 Enter the prep data into the LIMS system, double checking all volumes and spike amounts. After the prep data is checked, it can be approved and is available for use in the final calculations.

11.0 COLD VAPOR ANALYSIS PROCEDURE HYDRA II

11.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operators' manual.

11.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

11.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath must be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

11.1.3 Turn on the analyzer and allow it to warm up.

11.1.3.1 For the Hydra AA II, open the Envoy software. Go to Method and click Instrument Control. On the Instrument Control page, click the startup icon. This will turn on the lamp, gas, and pump. You may also turn on/off the lamp, gas and pump individually on the Instrument Control Page.

11.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not overtighten.

11.1.4.1 Go to the Instrument control tab and pick the gas control test option. The input must be approximately 0.25 LPM. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.5 Start a batch to save your data.

11.1.5.1 Create a new chapter (Data File) by clicking Analysis. The batch must normally be named H5 followed by the month date and year, followed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument for 3/24/03 would be named H5032403w1. The realtime print option can also be turned on from this tab.

11.1.5.2 Set up autosampler racks containing the samples that are going to be run.

11.1.5.3 Create a new sequence by clicking sequence--new. Type the sequence name. After typing the samples in to sequence page make sure to click update and save. CCV and CCB checks can be entered in the macro column of the sequence page.

11.1.6 Set up the calibration.

11.1.6.1 Go to the Method menu, enter or verify the standard concentration by clicking on the standard tab. Also select number of replicates to be run for each standard. Normally one replicate is run per standard. The check standard concentrations and acceptance ranges are also defined under this standard info tab. Make sure to always click apply when any changes are made in a tab.

11.2 Add hydroxylamine hydrochloride to all samples and standards as outlined below.

12.2.1 Add **1.8** ml of hydroxylamine hydrochloride solution to each standard and sample and swirl until the solution has been completely decolorized. Transfer to a calibrated glass cylinder and dilute to a final volume of **50** ml and swirl to mix.

12.2.2 They hydroxylamine hydrochloride can be added using a bottle pipettor which is accurate in a range of 90 to 110%.

11.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

11.4 Start the calibration.

12.4.1 Click run sequence. The instrument will run the calibration and then pause. Click stop. Go to the Calibration page. Accept the calibration and then print the calibration. Click the Document icon, then choose HG5-PDF. Rename the file as MA*****_cal.

11.5 After the calibration has been accepted, start to run the samples.

12.5.1 For the Hydra AA II, go to the Sequence page. Right click on the first sample (ie. ICV) and click start from here.

11.6 Review the data. Any samples that are over the range of the curve must be diluted with the dilution acid (see Section 9.3) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

11.7 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports must be transferred into the LIMS system where the final calculations are done.

11.7.1 Go to analysis-Click result-Click chapter. Then go to report and select report spec. The normal report spec is "ACCUTEST". Click OK. Click on chapter in order to select all samples. Then click report output and then csv.file. Save as MA*****.csv. To print, select printer output and then type the report title (i.e. MA*****) and enter OK.

11.8 The calculations are done in the LIMS as described below. A final volume of 30.0 ml is used for calculation purposes for graphite heating block digestions. (The volume of 50.0 ml is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 30.0 ml.)

Final sample concentration in mg/L =

$$\frac{\text{concentration in the digestate in ug/l x final volume in ml}}{\text{Initial volume in ml}}$$

11.9 Review the data in the LIMS, adding comments and accepting results as appropriate.

11.10 Shut down the instruments.

11.10.1 To shut down the Hydra AA II, move the stannous chloride line from the stannous chloride bottle to the 10% HNO_3 rinse bottle. Let the system rinse with 10% HNO_3 for several minutes. Then switch the line to DI water bottle and let rinse for several more minutes. Let the pump and gas run until the lines are completely dry. Then go to instrument control menu and click off icon for Lamp, Gas and Pump.

12.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

12.1 Instrument Detection Limits (IDLs). The instrument detection limits must be done a minimum of once per year or when instrument conditions change significantly. The IDL is generated by running 10 replicates of a digested blank. The IDL is then defined as 3 times the standard deviation of the 10 replicates of the blank.

12.2 Method Detection Limits (MDLs). MDLs are determined using the procedure specified in 40 CFR, Part 136, Appendix B, Revision 2 and lab SOP EQA075.

12.3 Instrument Calibration. The instrument must be calibrated daily or at a minimum of once every 24 hours and each time the instrument is set up. Calibration standards must be prepared fresh with each preparation batch. A minimum of a blank and 5 standards are required. The correlation coefficient of the curve must be a minimum of 0.995. No samples must be analyzed until all of the calibration criteria are met. Resloping is acceptable as long as it is immediately preceded and immediately followed by a complaint CCV and CCB. NOTE: method 245.1 calibration standards must not be digested.

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12.4 Linear Dynamic Range (LDR). For each instrument, the upper limit of the linear dynamic range must be established. A linear calibration must be prepared from 3 standards, one of which is close to the upper limit of the linear range. The LDR is determined by analyzing succeedingly higher standard concentrations of mercury until the observed analyte concentration is no more than 10 percent below the true value of the standard. Sample concentrations that are greater than 90% of the determined upper LDR limit must be analyzed using dilutions. The LDR must be verified annually or whenever there is a significant change in the instrument's analytical performance.

12.5 Quality Control Sample (also referred to as Initial Calibration Verification Standard (ICV)). At a minimum of once per quarter, a standard from a different source than the calibration standard must be analyzed. Normally this is analyzed at the beginning of the run after the CCV and CCB checks. The ICV must be within 10 percent of the true value. It is recommended that this standard be analyzed with each run so that it is included with all client reports. For SW846 7470A, this standard must be at a concentration near the midpoint of the calibration curve. If the ICV is outside of the acceptance limits, then the problem must be corrected and the ICV reanalyzed and shown to be within QC limits before any samples can be reported. All reported samples must be bracketed by an ICV which meets acceptance criteria.

12.5.1 If the ICV is biased high and all sample results are < RL, then, at the discretion of the data reviewer, data may be reported.

12.6 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain mercury at < 2.2 times the MDL or < ½ the RL, whichever is less. If the method blank value is over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit. (Note: Not all program codes allow this. Verify prior to proceeding.)

12.6.1 Note: For practical purposes, reviewing the method blank data to ½ RL will meet the 2.2 times MDL requirement.

12.7 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample (spike blank) with each set of samples. A minimum of one lab control sample is required for every 20 samples. For a running batch, a new lab control sample is required for each different digestion day. For method 245.1, the laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 85 to 115 percent. For method 7470A, the laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120 percent. In either case, if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag. If the lab control recovery is low or there are samples above the reporting limit, then all affected samples must be re-digested and reanalyzed.

12.8 Matrix Spike.

12.8.1 For method 245.1, the laboratory must add a known amount of each analyte to a

minimum of 1 in 10 samples. The spike recovery must be within the limits of 70 to 130. If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect.

12.8.2 For method 7470A, the laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The laboratory must assess the matrix spike recovery against limits of 75 to 125. (In house control limits are also generated on an annual basis and are used to support the default limits.) An exception to this rule occurs where the sample concentration exceeds the spike concentration by a factor of 4 or more. If the matrix spike fails this criterion, then the sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. An analyte spike is added to a portion of a prepared sample, or its dilution, and must be recovered to within 80-120% of the known value. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

12.8.3 Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculation shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

12.9 Matrix Spike Duplicate or Matrix Duplicate. The laboratory must digest a matrix spike duplicate or a duplicate sample for a minimum of 1 in 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. The relative percent difference (rpd) between the matrix spike duplicate and the matrix spike or between the duplicate and the sample must be assessed. The calculations for both rpds are shown below.

12.9.1 For method 245.1, the control limits for the matrix spike duplicates or the duplicates are calculated on an annual basis and are used to assess whether a matrix spike duplicate or a duplicate is in control. If it is out of control, then the results must be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

12.9.2 For method 7470A, the duplicate or matrix spike duplicate RPD must be assessed against a limit of 20% RPD. (In house control limits are also generated on an annual basis and are used to support the default limits.) If it is out of control, then the results must be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

12.9.3 Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculations shown below.

$$\frac{\text{(Sample Result - Duplicate Result)} \times 100}{\text{(Sample Result + Duplicate Result)} \times 0.5} = \%\ \text{RPD}$$

or

$$\frac{(|MS\ Result - MSD\ Result|) \times 100}{(MS\ Result + MSD\ Result)/2} = MSD\ RPD$$

12.10 Continuing Calibration Verification. (Also known as the instrument performance check solution.) The CCV must be from the same source as the calibration curve.

12.10.1 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within a method specified range of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentration must be at or near the mid-range of the calibration curve.

12.10.1.1 For methods 245.1 and 7470A, the CCV must be within 10 percent of the true value. Relative Error(%RE) must be 10% for CCV (See section 12.12.3 for calculation)

12.10.2 The ICCV check must also be analyzed at the beginning of the run, immediately after the instrument is calibrated. For method 245.1, this first check must be within 5 percent of the true value. If it is not and there is not a problem with the standard solution, the instrument must be recalibrated and rechecked.

12.10.2.1 This check is not required for method SW846 7470A.

12.11 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

12.12 CRA (Low) Check. For all runs, a low check at the level of the CRDL (0.20 ug/l) or reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. No specific acceptance criteria are listed in any of the methods for this standard at this time. The method criteria of 70-130% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check Relative Error(%RE) must be 30% for CRA (See section 12.12.3 for calculation.

12.12.1 If the CRA is biased high and there is no mercury found in the samples, then the sample results may be reported for mercury. If the CRA is biased high and there is mercury found in the samples, then the samples with Hg at levels ranging from the CCV to the high standard may be reported. Samples with levels of mercury between the CRA and the CCV standard may be biased high and cannot be reported.

12.12.2 Some client may require additional bracketing low checks to be analyzed. Client specific limits may also be required. Check with the area supervisor or manager for more information.

12.12.3 Measurement the Relative Error (%RE):
Relative error is calculated using the following equation:

$$\% \text{ Relative Error} = \frac{x'i - xi}{xi} \times 100$$

xi = True value for the standard
x'i = Measured concentration of the standard
The Relative Error for the CCV is 10% and for LLCCV (CRI/CRA) is 30%

13.0 DOCUMENTATION REQUIREMENTS

Refer to the laboratory Quality Assurance Manual for additional documentation requirements.

13.1 Sample Worksheets. Digestion data sheets for the Hg water samples must show all digestion information including the sample ID's, sample volumes, bottle numbers, start times, end times, and pressure or temperature, as appropriate for all digestions. The digestion method (i.e digestion block) must be indicated on the digestion sheet. All sample information must be clearly entered on these sheets. In addition, any unusual characteristics of the samples or the digestion procedure must be noted in the Comments sections. Make sure also that all dilutions are clearly documented.

13.2 Standards and Reagents. All stocks and reagents must be recorded in the reagent logbook. All standards must be recorded on the digestion log with the samples.

13.3 Any run comments must be written on the raw data for the analysis and on the run log in the LIMS.

13.4 Annual bottle calibration verifications must be documented in the Mercury Bottle calibration log.

14.0 DATA REVIEW AND REPORTING

14.1 All samples must be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for making sure that the raw data is fully documented, and it is loaded into the LIMS system. They are responsible for submitting samples for redigestion and reanalysis, when appropriate.

14.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The reviewer is also responsible for making sure that the QC calculations are done correctly and that appropriate flags are added.

14.3 After the reviewer completes their review, the data is released for client access in the LIMS. The raw data and the run log are submitted to the area manager. The manager periodically does an additional review on data for technical completeness. Any hardcopy raw data is transferred to the report generation department for scanning and storage. Instrument data is transferred electronically.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation

and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS 004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non-hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes.

15.2.3 Chlorinated organic solvents.

15.2.4 Non-chlorinated organic solvents.

15.2.5 Hazardous solid wastes.

15.2.6 Nonhazardous aqueous wastes.

16.0 ADDITIONAL REFERENCES

16.1 Leeman Hydra II instrument manual.

Current Version Revision Information

Changes / Edits made (this should include added or deleted information within a sentence or paragraph only):

Section / Subsection	Detailed description of what was revised
12.8.2	Added post digestion spike criteria

Sections or Subsections deleted:

Section / Subsection	Reason section or subsection was removed

Sections or Subsections added:

Section / Subsection	Reason section or subsection was added

History of Revisions

Version #	Date of Revision	Revised By
24	1/22/20	Olga Azarian
25	1/4/2021	Rakesh Pathak
26	2/14/22	Olga Azarian

END OF DOCUMENT

Honeywell PARSONS

STANDARD OPERATING PROCEDURE L-3H: STANDARD OPEARTING PROCEDURE FOR EXTRACTION OF VARIOUS MATRICES

AND

STANDARD OPERATING PROCEUDRE FOR FRACTIONATION

Standard Operating Procedure for Extraction of Various Matrices

Issue date: 02/11/2022
Revision: 7

SGS North America Inc.
5500 Business Drive
Wilmington, North Carolina 28405

Approved by:

Richard Ballard, Last Revised by	2/11/2022 Date
Greg Dickinson, Technical Director	02-11-2022 Date
Jeannie Milholland, Quality Assurance Director	2-11-2022 Date

(Official copies of final documents will contain all three signatures.)

TABLE OF CONTENTS

Revision History

- The following revisions were made effective on February 11, 2022:
  - Added Section 5.4 for soil sample container requirements
  - Updated Section 6.0 Equipment and supplies; removed redundant items and items that were not needed
  - Updated Section 7.0 Standards and Reagents; removed items that were no longer needed
  - Added Section 8.2 for balance calibration verification
  - Sections 9.16 and 9.5 removed WV specific requirements – no longer accredited in WV
  - Section 9.8.1 updated photograph procedure
  - Section 9.8 updated when in the process the ES is spiked into the thimble
  - Section 9.93 removed precise sample volume
  - Section 9.9.8 removed Hyrdromatrix
  - Section 9.10.3 added 60mL vial
  - Section 9.10.4 removed solvent exchange - done at clean up
  - Section 15 removed redundant definition
  - Section 16 added references for MI_1 and CARB 429
- The SOP was reviewed 12/10/2021
- The Sop was reviewed 12/2/2020
- The following revisions were made effective on June 1, 2020:
  - Section 4.1; reference MI_2
  - Section 7.22; reference DC_364
  - Section 9.2.1 & 9.2.13; updated section with batch QC
  - Section 9.3.10 and 9.4.5; added pH requirement
  - Section 9.3.12.1; added distilled water
  - Section 9.4.3, 9.4.6, 9.4.7, 9.6.1 & 9.13; added sections
  - Section 9.13.1; reference DC_353
  - Section 15.17; added definition
  - Section 16.6, 16.7, & 16.8; added references
- The following revisions were made effective on February 15, 2020:
  - Sections 5.2.5, 5.4.5, 5.5.4 and 17.18 - removed reference to method 8270 holding times
- The following revisions were made effective on December 5, 2018:
  - Added Section 9.1.4 for determination of oil / lipids
  - Added Section 11.2 for oil / lipids calculation
- The following revisions were made effective on April 10, 2018:
  - Section 7.24; added supply
  - Section 9.3.10; added details
  - Sections 9.5.3, 9.6.6; added criteria for residual chlorine
- Please refer to previous version of this SOP for revisions made on or before February 8, 2017.

1.0 Scope and Application

1.1 This method is intended to apply to all extractions performed at SGS, regardless of matrix. It is consistent with the Final Rule on the Methods Innovation Rule 40 CFR Parts 63, 268, et al.; June 14th, 2005; pp. 34538-34592.

1.2 To describe the procedures followed for the extraction of various matrices using Soxhlet Dean-Stark, Continuous Liquid-Liquid, temperature-assisted liquid-liquid extraction (TALEX) and/or other processes as applicable. This approach applies to air samples (e.g. XAD-2 resin, PUF, filters, wipes), soil, water, tissues and special matrices

1.3 Complex sample matrices may require special extraction techniques. Please see Technical Director and/or Senior Chemist in these cases.

1.4 This SOP is based on SW-846 Methods 3540C/3520C/3510C/3580A

1.5 See Document DC_139 Appendix D for a full list of definitions.

2.0 Summary of Method

2.1 The primary objective of sample extraction is to quantitatively remove the analytes of interest from the matrix into an appropriate solvent, which will then be reduced in volume so that it can be cleaned up prior to analysis. For solid samples, the percent solid is determined. The samples are conditioned appropriately, depending on matrix. The samples are fortified with extraction standards and then extracted by a number of means, depending on which is appropriate for the matrix in question. Following extraction, additional conditioning may be necessary, after which the sample extracts are concentrated and prepared for cleanup.

3.0 Safety Precautions

3.1 Follow all appropriate safety guidelines, as laid out in our safety plans.

3.2 Gloves must be worn when handling samples, standards, and reagents.

3.3 Safety glasses must be worn at all times when working in the laboratory.

3.4 A lab coat must be worn while dealing with samples, standards, and reagents.

3.5 In the interest of safety and pollution prevention, all spills must be cleaned up immediately.

4.0 Interferences and Preventive Measures

4.1 Solvents, reagents, incorrectly cleaned glassware, and other extraction techniques may yield interference components in the final extract. See SOP MI_2 for glassware cleaning.

4.2 Three types of interferences may cause problems with this method. The three kinds of interferences are specific, non-specific, and quantitative, and each is considered below.

4.2.1 *Specific Interferences*: Specific interferences are PCDD/Fs that appear in a final extract but did not originate with that sample. Two primary sources of specific interferences are cross-contamination from other samples and, less commonly, chemical reactions that form PCDD/Fs during sample preparation procedures (e.g., extraction).

4.2.2 *Non-specific interferences*: Non-specific interferences are compound present in the final extract that creates false positive signals for PCDD/Fs (e.g., polychlorinated diphenyl ethers). Ideally, sample preparation removes these interferences, but analysts should always be wary of them. An exhaustive list of non-specific interferences may be found in – *Environmental Carcinogens: Methods of Analysis and Exposure Measurement Volume 11: Polychlorinated Dioxins and Dibenzofurans* (IARC Scientific Publications), C. Rappe (Editor), H. R. Buser (Editor), B. Dodet (Editor), I. K. O'Neill (Editor).

4.2.3 *Quantitative Interferences*: Quantitative interferences cause alterations in the measured instrumental response for one or more target analyte instrument responses. These interferences result from the presence of compounds that in the final extract that either suppress ionization or upset the lock mass correction of the instrument. For more detail on these types of interferences, see "Hybrid HRGC/MS/MS Method for the Characterization of Tetrachlorinated Dibenzo-p-dioxins in Environmental Samples." Y. Tondeur, W.J. Niederhut, S.R. Missler, and J.E. Campana, *Mass Spectrom.* **14**, 449-456 (1987).

4.3 Care should be taken in cleaning any extraction vessel or equipment that the sample or sample extract may contact during the extraction process.

4.4 Interferences co-extracted from samples vary from matrix to matrix and from sample to sample. Additional cleanup may be required as needed or

specified by project.

4.5 Contamination or carry-over may occur by extraction of high level samples sequentially with clean or low level samples. Treat all samples as though they have the potential to cause cross-contamination, even when we are certain they cannot. Proper record keeping allows for review of how and in what order samples were extracted if a high level sample is discovered during analysis. This makes it possible to determine which samples may have carry over and need re-extraction.

4.6 Some PCBs are airborne. Use of a separatory funnel may result in contamination of samples with airborne PCBs. Lab method blanks should be monitored closely when using separatory funnels for PCBs.

5.0 Sample Collection, Preservation and Storage

5.1 Waste is disposed of in appropriate waste containers in accordance with the local, state and federal regulations. No sample or reagent is ever disposed of down a drain or in the trash. See document MI_278 for waste disposal, pollution prevention and spill clean-up.

5.2 Sample holding times and other storage requirements by method for solid samples are as follows:

5.2.1 Methods 1668 & 1613: holding time is up to 1 year, store in the dark at 4°C (± 2° C) until extracted then frozen (-10°C) until disposal

5.2.2 Method 8290: holding time is 30 days from collection to extraction, store in the dark at 4°C (± 2° C)

5.2.3 CARB 429 (air sample XAD and filters): holding time for extraction is within 21 days from collection, store at 4°C (± 2° C)

5.2.4 Method 1699: holding time is 1 year, store at 4°C (± 2° C) until extracted then frozen (-10°C) until disposal

5.2.5 Extracts should be analyzed within 40 days for Semivolatile organics and organochlorine pesticides. Extracts should be analyzed within 45 days for PCDDs and PCDFs.

5.3 Water samples are collected in 1 L amber glass (2 L size for DRBC) containers following conventional sampling practices.

5.4 Soil samples are collected in 1 4oz amber wide-mouth glass container.

5.5 Sample holding times and other storage requirements by method for aqueous samples are as follows:

5.5.1 Methods 1668 & 1613: holding time is up to 1 year, store in the dark at 4°C (± 2° C)

5.5.2 Method 8290: holding time is 30 days from collection to extraction, store in the dark at 4°C (± 2° C)

5.5.3 CARB 429 (water fractions of air sampling train): holding time for extraction is 21 days from collection, store at 4°C (± 2° C)

5.5.4 Method 1699: holding time is 7 days, store at 4°C (± 2° C)

5.6 Sample holding times and other storage requirements by method for tissue samples are as follows:

5.6.1 Methods 1668 & 1613: holding time is up to 1 year, store in freezer at -10°C

5.6.2 Method 8290: holding time is 30 days from collection to extraction, store in freezer at -10°C

5.6.3 Method 1699: holding time is 1 year, store in freezer at -10°C

6.0 Equipment and Supplies

6.1 Soxhlet setup

6.1.1 Soxhlet body equipped with drain tube and

6.1.2 Dean Stark

6.1.3 Condenser

6.1.4 500mL round bottom flask

6.2 Suitable personal protection equipment (PPE)

6.3 Clean stainless steel forceps

6.4 Aluminum foil

6.5 Drying Oven

6.6 Top-Loader Balance

6.7 Aluminum weight boats

6.8 Glass thimble (glass fritted at bottom)

6.9 Heating mantle

6.10 Chiller

6.11 Teflon Boiling chips

6.12 Concentrator

6.13 Table shaker
6.14 Graduated cylinder (various volumes)
6.15 Filtration device
6.16 Appropriate micropipette
6.17 Butcher knife
6.18 Meat grinder (Hobart or equivalent)
6.19 Fume hood
6.20 Freezer
6.21 Glass Beakers (various sizes)
6.22 40 or 60 ml vials
6.23 Diatomaceous earth (Hydromatrix™)
6.24 Borosilicate pipets, disposable, serological (various volumes)
6.25 Amber glass bottles, 1 L or 2.5 L(Teflon-lined screw cap)
6.26 separatory funnels varying sizes
6.27 Glass chromatographic columns
6.28 N-Evaporator, rocket evaporator or equivalent
6.29 Conical autosampler vials, ~2mL
6.30 Glass fiber filters
6.31 Glass wool plugs
6.32 Glass Funnels
6.33 Rotary Evaporator or Vacuum Centrifuge
6.34 15mL test tubes
6.35 Tissuemizer
6.36 Stainless Steel Spatula
6.37 pH Paper
6.38 CLLE extraction bodies
6.39 CLLE rack with condenser and water lines
6.40 Drying Adaptor
6.41 Water Heater
6.42 Snyder Column

6.43 Various sized micron filter papers (2 µm, 1 µm, 0.7 µm and 0.45 µm)

6.44 4 or 8 oz. jars

6.45 Semipermeable membrane

6.46 Membrane crimper

6.47 Heat sealer

6.48 Carbon Pellets

6.49 Carbopak carbon

6.50 Side arm Erlenmeyer flasks

6.51 Büchner funnels

6.52 Vacuum pump

6.53 Chlorine test strips

6.54 AX-21

6.55 Sonicator

6.56 Appropriately sized round bottom

6.57 Custom Talex column

6.58 Boiling stones

6.59 Glass beads

7.0 Standards and Reagents

7.1 Note: Not all reagents are used in every extraction type.

7.2 Hexane Highest available purity.

7.3 Toluene Highest available purity.

7.4 Isooctane Highest available purity

7.5 Methylene chloride Highest available purity.

7.6 Sulfuric acid, concentrated

7.7 Tetradecane Highest available purity.

7.8 Methanol Highest available purity.

7.9 Anhydrous Sodium Sulfate

7.10 DI water

7.11 Cleaned DI water/Distilled water

7.12 Acetone Highest available purity.

7.13 Silica gel. Highest purity grade.

7.14 Florisil

7.15 Pre-purified nitrogen gas.

7.16 Sodium Hydroxide. Highest available purity.

7.17 Diethyl Ether

7.18 Analytical standards, in toluene, (Cambridge Isotope Laboratory, Woodburn, MA, Wellington Laboratories, or other qualified vendor). See Table 3 of the dioxin/furan analysis SOP DC_364 for details on composition of standard solutions.

7.19 Extraction Standards (20ul@100pg/uL in Toluene for D/F, 20ul@100pg/ul in nonane for PCB) See project spike profile for exact details.

7.20 Sodium Thiosulfate, 99.99+%, powder

8.0 Calibration

8.1 Pipette Calibration

8.1.1 Refer to SGS document MI_46 for pipette and syringe calibration procedure.

8.2 Balance Calibration Verification

8.2.1 Refer to SGS document MI_1 for balance verification procedure.

9.0 Sample Preparation

9.1 Sample Examination

9.1.1 When first opening a sample, examine the sample for any qualities that may affect reliable analysis. A strong chemical odor may indicate that a sample will contain particularly high concentrations of PCDD/Fs or laboratory contaminants. It may also indicate potential interference problems, such as high fuel content. Note any large pebbles, rocks, twigs, shells and other matter that interferes with representative subsampling. For aqueous samples, note color and solids content. Record any observations you make that you believe may affect the analysis.

9.1.2 If you have reason to suspect that a sample may contain unusually high concentrations of PCDD/Fs, make note of this fact in the

documentation accompanying the sample and consult the Technical Director and/or Senior Chemist for instructions on how to proceed.

9.1.3 Determine the percent solids on all soil and sediment samples. Percents solids determinations are not necessary for air matrices. For other matrices, use your best scientific judgment to determine if a percent solids determination is necessary.

9.1.3.1 Pre-weigh an aluminum weighing boat.

9.1.3.2 Weigh out an appropriate mass of sample, target approximately 2-3g.

9.1.3.3 Dry the sample overnight in a 110 °C oven and re-weigh the remaining residue.

9.1.3.4 Determine percent solids using the calculations shown section 11.1.

9.1.3.5 All samples are extracted on a wet weight basis. For solid samples where a percent solids determination has been made, adjust the sample amount for extraction to yield a dry weight equivalent (DWE) based on the percent solids, usually defaulting to 10g DWE .

9.1.3.6 Ensure all samples are homogenized.

9.1.3.7 The lab will use a one gram dry-weight equivalent sample size for sediment samples believed to contain unusually high levels of PCBs (>80 ppb). In addition, in these cases, the lab will spike 10 ng of the ES instead of the usual 2 ng. Finally, the lab will use a final volume of 100 µL of nonane instead of the usual 20 µL. These enhancements are designed to prevent unnecessary extraction of samples and saturation of the HRMS detector).

9.1.4 Determination of percent oil or lipids if required.

9.1.4.1 Extract the entire contents of the sample using a soxhlet extraction apparatus.

9.1.4.2 Remove any residual water from the extract using sodium bisulfate to dry the sample.

9.1.4.3 Filter solid particulate from the extract and concentrate the sample down to 10mL.

9.1.4.4 Using a class A, 1.00mL syringe, transfer 1mL of the extract to a pre-tared aluminum weigh boat.

9.1.4.5 Concentrate the extract aliquot to “dryness” at room temperature.

9.1.4.6 Record the weight of the aluminum weigh boat and oil residue using an analytical balance accurate to 0.002g (+/- 0.0002g).

9.1.4.7 Place the weigh boat in a vacuum desiccator and allow to concentrate for at least 1 hour.

9.1.4.8 Re-weigh the sample and weigh boat to ensure that no additional evaporation has occurred, and the weight remains stable. If the second weight does not match within +/- 0.0002 of the first weight, repeat the process starting at 9.1.4.7 until criteria is met.

9.1.4.9 The residual oil weight is calculated by subtracting the weight of the boat from the total weight of the boat with dried oil residue.

9.1.4.10 Multiply the oil residue weight by 10 to correct the weight to the original sample volume, and calculate the oil or lipid content to the nearest three significant figures using calculation shown in section 11.2

9.1.5 Sub Sampling (if needed)

9.1.5.1 Water

9.1.5.1.1 Homogenize sample to incorporate and evenly distribute particulate matter.

9.1.5.1.2 Use a power shaker if desired (consider the possibility of incorporating airborne PCBs).

9.1.5.2 Soils and Sediments

9.1.5.2.1 The sample should be stirred thoroughly to ensure homogeneity. The sample is homogenized and a representative sample is taken after homogenization.

9.1.6 Aqueous or Effluent Samples (nominal volume of 1 liter)

9.1.6.1 If the sample contains >1.0 percent solids, treat the sample as a solid. If the particulate appears to be easily removed by filtration, SPE-C may be used prior to soxhlet extraction.

9.1.6.2 If the solid load is <1.0 percent, the sample may be extracted using the TALEX or CLLE approaches.

9.1.6.3 The details for these procedures are given below. The decision to follow one particular approach over the others is dictated by the client's requirements, the type of samples undergoing analysis, and the expertise of the laboratory staff.

9.1.6.4 All paper mill effluent samples should be filtered and the isolated solids extracted by SPE and SDS.

9.1.7 Extraction Solvents and heating mantle temperature settings:

9.1.7.1 D/Fs solids: Toluene with a keeper solvent such as Tetradecane.

9.1.7.2 PCBs/USVs/PAHs solids: Hexanes

9.1.7.3 Tissues (moderate to high %lipid content)- Hexanes. EU Tissues- Hexanes: Acetone.

9.1.7.4 The heater should be set to "40-55" for Methylene chloride and hexanes, "65-75" for toluene depending on the equipment being used.

9.2 **Soils & Sediments by Soxhlet and Soxhlet/Dean-Stark (SDS)**

9.2.1 Weigh the samples, and batch QC (LMB/OPR), in clean glass thimbles containing Hydromatrix™ or sodium sulfate. Batch QC is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and labeled compounds. Perform the following steps for each sample.

9.2.2 Stir the thimble's contents to thoroughly mix the sample with the Hydromatrix™ or sodium sulfate; dispersing the sample across the surface of the inert material. This step will have the secondary effect of absorbing the liquid present in the sample.

9.2.3 Transfer the thimble to a Soxhlet Extraction apparatus and add the Dean-Stark adapter if necessary.

9.2.4 Fortify the samples with the appropriate extraction standards. Extract the samples by SDS by adding ~300-400 mL of an appropriate solvent to a 500 mL Round Bottom Flask containing Teflon ™ chips. Extraction must be for a length of time sufficient to effect full recovery of extraction standards. By default, the extraction time is 16 hours, although shorter times may be used if they have been previously demonstrated through validation to provide adequate performance.

9.2.5 During the extraction, verify that the solvent cycles normally. The solvent must cycle through the system five times each hour.

9.2.6 Drain any water from the Dean-Stark as appropriate to prevent water from returning to the boiling flask.

9.2.7 At the end of the reflux cycle time, proceed with sample concentration as described below.

9.2.8 Drain the solvent present in the DS side arm directly to solvent waste. Open stopcock on thimble holder and continue to drain solvent to waste until ~25 mL of solvent is remaining in the round bottom flask.

9.2.9 Turn off the heater and allow the solvent to continue to concentrate

as low as ~5 mL. Do NOT allow to go "dry" for PCBs and/or PAHs.

9.2.10 Allow the flask to cool down.

9.2.11 If necessary, continue concentration of sample using a combination of TurboVap, rocket concentrator and/or rotovap. Solvent exchange to hexane, if necessary and spike with cleanup standards.

9.3 **Continuous Liquid-Liquid Extraction** (using extraction bodies with Snyder columns)

9.3.1 Remove samples from designated storage area and allow them to come to room temperature.

9.3.2 Make sure the individual water supply valves on the CLLE rack are closed.

9.3.3 Turn on the main pump valve to "on".

9.3.4 Add one large boiling chip to each concentrator.

9.3.5 Attach the extraction body, drying adapter (with sodium sulfate) and concentrator to the CLLE rack.

9.3.6 Attach the water supply and return lines to the concentrator, and open the valves.

9.3.7 Turn on the water heater and allow the temperature to come up to 160 ± 5°C.

9.3.8 Make sure the chiller is running at the proper temperature (10 ± 2°C).

9.3.9 Add 250 mL of methylene chloride to each extraction body.

9.3.10 Test for residual chlorine and Record the pH of the sample. If residual chlorine is present, then add 80 mg sodium thiosulfate per liter of water. If pH is > 9 for NPDES permit compliance samples then adjust the pH to < 9 using sulfuric acid.

9.3.11 Place sample jar on a balance and tare the scale.

9.3.12 Add the contents of the sample bottle to the extraction body, use 1L of deionized water for batch QC samples (LMB/OPR). Batch QC is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and labeled compounds.

9.3.12.1 Use the entire sample container for all DRBC samples, use 2L of distilled water for

9.3.13 Reweigh the sample jar on the tared scale and record the weight of the displaced sample volume.

9.3.14 Rinse the jar with Methylene Chloride and add to the extraction body.

9.3.15 Spike the sample with extraction standards as listed on the spike profile.

9.3.16 Attach the condenser to the extraction body and open the stopcock.

9.3.17 Allow the samples to extract for 16 to 18 hours, as validated. South Carolina samples will be extracted for 24 hours.

9.3.18 When the extraction is complete, close the stopcock and allow the extract to concentrate down to approximately 10 mL.

9.3.19 Turn off the water heater.

9.3.20 Turn off the power to the water pump.

9.3.21 Crack open the individual water return valves to allow air in, and water to drain out.

9.3.22 Close the individual water supply and return valves.

9.3.23 Transfer the extract to a 60 mL vial. Solvent exchange to hexane, if necessary and spike with cleanup standards.

9.3.24 Properly dispose of the remaining sample water and Methylene Chloride.

9.4 Separatory Funnel Extraction

9.4.1 Prepare drying funnels by packing the neck of a glass funnel with glass wool.

9.4.2 Add approximately 10-15 g of Na_2SO_4 on top of the glass wool and position over an appropriately labeled collection vial (containing keeper solvent if required).

9.4.3 Test for residual chlorine and Record the pH of the sample. If residual chlorine is present, then add 80 mg sodium thiosulfate per liter of water. If pH is > 9 for NPDES permit compliance samples then adjust the pH to < 9 using sulfuric acid.

9.4.4 Place the sample bottle on a balance and tare the scale.

9.4.5 Add the contents of the sample bottle to the separatory funnel, reweigh the bottle and record weight of the displaced sample

volume.

9.4.6 Rinse the jar with Methylene Chloride and add to the extraction body.

9.4.7 Use 1L of deionized water for batch QC samples (LMB/OPR). Batch QC is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, internal standards, and labeled compounds

9.4.8 Record the pH of the sample on the extraction sheet.

9.4.9 Add extraction standard to the sample, shake vigorously and allow it to integrate.

9.4.10 Add 60 mL of methylene chloride to the separatory funnel.

9.4.11 Shake for at least 2 min, periodically purging the separatory funnel of any excess pressure.

9.4.12 Allow the sample-solvent solution to settle out and form a distinct interface.

9.4.13 Drain the solvent through the sodium sulfate funnel into the collection vial.

9.4.14 Repeat the extraction twice more.

9.4.15 Proceed to concentration, solvent exchange to hexane if necessary, and spike with cleanup standards.

9.5 **SPE-C**

9.5.1 Obtain the weight of the sample and container. Transfer the sample to the extraction flask and re-weigh the empty container. Determine and record the weight of the sample by difference.

9.5.2 For composites of pulp and paper acid/alkaline aqueous samples, composite according to the ratio or amount specified in the COC.

9.5.3 Measure pH and residual chlorine using test strips. Record the information. If residual chlorine is present, then add 80 mg sodium thiosulfate per liter of water.

9.5.4 Fortify the sample with the ES (along with Ax for the OPR or MS/MSD when requested).

9.5.5 If the samples are for 2378-TCDD only add 1 g of the carbon pellets (~10 pellets). Pellets can be used for large volume samples also (i.e.. 4L)

9.5.6 If the samples are for a full list analysis add an appropriate amount of the carbo-pak carbon.

9.5.7 Allow the sample to agitate on the platform shaker for 2 hours(4 hours for large volume samples).

9.5.8 Filter through a 2 µm, 1µm, 0.7 µm filter then a 0.45 µm filter using an Erlenmeyer flask equipped with a Buchner funnel. Recover the filters and any cake/carbon pellets.

9.5.9 Rinse the bottle with toluene (10-25 mL) and add this rinse to the SDS toluene for the extraction of the solid catches.

9.5.10 Perform an SDS extraction on the filters/solids using toluene for 16 hours. Watch cycling for at least 1 hour to insure proper cycling, no loss of solvents, leakage, broken glassware.

9.5.11 At the end of the reflux cycle time, proceed with sample concentration/solvent exchange to hexane, if necessary and spike with cleanup standards.

9.6 **Aqueous Samples other than P&P Filtrates**

9.6.1 The following procedure is not applicable for South Carolina compliance samples.

9.6.2 Use the custom-designed TALEX column.

9.6.3 Prime the column with a few mL (usually 2-3 mL) of DI water.

9.6.4 Add 3 mL of toluene for PCDD/Fs or 3 mL isooctane for PCBs.

9.6.5 Add the demister in the mid section of the column (glass beads) and top the column with aluminum foil.

9.6.6 Obtain the weight of the sample and container. Transfer the water sample to the round bottom flask and re-weigh the empty container. Determine and record the weight of the sample by difference.

9.6.7 Measure pH and residual chlorine using test strips and record in the paperwork. If residual chlorine is present, then add 80 mg sodium thiosulfate per liter of water.

9.6.8 Fortify the aqueous samples with the extraction/analytes standards directly into the round bottom.

9.6.9 Add several boiling stones (Do not use Carborandum). Make sure there are enough stones sitting at the bottom of the flask. Floating chips do not regulate boiling.

9.6.10 Allow chiller water to circulate through the condenser making sure to check for leaks and /or cracks. Do not use water with a temperature higher than 15ºC.

9.6.11 Start heating by turning the knob to position "70" on the thermo controllers.

9.6.12 Record the time from the moment the water starts boiling. Allow the boiling to go on for 2-4 hours.

9.6.13 After 2-4 hours, turn off the heat and allow the system to cool down for approximately 30 minutes.

9.6.14 Open the stopcock on the condenser and slowly drain the water layer to waste.

9.6.15 Drain the toluene or isooctane into a 60-mL vial.

9.6.16 If necessary, tip the column to draw out most of the organic solvent.

9.6.17 Rinse the inside of the column with 2x3 mL of toluene for PCDD/Fs (or hexane for PCBs); draining into the vial with the original extract.

9.6.18 Concentrate and/or solvent exchange to hexane, if necessary and spike with cleanup standards.

Note: If the sample is a clean water sample (e.g., drinking water) additional cleanup is not necessary.

9.7 **Oil Samples**

9.7.1 Acid Partition

9.7.1.1 Weigh 1 g of oil (fish oil) into a VOA vial for PCBs or 5 g of fish oil if the analysis is for dioxins.

9.7.1.2 Dilute the oil with approximately 30 – 40 mL of hexanes.

9.7.1.3 Spike the diluted oil with extraction standards.

9.7.1.4 Perform an acid partition with concentrated H_2SO_4 until the solution appears clear.

9.7.1.5 Transfer the hexanes layer into a clean VOA

vial.

9.7.1.6 Wash with Talex water (PCBs) or deionized water (PCDD/Fs).

9.7.1.7 Run through Na_2SO_4 to remove any residual water.

9.7.1.8 Concentrate hexane and spike with cleanup standards.

9.7.2 Carbon Column

9.7.2.1 Weigh out the required amount of sample into a 60 mL vial. Use an equal amount of hexane for the LMB and OPR.

9.7.2.2 Spike the samples with the extraction standards as listed on the spike profile.

9.7.2.3 If the sample is significantly more viscous than hexane, dilute the sample with hexane (usually 1:1).

9.7.2.4 Pack a glass column with glass wool, 3-4 cm sodium sulfate, 3-4 cm furnaced silica, ~0.5 grams of 5% AX-21, 3-4 cm furnace silica, 3-4 cm sodium sulfate and a glass wool plug.

9.7.2.5 Secure the column in a clamp with the "clean" end down and place a "waste" beaker underneath it.

9.7.2.6 Pre-elute the column with20mL toluene, followed by 10mL hexane and allow to drip into the waste beaker. After the solvent has eluted, flip the column so that the "clean" side faces up.

9.7.2.7 Transfer the sample onto the column.

9.7.2.8 When the entire sample has been transferred, rinse the sample beaker two times with 1 mL hexane and transfer to the column.

9.7.2.9 Continue to rinse the column with hexane until all the oil has been rinsed off the column (approximately 20 mL).

9.7.2.10 Remove the waste beaker and flip the column.

9.7.2.11 Place a 60mL vial under the column and elute with 50 mL toluene.

9.7.2.12 Concentrate the toluene,solvent exchange to hexane if necessary, and spike with cleanup standards.

Note: This extraction procedure was designed to accommodate large amounts of oil. For smaller amounts of oil, the sample may be added directly to a cleanup column.

9.7.3 Florisil Column

9.7.3.1 Weigh out the required amount of sample (nominally 20g for Dioxin analysis) into a 250 mL flask and add 50 mL of Hexane. Use an equal amount of hexane for the LMB and OPR.

9.7.3.2 Spike the samples with the extraction standards as listed on the spike profile.

9.7.3.3 The use of mild heat and sonication may be required to speed the dissolving of the oil in the solvent.

9.7.3.4 Pack a glass column with glass wool, 2 g salt, 3 g of florisil, and 1 g of salt.

9.7.3.5 Secure the column in a clamp.

9.7.3.6 Position a waste collection beaker.

9.7.3.7 Pre-elute the column with 30 mL hexane and allow drip into the waste beaker.

9.7.3.8 Transfer the sample onto the column.

9.7.3.9 When the entire sample has been transferred, rinse the sample beaker with 2 mL hexane and transfer to the column.

9.7.3.10 Continue to rinse the column with hexane until all the oil has been rinsed off the column (approximately 60 mL).

9.7.3.11 Remove the waste beaker and position a sample collection flask.

9.7.3.12 Elute the sample with 240 mL methylene chloride.

9.7.3.13 Concentrate the methylene chloride, solvent

exchange to hexane and spike with cleanup standards.

Note: This extraction procedure was designed to accommodate large amounts of oil (5-20 g). For smaller amounts of oil, the sample may be added directly to a cleanup column.

9.8 Air Samples

9.8.1 Collect all the sample components.

Note: Usually, samples being prepared by EPA Method 23 are comprised of a filter, an XAD-2 resin trap, an acetone rinse for both the front and back halves, a toluene rinse for both the front and back halves, and sometimes a methylene chloride rinse for both the front and back halves. Method 0023A samples contain the same components, but the method requires the filter and front half rinses to be extracted and analyzed as a separate sample from the XAD-2 resin trap and back half rinses. For ambient air samples (Method TO-9A), a PUF and filter combination is typical.

For a Method 23 analysis (only), photograph the filter and XAD-2 resin trap together for documentation purposes prior to combination. Take a photograph of each sample's components immediately before unpacking and combining in the thimble. Follow the steps below as written. If the analysis is by Method 0023A, follow the steps below except for combining the resin and filter – these components (with their respective rinses) constitute two separate samples. Combine resin and filter in a glass SDS thimble.

9.8.2 If the client used spiked Carbon Rinse Jars, the acetone rinse jars will have TS spike in them.

9.8.2.1 To extract rinse jars, add methanol and extraction solvent (toluene or hexane). Then take pieces of glass wool and clean the inside of the jar then place glass wool into extraction thimble. Repeat this until the jar is completely clean. Finish by rinsing the jars with the extraction solvent (hexane or toluene) and pour it into the extraction thimble.

9.8.3 Concentrate the rinses to less than 5 mL using a rotovap or by other appropriate means.

9.8.4 Add the concentrated solvent rinses to the resin/filter in the thimble.

9.8.5 Use the glass wool that was packed into the XAD-2 trap to collect any stray XAD-2 particles and solvent and place the glass wool plug in the thimble on top of the resin.

9.8.6 Into the thimble, spike the appropriate amount of Extraction Standards, as indicated in the project documentation.

9.8.7 Assemble the DS and condenser components . Extract the samples by SDS by adding ~300-400 mL of an appropriate solvent to a 500 mL Round Bottom Flask containing Teflon^{TM} boiling chips. Extraction must be for a length of time sufficient to effect full recovery of extraction standards. By default, the extraction time is 16 hours, although shorter times may be used if they have been previously demonstrated through validation to provide adequate performance.

9.8.8 During the extraction, verify that the solvent cycles normally. The solvent must cycle through the system five times each hour.

9.8.9 Drain any water from the Dean-Stark as appropriate to prevent water from returning to the boiling flask.

9.8.10 At the end of the reflux cycle time, proceed with sample concentration as described below.

9.8.10.1 Drain the solvent present in the DS side arm directly to solvent waste. Open stopcock on thimble holder and continue to drain solvent to waste until ~25 mL of solvent is remaining

in the round bottom flask.

9.8.10.2 Turn off the heater and allow the solvent to continue to concentrate to a minimum of ~5 mL. Do NOT allow to go "dry" for PCBs and/or PAHs.

9.8.10.3 Allow the flask to cool down.

9.8.10.4 If necessary, continue concentration of sample and/or solvent exchange to hexane, if necessary and spike with cleanup standards. Quantitatively transfer the extract to a 60 mL vial and bring to a volume of 12 mL in hexane.

9.8.11 Split the extract per the project instructions, archive as necessary.

9.8.12 Store the archived extract at room temperature in the vial with a Teflon™-lined screw top.

9.9 **Tissue Samples**: Tissue samples received as whole material are ground and homogenized. Others can be used as received.

9.9.1 Grind fish (or other tissue received as whole tissues) using the Hobart meat grinder. Collect the ground tissue directly on cleaned aluminum foil.

9.9.2 Using a spatula, mix well.

9.9.3 Use the requested or necessary aliquot size if a larger aliquot is requested by the customer or necessary to meet customer data quality objectives.

9.9.4 Place two more aliquots of the ground tissue inside two 4-oz jars, label the jars and store in a freezer.

9.9.5 Using Tissuemizer blend meat into a creamy paste consistency.

9.9.6 Using a spatula, mix well.

9.9.7 Fortify the sample with ES directly.

9.9.8 Mix the sample with 20-25 g of sodium sulfate, stir until a dry, free-flowing consistency is achieved, adding more Hydromatrix™ or sodium sulfate as needed. Be careful not to exceed an amount that can fit into the thimble for the sample size used.

9.9.9 Soxhlet Dean-Stark using hexane with ~250 uL of the keeper solvent for 16h (or other duration previously demonstrated when appropriate).

9.9.10 For samples exceeding 50g, implement the following additional steps:

9.9.10.1 After spiking the sample and thoroughly integrating the spike, split the sample across enough thimbles such that no thimble holds more than 50g of tissue.

9.9.11 At the end of the reflux cycle time, proceed with sample concentration as described below.

9.9.11.1 Drain the solvent present in the DS side arm directly to solvent waste. Open stopcock on thimble holder and continue to drain solvent to waste until ~25 mL of solvent is remaining in the round bottom flask.

9.9.11.2 Turn off the heater and allow the solvent to continue to concentrate to a minimum of 5 mL. Do NOT allow to go "dry" for PCBs and/or PAHs.

9.9.11.3 Allow the flask to cool down.

Combine the extracts after the extraction is complete but before concentrating the extracts for cleanup.

9.9.11.4 Continue concentration of sample and/or solvent exchange to hexane, if necessary and spike with cleanup standards.

9.9.11.5 In case the tissue contains sediment particles, it is recommended to follow the hexane (-acetone) extraction with a toluene-acetone extraction.

9.10 **SPME Fibers**

9.10.1 SPME Fibers will be extracted by sonication, as follows:

9.10.2 **Water fraction**: Pour off water into a 60mL vial. Extract 3 times serially with 5 mL Hexane. Combine with the hexane extract of the fibers. Alternatively, if the liquid portion is too small to be transferred to a separate vial for extraction, the aqueous portion may be co-extracted by sonication with the fiber portion.

9.10.3 **Fibers:** Leave fibers and aqueous portion, if necessary, in the vial which it was received. Spike with ES solutions, per project specifications. Fill the vial (at least to fully cover the fibers) with

hexane and sonicate for at least 30 minutes. As soon as possible after sonication, transfer the hexane extract to a new 60 mL vial and rinse the vial again with additional hexane after transfer to ensure complete recovery of analytes and standards.

9.10.4 If necessary, and not already done, combine the extracts and remove any residual water by separation or addition of sodium sulfate.

9.10.5 Depending on the fiber composition and extract cleanliness, cleanup of the extract may be unnecessary and is optional. If cleanup is not needed, proceed to transfer steps.

9.10.6 Alternative spiking schema (e.g., use of FS as an ES) may be instituted to facilitate best scientific practice on customer request.

9.11 **Semipermeable Membrane**.

9.11.1 Using a heat sealer, seal the end of a semi permeable membrane (SPM) by pushing down the sealer quickly and releasing. Check for complete seal.

9.11.2 Clean the bags by filling with 10 mL hexane, close open end by rolling over the edges around forceps. Gently rock the bag back and forth to ensure the solvent covers the inside of the bag. At this time check for leaks at the sealed end. If a leak appears, reseal the bag.

9.11.3 Drain and repeat a second time.

9.11.4 The bag is now ready for use.

9.11.5 Slide the SPM into the extraction column. Open the top of the bag using forceps.

9.11.6 Prepare the sample by dissolving in an appropriate amount of hexane.

9.11.7 Using a 25 mL Borosilicate glass pipette, transfer the sample to the SPM bag.

9.11.8 Seal top of bag, leaving seal outside of column. Tape top of bag to outside of column.

9.11.9 Fill the column with 300 mL hexane.

9.11.10 Cover the top of the column with foil.

9.11.11 Allow to stand for 12-16 H.

9.11.12 Drain the hexane and refill with 300 mL of fresh hexane.

9.11.13 Allow to stand for another 12-16 H.

9.11.14 Drain the hexane and refill with 300 mL of fresh hexane.

9.11.15 Allow to stand for 12-16 H.

9.11.16 Drain off the hexane into the same collection container as the previous hexane recovery.

9.11.17 Concentrate the hexane and combine all fractions into one sample.

9.11.18 Spike with Cleanup Standard and proceed with cleanup.

9.12 CLEANUPS and TRANSFERS

9.12.1 See SOP DC_365

9.13 Fortification

9.13.1 See SOP DC_353

10.0 Analytical Procedure

10.1 See the SOP for the determinative method(s) for analytical procedures. Details of Calculations

10.2 Percent solids:

$$\%Solids = \left(\frac{dry - tare}{wet - tare} \right) \times 100$$

where,

dry = weight after drying
wet = wet weight of sample
tare = weight of pan

10.3 Oil/Lipid Content:

$$\%Oil / Lipid = \left(\frac{final - tare}{initial - tare} \right) \times 100$$

where,

final = weight after drying
initial = initial weight of sample
tare = weight of pan

11.0 Quality Control Requirements

11.1 Data outside of QC limits may be addressed by one or more of the following options:

11.1.1 Re-preparation and re-analysis of sample

11.1.2 Client notification

11.1.3 Discussion and qualification of data by case narrative

11.1.4 Re-sampling and reanalysis (client decision)

11.2 Data outside of QC limits may be reported if directed by the client. It must be qualified by a case narrative detailing the QC problems with advice on the usability of the data.

11.3 See the SOP of the associated determinative method(s) for specific requirements.

12.0 Data Review and Reporting Requirements

12.1 Refer to SGS document MI_141, Data review SOP

13.0 Preventative Maintenance

13.1 Cleanup pumps calibrated semi-annually

13.2 Pipettes calibrated quarterly

13.3 Balance verification performed daily or when in use

14.0 Tables

14.1 Not applicable

15.0 Definitions

15.1 SDS – Soxhlet-Dean Stark

15.2 PPE – Personal protective equipment

15.3 XAD – Experimental and Development

15.4 PCB – Polychlorinated Biphenyls

15.5 DI – Deionized (cleaned DI water by TALEX for PCBs)

15.6 GC – Gas chromatograph

15.7 SPM – Semipermeable membrane

15.8 CLLE - Continuous liquid-liquid extraction

15.9 DRBC – Delaware River Basin Commission

15.10 H_2SO_4 - Sulfuric Acid

15.11 Na_2SO_4 - Sodium Sulfate

15.12 PCDD/Fs - polychlorinated dibenzo-p-dioxin/furan

15.13 PAH – Polynuclear aromatic hydrocarbon

15.14 SPE – Solid phase extraction

15.15 P&P – Pulp and paper

15.16 Fortification – Spiking of samples with labeled standards

15.17 Fractionation – Clean up procedures used to remove interfering compounds from an extract

16.0 References

16.1 SGS document DC_139, Appendix D Definitions.

16.2 SGS document MI_278, Waste Disposal, Pollution Prevention and Spill Clean up.

16.3 SGS document MI_141, Review of Analytical Data.

16.4 SGS document MI_46, Pipette and Syringe Calibration.

16.5 SGS document MI_254, Chemical Hygiene Plan

16.6 SGS document DC_353, Fortification

16.7 SGS document MI_2, Preparation of Glassware and Reusable Sample Prep Equipment.

16.8 SGS document DC_365, Fractionation

16.9 SGS document MI_1, Daily Monitoring of Support Equipment

16.10 EPA Method 1613B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, October 1994

16.11 EPA Method 1668A, Chlorinated Biphenly Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, December 1999

16.12 EPA Method 8290A, Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS), February 2007

16.13 EPA Method 1668B, Chlorinated Biphenly Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, November 2008

16.14 EPA Method 1668C, Chlorinated Biphenly Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, April 2010

16.15 SW-846 Method 3510C Revision 3, December 1996

16.16 SW-846 Method 3540C Revision 3, December 1996

16.17 SW-846 Method 3580A Revision 1, July 1992

16.18 SW-846 Method 3520C Revision 3, December 1996

16.19 California Air Resources Board (CARB) Method 429 (9/89)

16.20 Final Rule on the Methods Innovation Rule 40 CFR Parts 63, 268, et al.; June 14th, 2005; pp. 34538-34592

16.21 *Environmental Carcinogens: Methods of Analysis and Exposure Measurement Volume 11: Polychlorinated Dioxins and Dibenzofurans* (IARC Scientific Publications), C. Rappe (Editor), H. R. Buser (Editor), B. Dodet (Editor), I. K. O'Neill (Editor)

16.22 Hybrid HRGC/MS/MS Method for the Characterization of Tetrachlorinated Dibenzo-p-dioxins in Environmental Samples." Y. Tondeur, W.J. Niederhut, S.R. Missler, and J.E. Campana, *Mass Spectrom.* **14**, 449-456 (1987)

Standard Operating Procedure for Fractionation

Issue date: 02/11/2022
Revision: 11

SGS North America Inc.
5500 Business Drive
Wilmington, North Carolina 28405

Approved by:

Richard Ballard, Last Revised by — Date: 2/11/2022

Greg Dickinson, Technical Director — Date: 02-11-2022

Jeannie Milholland, Quality Assurance Director — Date: 2-11-2022

(Official copies of final documents will contain all three signatures.)

TABLE OF CONTENTS

Revision History

- The following changes were made effective on February 11, 2022:
  - Deleted Section on ASECS pumps as we no longer use these in the clean-up procedure
  - Section 6.0 and 7.0; updated sections
  - Section 8.2.2 added Post Clean-up clarification
  - Section 8.2.3 added Pre-Clean-up clarification
  - Section 8.2.2.3; added boiling information for Hexane
  - Section 8.2.4.5 updated volume and clarification that this keeper solvent is only for Dioxins
  - Section 8.3 added requirement for spike witness
  - Section 8.3.1.5 and 8.3.1.6; added distilled water
  - Section 8.3.2 removed ASECS instructions
  - Section 8.3.3 moved PCU methods to this section
  - Section 8.3.9.1 corrected volume
  - Section 8.3.10.1 Added details of sulfur removal
  - Section 8.3.12.8; updated volume
- This document was reviewed on 12/2/2020
- The following changes were made effective on May 19, 2020:
  - Updated Section 5.2 clarified procedure
  - Added Section 9.1 manual fractionations
  - Added Section 9.2 details of concentration procedures
  - Updated section 9.3 with spike concentrations
  - Updated Section 9.4 with clarification of the transfer procedures
- The following changes were made effective on February 15, 2020:
  - Section 6.0; updated equipment and supplies list
  - Section 7.0; updated standards and reagents list
  - Sections 9.2.2.13, 9.2.12.8; added “up to” for percent of DCM/ Hexane
  - Section 9.2.7; added section for micro alumina clean up
  - Section 9.2.8.16; updated to 50mL of toluene
  - Section 9.3.3.3; updated solvent
- The following changes were made effective on February 19, 2019:
  - Sections 9.2.2.13, 9.2.2.21, 9.2.2.22: updated DCM/Hexane ratio
  - Sections 9.2.11.8-9.2.11.10: updated sections to reflect current practices
- The following changes were made effective on May 30, 2018.
  - Sections 6.15-6.18; added supplies
  - Section 9.2.12; added section and subsections for GPC cleanup
- For changes made on or before March 10, 2017 please refer to archived SOP(s)

1.0 Scope and Application

1.1 This SOP outlines procedures designed to remove interfering compounds/substances from an extract.

1.2 See Document DC_139 Appendix D for a full list of definitions.

2.0 Summary of Method

2.1 Following extraction, additional conditioning may be necessary, after which the sample extracts are concentrated and fortified with additional standards for clean-up. A variety of clean-up procedures, usually including gravity-fed column chromatography with acid and base impregnated silica are employed, depending on the nature of the extract. Extracts are then concentrated, fortified with injection standards, and undergo final preparations for HRGC/HRMS. The extracts are analyzed by HRGC/HRMS.

3.0 Safety Precautions

3.1 Gloves must be worn when handling samples, standards, and reagents.

3.2 Safety glasses must be worn at all times when working in the laboratory.

3.3 A lab coat must be worn while dealing with samples, standards, and reagents.

3.4 In the interest of safety and pollution prevention, all spills must be cleaned up immediately.

4.0 Interferences and Preventive Measures

4.1 Three types of interferences may cause problems with this method. The three kinds of interferences are specific, non-specific, and quantitative, and each is considered below.

4.2 *Specific Interferences*: Specific interferences are PCDD/Fs that appear in a final extract but did not originate with that sample. Two primary sources of specific interferences are cross-contamination from other samples and, less commonly, chemical reactions that form PCDD/Fs during sample preparation procedures (e.g., extraction).

4.3 *Non-specific interferences*: Non-specific interferences are compound present in the final extract that creates false positive signals for PCDD/Fs (e.g., polychlorinated diphenyl ethers). Ideally, sample preparation removes these interferences, but analysts should always be wary of them. An exhaustive list of non-specific interferences may be found in – *Environmental Carcinogens: Methods of Analysis and Exposure Measurement Volume 11: Polychlorinated Dioxins and Dibenzofurans* (IARC Scientific Publications), C. Rappe (Editor), H. R. Buser (Editor), B. Dodet (Editor), I. K. O'Neill (Editor).

4.4 *Quantitative Interferences*: Quantitative interferences cause alterations in the measured instrumental response for one or more target analyte instrument responses. These interferences result from the presence of compounds that in the final extract that either suppress ionization or upset the lock mass correction of the instrument. For more detail on these types of interferences, see "Hybrid HRGC/MS/MS Method for the Characterization of Tetrachlorinated Dibenzo-p-dioxins in Environmental Samples." Y. Tondeur, W.J. Niederhut, S.R. Missler, and J.E. Campana, *Mass Spectrom.* **14**, 449-456 (1987).

5.0 Sample Collection, Preservation and Storage

5.1 Waste is disposed of in appropriate waste containers in accordance with the local, state and federal regulations. No sample or reagent is ever disposed of down a drain or in the trash. See document MI_278 for waste disposal, pollution prevention and spill cleanup.

5.2 Sample extracts should be stored at room temperature during the cleanup and fractionation process. (i.e. PCDD/Fs and PCBs).

5.3 Sample extracts containing “volatile” compounds should be stored in the refrigerator at -2 to 4°C until analysis (i.e. Pesticides, PAHs, QuanTics, etc).

6.0 Equipment and Supplies

6.1 Glass wool

6.2 Sodium sulfate

6.3 Acidic silica gel

6.4 5 % AX-21 Carbon on silica gel

6.5 Alumina

6.6 Basic silica gel

6.7 5 % Silver nitrate on silica gel

6.8 Florisil/ 2% Deactivated Florisil

6.9 Tetrabutylammonium hydrogen sulfate

6.10 Sodium sulfite

6.11 Appropriate micropipettes

6.12 Class “A” Graduated Cylinder

6.13 Timer

6.14 10, 25, and 50ml drying column

6.15 0.45µm syringe filter

6.16 5ml syringe

6.17 Gilson: GX-271 liquid Handler

6.18 J2 Scientific: PrepLinc GPC

6.19 TurboVap

6.20 Genevac Rocket Evaporation System

7.0 Standards and Reagents

7.1 Hexane

7.2 Toluene

7.3 Methylene chloride - CH_2Cl_2

7.4 Tetradecane

7.5 TBA sulfite solution

7.6 2-propanol

7.7 Sulfuric Acid - H_2SO_4

7.8 Sodium Sulfate - Na_2SO_4

7.9 Silica Gel - SiO_2

7.10 Alternate standard (AS) or Cleanup standard (CS)

7.11 Isooctane

7.12 Distilled H2O

7.13 Talex Cleaned DI H2O

8.0 Sample Preparation

8.1 Use a manual fractionation process any time samples suspected to have unusually high native concentrations are being cleaned up.

8.2 Concentration

8.2.1 Turbovap

8.2.1.1 Set the water bath to the appropriate temperature for the solvent used and allow the bath to come to temperature (approximately 45°C for hexane and methylene chloride, 65°C for toluene).

8.2.1.2 Clean the nitrogen needles with toluene before use.

8.2.1.3 Place the 40- or 60-mL sample vials into the TurboVap. (Note: Be sure the correct vial rack is used.)

8.2.1.4 Set the nitrogen at 1-2 psi and set the time to allow the samples to evaporate down 5-10 mL. This will help prevent cross contamination. Once the samples have evaporated enough that solvent will not splash out of the vials, turn the nitrogen flow up to a maximum of 15 psi and set the time to allow the sample to evaporate to near dryness. The TurboVap will beep to signal that time is up. Additional time may be added if samples are not completely evaporated.

8.2.1.5 Once the samples have evaporated, remove the vials, and rinse the nitrogen needles with toluene.

8.2.2 Rocket Concentrator- Post Clean-up

8.2.2.1 The Rocket concentrator is a pre-programmed automated centrifugal sample concentration device.

8.2.2.2 Place samples in the vial holding "pucks" and insert into the rocket concentrator.

8.2.2.3 Select the option for "Very Low Boiling Point" (For CH2Cl2) or "Low Boiling Point" (For Hexane) solvent concentration.

8.2.2.4 The Rocket will automatically calculate the appropriate time to stop the concentration based upon the change in evaporated solvent temperature and stop when concentration is complete.

8.2.3 Roto-Vap- Pre-Clean-up

8.2.3.1 Set the water bath to the appropriate temperature for the solvent used and allow the bath to come to temperature (approximately 25°C for PCB/PAH's, 45°C for D/F analysis).

8.2.3.2 Add the solvent trap to the round-bottom flask containing the extract to prevent cross-contamination and attach to the Roto-vap concentrator.

8.2.3.3 Set the rotation to ~150rpm, turn the vacuum pump to the on position, and allow the sample to concentrate to approximately 5mL.

8.2.4 Solvent Exchange

8.2.4.1 If the sample extract is received in a solvent that is not compatible with the appropriate cleanup procedure, a solvent exchange must be performed.

8.2.4.2 Concentrate the sample to the smallest volume ("near dryness") possible depending on the concentration technique being used.

8.2.4.3 Add at least double the volume of the new, desired solvent to the residual solvent remaining in the extract and repeat 9.2.4.2

(Ex. 5mL of residual solvent should be exchanged with no less than 10mL of the desired solvent).

8.2.4.4 Repeat step 9.2.4.3 and proceed to the desired cleanup.

8.2.4.5 Alternatively, ~400uL of a "keeper solvent" compatible with the desired cleanup system may be used to assist with the solvent exchange. If this process is used the extract can be concentrated to the volume of keeper solvent, the cleanup solvent can be added, and the sample can proceed to cleanup immediately. This is for Dioxins/Furans only.

8.3 Sample cleanup

Note: If not already done, add the Cleanup Standards and/or Alternate Standards (typically 20ul@100pg/uL for D/F and PCB analysis). See project spike profile for exact spiking instructions. Always spike witness.

8.3.1 Acid Partition

8.3.1.1 Consider this technique for samples high in hydrocarbons, lipids, and other oily substances.

8.3.1.2 Dilute extracts at least 5-fold with hexane, including QC samples.

8.3.1.3 Add ~5 to 10 mL concentrated sulfuric acid to each sample. Alternatively, acid coated silica may be used as a substitute for concentrated sulfuric acid when emulsions are a concern

8.3.1.4 Shake the container vigorously. Remember to vent the container to relieve pressure during the shaking process.

8.3.1.5 Let the sample sit until the acid separates from the hexane. Take care not to let PCB samples sit in contact with the acid for too long, as lower homologue PCBs are susceptible to losses if in contact with the acid for long periods of time. Carefully add DI water (Talex cleaned DI water or Distilled water for PCB analysis) to the sample and swirl.

8.3.1.6 Remove the acid layer and retain the hexane layer.

8.3.1.7 If needed, repeat previous steps until the extract color has changed to a clear or yellow color.

8.3.1.8 Add ~5 to 10 mL DI water to the retained hexane portion (Talex cleaned DI water or Distilled water for PCB analysis).

8.3.1.9 Shake the container vigorously. Remember to vent the container to relieve pressure during the shaking process.

8.3.1.10 Let the sample sit until the water separates from the hexane.

8.3.1.11 Remove and retain the hexane layer. Run hexane layer through sodium sulfate plug.

8.3.1.12 Concentrate the sample and proceed with the clean-up and transfer steps.

8.3.2 Acid Base Columns

8.3.2.1 Build the standard acid/base column in the following order:

8.3.2.1.1 0.5 g (~1/4 teaspoon) silica gel

8.3.2.1.2 1.5 g base silica

8.3.2.1.3 0.5 g (~1/4 teaspoon) silica gel

8.3.2.1.4 12 g (~1 tablespoon) acid silica

8.3.2.1.5 0.5 g (~1/4 teaspoon) silica gel

8.3.2.1.6 1.25 g (~2cc scoop) 5% silver nitrate/silica - D/F only

8.3.2.1.7 1 g sodium sulfate

8.3.2.2 Rinse columns with 85 ml of hexane

8.3.2.3 Prepare Florisil columns.

8.3.2.3.1 Load each small column with ~1.70 g (+/- .04) florisil; followed by small amount sodium sulfate.

8.3.2.3.2 Rinse with 20 mL CH_2CL_2 followed by 20 mL hexane.

8.3.2.4 Review paperwork for projects to be cleaned up.

8.3.2.5 Verify type of projects for the run(s) and double check for any special instructions and confirm that all samples for clean-up have been spiked and are ready for cleanup procedure.

8.3.2.6 Remember if project has a PCB portion to put matching round bottoms60mL vials under each sample BEFORE loading the sample.

8.3.2.7 Load samples onto columns. Rinse each sample vessel twice with 1 mL hexane.

8.3.2.8 Elute with 85 mL hexane. Swap vials when needed to collect.

8.3.2.9 When hexane elution is complete remove acid/base column. Collect 20mL 5% DCM/ Hexane if PCB. D/F only 3% DCM hexane to waste.

8.3.2.10 When 5% portion is complete, remove the waste jars or PCB vials.

8.3.2.11 Place the appropriate dioxin collection new vial under columns

for final elution of 55mL DCM

8.3.3 PCU

8.3.3.1 1613/8290(soils) - Load method: DX_only_clean-up.txt

8.3.3.2 1668 (soils) - Load method: PCB_only_clean-up.txt

8.3.3.3 Dual extraction – Load method: PCB-DX_clean-up.txt

8.3.4 PCU-F

8.3.4.1 Assemble the acid/base silica column.

8.3.4.2 Assemble the florisil column.

8.3.4.3 Assemble waste collection setup.

8.3.4.4 Wet columns with hexane

8.3.4.5 Fill 4% DCM line.

8.3.4.6 Flush center fitting.

8.3.4.7 Load sample plus two vial rinses.

8.3.4.8 Elute acid base column with hexane.

8.3.4.9 Elute florisil with 4% DCM in hexane.

8.3.4.10 Position collection vial

8.3.4.11 Elute sample with 100% CH_2Cl_2.

8.3.4.12 Note: To perform method, start PCU software, load the desired method and hit start. When method is complete, concentrate the samples.

8.3.5 PCU-A

8.3.5.1 Assemble the acid/base silica column.

8.3.5.2 Assemble the alumina column.

8.3.5.3 Note: For tissue samples (e.g., fish) use the anthropogenic isolation column.

8.3.5.4 Assemble waste collection setup.

8.3.5.5 Wet columns with hexane

8.3.5.6 Fill 4% DCM line.

8.3.5.7 Flush center fitting.

8.3.5.8 Load sample plus two vial rinses.

8.3.5.9 Elute acid base column with hexane.

8.3.5.10 Elute alumina with 4% DCM in hexane.

8.3.5.11 Position collection vial

8.3.5.12 Elute sample with 100% CH_2Cl_2.

8.3.5.13 Note: To perform method, start PCU software, load method PCU-abal.txt, and hit start. When method is complete, concentrate samples.

8.3.6 Alumina Column Cleanup

8.3.6.1 Plug a 50 mL drying column with glass wool.

8.3.6.2 Add 10 g alumina followed by 1 g of Na_2SO_4 to the column.

8.3.6.3 Elute the column with 50 mL of hexanes.

8.3.6.4 Add the sample to the column.

8.3.6.5 Rinse the sample container with 2 x 1 mL aliquots of hexane and transfer to the column.

8.3.6.6 Elute with 15 mL of hexane to waste or another container if it is to be saved.

8.3.6.7 Elute with 100 mL CH_2Cl_2 and collect this fraction in the appropriate container.

8.3.7 Micro Alumina Column Cleanup

8.3.7.1 Plug a 50 mL drying column with glass wool.

8.3.7.2 Add 6 g alumina followed by 1 g of Na2SO4 to the column.

8.3.7.3 Elute the column with 20 mL of hexane.

8.3.7.4 Add the sample to the column.

8.3.7.5 Rinse the sample container with 2 x 1 mL aliquots of hexane and transfer to the column.

8.3.7.6 Elute with 10 mL of hexane to waste or another container if it is to be saved.

8.3.7.7 Elute with 50 mL CH_2Cl_2 and collect this fraction in the appropriate container.

8.3.8 Carbon Cleanup (PCDD/Fs and Co-Planar PCBs ONLY)

8.3.8.1 Plug one end of a glass tube with glass wool.

8.3.8.2 Add 1 g of Na_2SO_4 followed by 1g furnaced silica

8.3.8.3 Add ~.25 g of 5 % AX-21 carbon on silica gel (1/8tsp stainless steel scoop may be used).

8.3.8.4 Rinse with methanol.

8.3.8.5 Rinse carbon residue from sides of column using methanol, add

1 g furnace silica, followed by 1 g of Na_2SO_4

8.3.8.6 Rinse with toluene.

8.3.8.7 Plug the end of the column with glass wool and pack with a stirring rod.

8.3.8.8 Rinse with toluene

8.3.8.9 Prep collection vessels and spike with 20 µL of tetradecane

8.3.8.10 Set up waste jars

8.3.8.11 Prepare solvents

8.3.8.12 Pre-elute with 20 mL toluene flip the column and follow with 10 mL hexane pre-elution, making sure 'clean' side of glass wool is on top (clean in, clean out)

8.3.8.13 Load the sample in hexane, rinse with hexane, load, and repeat.

8.3.8.14 Elute with 10 mL of hexane and allow to flow into waste.

8.3.8.15 Flip column over and place collection vessel under the column. (Clean side should be DOWN)

8.3.8.16 Elute with 50 mL of toluene into collection vessel.

8.3.8.17 If column is not flipped over for toluene elution; elute with 100-150 mL of toluene and collect.

8.3.9 Mini-acid silica cleanup

8.3.9.1 Place a glass wool plug in a 25 mL drying column.

8.3.9.2 Add 4 g of acid coated silica gel to the column, followed by 1 g of Na_2SO_4.

8.3.9.3 Position waste collection vial under silica column.

8.3.9.4 Pre-elute column with 30 mL of hexane

8.3.9.5 Position properly labeled collection vial under column.

8.3.9.6 Load sample, rinse sample container with hexane, load, and repeat.

8.3.9.7 Flush column with 30 mL of Hexane.

8.3.9.8 Concentrate sample and proceed with the Transfer steps.

8.3.10 Sulfur removal

8.3.10.1 Add ½ gram of cooper to sample extract. Agitate and let sit. Proceed to clean up as normal.

8.3.10.2 Tetrabutylammonium hydrogen sulfate cleanup

8.3.10.2.1 Dissolve 3.39 g of tetrabutylammonium hydrogen sulfate $[CH_3(CH2)_3]_4$ $NHSO_4$ (TBA sulfite) in 100 mL of Talex cleaned DI water in a 250-mL amber bottle with a Teflon™-lined screw cap. Extract this solution three times with 20 mL each of hexane. Discard the hexane appropriately and then add sodium sulfite until saturation (~ 25 g). [Note: The solution can be kept at room temperature for up to 2 months.]

8.3.10.2.2 Transfer the sample extract to a 40 mL VOA vial using Hexane. Rinse the sample container 2 times with ~1.5 mL of hexane. (Note: the VOA vial should now have ~5.0 mL of hexane). Add 1.0 mL of the TBA sulfite solution and 2.0 mL of 2-propanol to the VOA vial. Shake for 1 minute. If crystals are present, then enough sodium sulfite is present; if not, add 0.1 g of sodium sulfite. Shake for 1 minute. If there are still no crystals, repeat adding sodium sulfite and shaking.

8.3.10.2.3 Add 5.0 mL Talex cleaned DI water and shake for 1 minute. Allow the sample to settle for 10 minutes. 2 layers will form. Transfer the hexane layer (top) to a round bottom through a sodium sulfate plug (to remove any water). Concentrate sample and proceed with the Transfer Steps Discard the bottom layer as waste down the drain.

8.3.11 PAH Clean up

8.3.11.1 Place a glass wool plug in a 25 mL drying column.

8.3.11.2 Add ~6 g (1 tablespoon) of furnaced silica to the drying column followed by 1 g of Na_2SO_4.

8.3.11.3 Pre-elute with 30 mL of DCM followed by 30 mL of hexane into waste container and remove

8.3.11.4 Place properly labeled 60mL vial under column. Load sample, rinse sample container with hexane, load, and repeat

8.3.11.5 Elute with 25 mL of hexane followed by 30 mL of 40% DCM in hexane.

8.3.11.6 Concentrate sample and proceed with the Transfer step.

8.3.11.7 Acid silica with florisil cleanup for dioxin and/or PCB waters

8.3.11.8 Dioxin and PCB water sample extract cleanup is accomplished by passing the extract through the column under controlled

conditions described below.

8.3.11.9 Assemble the column as follows from bottom: glass wool, 5mm silica(~0.5g), 15mm florisil(~1.7g), 5mm silica(~0.5g), 80mm acid silica(~4g), 10mm sodium sulfate(~1g).

8.3.11.10 Position waste collection vial under silica column.

8.3.11.11 Rinse the column with 30mL of dichloromethane and flow to waste.

8.3.11.12 Rinse the column with 30mL of hexane and flow to waste.

8.3.11.13 Position PCB collection vial and load the sample from the 60mL vial. If the samples do not contain a PCB portion allow this fraction to flow to waste.

8.3.11.14 Rinse vial with 2x 1mL rinses of hexane and apply to column.

8.3.11.15 Flush column with 30mL of hexane, followed by 20mL of up to 5% DCM in Hexane, and collect. If the samples do not contain a PCB fraction, flush the column with 40mL of hexane (without using up to 5% DCM in Hexane) and allow this fraction to flow to waste.

8.3.11.16 To collect the dioxin fraction, position a properly labeled 60mL vial under column, and elute the column with 55mL of 100% DCM.

8.3.11.17 Concentrate the samples and proceed to sample transfer.

8.3.12 GPC Clean-up – For Solid samples and additional cleanup of samples with large quantitative interferences.

8.3.12.1 If not previously performed, add the cleanup standard (CS).

8.3.12.2 Solvent exchange each sample to DCM and bring volume to 5 mL. Samples should not contain any residual solvent, as this will affect the GPC packing material and elution pattern of the analytes.

8.3.12.3 Samples must be free of any particulate matter and may require filtering through a 0.45 µm filter to remove particulates. Any particles not removed will remain on the column and may also clog the inlets.

8.3.12.4 Prior to running the GPC check to make sure the column media is saturated with solvent, and a valid calibration (within 30 days) is available.

8.3.12.5 Determine the appropriate fractions to be collected using the “chromatogram” feature in the GPC software and update or create a new GPC method.

8.3.12.6 Create a data sequence using the "sequence editor" function in the GPC software, and program a blank sample. This sample is used to prime the GPC Column, and check the elution times and quantities. Details on the use of the GPC software may be obtained from the user's manual.

8.3.12.7 Load the samples and QC into the GPC sample tray and check to make sure all solvent reservoirs are at the appropriate volume.

8.3.12.8 Position collection vials in the GPC collector tray and start the GPC sequence.

8.3.12.9 After the sequence has been completed, concentrate the samples in a TurboVap or rotovap at 25^{o}C and low pressure. Do not let the samples go dry.

8.3.12.10 If further cleanup is needed spike the samples with appropriate amount of injection standard (JS) and filter samples using a 0.45µm syringe filter directly into labeled GC/MS vials with at least 2-3 rinses of hexane.

8.3.12.11 If no further cleanup is required spike the samples with appropriate amount of injection standard (JS) and gently concentrate extract under nitrogen blow-down to a final volume of 50 µL.

8.4 TRANSFER

8.4.1 After concentrating the extract resulting from the clean-up process to volume of approximately 0.5 mL.

8.4.2 Spike the extract with 2ng of injection standards (JS) and transfer to a GC/MS vial.

8.4.3 Using the mini-vap (nitrogen blow-down), set the flow to approximately 10 L/min and concentrate the extract to the correct final volume (depending on analysis). Use caution to avoid over-concentrating the extract at this stage, as you may cause losses of compounds if the extract is over-concentrated.

8.4.3.1 20 µL in Tetradecane for PCDD/PCDFs

8.4.3.2 20 µL in Nonane for PCBs

8.4.3.3 100 µL in Isooctane for PAHs

8.4.3.4 100 µL in Isooctane for QuanTics

8.4.3.5 50µL in Nonane for Pesticides

9.0 Quality Control Requirements

9.1 Data outside of QC limits may be addressed by one or more of the following options:

9.1.1 Re-preparation and re-analysis of sample

9.1.2 Client notification

9.1.3 Discussion and qualification of data by case narrative

9.1.4 Re-sampling and reanalysis (client decision)

9.2 Data outside of QC limits may be reported if directed by the client. It must be qualified by a case narrative detailing the QC problems with advice on the usability of the data.

10.0 Data Review and Reporting Requirements

10.1 Refer to SGS document MI_141, Data review SOP

11.0 Definitions

11.1 ASECS – Automated Sample Extract Cleanup System

11.2 PCU – Paradigm Cleanup

11.3 PCU-F – Paradigm Cleanup with Florisil

11.4 PCU-A – Paradigm Cleanup with Alumina

11.5 DCM – Dichloromethane - CH_2Cl_2

11.6 DI - Deionized

11.7 PCDD/PCDF- polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran

11.8 PCB- Polychlorinated Biphenyl

11.9 PAH- Polynuclear Aromatic Hydrocarbon

11.10 QuanTIC = selected SVOAs by full-scan GC/MS (ID-HRMS)

12.0 References

12.1 SGS document DC_139, Appendix D Definitions.

12.2 SGS document MI_278, Waste Disposal, Pollution Prevention and Spill Clean up.

12.3 SGS document MI_141, Review of Analytical Data.

12.4 SGS document MI_2, Glass Prep

12.5 EPA Method 1613B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, October 1994

12.6 EPA Method 1668A, Chlorinated Biphenyl Congeners in Water, Soil, Sediment

and Tissue by HRGC/HRMS, December 1999

12.7 EPA Method 8290A, Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS), February 2007

12.8 EPA Method 1668B, Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, November 2008

12.9 EPA Method 1668C, Chlorinated Biphenyl Congeners in Water, Soil, Sediment and Tissue by HRGC/HRMS, April 2010

STANDARD OPERATING PROCEDURE L-3I: HOMOGENIZATION OF BIOTA/TISSUE

Standard Operating Procedure for the Preparation of Fish Tissue samples for HRMS/ID analyses

Issue date: 09/22/2022
Revision: 5

SGS North America Inc.
5500 Business Drive
Wilmington, North Carolina 28405

Approved by:

Jeannie Milholland
Jeannie Milholland, Last Revised by — Date

Greg Dickinson
Greg Dickinson, Technical Director — 09-22-2022` Date

Jeannie Milholland
Jeannie Milholland, Quality Assurance Director — Date

(Official copies of final documents will contain all three signatures.)

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Revision History

- The following change was made effective on September 22, 2022
  - Section 3.5: added safety precautions
  - Section 6.0: Updated equipment and supplies
  - Sections 7.6.3, 7.6.3.1, 7.6.4, 7.6.5 and 7.6.6: updated homogenization process to be specific to fish and preparation
  - Sections 7.4.2, 7.4.3, 7.4.5: updated sections
  - Section 8.3: added section on personnel qualifications and capability
- The following change was made effective on July 8, 2022
  - Typo revision made to section 4.2 – New SOP version not required
- The following changes were made effective on June 21, 2022
  - Added section 7.6 specific to NYSDEC homogenization
- The following changes were made effective on June 21, 2022
  - Section 3 – Added requirement for cut-resistant gloves and chainmail gloves
  - Added Section 4 – Interference and Preventative Measures
  - Added Section 7.2.3 – NYSDEC homogenization requirements
  - Added Sections 7.3 & 7.4 – specific filleting requirements for NYSDEC samples
  - Section 11 – Added reference to NYSDEC SOP
- Review was completed on March 21, 2020, by Ricky Ballard and no updates needed
- The following changes were made effective on January 4, 2017
  - Section 6.3: removed references to fish fillets as this section is for whole body fish
- The following changes were made effective on May 26, 2015
  - Section 6.3.1: added ‘if’ before debris
  - Section 6.3.2: new section inserted, renumbering rest of section
  - Section 6.3.3: ‘sample’ changed to ‘fillets’
  - Section 6.3.4: ‘The sample is’ changed to ‘All fillets are’ and ‘together’ added

1.0 Scope and Application

1.1 This standard operating procedure describes procedures for the initial preparation of fish tissue or other marine biota submitted to the laboratory which will be extracted and analyzed for ultra-trace levels of PCDD/Fs, PCBs, and/or other ultra-trace analytes by HRMS-ID technique.

1.2 This SOP is intended to provide guidance for the preliminary preparation of tissue samples prior to the sample aliquotting and analytical preparation described in individual analytical SOPs.

1.3 Customer specific QAPP/SAP/SOW/protocols with alternate procedures will take precedence over this SOP.

2.0 Summary of Method

2.1 Fish tissue samples are inherently nonhomogeneous and require special treatment to obtain a representative sample for analysis. This SOP provides guidance on appropriate procedures to follow to obtain a representative sample for extraction and analysis for samples analyzed by HRMS-ID methods.

3.0 Safety Precautions

3.1 Gloves must be worn when handling samples, standards, and reagents.

3.2 Safety glasses must be worn at all times when working in the laboratory.

3.3 A lab coat must be worn while dealing with samples, standards, and reagents.

3.4 Cut gloves are to be worn when filleting fish using a knife. Chainmail gloves are to be worn when using a cleaver.

3.5 Avoid distractions when working with sharp equipment to minimize the loss of focus to the task. Do not place any spoons, spatulas, knives, or any other devices into a food processor when in operation. Be certain the unit has stopped rotating BEFORE opening the lid.

3.6 In the interest of safety and pollution prevention, all spills must be cleaned up immediately.

3.7 Waste is disposed of in appropriate waste containers in accordance with the local, state and federal regulations. No sample or reagent is ever disposed of down a drain or in the trash. See document MI_278 for waste disposal, pollution prevention and spill cleanup.

4.0 Interference and Preventative Measures

4.1 Conduct all work in a clean laboratory environment. All worksurfaces, utensils and grinder work bowls and covers should be cleaned with soap and water, then rinsed with clean water, prior to working with samples, between each sample, and upon completion of sample preparation for the day. Alternatively, between samples aluminum foil may be placed on the work surface for the succeeding fish sample; discard foil after one use.

4.2 Wear nitrile or latex gloves at all times while preparing samples. Dispose of gloves between samples and place new gloves on hands. If a glove is torn or punctured, immediately discard the glove and replace with a new glove. Discard gloves at the end of the day, or earlier if they become unsuitable for clean preparation of samples.

4.3 Rinse fish samples in clean DI water if soil, debris or other matter are evident on the exterior surfaces. Allow water to run off and dry exterior surface.

4.4 Following preparation of sample portions, place sample in clean containers of suitable size for the sample. Place small samples in chemically clean glass jars, cover, and label immediately. Jars should have PTFE-lined caps and be recleaned and certified. For large samples, wrap in Acetone or methanol rinsed aluminum foil and label externally. For NYSDEC samples rinse the aluminum foil with Hexane. Place foil wrapped sample in a labeled food-grade plastic bag for subsequent storage and transport. If hexane-rinsed aluminum foil is unavailable, and samples are not to be analyzed for phthalates, the excised sample may be placed in a food grade plastic bag, labeled externally and placed in frozen storage.

5.0 Sample Preservation and Storage

5.1 Fish samples are kept frozen until ready for extraction in which they are placed in refrigeration at 4°C (+/- 2°C) to thaw for 2 days.

5.2 After extraction, the samples are placed in the freezer and kept frozen until disposal.

6.0 Equipment and Supplies

6.1 Hobart food chopper, or comparable device (blades must be sharp)

6.2 Tissuemizer (blades must be sharp)

6.3 Waring blender, or similar device (blades must be sharp)

6.4 Glass or PTFE cutting boards

6.5 Knives and cutting implements, stainless steel (blades must be sharp)

6.6 Standard laboratory glassware, amber glass jars/bottles

6.7 Heavy duty aluminum foil

6.8 Pesticide grade or better, acetone and/or methanol

6.9 Balance capable of weighing to 0.1 g

6.10 Blade sharpener

7.0 Sample Preparation

7.1 Cleaning

7.1.1 Prior to handling samples, any utensils, knives, cutting boards and bench surfaces should be thoroughly cleaned and rinsed/wiped with acetone or methanol.

7.1.2 Implements should be washed in detergent hot water solution, rinsed with tap water, followed by rinsing with DI water, and acetone or methanol before use and in between each individual sample that is prepared.

7.1.3 Pre-cleaned certified amber glass jars or bottles may be used without any further cleaning.

7.1.4 Heavy duty aluminum foil should be rinsed with acetone or methanol prior to use or before contact with any sample.

7.2 Fish Fillets

7.2.1 Fish samples often arrive at the lab having already been filleted and packaged by the client. Instructions from the client and/or project manager should be followed for appropriate compositing.

7.2.2 Samples may be ground and homogenized using the Hobart or Waring blender, depending on the size of the sample(s).

7.2.3 For NYSDEC samples Mix the tissue and repeat the grinding step at least two more times and until the sample appears to be homogeneous.

7.2.4 Samples should be kept cold. Partially frozen tissue is typically more readily homogenized.

7.2.5 Individual (single) fillets are ground and homogenized to fine paste-like consistency to ensure that the sample is thoroughly homogenized and mixed.

7.2.5.1 The entire fillet received should be homogenized. Large fillets may be cut with a knife into smaller pieces to facilitate homogenization.

7.2.5.2 If enough homogenized sample is available, the sample should be placed into three labeled 4-ounce amber jars then moved to appropriate cold storage.

7.2.5.3 Any remaining sample may be discarded, unless directed otherwise.

7.2.6 Composited/multiple fillets are ground and homogenized to fine paste-like consistency to ensure that the sample is thoroughly homogenized and mixed.

7.2.6.1 Whole fillets received should be used and not sub-sampled prior to homogenization.

7.2.6.2 Large fillets may be cut with a knife into smaller pieces to facilitate homogenization.

7.2.6.3 Component fillets may be homogenized together if the fillets are small enough to fit into the Hobart or Waring blender. Care must be taken to ensure that component fillets are thoroughly homogenized and mixed to provide a representative composited sample.

7.2.6.4 If enough of the sample is available, the composited sample should be placed into three labeled 4-ounce amber jars then moved to appropriate cold storage.

7.2.6.5 Any remaining sample may be discarded, unless directed otherwise.

7.3 Standard Fillet for NYSDEC samples

7.3.1 Remove scales from the fish making sure not to remove the skin.

7.3.2 Take the fillet from the left side of the fish

7.3.3 Make a cut along the ventral midline of the fish from the vent to the base of the jaw.

7.3.4 Make a diagonal cut from the base of the cranium following just behind the gill to the ventral side just behind the pectoral fin.

7.3.5 Remove the flesh and ribcage from the left side of the fish by cutting from the cranium along the spine and dorsal rays to the caudal fin. The ribs should remain on the fillet.

7.3.6 Score the skin and homogenize the entire fillet.

7.4 Modifications to the Standard Fillet for NYSDEC samples

7.4.1 Four modifications of the standard fillet procedure above are designed to account for variations in fish size or known

preferred preparation methods of the fish for human consumption.

7.4.2 Some fish are too small to fillet by the above procedure. Fish less than approximately 6 inches long and rainbow smelt are analyzed by descaling, cutting the head off from behind the pectoral fin and eviscerating the fish. Ensure that the belly flap is retained on the carcass to be analyzed.

7.4.3 Some species are generally eaten by skinning the fish. The skin from these species is also relatively difficult to homogenize in the sample. Hence, for the following list of species, the fish is first skinned prior to homogenization: Brown Bullhead, Yellow Bullhead, Black Bullhead, Atlantic Sturgeon, White Catfish, Channel Catfish and Lake Sturgeon. Note: For the catfish and bullhead it can be easier to remove the skin after filleting. Either before or after filleting is fine if muscle is not lost in the removal of the skin.

7.4.4 American eel are analyzed by removing the head, skin, and viscera; filleting is not attempted.

7.4.5 Forage fish and young-of-year fish are analyzed whole. Small prey fish should have been composited prior to delivery to the laboratory. Individuals should be of the same species.

7.5 Whole body fish

7.5.1 Partially frozen whole body fish samples should be rinsed with DI water if debris or mucus are visible.

7.5.2 All whole body fish are thoroughly ground and homogenized together in the Hobart or Waring blender. Fish skin may be difficult to thoroughly homogenize. Care will be taken to homogenize the sample to the extent possible with the ideal final consistency being paste-like.

7.5.3 The sample should be placed into three labeled 4-ounce amber jars then moved to appropriate cold storage.

7.5.4 Any remaining sample may be discarded, unless directed otherwise.

7.6 NYSDEC Fish Homogenate criteria

7.6.1 Sample must be uniform.

7.6.2 No whole fish or fish organs may be present.

7.6.3 All sport fish must be descaled including those under 6 inches in length.

7.6.3.1 Sport fish fillets (e.g., smallmouth bass, walleye, pumpkinseed), small sport fish with head and viscera removed. Retain belly flap for homogenization. Samples are blended for approximately 15 – 30 seconds per cycle, followed by scraping down the sides of the blender and repeating, until homogenized sample meets requirements below. If the grinder is used samples are processed through the grinder 3 times or until the sample meets requirements below.

7.6.3.2 Requirements: Three or fewer pieces less than 1 cm of skin or bone may be present.

7.6.4 Carp and fillet fish –Descale, prepare left side fillet (right side for samples with no left side remaining) by cutting into small fragments (1 square inch). Blend or grind in multiple aliquots, if necessary, based on the size of the sample. Samples are blended for approximately 15 – 30 seconds per cycle, followed by scraping down the sides of the blender and repeating, until homogenized sample meets requirements below. If the grinder is used samples are processed through the grinder 3 times or until the sample meets requirements below. Requirements: Four to Six or fewer pieces less than 2-3 cm of skin or bone may be present.

7.6.5 Large whole body prey fish – Remove head and break skull bones, cut fish into five parts of equal size. Add to blender or grinder in units (starting with the head). If using blender pause as necessary to scrape down the sides of the blender in order to ensure that the sample is actively making contact with the blades and not stuck to the sides. Cooling intervals, at approximately 10 minutes each, will be necessary to ensure that the blender does not heat the sample. Continue the blending and cooling intervals until homogenized sample meets requirements below. If the grinder is used samples are processed through the grinder 3 times or until the sample meets requirements below. Requirements: Large whole body prey fish are expected to have some larger pieces of skin or bone (3 – 6 cm) but must be evenly distributed; occasional occurrence of fins is also acceptable.

7.6.6 Small whole-body fish (prey fish) -Whole body fish to blender. Samples are blended for approximately 15 – 30 seconds per cycle, followed by scraping down the sides of the blender and repeating, until homogenized sample meets requirements below.

Requirements: Three or fewer pieces less than 1 cm of skin or bone may be present.

8.0 Quality Control Requirements

8.1 Data outside of QC limits may be addressed by one or more of the following options:

8.1.1 Re-preparation and re-analysis of sample

8.1.2 Client notification

8.1.3 Discussion and qualification of data by case narrative

8.1.4 Re-sampling and re-analysis (client decision)

8.2 Data outside of QC limits may be reported if directed by the client. It must be qualified by a case narrative detailing the QC problems with advice on the usability of the data.

8.3 SGS personnel performing this procedure must have documented demonstration of capability and must have signed attestation for current revision of this SOP.

9.0 Data Review and Reporting Requirements

9.1 This section addresses any criteria that must be met before the analytical results can be reported and should also reference our Data Review SOP (MI_141).

10.0 Definitions

10.1 QAPP – Quality Assurance Project Plan

10.2 SAP – Sampling and Analysis Plan

10.3 SOW – Scope of Work

10.4 SOP – Standard Operating Procedure

10.5 PTFE – Polytetrafluoroethylene (Teflon)

10.6 PCDD/F - Polychlorinated dibenzo-p-dioxin/furan

10.7 PCB - Polychlorinated biphenyl

10.8 HRMS-ID – High-resolution Mass Spectrometry Isotope Dilution

11.0 References

11.1 Prep Lab Standard Operating Procedure NYS Department of Environmental Conservation, Hale Creek Field Station ; SOP PrepLab-4 (5-28-2014)

11.2 SGS document DC_139, Appendix D Definitions.

11.3 SGS document MI_278, Waste Disposal, Pollution Prevention and Spill Clean up.

11.4 SGS document MI_141, Review of Analytical Data.

PREP LAB STANDARD OPERATING PROCEDURE
NYS DEPARTMENT OF ENVIRONMENTAL CONSERVATION
Hale Creek Field Station

Name of document: SOP PrepLab4 (5-28-2014)
Revision date: 5/28/2014
Previous revision: SOP PrepLab3 (3-16-2011)
Reason for this revision:

- Revise Section III. B) 1) to indicate that the standard fillet is taken from the left side of a fish.

Reference: *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1, 3rd edition* (USEPA Office of Water, November 2000)

Summary: Samples are received at Hale Creek Field Station and dissected, ground and homogenized for future chemical analysis. In addition, samples for organochlorine analysis are freeze-dried to remove moisture.

Background:
New York State Department of Environmental Conservation conducts studies requiring chemical analysis on fish or other biological tissues. Routine monitoring and surveillance studies develop data on contaminants in fish for several reasons:

1. To identify sources of environmental contamination;
2. To identify the geographic extent of environmental contamination;
3. To identify temporal trends of contaminants in fish and wildlife;
4. To identify potential impacts to fish and their consumers; and
5. To provide information regarding human consumption advisories.

Chemical analyses of edible fish flesh have been determined to be the most appropriate analyses for satisfying all of these objectives. The following methodology has been developed in order to standardize the tissues under analysis and to adequately represent the contaminant levels of fish flesh. The portion of edible flesh analyzed will be referred to as the standard fillet unless otherwise noted. For some species, the procedure is modified as indicated below.

I. SAMPLE RECEIPT

A) All samples received by the lab are to be accompanied by a Collection Record and Continuity of Evidence form.

B) After comparison of samples received with the Collection Record, the Continuity of Evidence form is signed and dated.

C) The original forms are to be retained by the lab. Copies may be returned to the delivery person.

D) Depending upon sample type, the samples are to be stored locked in either the cooler or freezer.

II. SAMPLE LOG IN

A) All samples are assigned a unique serial Lab # which corresponds to a specific Tag # or ID # on the sample or sample container.

B) The Lab #s are to be indicated on the Continuity of Evidence form and the Collection Record.

C) From the Collection Record the Lab #, Tag #, Species, Location, Program, Length, Weight, Sex, and Age are entered into the computer Log file.

III. SAMPLE DISSECTION

A) Samples are removed from the freezer and allowed to partially thaw (large samples may be removed the previous night).

B) FISH: The portion of edible flesh analyzed will be referred to as the standard fillet unless otherwise noted. For some species, the procedure is modified as indicated below.

1) Standard Fillet – Take the fillet from the left side of the fish as follows:

a) Remove scales from the left side of the fish. Do not remove the skin.

b) Make a cut along the ventral midline of the fish from the vent to the base of the jaw.

c) Make a diagonal cut from the base of the cranium following just behind the gill to the ventral side just behind the pectoral fin.

d) Remove the flesh and ribcage from the left side of the fish by cutting from the cranium along the spine and dorsal rays to the caudal fin. The ribs should remain on the fillet.

e) Score the skin and homogenize the entire fillet.

2) Modifications to the Standard Fillet

a) Four modifications of the standard fillet procedure (see b,c,d,e) are designed to account for variations in fish size or known preferred preparation methods of the fish for human consumption.

b) Some fish are too small to fillet by the above procedure. Fish less than approximately 6 inches long and rainbow smelt are analyzed by cutting the head off from behind the pectoral fin and eviscerating the fish. Ensure that the belly flap is retained on the carcass to be analyzed.

c) Some species are generally eaten by skinning the fish. The skin from these species is also relatively difficult to homogenize in the sample. Hence, for the following list of species, the fish is first skinned prior to homogenization:

Brown Bullhead	White Catfish
Yellow Bullhead	Channel Catfish
Black Bullhead	Lake Sturgeon
Atlantic Sturgeon	

d) American eel are analyzed by removing the head, skin, and viscera; filleting is not attempted.

e) Forage fish and young-of-year fish are analyzed whole.

C) Wildlife/Other: Generally non-fish samples that are to be prepared have already been dissected. See supervisor for appropriate instructions.

D) All dissection tools are to be rinsed, washed with soap, rinsed, rinsed with DI water and dried between each sample dissection.

IV. HOMOGENIZATION

A) Thoroughly grind and homogenize fish fillets using a Waring commercial chopper/grinder model WCG75. Alternatively, a comparable food chopper, food processor, grinder, blender or homogenizer may be used.

B) Mix the tissue and repeat the grinding step at least two more times and until the sample appears to be homogeneous.

C) The homogenized sample is then subsampled into appropriate glass bottles. Generally 2-10 g is needed for metals analysis and 20g for organochlorine analysis. For the OC sample label and weigh an empty sample bottle. Add ca 20g of sample into the bottle and

weigh again.

D) The bottles are capped and stored in the freezer.

E) All homogenization tools are to be rinsed, washed with soap, rinsed, rinsed with DI water and dried between each sample.

V. FREEZE DRYING

A) Generally samples for organochlorine analysis are freeze dried.

B) Make sure that the unit has been drained, all valves closed and the vacuum pump oil is clear and within the acceptable markings on the site vial.

C) Turn the refrigeration unit on. After the temperature OK light comes on (less than -40 C) turn the vacuum pump on. After the vacuum OK light comes on (less than 100 millitorr) the samples may be placed on the freeze dryer (make sure samples are frozen).

D) The samples are freeze dried ca 16 hours or until the samples reach a constant weight.

E) When freeze dried, the sample bottle is weighed again.

F) The sample is stored in the freezer until analysis is started.

VI. MINIMIZING SAMPLE CONTAMINATION DURING SAMPLE PREPARATION

A) Conduct all work in a clean environment, preferably a laboratory setting. All work surfaces, utensils and grinder work bowls and covers should be cleaned with soap and water, then rinsed with clean water, prior to working with samples, between each sample, and upon completion of sample preparation for the day. Alternatively, between samples aluminum foil may be placed on the work surface for the succeeding fish sample; discard foil after one use. DO NOT use aluminum foil if metals analyses are to be conducted on the sample.

B) Wear a clean laboratory coat for protection of clothing. Wear nitrile or latex gloves at all times while preparing samples. Clean gloves with soap and water between each sample, or discard gloves between samples and place new gloves on hands. If a glove is torn or punctured, immediately discard the glove and replace with a new glove. Discard gloves at the end of the day, or earlier if they become unsuitable for clean preparation of samples..

C) Rinse fish or other biological samples in clean water if soil, debris or other matter are evident on the exterior surfaces. Allow water to run off and dry exterior surface.

D) Following preparation of sample portions, place sample in clean containers of suitable size for the sample. For example, place small samples in chemically clean glass jars, cover and label immediately. Jars should have PTFE-lined caps and be precleaned and certified to meet EPA standards for metals, pesticides and semi-volatiles. For large samples (e.g., a fish fillet), wrap in hexane-rinsed aluminum foil and label externally. Place foil wrapped sample in a labeled food-grade plastic bag for subsequent storage and transport. If hexane-rinsed aluminum foil is unavailable, and samples are not to be analyzed for phthalates, the excised sample may be placed in a food grade plastic bag, labeled externally and placed in frozen storage. DO NOT use aluminum foil if metals analyses are to be conducted on the sample.

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NYS DEPARTMENT OF ENVIRONMENTAL CONSERVATION
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H-1 CONTAINERS, PRESERVATION, PROCESSING AND TRACKING OF SAMPLES FOR ANALYSIS

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the standard operating procedure (SOP) for containment, preserving, handling and shipping samples collected for analysis. Samples are defined as biota, sediment or water samples collected or generated at the site for chemical or geotechnical analysis. This procedure describes the essential steps that could affect tracking, documentation, or integrity of samples and is intended to provide sufficient instructions for sampling personnel to follow reliably, and consistently.

This procedure is to be followed, and any substantive modification to the procedure shall be approved and documented by the Field Team Leader.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Field Team Leader is responsible for assigning field personnel to handle samples at the site. Field personnel assigned to handle samples for laboratory analysis are responsible for completing their tasks according to this and other appropriate procedures. Field personnel are responsible for reporting deviations from the procedure to the Field Team Leader.

Only qualified personnel shall be allowed to perform this procedure. Qualifications will be based on previous experience and appropriate health and safety training. These considerations are discussed in more detail in the Project Safety Plan (PSP).

3.0 SAMPLE HANDLING PROCEDURES

3.1 Equipment List

- Inert packing material
- Sample containers (glass jars, plastic bottles, Encore samplers, preservatives and temperature blanks (as specified in the QAPP))
- Sample labels
- Chain of Custody (COC)/Analytical Request Forms
- Ice chest(s)
- Custody seals
- Marking pens (permanent markers and black ballpoint pens)
- Hacksaw and linoleum or carpet knives, spare blades
- Electric shears
- Plastic sheeting and/or aluminum foil
- Processing table(s)
- Stainless steel spoons

- Stainless steel spatulas
- Paddle for homogenization/mixing
- Shipping tape
- Sealable plastic bags
- Field logbook
- Wet ice (frozen H_2O)
- Food grade plastic lining material
- Shipping forms for selected carrier
- Sampling Plan
- Disposable cloth and/or paper towel
- Clean plastic and/or aluminum foil
- Shelby tube cutter or large enough pipe cutter
- Spatulas large enough for Shelby tube, at least 5-inch blade
- Shelby tube caps

3.2 Documentation

All sample identification information (i.e., sampling location, sample number/ designation, sample time, and analysis) will be written into a bound, paginated field logbook. Sampling locations and samples collected will be named in general conformance with the convention outlined below. Information will also be maintained electronically with data management software discussed in detail in SOP D-1. If the samples are taken from core or boring the sample ID will also be recorded on the boring log.

3.3 Sample Labeling

Each bottle used for sampling will have a label attached. The sample coordinator will have the project name, location ID, field sample ID (see below), matrix, preservative, analysis requested, sampler's initials, laboratory designation, sample data and time printed onto the label in the field. Alternatively, the sample container will be hand labeled at the time of collection and a complete label will be affixed before packing for shipment. The label will be protected from water and solvents with clear label protection tape.

3.4 Management of COC Data - Sample Nomenclature System

A sample nomenclature system has been developed to ensure consistency in field sample ID assignment and compatibility with EQuIS developed for Honeywell. Two identification labels will be associated with field samples: the Location ID, and Field Sample ID.

Location ID: The Location ID will represent the physical location where samples are collected, such as a monitoring well or sediment boring. Each unique field sample will be associated with a Location ID, which will be identified prior to fieldwork or at the time of sampling, and entered into EQuIS prior to field sample information input. The Location ID will consist of a description of the site (Site ID), the remediation area, the sample location type (such as a well or boring), and a five-digit sample location number that starts with the former SMU designation:

- # # # - # # # - # # # #

Site ID - Remediation Area- Location type - Location number

The first part of the Location ID is the Site ID, which will be OL, for Onondaga Lake, for all the sample locations. The second part of the Location ID is the Remediation Area which will be abbreviated as RA followed by a letter for the area (RAA). The third part of the Location ID is the Location Type. The location type will be based on what activity(s) will occur at the location, based on a predetermined list of database specific options . The list of location types is as follows:

- S-SB: sediment or soil boring
- W-SW: surface water
- SED: surface sediment
- T-FT: fish tissue
- T-IT: invertebrate tissue
- T-ZP: zooplankton tissue

Other location type naming will be consistent with that used during the PDI/baseline sampling, as applicable. At locations where more than one activity will take place the location type is STA for station. A list of valid site IDs, Location Types, and Location Numbers will be available to the field team from the Data Manager.

For all other Honeywell sites, the locations ID is the same structure but without the remediation area or SMU designation as follows:

- # # # - # # # #

Site ID - Location type - Location number

Field Sample ID

The Field Sample ID is the unique label assigned to each individual sample. The Field Sample ID will consist of the site description abbreviation (Site ID), the COC #, and a COC sample number.

- # # # # - #

Site ID - COC # - COC sample #

During the selection of samples the COC will be kept on hand, or in the field database within the sampling computer. As the samples are generated and the field database is updated the filed sample ID will be created. For further details on the procedures of the field database see SOP D-1.

Upon collection of the sample(s), a field team member will affix an identification label to the sample container(s). In the case of failure of the field database or other circumstances where the field database is not available a label provided by the laboratory may be used or any other label that includes the information provided herein. This label must contain, as a minimum, the following information:

- Client Name - Honeywell
- Project Name – *The site/project that the sampling is a part of*
- Location ID - *The unique number that identifies the sample location*
- Field Sample ID - *The unique number that identifies the sample*
- Date of sample collection - *use six digit date (mm/dd/yy)*
- Time of sample collection - *use 24-hour format (hh:mm)*
- Sample Type - Water, Sediment, sediment, sludge, leachate, fish tissue, invertebrate tissue, etc.
- Sample Prep - Grab *or* Composite
- Specimen type: whole body, composite, fillet, etc.
- Preservation - *Type of preservation added*

- Analyses - *use the method reference from the COC, (such as VOA-624 Full Scan, or A2340C Hardness)*
- Initials - *The initials of the sample collector*

Sample purpose is to be completed on the COC. A sample purpose of REG will be used for all regular environmental field samples, "EB" will be used to indicate an equipment blank, "TB" will be used to designate a trip blank, and "FD" will be used to indicate a field duplicate sample. The lab will not be able to associate this duplicate with a particular sample. The location ID to be used for all blanks (EB, TB) is QC. For MS/MSD samples, a separate line item is not necessary on the COC. The field crew can simply use the comment area of the COC to indicate which field sample will have the MS/MSD run.

The field team leader will create the COC using the Honeywell approved format provided in the QAPP. The field team leader will be responsible for verifying that information on the COC is consistent with the information recorded in the field book, on the sample log sheets, and on the bottle labels. The COC will be printed, signed and included in the sample shipment cooler.

The field team leader will transmit the electronic COC to the Data Manager within 24 hours of COC completion. The Data Manager will enter the field sample information into the system and create COC data in EQuIS. The sample order will match the COC.

Upon entry of COC data, a text file will be generated by the Data Manager who transmits this text file via e-mail to the laboratory for entry in the laboratory information system (LIMS). The text file must be received by the laboratory within 48 hours of receipt of samples.

Within 24 hours of receipt of the text file, the laboratory must send an acknowledgement to the Data Manager indicating all the sample identification numbers and the analyses to be conducted on each sample. The Data Manager will review the acknowledgement and confirm that no errors have been made. If errors are detected, the Data Manager will coordinate with the laboratory to resolve the issue.

The Data Manager will track receipt of preliminary data and EDDs against the sample receipt date indicated by the laboratory for compliance with contract terms. The Data Manager will issue weekly reports of any data not received within contract terms and elevate any occurrence of non-compliance to the attention of the Field Team Leader or Project Manager.

4.0 SAMPLE CONTAINERS AND PRESERVATION

4.1 Sample Containers

Certified, pre-cleaned containers will be supplied from commercial suppliers or laboratories for the collection of all sediment and water samples. Certification of sample container quality will be provided by the laboratory if requested. Bulk sediment and water samples will also be placed in containers provided by the laboratory. Food grade plastic liners may be used inside 5-gallon buckets or various sized drums to minimize impacts from phthalates or other residual compounds that may be present in the plastic buckets or drums during mixing or storage and shipment. The QAPP provides further information on the laboratory-provided containers to be used for the samples that will be collected.

4.2 Sample Preservation

The sample preservation methods for samples for chemical analysis to be used are summarized in the QAPP. Samples requiring preservation will be collected in sample containers provided by the analytical laboratory that already contain sufficient quantities of the appropriate preservative(s) to ensure that the sample is preserved in accordance with the method requirements. The laboratory must provide an adequate amount of pre-preserved bottles with traceable high-purity preservatives, and additional preservative for use if the added amount is not sufficient, based on request by the Field Team Leader and on an as-needed basis if additional bottle ware is needed during the field activities. The field team must verify that the preservative has been added appropriately. Documentation of equipment and methods used in the field for treating the samples, such as filtering equipment (if used), will be maintained in the field logbooks. The brand name, pore size, and number of filters (if used) used will be recorded. If refrigeration is necessary, samples will be placed on ice or in a trailer after collection, and shipping containers will be packed with additional ice, if needed, prior to transfer.

4.3 Preservation of Aqueous Samples

Preservatives required for aqueous samples will be added to the pre-labeled laboratory-provided containers prior to shipment to the site and sampling. For aqueous samples including field rinsate blanks, the field sampler will ensure that nitric acid (i.e., for metals) or other appropriate preservative has been added to the sample containers by the analytical laboratory.

SECTION 5.0 SAMPLE HANDLING AND SHIPPING

Sample packaging and shipping will be performed as follows:

- After filling, securely seal sample bottle caps. Affix the completed sample labels to the bottles if they were not affixed before the bottle was filled. Cover sample label with plastic tape.
- VOC vials for aqueous samples (including blanks) will be checked for headspace prior to shipment. If headspace is present, collect a new sample, if practical. If not, the presence of headspace should be recorded on the COC, and the QAO should be notified.
- Wipe off any sediment, water, etc. from the outside of the sample containers with a cloth or paper towel.
- Transfer the samples to an ice chest that will be used as a shipping container. For samples leaving the site, use inert packaging material to cushion the samples and minimize potential breakage.
- Place the samples and the laboratory-provided temperature blank upright in the sample cooler. The temperature blank should be placed in the center (horizontally and vertically) with the samples surrounding it.
- If refrigeration is necessary, ice chests will contain sufficient ice or similar chilling sources to maintain approximately 4°C (but not frozen) inside cooler during transport. The bags of ice will be double bagged to prevent leaking of liquid during shipment.
- Complete sample tracking documentation as described in this SOP and data management SOP.
- Place the documents in a sealable plastic bag inside the ice chest taped to the inside lid. Prior to sealing for shipment, the list of samples will be checked against the container contents to verify the presence of each sample listed on the COC.
- Secure chest top and seal the top and the drain spout (if present) with duct tape and affix custody seals to the cooler.

- Arrange for sample pickups at the site by an approved courier or shipper or hand deliver sample coolers to an approved courier service or overnight delivery service such as FedEx. Samples will be shipped for arrival at the laboratory within two business days from the time of sample collection.
- For international shipments, an International Air Waybill and a packaging list form for customs must be filled out and attached to the package or sample cooler. FedEx or other shippers can provide these blank forms and may offer assistance in completing the paperwork.

SECTION 6.0 SAMPLE TRACKING

All samples collected for analysis will be continuously tracked in the field and in transit to the laboratory as follows:

- Individual sample bottles will be properly labeled and securely sealed before being placed in the container for shipment to the laboratory.
- All pertinent information (see requirements in next bullet) will be entered on the Honeywell COC form in the field. Assignment of the matrix spike/matrix spike duplicate/laboratory duplicates (MS/MSD/LD) and all of the analyses requested for each sample will be made on the COC form. Blind duplicates that are to be collected will be identified in the field logbook but will be assigned a field sample id according to the standard nomenclature described above on the COC. A notation will be added to the third copy (pink copy) that will be retained by the sampler. The notation will indicate which sample the duplicate correlates to.
- COC forms must include the following, as required by guidance in SW-846, Test Methods for Evaluating Solid Waste (USEPA, Third Edition, including Promulgated Update IIIB, June 2005, Chapter One): 1) the project name; 2) signatures of samplers; 3) the sample number, date and time of collection, and grab or composite sample designation; 4) signatures of individuals involved in sample transfer; and 5) if applicable, the air bill or other shipping number.
- The completed COC form will be signed, dated, enclosed in a sealable plastic bag and placed in the shipping container prior to shipment. A copy of the COC form will be retained by field personnel and an additional copy transmitted to the Contractor Project Manager (CPM) or the manager's designee.
- Samples will be considered in the sampler's custody while in sight, or locked in a secure area prior to shipment. If the person packing the container and verifying the sample list is different than the sampler, both the sampler and the packer will sign the COC form.
- Upon receipt at the laboratory, sample receiving personnel will inspect the samples for integrity of the custody seal and will check the shipment against the COC. Using the temperature blank in each cooler, the temperature will be measured and will be verified to be approximately 4°C (not frozen) during sample receipt/log-in procedures prior to samples being placed in the laboratory cold storage. Similarly, the laboratory will maintain documentation that their cold storage facilities are being maintained at approximately 4°C (not frozen) through daily (at minimum), documented temperature measurements using a calibrated thermometer.
- The pH of acid or base preserved aqueous samples will be measured and documented on the COC. Any problems observed during sample receipt must be communicated to the Quality Assurance Officer (QAO), verbally and either by fax transmission or e-mail within 24 hours (preferably three hours, beginning with the normal business day, immediately following for problems noted during second shifts or weekends) after discovery and before samples are released to the laboratory for analysis. Problems may include but are not limited to: broken bottles, errors or ambiguities in paper work, insufficient sample volume/weight, presence of headspace in VOC vials, and inappropriate pH and/or elevated temperature. When the shipment is

inspected and the COC are in agreement, the sample receiving personnel will enter the sample and analysis information into the laboratory information management system (LIMS) and will assign each sample a unique laboratory number. This number will be affixed to each sample bottle. While in the laboratory, the samples and aliquots that require cold storage will be maintained in a secured refrigerator unless they are being used for preparation and/or analysis.

- A copy of the COC form shall be returned from the laboratory to the Parsons QAO or the officer's designee(s). The original shall be retained by the laboratory's sample custodian.

SECTION 7.0 DOCUMENTATION OF SAMPLES COLLECTED - FIELD NOTES

The Sample Manager or the manager's designee is responsible for documenting sample handling activities. Observations and data will be recorded with waterproof ink in a hardbound field logbook with consecutively numbered pages. Incomplete lines and pages will be lined out with a single line and initialed. Changes will be lined out with a single line, dated, and initialed. The information in the field logbook will include the following as a minimum:

- Site name
- Date
- Brief report of weather conditions and lake conditions (if working on the lake)
- Responsible person's name
- Date and time of activity
- Information coordinating container numbers with sample numbers
- Information coordinating sample handling activities with the appropriate field activities and COC documentation
- Equipment and methods used for field preparation of samples
- Field measurements of samples (e.g., pH, ORP, temperature)

SECTION 8.0 REFERENCES

United States Environmental Protection Agency (USEPA). 1980. Office of Emergency and Remedial Response, OSWER Directive # 9240.0-05A, "Specifications and Guidance for Contaminant-Free Sample Containers." EPA 540/R-93/051. Washington, D.C.

United States Environmental Protection Agency (USEPA). 1986. SW-846, Test Methods for Evaluating Solid Waste, Third Edition, including subsequent updates.

United States Environmental Protection Agency (USEPA). 2003. Methods for Collection, Storage, and Manipulation of Sediment for Chemical and Toxicological Analyses: Technical Manual, Office of Water 4305, EPA-823-F-01-023, October 2001, last update December 2003.

SECTION 9.0 REVISIONS/REVIEWS

Doc Number: Rev No.: 0 Date: June 23, 2022

Reviewer: Parsons

What was changed: N/A

D-1 DATA MANAGEMENT

This data management procedure has been prepared to support the investigation and sampling program for the Syracuse Portfolio, which consists of various sites located in and around Onondaga Lake. This document is intended to serve as a standard for all data management activities taking place for the environmental programs of the Syracuse Portfolio.

The environmental programs of the Syracuse Portfolio will generate analytical and field data, which will require both storage and project team accessibility. Electronic data management systems will be implemented to effectively process the information without loss or alteration. The approach outlined in this procedure is designed to provide an organized method of data management for the large amounts of data that will be generated during the environmental programs.

The objectives of this procedure are to define:

- The electronic data management system that will be used
- The data management team organization
- The flow path of the data and the data types
- The data management procedures that will be implemented

SECTION 1.0 DATA MANAGEMENT SYSTEMS

1.1 EQuIS

Honeywell has selected Earthsoft's Environmental Quality Information Systems (EQuIS) software as its preferred environmental data management system. EQuIS was developed by Earthsoft, who have an extensive background in environmental remediation projects and the associated data collection and processing requirements. Honeywell Technical Services (HTS) will provide technical support associated with the use of EQuIS for the Syracuse Portfolio.

EQuIS is designed to manage the following data types:

- Chain-of-custody data
- Laboratory Analytical Data for various media such as soil, water, soil vapor, sediment, and sludge
- Field Measurement data such as pH, dissolved oxygen, turbidity, water levels, etc.
- Geotechnical data such as Surface or subsurface soil, or geologic characterizations/lithology
- Survey Data: Geographic or location data

Additional data types may be added to EQuIS as appropriate. Historical data related to the Syracuse sites, including all chemical analytical data from previous investigations, has been integrated into the EQuIS database. Procedures for data management using EQuIS are available in the Honeywell SharePoint site. The remaining sections of this procedure specify the applicable procedures.

1.2 EQuIS Database Setup

Database settings control how information is stored in EQuIS and determine the structure of the database. Configuration of the settings for the Syracuse Portfolio database will be limited to the HTS. Changes to the Syracuse database settings will be reviewed by HTS before implementation.

In order to use EQuIS efficiently, the project must be properly set up before field activities begin. Database settings that will be established in EQuIS include:

- Valid Values List
- Location Groups
- Parameter and Field Parameter Groups
- Project Analytical Groups
- Site Groups

Once these setup tasks have been accomplished, the database will be ready for data input by the Database Manager.

1.3 Database User Access

The next step in preparing the EQuIS database for use is to assign access rights to the end users. Access to EQuIS is restricted and a username and password will be required. To request access to the Syracuse Portfolio, users will contact HTS. In general, "Guest" (read-only) privileges will be granted to team members. Members of the data management team will be granted privileges to add data to EQuIS.

1.4 Required QC for Laboratory Analytical Data

Electronic Data Deliverables (EDDs) from laboratories working on behalf of Honeywell are required to contain the applicable QC that are necessary for EQuIS to validate the electronic dataset. A list of QC valid values that EQuIS uses to validate uploaded analytical data files, along with a list of field names and required fields that are to be included in the Honeywell EQ EDD, will be provided directly to all labs.

With respect to QC data, please note the following requirements:

- Honeywell requires analytical laboratories to report every QC parameter both electronically and in hardcopy.
- The hardcopy QC and hardcopy analytical result must be identical with the EDD in every respect for Level 1 - 3 deliverables. We are defining a Level 4 deliverable as that level requiring calibration data, MDL studies, raw data such as lab notebooks evidencing standard validity and GC/GCMS chromatograms. EQuIS does not incorporate Level 4 items but may in the future.
- Any fields left blank in the EDD, are assumed not to be required of the laboratory and shall not be included in the hardcopy.
- Data are to be batched for analytical preparation in groups of, at most, 20 field samples. Honeywell is requiring the laboratory to have, at a minimum, all of the project-required QC for each batch – even if the batch consists of one sample. The only permitted exception is the MS and MSD. However, if sufficient sample is available, this must also be included. If sufficient sample is available, the Honeywell Laboratory Services Contract requires analyses of the MS/MSD at no additional charge to Honeywell.

1.5 Honeywell EQEDD Format Requirement

To facilitate data loading, the following electronic file formats must be observed:

- The file format must be ASCII with no header or footer, and with each record alike with respect to format.
- Every analytical result is to be a single record.
- No field will be enclosed in quotation marks.
- Every field must be separated by a semi-colon delimiter (a comma must not be used – owing to its frequent appearance in chemical names).
- Each record must be terminated with a carriage return.
- In instances where a CAS number does not exist, Honeywell has defined the nomenclature that must be used. The remaining parameters have CAS numbers.

Assignment of Sample Names: A sample nomenclature system has been developed to ensure consistency in field sample ID assignment and compatibility with EQuIS. Unique sample names will be assigned to each sample according to the sample identification protocol described in this QAPP. Sample nomenclature will include the following:

- **Location ID:** Site ID – Remediation Area-Location Type – Location #. For example, location ID OL-RAA-STA-1001 indicates that the sample came from Onondaga Lake, Remediation area A, STA is the location type identification, 1001 is the first location in SMU 1. For water samples from the profundal zone, the location ID can be Deep_S for South Deep or ISUS for one of the ISUS locations. For locations where more than one matrix is sampled, STA is to be used for the location type indicating a sample station.
- **Field Sample ID:** Site ID – chain-of-custody form # - Sample #. For example, field sample ID OL-12345-01 indicates that the sample came from Onondaga Lake, chain-of-custody number 12345, line 1 on the chain-of-custody form. Depth interval will be shown in a separate area of the chain-of-custody form.

1.6 Data Output

In general, the Database Manager will provide a single point of contact for team members to obtain data outputs on an as needed basis.

Secondly, Individuals may also access EQuIS directly through Enterprise. Any team member with access to Enterprise may retrieve data in EQuIS. The EQuIS database, unlike other data management systems, represents a dynamic data set. Therefore, users that output data sets from EquIS for the purposes of an engineering or design calculation must date the query.

Each EDD from each laboratory will be loaded to EQuIS where the data manager can generate a file for the chemist to conduct their validation. Once the validation is complete, the dataset is reloaded to the EQuIS database.

EDDs provided to NYSDEC have a format that is separate from the Honeywell EDD format (NYSDEC 2018). The Database Manager prepares EDDs for NYSDEC from EQuIS and sends the EDDs to 'NYENVDATA' at the direction of the Project Manager or Task Manager.

SECTION 2.0 REFERENCES

NYSDEC. 2018. NYSDEC Electronic Data Deliverable Manual Format V.4. November, 2018.

SECTION 3.0 REVISIONS/REVIEWS

Doc Number: Rev No.: 0 Date: June 23, 2022

Reviewer: Parsons

What was changed: N/A

ATTACHMENT 1: USE OF STANDARD REFERENCE MATERIALS IN NYSDEC FISH STUDIES

***A**nalytical and **E**nvironmental **S**ervices, Inc.*
908 Shinnecock Hills Dr.
Georgetown TX 78628
e-mail: renesurgi@aesi.us

847.835.0983 *Mobile: 847-254-0934*

Date: 10/21/2020
To: Anne Burnham, Mark Arrigo
From: Rene Surgi
RE: Use of Standard Reference Materials in NYSDEC Fish Studies

Upon recommendation by New York State Department of Environmental Conservation (NYSDEC) Honeywell will be using Standard Reference Materials (SRM) and Certified Reference Materials (CRM) for the evaluation of laboratory performance. CARP-2 is a Certified Reference Material made from ground whole carp ***(1)***. SRM-1947 is a frozen fish tissue homogenate from fish collected from Lake Michigan ***(2)***. DORM-4 is a CRM prepared from fish protein ***(3)***. Our intent is to use SRM-1947 for PCBs, pesticides and lipids, to use CARP-2 for PCDDs and PCDFs, and to use DORM-4 for Hg. These materials will be referred to collectively as reference materials.

Analyses Frequency
Reference materials will be analyzed and evaluated with each analytical batch not to exceed 20 samples.

Acceptable Performance
The analytes in the CARP-2, DORM-4 and NIST 1947 for Hg, PCDD/Fs, pesticides, and lipids reference materials present a 1:1 correspondence between certificate analytes and analytes reported by the laboratory. PCBs do not present this 1:1 correspondence and are discussed below.

Sloan *et al.* ***(4)*** have evaluated the total PCBs in NIST 1947 as detailed in Table 13 of reference 4. Table 13 lists total PCBs as 2236 ug/kg as aroclors using SW 846 Method 8082 and 2093 ug/kg using three analytical methods (aroclors, homologs and congeners). Since this study will utilize SW-846 Method 8082 and quantify results in terms of aroclors, we originally proposed using 2236 ug/kg total PCBs as the most applicable value to assign to NIST 1947 as it maintains the reference value for the method to be used. For consistency with Fish Consumption Advisory Studies, DEC has requested the composite value of 2093 ug/kg from the three methods be used, hence we will adopt 2093 ug/kg as the true value for total PCBs by SW846 Method 8082. Sloan obtains this result from the predominant contributions of aroclors 1248, 1254 and 1260. Integration run time and aroclor identifications vary among labs so the total PCBs in one lab may be from a combination of, for example, aroclors 1254 and 1260 and subsume some of the aroclor 1248 peaks in aroclor 1254. Other labs may identify three separate aroclors (1248, 1254, and 1260). In any event the lab must identify total aroclors by a summation of the aroclors identified. Sloan *et al.* ***(4)*** provides the basis for the PCB concentrations based on total aroclors. DEC has requested Honeywell retain an acceptance window of ±30%. The acceptance range for NIST 1947 would be 2093 ug/kg (average) with a ± 30% window of 1465 to 2721 ug/kg. Recoveries exceeding ±30% will be J-flagged. Recoveries below 25% will be rerun.

Since CARP-2 is a sample matrix similar to NIST 1947, the same windows would be used for each analyte of CARP-2 (PCDDs and PCDFs): ± 30% of the reported true value. For DORM-4 the analyte is Hg. The recovery window for Hg in DORM-4 is ± 20%, and lipids in NIST 1947 would be ± 30%.

In addition to the criteria discussed above, the lab would continue its own control chart using total PCBs, individual pesticides, lipids PCDFs/PCDDs and Hg and implement these control criteria in accord with the current laboratory SOP for recovery and control charting. The lab would supplement reference material recoveries obtained with each batch with the control chart. If the lab reports a narrower recovery range than ±30%, the 30% criteria will control.

Corrective Action

Where recoveries exceed the stated criteria of ±30%, a J-flag will be applied. Recoveries below 25% and above 175% will be rerun unless the recovery is above 175% and the result is ND or below an established criteria.

Additional Quality Control

Other batch QC will remain as indicated in the current QAPP. Such QC includes MS/MSD, method blanks, LCS/LCSD and are also among requirements by outside agencies, by the laboratory's other clients, and are in the methods themselves. The laboratory QC requirements and this program QAPP will continue to apply to these studies.

Field duplicates are synonymous with sample duplicates in this case and will be split after homogenization at the bench. This is in addition to the MS/MSD currently run by the lab as part of the ordinary QC in a preparation batch. The MS/MSD is a requirement of many clients, SOPs and methods; however, the MS/MSD may not be a Honeywell sample from this program owing to mass of sample available. Parsons will provide guidance on which samples to use for the sample/sample duplicate or MS/MSD based on mass. Where the MS/MSD is not a Honeywell sample, no MS/MSD or sample/sample duplicate criteria will be applied to qualify Honeywell results. For Honeywell samples, the historical laboratory windows will be applied to J-flag results.

The laboratory will maintain a five point initial calibration for aroclors 1248 (for consistency with historical trends), 1254 (an aroclor described in Sloan *et al.*), 1242 (a NYSDEC request) in addition to the five-point initial calibration for 1016 and 1260 (an aroclor identified by Sloan *et al*). Owing to the importance of aroclors 1016 and 1260 in Method 8082 and in the laboratory's certification programs for soils and waters, in consideration of the laboratory workflow, these aroclors will be retained. Retention of aroclor 1248 calibration is optional and will prevent a low bias if future results are compared to historical trends. We recognize that some aroclors such as 1016 and 1242 have overlapping congeners. Such aroclors will be run separately and not mixed. Only 1016 and 1260 will be mixed.

Discussion of Quality Control Criteria in the Case Narratives of the Data Usability Report (DUSR)

The DUSR will discuss the recovery requirements, the accepted true value of the reference materials, the result of the laboratory analyses of the reference material and the date range covered by the analyses. Both lab and validator qualifiers will be retained in separate fields in the EQuIS EDD.

For the remaining quality control, the general approach will be to use flags as follows:
a) high recovery and non-detect: no flag;
b) high recovery and detect: J+ flag (high bias);
c) low recovery and detect: J- flag (low bias; no further action if the result is not within ± 10% of an action limit);
d) low recovery and non-detect: UJ (bias); reject if recovery <25%: samples would be rerun if outside 25 – 175% window);
e) P flags applied for pesticides as described for 4,4'-DDT below.

Discussion of Pesticide Dual Column Quantitation

For NIST1947, 4,4'-DDT was shown to initially coelute with what was assigned as a PCB congener biasing the recovery and concentration for 4,4'-DDT high on one of the two columns. After adjustments of the run time and

thermal program, 4,4'-DDT separated forming a fused peak which was discernable and manually quantitated consistent with ELLI's SOP for manual integration. When this coelution occurs during analyses, the lower value will be reported, a P-flag assigned when the RPD between the results for the two columns exceeds 40%, and the fused peak be manually integrated consistent the ELLI's SOP for manual integration.

While this coelution was discovered for 4,4'-DDT in NIST 1947, this may not manifest in actual samples that may be less complex that NIST 1947.

QC Summary

QC Element	Criteria	Frequency	Impact on Data
MS/MSD	Hg: 80 - 120% R and 20% RPD; PCB & pesticides: Lab control limits for recovery and 30% RPD; PCDD/PCDF: method % recovery and 20% RPD	1 in 20 prepared samples	Insufficient mass of Honeywell sample if used for sample and sample duplicate. Recovery and RDP on other client sample has no impact on Honeywell samples. RPD is relative percent differene.
LCS/LCSD (general)	Hg: 80 - 120% R and 20% RPD; PCB & pesticides: Lab control limits for recovery and 30% RPD; PCDD/PCDF: method % recovery and 30% RPD	1 in 20 prepared samples	a) High recovery and non-detect: no flag. b) High recovery and detect: J+ (high bias). c) Low recovery and detect: J- (low bias, no further action is result not within 10% of an action limit, otherwise redigest sample in new batch. d) Low recovery and non-detect: UJ (bias). Reject (R) if recovery < 10%.
MB	RL or 1/10 sample concentration whichever is greater	1 in 20 prepared samples	No flag if below the RL of less than 1/10 sample concentration. Flag for blank contamination otherwise.
Sample duplicate	RPD 30% (PCB, OCP, PCDD/F) 20% (Hg); sample to be selected by Parsons depending on mass and availability of fish type	1 duplicate per 20 prepared samples	If run in triplicate or greater frequency, one duplicate is allowed outside 50%, otherwise J-flag (estimated).
CARP-2 (project specific)	Recovery +/-30% of true value for PCDD/PCDF	Run once per batch of 20 samples	Recovery outside limits - J flag results. Redigest if recovery <25% or greater than 175%.
DORM-4	Recovery +/-20% of true value for Hg	Run once per batch of 20 samples	Recovery outside limits - J flag results. Redigest if recovery <25% or greater than 175%.
NIST 1947	Recovery +/-30% of true value for total PCBs (Sloan et al) and pesticides. Recovery of +/- 30% for lipids	Run once per batch of 20 samples	Recovery outside limits - J flag results. Redigest if recovery <25% or greater than 175%. For pesticides, the lower value of the two columns will be reported with a P-flag.
Aroclor 1248	+/-20% of response factor in ICAL.	Run as a 5-point ICAL with Aroclor 1660 and spiked into LCS on rotating basis.	Results must bracket successful ICAL and CCV. Only failing aroclor is impacted, remainder can be reported. Optional spike into clean matrix.
Aroclor 1254	+/-20% of response factor in ICAL.	Run as a 5-point ICAL with Aroclor 1660 and spiked into LCS on rotating basis.	Results must bracket successful ICAL and CCV. Only failing aroclor is impacted, remainder can be reported. Optional spike into clean matrix.
Aroclor 1242	+/-20% of response factor in ICAL.	Run as a 5-point ICAL with Aroclor 1660 and spiked into LCS on rotating basis.	Results must bracket successful ICAL and CCV. Only failing aroclor is impacted, remainder can be reported. Optional spike into clean matrix.

References

(1)NRC-CNRC. Certificate of Analysis: CARP-2. March, 2016.

(2) National Institute of Standards and Technology: Standard Reference Material 1947 Lake Michigan Fish Tissue. May 31, 2017.
(3))NRC-CNRC. Certificate of Analysis: DORM-4. June, 2012.
(4) Sloan, R.; Bauer, R.; Schantz, M. **Development of Hudson River Fish Reference Material (HRMs) for PCB Analyses Quality Assurance/Quality Control Purposes.** November 22, 2007.
(5) Eurofins Lancaster Laboratories, LLC (ELLI). 2425 New Holland Pike. Lancaster PA 17605.

Please call me if you have any questions.

Rene Surgi

Rene Surgi, Ph.D.
AESI

***A**nalytical and **E**nvironmental **S**ervices, Inc.*
908 Shinnecock Hills Dr.
Georgetown TX 78628
e-mail: renesurgi@aesi.us

847.835.0983 *Mobile 847-254-0934*

Date: 3/21/23
To: Anne Burnham
From: Rene Surgi
RE: Use of DORM-5 as a Standard Reference Material in NYSDEC Fish Studies

As per the Memorandum from Analytical and Environmental Services, Inc dated October 21, 2020, DORM-4 is to be utilized as a reference material, and was to be analyzed and evaluated with each analytical batch not to exceed 20 samples. DORM-4 is no longer available for purchase. Therefore, DORM-5 is to be utilized. All frequencies, acceptable performance measures, and corrective actions will apply.
In summary:

QC Element	Criteria	Frequency	Impact on Data
DORM-5	Recovery +/- 20% of true value for Hg	Run once per batch of 20 samples	Recovery outside limits- J flag results. Redigest if recovery <25% or greater than 175%

Please call me if you have any questions.

Rene Surgi

Rene Surgi, Ph.D.
AESI
908 Shinnecock Hills Dr.
Georgetown TX 78628

***A**nalytical and **E**nvironmental **S**ervices, Inc.*
908 Shinnecock Hills Dr.
Georgetown TX 78628
e-mail: renesurgi@aesi.us

847.835.0983 *Mobile 847-254-0934*

Date: 8/26/23
To: Anne Burnham
From: Rene Surgi
RE: Use of CARP 2 as a Standard Reference Material in NYSDEC Fish Studies for Lipids

As per the Memorandum from Analytical and Environmental Services, Inc dated October 21, 2020, NIST 1947 was to be utilized as a reference material for PCBs, pesticides and lipids, and was to be analyzed and evaluated with each analytical batch not to exceed 20 samples. As supplies of NIST 1947 are limited, supplies are being prioritized for use with PCB and pesticide analysis. NIST 1947 will no longer be used as the reference material for lipid analysis; CARP 2 will be used instead. All frequencies, acceptable performance measures, and corrective actions will apply.
In summary:

QC Element	Criteria	Frequency	Impact on Data
CARP-2 (project specific)	Recovery +/- 30% of true value for lipids	Run once per batch of 20 samples	Recovery outside limits- J flag results. Redigest if recovery <25% or greater than 175%

Please call me if you have any questions.

Rene Surgi

Rene Surgi, Ph.D.
AESI
908 Shinnecock Hills Dr.
Georgetown TX 78628