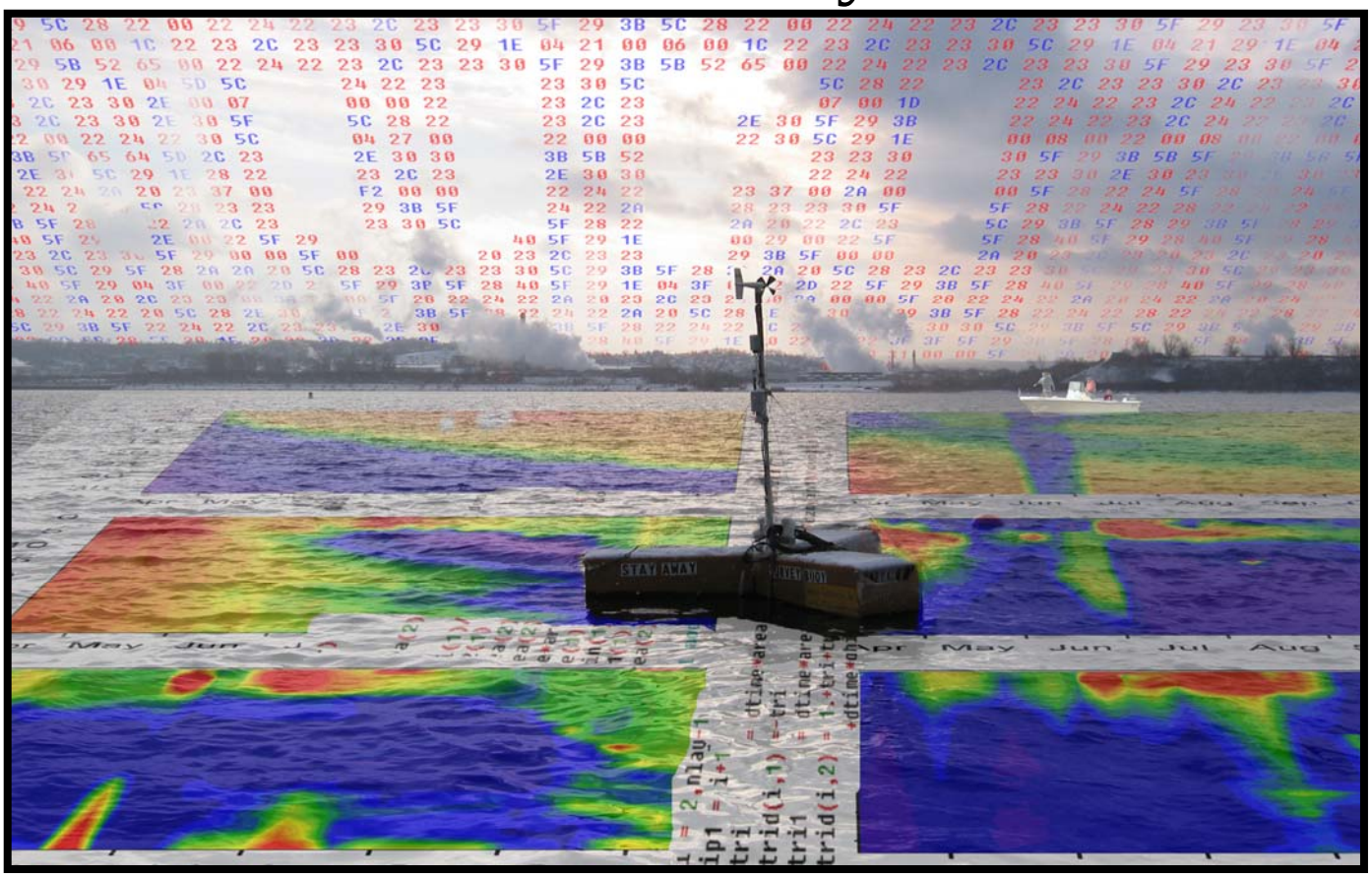
Appendix B
Work Plan for Evaluation of Nitrate Addition to Control Methylmercury Production in Onondaga Lake, 2007 Study



UPSTATE FRESHWATER INSTITUTE
P.O. Box 506
Syracuse, New York 13214

SYRACUSE UNIVERSITY
SUOS CULTORES SCIENTIA CORONAT
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January 2008

Quality Assurance Project Plan

Evaluation of Nitrate Addition to Control Methyl Mercury Production in Onondaga Lake – 2007 Study

Syracuse University
and
Upstate Freshwater Institute
for
Honeywell

Based on the Intergovernmental Data Quality Task Force
Uniform Federal Policy for Quality Assurance Project Plans

January 22, 2008

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QAPP Worksheet #1
Title and Approval Page

Site Name/Project Name: Onondaga Lake Nitrate Evaluation 2007
Site Location: Onondaga Lake

Title: Evaluation of nitrate addition to control methyl mercury production in Onondaga Lake – 2007 Study
Revision Number: 2
Revision Date: January 22, 2008

Quality Assurance Project Plan, Evaluation of Nitrate Addition to Control Methyl Mercury Production in Onondaga Lake
Document Title

Syracuse University (SU)
Lead Organization

M.G. Perkins, Upstate Freshwater Institute (UFI), and Mario Montesdeoca, SU
Preparer's Name and Organizational Affiliation

UFI: 224 Midler Park Drive, Syracuse, NY 13206 (315-431-4962), mgperkins@upstatefreshwater.org and SU: Department of Civil and Environmental Engineering, 419 Link Hall, Syracuse University 13244 (315-443-9975), mmontesd@syr.edu
Preparer's Address, Telephone Number, and E-mail Address

January 22, 2008
Preparation Date (Day/Month/Year)

Investigative Organization's Project Manager: _____
Signature

_____
Signature

Steven Effler, UFI, and Charles Driscoll, SU
Printed Name/Organization/Date

Investigative Organization's Project QA Officer: _____

_____
Signature

M.G. Perkins, UFI, and Edward Mason, SU
Printed Name/Organization/Date

Lead Organization's Project Manager: _____
Signature

Charles Driscoll, SU
Printed Name/Organization/Date

QAPP Worksheet #1
Title and Approval Page
(continued)

Site Name/Project Name: Onondaga Lake Nitrate Evaluation 2007
Site Location: Onondaga Lake

Title: Evaluation of nitrate addition to control methyl mercury production in Onondaga Lake - 2007 Study
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Approval Signatures: _____
Signature

_____
Printed Name/Title/Date

_____
Approval Authority

Other Approval Signatures: _____
Signature

_____
Printed Name/Title/Date

Document Control Number: UFI 018

QAPP Worksheet #2
QAPP Identifying Information

Site Name/Project Name: Onondaga Lake Nitrate Evaluation 2007
Site Location: Onondaga Lake
Site Number/Code: N/A
Operable Unit: N/A
Contractor Name: UFI and SU
Contractor Number: N/A
Contract Title: N/A
Work Assignment Number: N/A

Title: Evaluation of nitrate addition to control methyl mercury production in Onondaga Lake - 2007 Study
Revision Number: 2
Revision Date: January 22, 2008

1. Identify guidance used to prepare QAPP:
Uniform Federal Policy for Quality Assurance Project Plans

2. Identify regulatory program: CERCLA

3. Identify approval entity:
New York State Department of Environmental Conservation (NYSDEC) and U.S. EPA Region 2

4. Indicate whether the QAPP is a generic or a project-specific QAPP. (circle one)

5. List dates of scoping sessions that were held: January 31, 2007 and others

6. List dates and titles of QAPP documents written for previous site work, if applicable:

Title	Approval Date
Onondaga Lake Nitrate Evaluation 2006	March 6, 2007

7. List organizational partners (stakeholders) and connection with lead organization:
Exponent, Parsons, NYSDEC, U.S. EPA

8. List data users: Exponent, Parsons, NYSDEC, U.S. EPA

9. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below:

QAPP elements and required information that are not applicable to the project are circled and an explanation is provided in the QAPP.

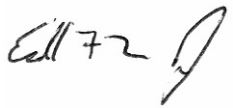
Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
Project Management and Objectives		
2.1 Title and Approval Page	- Title and Approval Page	QAPP Worksheet #1
2.2 Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.4 QAPP Identifying Information	- Table of Contents - QAPP Identifying Information	QAPP Worksheet #2
2.3 Distribution List and Project Personnel Sign-Off Sheet 2.3.1 Distribution List 2.3.2 Project Personnel Sign-Off Sheet	- Distribution List - Project Personnel Sign-Off Sheet	QAPP Worksheet #3 & #4
2.4 Project Organization 2.4.1 Project Organizational Chart 2.4.2 Communication Pathways 2.4.3 Personnel Responsibilities and Qualifications 2.4.4 Special Training Requirements and Certification	- Project Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications Table - Special Personnel Training Requirements Table	QAPP Worksheet #5, #6, #7 & 8
2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	- Project Planning Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History, and Background - Site Maps (historical and present)	QAPP Worksheet #9 & #10
2.6 Project Quality Objectives and Measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	- Site-Specific PQOs - Measurement Performance Criteria Table	QAPP Worksheet #11 & #12
2.7 Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations Table	QAPP Worksheet #13

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation Table - Project Schedule/Timeline Table	QAPP Worksheet #14 & #15
Measurement/Data Acquisition		
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	- Sampling Design and Rationale - Sample Location Map - Sampling Locations and Methods/ SOP Requirements Table - Analytical Methods/SOP Requirements Table - Field Quality Control Sample Summary Table - Sampling SOPs - Project Sampling SOP References Table - Field Equipment Calibration, Maintenance, Testing, and Inspection Table	QAPP Worksheet #17, #18, #19, #20, #21, #22
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	- Analytical SOPs - Analytical SOP References Table - Analytical Instrument Calibration Table - Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	QAPP Worksheet #23, #24, #25 and SOPs in Appendix A
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample Handling and Tracking System 3.3.3 Sample Custody	- Sample Collection Documentation Handling, Tracking, and Custody SOPs - Sample Container Identification - Sample Handling Flow Diagram - Example Chain-of-Custody Form and Seal	QAPP Worksheet #19, #26, #27 and SOPs in Appendix A
3.4 Quality Control Samples 3.4.1 Sampling Quality Control Samples 3.4.2 Analytical Quality Control Samples	- QC Samples Table - Screening/Confirmatory Analysis Decision Tree	QAPP Worksheet #28

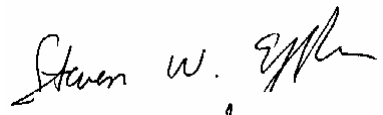
Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	- Project Documents and Records Table - Analytical Services Table - Data Management SOPs	QAPP Worksheet #29, #30
Assessment/Oversight		
4.1 Assessments and Response Actions 4.1.1 Planned Assessments 4.1.2 Assessment Findings and Corrective Action Responses	- Assessments and Response Actions - Planned Project Assessments Table - Audit Checklists - Assessment Findings and Corrective Action Responses Table	QAPP Worksheet #32, #28,
4.2 QA Management Reports	- QA Management Reports Table	QAPP Worksheet #33
4.3 Final Project Report		
Data Review		
5.1 Overview		
5.2 Data Review Steps 5.2.1 Step I: Verification 5.2.2 Step II: Validation 5.2.2.1 Step IIa Validation Activities 5.2.2.2 Step IIb Validation Activities 5.2.3 Step III: Usability Assessment 5.2.3.1 Data Limitations and Actions from Usability Assessment 5.2.3.2 Activities	- Verification (Step I) Process Table - Validation (Steps IIa and IIb) Process Table - Validation (Steps IIa and IIb) Summary Table - Usability Assessment	QAPP Worksheet #34, #35, #36, #37
5.3 Streamlining Data Review 5.3.1 Data Review Steps To Be Streamlined 5.3.2 Criteria for Streamlining Data Review 5.3.3 Amounts and Types of Data Appropriate for Streamlining		

QAPP Recipients	Title	Organization	Telephone Number	Fax Number	E-mail Address	Document Control Number
Charles Driscoll	Project Manager	SU	315-443-3434	315-443-4936	ctdrisco@syr.edu	
Mario Montesdeoca	Laboratory Director	SU	315-443-9975	315-443-1234	mmontesd@syr.edu	
Edward Mason	Quality Assurance Officer	SU	315-443-1247	315-443-1234	efmasonj@mailbox.syr.edu	
Svetoslava Todorova	Scientific/Technical Manager	SU	315-443-4121	315-443-1234	stodorov@ecs.syr.edu	
Steven W. Effler	Project Manager	UFI	315-431-4962 ext. 102	315-431-4969	sweffler@ upstatefreshwater.org	018
MaryGail Perkins	Quality Assurance Officer, Field Manager, Laboratory Director	UFI	315-431-4962 ext. 104	315-431-4969	mgperkins @upstatefreshwater.org	018
David Matthews	Scientific/ Technical Manager	UFI	315-431-4962 ext. 107	315-431-4969	damatthews@ upstatefreshwater.org	018
Betsy Henry	Project Manager	Exponent	518-370-5132	518-381-4115	henryb@exponent.com	
Ed Glaza	Project Manager	Parsons	315-451-9560	315-451-9570	edward.glaza@ parsons.com	
John McAuliffe	Project Manager	Honeywell	315-431-4443	315-431-4777	john.mcauliffe@ honeywell.com	
Tim Larson	Project Manager	NYSDEC	518-402-9767	518-402-9020	tjlarson@gw.dec.state.ny.us	
Robert Nunes	Project Manager	U.S. EPA Region 2	212-637-4254	212-637-3966	nunes.robert@epa.gov	

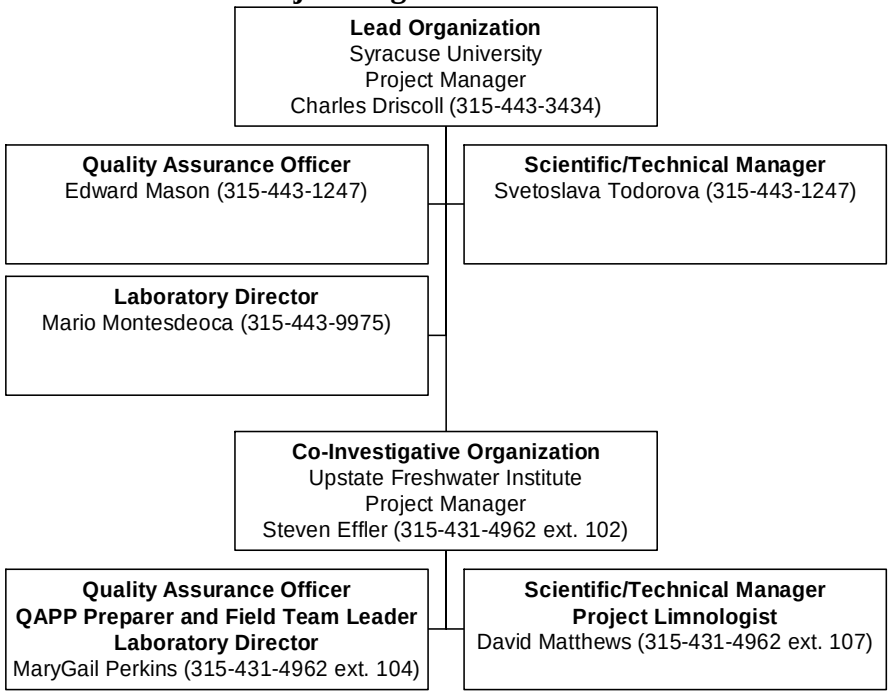
Organization: Syracuse University (SU)

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Mario Montesdeoca	SU Laboratory Manager	315-443-9975		1/30/08
Edward Mason	SU Quality Assurance Officer	315-443-1247		1/30/08
Svetoslava Todorova	SU Scientific/Technical Manager	315-443-4121		1/30/08

Organization: Upstate Freshwater Institute (UFI)

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Steven W. Effler	UFI Project Manager	315-431-4962 ext. 102		1/29/08
David Matthews	UFI Scientific/ Technical Manager	315-431-4962 ext. 107		1/29/08
MaryGail Perkins	UFI Quality Assurance Officer, Field Manager, Laboratory Director	315-431-4962 ext. 104		1/29/08

Project Organizational Chart



Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Point of contact with data users	Lead Organization and Co-Investigative Project Manager	Charles Driscoll	315-443-3434	All materials and information about the project will be forwarded to the data users by Charles Driscoll.
Manage all project phases	Lead Organization and Co-Investigative Project Manager	Charles Driscoll	315-443-3434	Charles Driscoll will be SU's liaison with data users and Steven Effler.
Manage all UFI project tasks	Co-Investigative Project Manager	Steven Effler	315-431-4962 ext. 102	Notify Charles Driscoll of field-related problems by phone, email, or fax by COB the next business day.
QAPP changes in the field	Field Team Leader	MaryGail Perkins	315-431-4962 ext. 104	Notify Steven Effler by phone or email of changes to QAPP made in the field and the reasons within one business day.
Daily field progress reports	Field Team Leader	MaryGail Perkins	315-431-4962 ext. 104	Notify David Matthews of any problems or issues.
Reporting SU lab data quality issues	SU Laboratory Director	Mario Montesdeoca	315-443-9975	Notify Edward Mason when problems occur, report data and supporting quality assurance information as specified in this QAPP.

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Field and UFI analytical corrective actions	UFI Quality Assurance Officer/UFI Technical Director	MaryGail Perkins	315-431-4962 ext. 104	The need for corrective action for field and UFI analytical issues will be determined by MaryGail Perkins and David Matthews.
SU analytical corrective actions	SU Quality Assurance Officer	Edward Mason	315-443-1247	The need for corrective action for SU analytical issues will be determined by Edward Mason.
Release of SU analytical data	SU Quality Assurance Officer	Edward Mason	315-443-1247	No SU analytical data can be released until validation is completed and Edward Mason has approved the release.
Release of UFI analytical data	UFI Quality Assurance Officer	MaryGail Perkins	315-431-4962 ext. 104	No UFI analytical data can be released until validation is completed and MaryGail Perkins has approved the release.
QAPP Amendments	Lead Organization and Co-Investigative Project Manager	Charles Driscoll	315-443-3434	Any major changes to the QAPP must be approved by Charles Driscoll before changes can be implemented.

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Steven Effler	UFI Project Manager	UFI	Overall responsibility for UFI activities. Provide approval of all necessary actions and adjustments for activities to accomplish project objectives. Provide management support of all project-related QA/QC activities.	Ph.D. Environmental Engineering; 30 years experience, 27 years Director of Research for UFI, 84 publications on Onondaga Lake
David Matthews	UFI Scientific/Technical Manager and Project Limnologist	UFI	Oversight of daily project activities to ensure compliance with project objectives. Provide technical oversight and consultation on major technical and scientific issues, and oversight of field and laboratory progress; deliver data to project participants; organize and maintain project database. Authorize and document minor adjustments to the field/laboratory program in response to changing field conditions.	Ph.D. Environmental Engineering; 11 years experience on Onondaga Lake; 15 publications on Onondaga Lake
MaryGail Perkins	UFI Project Administrator, Quality Assurance Officer, and Field Manager	UFI	Coordinate and supervise field activities; ensure that field procedures are completed in accordance with the work plan and QAPP. Coordinate field and laboratory activities and notify Technical Manager of any problems or issues. Provide technical quality assurance assistance, develop and review QAPP, oversee quality assurance activities to ensure compliance with QAPP, review and submit quality assurance reports as required, supervise data validation. Maintain the official, approved QAPP.	M.S. Hydrogeology; 26 years experience on Onondaga Lake, 12 publications on Onondaga Lake

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
MaryGail Perkins	UFI Laboratory Director	UFI	Oversee all UFI laboratory personnel, activities, equipment, and records; track submittal and receipt of samples to the laboratory; retain all chain-of-custody records; and ensure that sample receipt and custody records are properly handled and data are reported within the specified turnaround times. Ensure that laboratory staff maintain and calibrate instruments as necessary, perform internal quality control measures and analytical methods as required, take appropriate corrective actions as necessary, notify QA/QC officer when problems occur, report data and supporting quality assurance information as specified in this QAPP.	M.S. Hydrogeology; 26 years experience on Onondaga Lake, 12 publications on Onondaga Lake
Charles Driscoll	SU Project Manager	UFI	Overall responsibility for SU activities. Approve all necessary actions and adjustments for activities to accomplish project objectives. Provide management support of all project-related QA/QC activities.	Ph.D. Environmental Engineering; 27 years experience. Over 270 publications (authored or co-authored), PI of the LTER project at Hubbard Brook, CESE Director

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Mario Montesdeoca	SU Laboratory Director	SU	Oversee all SU laboratory personnel, activities, equipment, and records; track submittal and receipt of samples to the laboratory; retain all chain–of-custody records; ensure that sample receipt and custody records are properly handled and data are reported within the specified turnaround times. Ensure that laboratory staff maintain and calibrate instruments as necessary, perform internal quality control measures and analytical methods as required, take appropriate corrective actions as necessary, notify QA/QC officer when problems occur, and report data and supporting quality assurance information as specified in this QAPP.	M.A. Engineering Management, 12 years experience managing commercial laboratories, 5 years managing research laboratories
Svetoslava Todorova	SU Scientific/Technical Manager	SU	Oversee daily project activities to ensure compliance with project objectives. Provide technical oversight and consultation on major technical and scientific issues; oversee field and laboratory progress; deliver data to project participants; organize and maintain project database. Authorize and document minor adjustments to the field/laboratory program in response to changing field conditions.	M.S. Environmental Engineering, 4 years research experience, 2 years work experience as environmental engineer, Ph.D. candidate
Edward Mason	SU Quality Assurance Officer	SU	Provide technical quality assurance assistance, develop and review QAPP, oversee quality assurance activities to ensure compliance with QAPP, review and submit quality assurance reports as required, supervise data validation.	B.S. Environmental Science, 2 years QA experience, 5 years supervisory experience

Project Function	Specialized Training – Title or Description of Course	Training Provider	Training Date	Personnel/Groups Receiving Training	Personnel Titles/ Organizational Affiliation	Location of Training Records/Certificates[1]
Collection of water samples for mercury analysis	Instruction received on "clean hands-dirty hands" sampling protocol	Svetla Todorova	April 2006	BAW, MES, MTP, TP, DAM	UFI field staff	UFI – no records or certificates of this training are available

[1]If training records and/or certificates are on file elsewhere, document their location in this column. If training records and/or certificates do not exist or are not available, then this should be noted.

Project Name: Evaluation of nitrate addition to control methyl mercury production in Onondaga Lake **Projected Date(s) of Sampling:** April–November 2007 **Project Managers:** Charles Driscoll, SU, and Steven Effler, UFI	**Site Name:** Onondaga Lake **Site Location:** Onondaga Lake, Syracuse, NY

Date of Session: Numerous (see comments below)
Scoping Session Purpose: To discuss work plan for 2007 field investigation

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
Charles Driscoll	Project Manager	SU	315-443-3434	ctdrisco@ syr.edu	SU Project Manager
Steve Effler	Project Manager	UFI	315-431-4962 ext. 102	sweffler@ upstatefreshwater.org	UFI Project Manager
Dave Matthews	Scientific/Technical Manager	UFI	315-431-4962 ext. 107	damatthews@ upstatefreshwater.org	UFI Scientific/ Technical Manager
John McAuliffe	Project Manager	Honeywell	315-431-4443	John.mcauliffe@ honeywell.com	Overall Project Manager
Betsy Henry	Project Manager	Exponent	518-370-5132	henryb@ exponent.com	Technical support to Honeywell
Ed Glaza	Project Manager	Parsons	315-451-9560	edward.glaza@ parsons.com	Technical support to Honeywell
Tim Larson	Project Manager	NYSDEC	518-402-9767	tjlarson@ gw.dec.state.ny.us	NYSDEC Project Manager
Robert Montione	Scientist	Earth Tech	518-951-2226	robert.montione@ earthtech.com	Technical support to NYSDEC
Michael Spera	Senior Project Director	Earth Tech	212-798-8577	michael.spera@ earthtech.com	Technical support to NYSDEC

Comments/Decisions: From December 2006 through April 2007, several conference calls took place to discuss the 2007 work plan. Participants varied, but included representatives from Syracuse University, Upstate Freshwater Institute, Exponent, Parsons, NYSDEC, USEPA, EarthTech, and USFWS. Work Plan 2007 was revised on May 23, 2007 and conditionally approved by NYSDEC on June 6, 2007.

Action Items: SU/UFI will prepare work plan

Consensus Decisions: _____

Problem Definition and Background

The sediments, water column, and biota of Onondaga Lake (Figure 1) are contaminated with mercury (Hg). Mercury cycling in the lake is influenced by metabolic activity, including primary production and decomposition processes. One remediation initiative (aimed at abating the impacts of domestic waste discharged to the lake) has greatly altered lake metabolism by (1) changing the level of primary production, and thereby the supply of organic carbon delivered to the lake sediments, and (2) shifting the metabolic pathways by which this organic matter is decomposed. These effects have diminished the role of sulfate (SO_4^{2-}) reduction in decomposition. Sulfate-reducing bacteria are responsible for the methylation of ionic mercury. Recent mercury measurements from the water column of the lake suggest that noteworthy changes in the cycling of mercury, and perhaps levels of contamination, may have occurred since the early 1990s.

In September and October of 2005, the Upstate Freshwater Institute (UFI) and Syracuse University (SU) made presentations to the regulatory community (including NYSDEC and USEPA) and Honeywell Inc. concerning changes in the oxygen resources and decomposition pathways of the lake. As part of those presentations, a new approach was suggested to potentially abate the accumulation of methyl mercury (MeHg or CH_3Hg) in the hypolimnion of the lake. In this approach, nitrate (NO_3^-) would be added to the hypolimnion of the lake to inhibit sulfate reduction and control production and transport of methyl mercury. In 2006, UFI and SU conducted a water quality-monitoring program to evaluate the role of nitrate in controlling methyl mercury production in Onondaga Lake. Nitrate addition and hypolimnetic oxygenation will be evaluated as methods to reduce internal methyl mercury production (NYSDEC 2006 Consent Decree). Regardless of the means used to control methyl mercury, major demands will be placed on monitoring to effectively represent spatial and temporal patterns of key substances. Such information will need to be comprehensive and available in a timely manner. The scope of work presented here for 2007 includes components that will address these needs.

The objectives of the proposed 2007 investigation are to:

- Continue to stay apprised of the role of nitrate in controlling methyl mercury production in Onondaga Lake;
- Continue to investigate the interaction between methyl mercury production and related metabolic and redox processes, with particular emphasis on oxygen and nitrate;
- Assess spatial differences in water chemistry based on five paired profiles from the north and south basins of the lake collected over the spring to fall interval and the collection of 10 samples on two occasions from multiple locations in the lake;

Problem Definition and Background *(continued)*

- Assess spatial patterns of nitrate, bisulfide (HS-), and ancillary parameters through collection and interpretation of weekly gridding data from the ISUS rapid profiling instrument;
- Specify mercury concentrations and taxonomy of the pelagic zooplankton community, including seasonal patterns.

UFI has measured sulfide in Onondaga Lake since 1980, using the titration method (SM 18 4500 S2- E). Despite the high detection limit of this method, it was adequate given the high concentrations present in Onondaga Lake. Because sulfide concentrations in the lake have decreased substantially since 2004, UFI felt that it was necessary to achieve a lower detection limit through the use of an ISE (SM 18 4500 S2- G). UFI ran samples by both methods in 2006 because of uncertainties associated with comparability of the two methods, and to maintain consistency with the long-term data set. While results from the two methods were highly correlated, there were major discrepancies in concentrations, particularly at higher concentration levels. The reasons for these large differences are not yet understood. APHA (1992, 1998) suggests that both methods measure total dissolved sulfide ($H_2S+HS^{-}+S^{2-}$). Prior to and during the 2007 Study, UFI will continue to investigate the cause for the observed discrepancies between the two methods and will explore options for running some quality control samples using the titration method. Both sulfide methods are proposed for the 2007 Study because the titration method data are necessary for assessing long-term changes in Onondaga Lake.

Project Description

The nitrate/methyl mercury-monitoring program for 2007 is partitioned into three components: water column, zooplankton, and gas. The water column component has two subcomponents, laboratory analyses of lake samples and spatially detailed monitoring with the ISUS rapid profiling instrument. The laboratory analyses program includes selected features of the Upstate Freshwater Institute's (UFI's) long-term lake metabolism program, as well as a fully integrated mercury monitoring effort. The second component of the project consists of zooplankton sampling to assess mercury concentrations of the pelagic communities and their seasonal patterns in the lake. The gas monitoring component has a single element – the assessment of gas ebullition (gas bubble release from the sediment). Ebullition has been considered a potentially important recycling pathway for mercury in the lake.

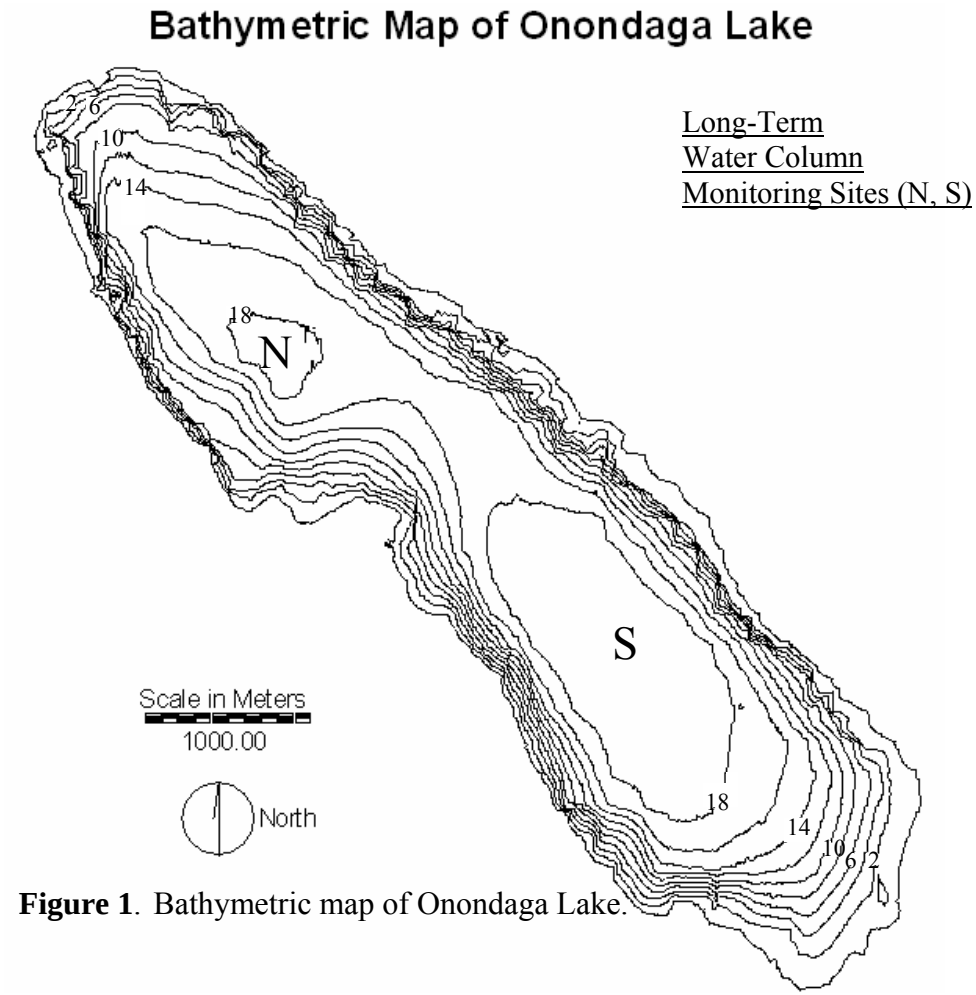


Figure 1. Bathymetric map of Onondaga Lake.

Who will use the data?

The results of the 2007 study will be analyzed by an interdisciplinary team of experts to identify and evaluate noteworthy findings consistent with the overarching and specific goals identified for the study above. The details of these analyses will doubtless evolve, and in some cases shift, through the study interval based on continuing inputs from the Honeywell team, and perhaps other parties, and observed lake conditions.

What will the data be used for?

Evaluation of the feasibility of nitrate addition to control methyl mercury production in Onondaga Lake

Water-Column Monitoring—Laboratory analyses of lake water samples

1) Assess temporal and spatial patterns of mercury speciation in Onondaga Lake
2) Assess temporal and spatial patterns of an array of constituents that include important redox constituents and indicators of primary production and decomposition processes
3) Continue to assess significant disparities observed in the 2006 study between sulfide concentrations determined by the titration (SM 18 4500-S^{2-} E) and electrode (SM 20 4500-S^{2-} G) methods.
4) Further establish relationship(s) between the patterns of mercury and redox constituents

***In situ/in vivo* Monitoring**—Measurements with rapid profiling instrumentation

1) Validate ISUS measurements of nitrate and bisulfide (HS-)
2) Assess spatial patterns of nitrate, bisulfide (HS-), beam attenuation coefficient (i.e., a surrogate of total suspended solids and turbidity), specific conductance, and ancillary parameters, with high spatial resolution, over short time intervals (three dimensional resolution within several hours)
3) Develop monitoring protocols with this instrumentation capable of assessing the efficacy of nitrate treatment, through resolution of the spatial patterns of nitrate and primary by-products of sulfate reduction (e.g., bisulfide); for monitoring during implementation of rehabilitation
4) Develop rapid-results-turn-around capabilities with this instrumentation to potentially assist in future nitrate and/or oxygenation pilot studies

What will the data be used for? *(continued)*

Zooplankton—Zooplankton taxonomy and mercury concentrations

1) Specify seasonal patterns in the taxonomy and biomass of the pelagic zooplankton community through enumeration of five samples to genus or species (in most cases) level
2) Determine concentrations of total and methyl mercury in the pelagic zooplankton assemblage on a seasonal basis
3) If possible, determine concentrations of total and methyl mercury in large daphnids

Gas Monitoring—Assessment of gas ebullition with inverted cones

1) Quantify the upward fluxes of ebullitive gas (approximately weekly), including its major components
2) Support the evaluation of the potential for increases in ebullition associated with a shift to an increased role for nitrate in supporting decomposition in the hypolimnion (a potential impact of nitrate treatment)

What type of data are needed?

Water-Column Monitoring—Laboratory analyses of lake water samples

1) Timing—monthly from April–November
2) Space—Samples will be collected at long-term monitoring sites, South Deep from April–November and North Deep during April, May, July, September and November (S and N, respectively on Figure 1); approximate dates and depths as specified according to analyte in Tables 1 - 3 of the work plan; in addition, 10 locations in the lake will be sampled in August and October, in conjunction with ISUS gridding, to evaluate lateral heterogeneity. These locations will be discussed with and approved by NYSDEC prior to sampling
3) Sample collection per National Environmental Laboratory Accreditation Conference (NELAC) and EPA specifications
4) Parameters
    - Chlorophyll a (EPA 445)
    - NO_x and NO_2 (EPA 353.2)

What type of data are needed? Water-column monitoring parameters *(continued)*

- T-NH_3 (EPA 350.1)
- DOC and TIC (SM 18–20 5310C)
- Chloride (SM 18–20 4500 Cl^- C)
- Ferrous Iron (Heaney and Davidson, 1977)
- Sulfide (SM 18 4500 S E)
- Sulfide (SM 20 4500 S G)
- Dissolved and ebullitive CH_4 and N_2 (Addess, 1990)
- Total mercury in water (EPA Method 1631E)
- Methyl mercury (EPA Method 1630)

***In situ/in vivo* Monitoring**—Measurements with rapid profiling instrumentation

1) Timing—weekly from April–November
2) Space—south deep, north deep, and X-Y gridding (15–30 sites)
3) Protocol—vertical resolution ~0.25 m
4) Parameters measured by sensors
    - Nitrate (Satlantic ISUS V2)
    - Bisulfide (Satlantic ISUS V2)
    - Temperature (SBE 3F)
    - Specific conductance (SBE 4)
    - Transmissivity (Wetlabs C-Star)
    - Turbidity (D&A OBS-3)
    - Chlorophyll (Wetlabs WETstar)
    - Light penetration (Li-Cor LI-193)

What type of data are needed? ***(continued)***

Zooplankton—Zooplankton taxonomy and mercury concentrations

1) Timing and space—Five samplings in duplicate will be collected at south deep under different water quality conditions – prior to thermal stratification (April); stratified conditions with oxygen present in the hypolimnion (early June); stratified conditions without oxygen, but with nitrate in the hypolimnion (late June or early July); stratified conditions without oxygen or nitrate in the hypolimnion (August); and following fall turnover (November); one sampling will be conducted at north deep in August.
2) Sampling
   - 13 m vertical tows with non-metallic 64µm mesh zooplankton net
   - Three tows per sampling: two tows for mercury analyses (i.e., field duplicates) and one tow for enumeration
3) Parameters
   - Taxonomy
   - Total mercury in zooplankton
     - Zooplankton assemblages (freeze dry, and analysis by EPA 7473)
     - Daphnia (Preparation using Watras and Bloom 1992, and analysis by EPA 1631E)
   - Methyl mercury in zooplankton (Digestion using Watras and Bloom 1992, and analysis by EPA 1630)

Gas Monitoring—Assessment of gas ebullition with inverted cones

1) Inverted cone design per long-term UFI program, LEXAN construction, 0.75 m diameter, inverted graduate separatory funnel
2) Deployment/collection – 1 m above bottom in south and north deep basins
3) Timing – weekly collections April – November
4) Parameters
   - Upward flux for each cone (approximately weekly)
   - Composition – primary constituents (e.g., CH_4 and N_2) according to Addess and Effler (1996)

How "good" do the data need to be in order to support the environmental decision?
The data must support an evaluation regarding nitrate addition for control of methyl mercury production in Onondaga Lake, and a feasibility and impact analysis of nitrate addition as a management option.
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 will be collected from Onondaga Lake and analyzed by UFI and SU between April–December 2007.
Who will collect and generate the data?
UFI will collect the samples and analyze all analytes, except mercury, which will be analyzed by SU.
How will the data be reported?
The data will be presented in the Data Report referenced in the Work Plan.
How will the data be archived?
All field and UFI laboratory data are stored on the UFI server. Data are protected from corruption through routine data backups via computer and secure storage of data in hardcopy. All raw field and analytical data are stored in hardcopy form and, depending on format, on the UFI local area network (LAN). All data are managed and stored on the network system. Field and laboratory data are usually in the form of an Excel spreadsheet. Near-real-time data and some UFI laboratory data are stored in a database. The database is stored in a MySQL (v.4.1) server. The UFI server runs the Linux operating system on an AMD Athlon computer. SU stores chain-of-custody forms and laboratory data in hard copy, and the electronic data are stored in the College of Engineering and Computer Science (ECS) computer network system. Data backups are conducted by College of Engineering and Computer Science (ECS) computer and the Computer and Information Technology Services (CIT) computer

Analytes can be NELAC (National standards) certified, ELAP (NYSDOH standard) certified, or non-certified methods that follow a standard industry (EPA, ASTM, Standard Methods, etc) acceptable protocol. All NELAC certified methods are also ELAP certified methods. Not all ELAP certified methods are NELAC certified. Many traditional water quality parameters do not have NELAC or ELAP certified methods. UFI and SU are certified for all NELAC/ELAP certifiable analytes listed here.

Matrix	Water
Analytical Group[1]	Chlorophyll a
Concentration Level	Low

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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-1	L-8	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Reference sample	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	Field trip blanks	S&A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	NO_x
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	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-1	L-2	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value) for warning limits and 3 for control limits	Matrix spike and matrix spike duplicates	A
				Laboratory control samples	A
				Reference sample	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	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

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

Matrix	Water
Analytical Group[1]	NO_2
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	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-1	L-2	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Matrix spike and matrix spike duplicates	A
				Laboratory control samples	A
				Reference sample	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	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]ELAP only certified method.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	T-NH_3
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	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-1	L-3	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Matrix spike and matrix spike duplicates	A
				Laboratory control samples	A
				Reference sample	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	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

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

Matrix	Water
Analytical Group[1]	DOC
Concentration Level	Low

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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-1	L-4	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Matrix spike and matrix spike duplicates	A
				Laboratory control samples	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]There is no NELAC/ELAP certification available for DOC. UFI is NELAC and ELAP certified for TOC. DOC samples are filtered and run as a TOC.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	TIC
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	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-1	L-7	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Reference sample	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	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Chloride
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	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-1	L-1	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Matrix spike and matrix spike duplicates	A
				Laboratory control samples	A
				Reference sample	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Completeness	95% for all analyses	Data completeness check	S&A

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

Matrix	Water
Analytical Group[1]	Ferrous iron
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	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	L-10	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Reference sample	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	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value (based on monthly moving average with n≥10) for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses the accepted procedure Heaney and Davidson (1977). Heaney, S,I. and Davidson, W. 1977. The determination of ferrous iron in natural waters with 2, 2' bipyridyl. *Limnol. Oceanogr.* 22(4):753–759.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Sulfide Method 1[2]
Concentration Level	High

Sampling Procedure[3]	**Analytical Method/SOP**[4]	**Data Quality Indicators (DQIs)**	**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	L-5	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Reference sample	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]All sulfide samples will be run using two sulfide methods (Method 1 - SM 18 4500 S^{2-} E and Method 2 - SM 20 4500 S^{2-} G) to assess comparability between the two methods over the observed concentration range. The SM 18 4500 S^{2-} E is UFI's historic long-term method. Method 2 is an NELAC and ELAP certified method, but Method 1 does not have a NELAC/ELAP certification available.
[2]Method 1 sulfide data will be used for comparison to historic analyses.
[3]Reference number from QAPP Worksheet #21.
[4]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Sulfide Method 2[2]
Concentration Level	Low

Sampling Procedure[3]	Analytical Method/SOP[4]	Data Quality Indicators (DQIs)	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	L-6	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Reference sample	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	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]All sulfide samples will be run using two sulfide methods (Method 1 - SM 20 4500 SE and Method 2 - SM 20 4500 S G) to assess comparability between the two methods over the observed concentration range. The SM 20 4500 S E is UFI's historic long-term method. Method 2 is an NELAC and ELAP certified method, but Method 1 does not have a NELAC/ELAP certification available.
[2]No measurement performance criteria are available for Method 1. Method 1 Sulfide data will be used for comparison to historic analyses.
[3]Reference number from QAPP Worksheet #21.
[4]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Dissolved and ebbulitive methane and nitrogen gas
Concentration Level	Low

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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 and S-5	L-9	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Method Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks (methane only)	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses the accepted procedure Addess (1990). Addess, J.M., 1990. Methane Cycling in Onondaga Lake, New York. M.S. Thesis, State University of New York, College of Environmental Science and Forestry. 111p.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Total mercury
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	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-3	L-11	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 20%	Laboratory duplicate samples	A
			82–122%	Ongoing precision and recovery samples	A
		Accuracy/Bias	Five standards with the RSD ≤15% and low standard recovery 75–125%	Initial calibration standards	A
			Control limit recovery 76–128%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 82-122%	Laboratory control samples	A
		Contamination	Less than reporting limit (0.5 ng/L)	Field, method, and instrument blanks	A
		Sensitivity	90–110% of expected value	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]ELAP only certified method.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Methyl mercury
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	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-3	L-12	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 20%	Laboratory duplicate samples	A
			53-125%	Ongoing precision and recovery samples	A
		Accuracy/Bias	Five standards with the RSD ≤15% and low standard recovery 85-115%	Initial calibration standards	A
			Control limit recovery 40-150 %	Matrix spike and matrix spike duplicates	A
			Control limit recovery 53-125%	Laboratory control samples	A
		Contamination	Less than reporting limit (0.05 ng/L)	Field, method, and instrument blanks	A
		Sensitivity	85–115% of expected value	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Zooplankton
Analytical Group[1]	Total mercury
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	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-4	L-13	Precision – Field	RSD 35%	Field duplicate samples	S&A
		Precision – Lab	RPD 20%	Laboratory duplicate samples	A
			86-115%	Ongoing precision and recovery samples	A
		Accuracy/Bias	Five standards with the RSD ≤15% and low standard recovery 75–125%	Initial calibration standards	A
			Control limit recovery 75–125%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 86-115%	Laboratory control samples	A
		Contamination	Less than reporting limit	Method and instrument blanks	A
		Sensitivity	90–110% of expected value	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Zooplankton
Analytical Group[1]	Methyl mercury
Concentration Level	Low

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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-4	L-15	Precision – Field	RSD 35%	Field duplicate samples	S&A
		Precision – Lab	RPD 20%	Laboratory duplicate samples	A
			69-110%	Ongoing precision and recovery samples	A
		Accuracy/Bias	Five standards with the RSD ≤15% and low standard recovery 65–135%	Initial calibration standards	A
			Control limit recovery 52-126%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 69-110%	Laboratory control samples	A
		Contamination	Less than reporting limit	Method and instrument blanks	A
		Sensitivity	85–115% of expected value	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Nitrate
Concentration Level	Low

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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)**
NA	L-15	Precision – Field	+/-0.05 umol/L	Field duplicate samples	A
		Accuracy/Bias	+/- 2 umol/L	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses the procedure described in Johnson and Coletti (2002).
[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]	Bisulfide (HS^-)
Concentration Level	Low

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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)**
NA	L-15	Precision – Field	+/-0.05 umol/L	Field duplicate samples	A
		Accuracy/Bias	+/- 2 umol/L	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses the procedure described in Johnson and Coletti (2002).
[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]	Temperature
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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)**
NA	L-15	Precision – Field	± 0.0003ºC	Field duplicate samples	A
		Accuracy/Bias	± 0.002ºC	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[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]	Specific conductance
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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)**
NA	L-15	Precision – Field	± 0.1 µS/cm	Field duplicate samples	A
		Accuracy/Bias	± 3 µS/cm	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[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]	Transmissivity (beam attenuation coefficient at 660 nm)
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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)**
NA	L-15	Precision – Field	± 0.1% transmission	Field duplicate samples	A
		Accuracy/Bias	± 0.1% transmission	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[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]	Turbidity (optical backscattering)
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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)**
NA	L-15	Precision – Field	± 0.1 NTU	Field duplicate samples	A
		Accuracy/Bias	± 0.25 NTU	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[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]	Chlorophyll fluorescence
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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)**
NA	L-15	Precision – Field	± 0.1 µg/L	Field duplicate samples	A
		Accuracy/Bias	NA		
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[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]	Light penetration (photo-synthetically active irradiance)
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**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)**
NA	L-15	Precision – Field	± 5% reading	Field duplicate samples	A
		Accuracy/Bias	± 5% reading	Check sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI/SU uses an accepted procedure.
[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.

There are no plans to use secondary data as part of this study, although daily *in situ* robotic measurements from multiple depths, in Onondaga Lake will be collected and available for use as part of this program.

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Org., Data Types, Data Generation/Collection Dates)	How Data Will Be Used	Limitations on Data Use
Daily robotic measurements from multiple depths	UFI; available on www.ourlake.org	UFI; data includes dissolved oxygen, temperature, specific conductance, pH, fluorometric chlorophyll, and turbidity	Seasonality of thermal stratification, oxygen depletion, plunging inflows, and phytoplankton biomass	No limitations

Sampling Tasks

1. Water column sampling by boat using standard techniques. Surface water parameters: chlorophyll, NO_x, NO_2, T-NH_3, DOC, DIC, chloride, ferrous iron, sulfide, total mercury, and methyl mercury.
2. Field instrument profiles
3. Zooplankton sampling by boat using vertical tows with a zooplankton net. Zooplankton taxonomy will be determined and tissue samples will be analyzed for total mercury and methyl mercury.
4. Gas monitoring component has a single element, assessment of gas ebullition with inverted cones. Parameters: dissolved and ebullitive methane and nitrogen gas.
5. *In situ/in vivo* monitoring analysis by ISUS (rapid robotic profiling instrumentation). Parameters: nitrate, bisulfide (HS-), temperature, specific conductance, transmissivity, turbidity, chlorophyll, and light penetration.
6. UFI will document the details of sample locations, depths, SOPs, and water sample collection.

Analysis Tasks

1. UFI will analyze water samples for chlorophyll, NOx, NO_2, T-NH_3, DOC, TIC, chloride, ferrous iron, sulfide, and dissolved methane and nitrogen gas. In addition, UFI will conduct the zooplankton taxonomy determinations.
2. The Center for Environmental Science and Engineering at SU will analyze water and zooplankton samples for total mercury and methyl mercury.

Quality Control Tasks

1. UFI field team leader will evaluate all samples and applicable field quality control samples for acceptability for transport/submission to the laboratory.
2. Implement SOPs for sample collection, packaging, transport, and storage prior to analysis. QC sample handling protocols are described on Worksheet #26.

Secondary Data

See Worksheet #13.

Documentation and Records

1. The QAPP is a UFI and SU controlled document and is subject to all requirements of a controlled document as specified by NELAC.
2. Procedures, observations, and test results will be documented for all sample collection activities, laboratory analyses, and reporting. In addition to data reports provided by the laboratory, reports will be prepared that address data quality and usability and that provide tabulated laboratory and field data.
3. Field data and field profiling instrumentation-related sampling information will be recorded on pre-printed forms, which provide space for comments and suggestions, pertinent observations, and performance and maintenance indicators. Field records will be maintained during all stages of sample collection and preparation for transport to the laboratory.
4. Field records will include the following items:
   a. Field notebook to record daily sampling activities and conditions;
   b. Combined station/sample log to document station locations, depth, date, and time of collection; and
   c. Combined chain-of-custody/sample analysis request forms.

Laboratory Data Reports

1. 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.
2. Material amendments to a test report after issue are made only in the form of a further document, or data transfer including the statement "Supplement to Test Report, report number __". Clients are notified promptly, in writing, of any event, such as the identification of defective measuring or test equipment that casts doubt on the validity of the results given in any test report or amendment to a report.

Data and Document Management Tasks

Records generated during sample collection and analyses document the validity and authenticity of the project data. The field and laboratory (electronic and hard-copy) data generated for this study will be retained at UFI's or SU's facility in the custody of the respective project manager. Field logs, sample records, and chain-of-custody records will be kept at UFI's facility for a period of five years.

Data Review Tasks

1. The laboratories 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 are certified to meet all requirements of the NELAC standards, or reasons are provided if they do not.

Assessment/Audit Tasks

1. 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 documented procedures, and the rationale for the changes.
2. Exponent on behalf of Honeywell will assess the quality of the analytical chemistry data. The goal of data assessment is to determine the quality of each data point and to identify data points that do not meet the project data quality objectives. Exponent staff will perform data assessment prior to finalization and release of the analytical data. The data will be assessed in accordance with the general guidance specified by the Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (National Functional Guidelines) (U.S. EPA 2002). EPA has not published data validation guidelines for any of the project-specific analytes included in this program (i.e., low-level total mercury, methylmercury, and the conventional parameters). Therefore, chemical data for these analytes will be assessed following the general evaluation procedures described in the National Functional Guidelines. Specifically, the following quality control indicators will be evaluated when available: holding times, calibration check standards, method and field blanks, LCSs, matrix spike samples, laboratory duplicate analyses, and field replicate analyses. For these data quality indicators, method-specific quality control requirements and laboratory-established control limits were used to assess the data. Instrument calibrations, calculations, and transcriptions will not be assessed by Exponent because the laboratories are responsible for 100-percent verification of these results and procedures.
3. Exponent on behalf of Honeywell will prepare the data quality and usability report. The report will summarize the results of the data assessment and data quality review and will describe any significant quality assurance problems that were encountered.

Matrix: Water
Analytical Group: Chlorophyll a
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Chlorophyll a	479-61-8	0.2 µg/L	0.5 µg/L	0.1 µg/L	0.2 µg/L	0.2 µg/L	0.5 µg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Nitrogen (NO_x and NO_2)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
NO_x	11104-93-1	NA	16 µg/L	1 µg/L	5 µg/L	5 µg/L	16 µg/L
NO_2	10102-44-0	NA	9 µg/L	1 µg/L	5 µg/L	3 µg/L	9 µg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

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

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
$T\text{-}NH_3$	7664-41-7	NA	41 µg/L	2 µg/L	NA	12 µg/L	41 µg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Carbon (DOC and TIC)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
DOC	None	NA	0.9 mg/L	0.002 mg/L	NA	0.3 mg/L	0.9 mg/L
TIC	None	NA	1.8 mg/L	0.002 mg/L	NA	0.5 mg/L	1.8 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Chloride
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Chloride	16887-00-6	10 mg/L	NA	NA	100 mg/L	NA	100 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Ferrous iron
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Ferrous iron	15438-31-0	NA	0.006 mg/L	NA	0.028 mg/L	0.002 mg/L	0.006 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Sulfide
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Sulfide Method 1	H_2S 7783-06-4 S^{2-} 18496-25-8	NA	1 mg/L	NA	1 mg/L	0.5 mg/L	1 mg/L
Sulfide Method 2	H_2S 7783-06-4 S^{2-} 18496-25-8	NA	0.032 mg/L	NA	0.032 mg/L	0.016 mg/L	0.032 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Dissolved and ebullitive methane and nitrogen
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Dissolved methane	74-82-8	NA	0.5 mg/L	NA	NA	NA	0.5 mg/L
Dissolved nitrogen	7727-37-9	NA	6 mg/L	NA	NA	NA	6 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods; this information is not available for these specific parameters.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Mercury
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	0.7 ng/L	0.5 ng/L	0.2 ng/L	0.5 ng/L	0.14 ng/L	0.5 ng/L
Methyl mercury	22967-92-6	0.7 ng/L	0.05 ng/L	0.02 ng/L	0.05 ng/L	0.015 ng/L	0.05 ng/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Zooplankton
Analytical Group: Mercury
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	NA		3 ng/g	9 ng/g	0.031 (low), 0.0125 ng (ultra low)[3]	0.09 ng (low), 0.0375 ng (ultra low)[3]
Methyl mercury	22967-92-6	NA		3.0 ng/g	9 ng/g	0.0015 ng[4]	0.0045 ng[4]

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.
[3]The MDL and QL concentrations are depending on amount of zooplankton collected. For an analysis of 10 mg, the MDL is 3.0 ng/g. If a lower MDL is needed a larger sample amount can be used, or if only a small amount of sample is present (for example 10-20 daphnia), the sample will be digested, and the digested solution will be analyzed by EPA 1631E method to quantify the concentration.
[4]The MDL and QL concentrations are dependent on amount of zooplankton collected or the volume of digest used during analysis. For an analysis of 5 mg, the MDL is 3.0 ng/g.

Matrix: Water
Analytical Group: Nitrate
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Nitrate	14797-55-8	NA	0.007 mg/L	NA	0.007 mg/L	NA	0.007 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Bisulfide
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Bisulfide (HS-)		NA	0.016 mg/L	NA	0.016 mg/L	NA	0.016 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Activities	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Develop work plan for 2007 study	UFI and SU	1/2007	6/2007	Work plan and QAPP	6/2007
Study set-up	UFI	1/1/07	4/30/07	NA	NA
Water-column monitoring	UFI	4/15/07	11/30/07	NA	NA
Zooplankton sampling	UFI	4/15/07	11/30/07	NA	NA
In situ/in vivo monitoring	UFI	4/15/07	10/31/07	NA	NA
Scientific oversight	Exponent	3/15/07	11/30/07	NA	NA
Data handling/analysis	UFI/SU	4/15/07	1/7/08	Data Summary Tables	Quarterly
Data Usability Assessment Report	Exponent	11/20/07	2/29/08	Data Report	3/2008
Data analysis/interpretation	UFI/SU	4/15/07	4/7/08	NA	NA

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

The primary sample locations are the south and north deep basins. Lake water is generally considered to be well mixed horizontally; however the north basin samples will provide data to assess this assumption. The ISUS gridding and associated mercury samples will also evaluate horizontal homogeneity in the water column. In previous investigations, gas ebullition measurements varied significantly between the two basins, therefore both basins will be sampled in this program. With regard to timing, water column and zooplankton samples will be collected monthly in the south basin and less frequently in the north basin. In both cases, samples will be collected in each of five water quality regimes: (1) spring turnover; (2) stratified conditions with both DO and NO_3^- present throughout the hypolimnion; (3) stratified conditions with NO_3^- present and DO depleted from the hypolimnion; (4) stratified conditions with both DO and NO_3^- depleted from the hypolimnion; and (5) fall turnover.

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) [May refer to map or Worksheet #18 for details]:

See Worksheet #18

Sampling Location/ID Number	Matrix	Depth (units)[1]	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)	Sampling SOP Reference[2]	Rationale for Sampling Location
South Deep	Water	2, 10, 18 m (April, May, November) 2, 6, 10, 18 m (June–October)	Chlorophyll a	Low	59 (32 env + 18 dups + 9 blanks)	S-1	See Worksheet #17
South Deep	Water	2, 10, 18 m (April, May, November) 2, 6, 10, 12, 14, 16, 17, 18 m (June–October)	NO_x and NO_2	Low	79 (52 env + 18 dups + 9 blanks)	S-1	
			$T\text{-}NH_3$	Low	79 (52 env + 18 dups + 9 blanks)		
			DOC and TIC	Low	79 (52 env + 18 dups + 9 blanks)		
			Chloride	Low	79 (52 env + 18 dups + 9 blanks)		
			Total mercury	Low	52(+9 dups)	S-3	
			Filtered total mercury	Low	10		
			Methyl mercury	Low	52 (+9 dups)		
			Filtered Methyl mercury	Low	10		

Sampling Location/ID Number	Matrix	Depth (units)[1]	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)	Sampling SOP Reference[2]	Rationale for Sampling Location
South Deep	Water	Anoxic depths 1-m intervals	Ferrous iron[3]	Low	54 (42 env + 8 dups + 4 blanks)	S-1 S-2	
			Sulfide method 1[3] Sulfide method 2[3]	Low Low	54 (42 env + 8 dups + 4 blanks) 79 (67 env + 8 dups + 4 blanks)		
			Dissolved methane[3]	Low	54 (42 env + 8 dups + 4 blanks)		
			Dissolved nitrogen[3]	Low	54 (42 env + 8 dups + 4 blanks)		

Sampling Location/ID Number	Matrix	Depth (units)[1]	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)	Sampling SOP Reference[2]	Rationale for Sampling Location
South Deep	Zooplankton	Variable	Total mercury	Low	5 (+5 dups)	S-4	
			Methyl mercury	Low	5 (+5 dups)		
South Deep	Water	18 m	Ebullitive methane[4]	Low	54 (42 env + 8 dups + 4 blanks)	S-5	See Worksheet #17
			Ebullitive nitrogen[4]	Low	54 (42 env + 8 dups + 4 blanks)	S-5	
ISUS Gridding	Water	Variable	NO_x and NO_2	Low	20 (+2 dups)	S-1 S-2	See Worksheet #17
			T-NH_3	Low	20 (+2 dups)		
			Sulfide[3]	Low	20 (+2 dups)		
			Total mercury	Low	20 (+2 dups)	S-3	
			Methyl mercury	Low	20 (+2 dups)		
North Deep	Water	2, 10, 17m (April, May, November) 2, 6, 10, 17 m (July, September)	Chlorophyll a	Low	17 (all env)	S-1	See Worksheet #17
North Deep	Water	2, 10, 17 m (April, May, November) 2, 6, 10, 12, 14, 16, 17 m (July, September)	NO_x and NO_2	Low	23 (all env)	S-1	See Worksheet #17
			T-NH_3	Low	23 (all env)		
			DOC and TIC	Low	23 (all env)		
			Chloride	Low	23 (all env)		

Sampling Location/ID Number	Matrix	Depth (units)[1]	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)	Sampling SOP Reference[2]	Rationale for Sampling Location
North Deep	Water	2, 10, 17 m (April, May, November) 2, 6, 10, 12, 14, 16, 17 m (July, September)	Total mercury	Low	28	S-3	
			Filtered total mercury	Low	4		
			Methyl mercury	Low	28		
			Filtered methyl mercury	Low	4		
North Deep	Water	Anoxic depths 1-m intervals	Ferrous iron[3]	Low	24 (all env)	S-1 S-2	
			Sulfide[3]	Low	24 (all env)		
			Dissolved methane[3]	Low	24 (all env)		
			Dissolved nitrogen[3]	Low	24 (all env)		
South Deep	Water	18 m	Ebullitive methane[4]	Low	20 (all env)	S-5	See Worksheet #17
			Ebullitive nitrogen[4]	Low	20 (all env)	S-5	
North Deep	Zooplankton	Variable	Total mercury	Low	1 (+1 dup)	S-4	
			Methyl mercury	Low	1 (+1 dup)		

[1]Samples will be collected at 1-m intervals at anoxic depths (total number of samples from water-column anoxic depths will depend on the time of year and extent of anoxia); table shows oxic depths only.
[2]From the Project Sampling SOP References table (Worksheet #21).
[3]Reduced species (CH_4, N_2, H_2S, Fe^{2+}) are collected at all anoxic depths, and 1 m above the uppermost anoxic depth (oxic sample); total number of samples will depend on the time of year and extent of anoxia.
[4]Ebullitive gas composition (CH4 and N2) will be measured on gas samples collected from one gas cone at south deep and one at north deep on approximately 20 occasions.

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference[1]	Sample Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Water	Chlorophyll	Low	L-8	25 mL–4 L	Opaque plastic bottle (2 or 4 L)[2]	Filter and freeze	21 days
Water	Nitrate/Nitrite as N (NO_x and NO_2)	Low	L-2	2 mL	Opaque plastic bottle (2 or 4 L)[2]	Cool, 4°C	48 hours
Water	Ammonia as N ($T\text{-}NH_3$)	Low	L-3	2 mL	Opaque plastic bottle (2 or 4 L)[2]	Cool, 4°C	48 hours
Water	Organic Carbon, Total/Total Dissolved as C (DOC)	Low	L-4	40 mL	Opaque plastic bottle (2 L)	Cool, 4°C may be preserved	28 days
Water	Carbon, Inorganic Dissolved and Total (TIC)	Low	L-7	40 mL	Glass sample tube (40 mL)	Cool, 4°C	48 hours
Water	Chloride	Low	L-1	250 mL	Opaque plastic bottle (500 mL)	Cool, 4°C	28 days
Water	Ferrous iron	Low	L-10	20 mL	Dark BOD bottle (300 mL)	Cool, 4°C	7 days
Water	Sulfide as S (Method 1)	Low	L-5	300 mL	BOD bottle (300 mL)	Cool, 4°C	7 days
Water	Sulfide as S (Method 2)	Low	L-6	150 mL	BOD bottle (300 mL)	Cool, 4°C	7 days

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference[1]	Sample Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Water	Dissolved Gas (methane, carbon dioxide, and nitrogen)	Low	L-9	20 mL	BOD bottle (300 mL)	Cool, 4°C	7 days
Water	Ebullitive methane and nitrogen	Low	L-9	2 mL	Syringe (5 or 10 mL)	Cool, 4°C	7 days
Water	Total mercury	Low	L-11	500 mL	Teflon bottle (500 mL or 1 L)	HCl, cool, 4°C	28 days (unpreserved), 90 days (preserved)
Water	Methyl mercury	Low	L-12	500 mL	Teflon bottle (500 mL or 1 L)	HCl, cool, 4°C	6 months (preserved)
Zooplankton	Total and methyl mercury	Low	L-13, L-14	250-500 mL	Plastic or Teflon bottle (250 - 500 ml)	cool, 4°C, freeze, and freeze dry	6 months (preserved)

[1]From the Analytical SOP References table (Worksheet #23).
[2]Bulk bottle is a 2-L bottle at 2, 6, 10, 12, 14, and 18 m; 4-L bottle at 0, 4, 8, and 16 m.

Matrix	Analytical Group	Concen-tration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	Inorganic No. of MS	No. of Field Blanks[3]	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Water	Chlorophyll	Low	L-8	2 stations, 3–4 depths, 9 sampling trips	Triplicate sets 9 (18 samples)		9			76[4]
Water	Nitrate/Nitrite as N (NO_x)	Low	L-2	2 stations, 3–8 depths, 9 sampling trips; 10 ISUS gridding stations, 2 samples per station	Triplicate sets 9 (18 samples)		9			122[4]
Water	Nitrate as N (NO_2)	Low	L-2	2 stations, 3–8 depths, 9 sampling trips 10 ISUS gridding stations, 2 samples per station	Triplicate sets 9 (18 samples)		9			122[4]

Matrix	Analytical Group	Concen-tration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	Inorganic No. of MS	No. of Field Blanks[3]	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Water	Ammonia as N ($T\text{-}NH_3$)	Low	L-3	2 stations, 3–8 depths, 9 sampling trips; 10 ISUS gridding stations, 2 samples per station	Triplicate sets 9 (18 samples)		9			122[4]
Water	Organic Carbon, Total/Total Dissolved as C (DOC)	Low	L-4	2 stations, 3–8 depths, 9 sampling trips	Triplicate sets 9 (18 samples)		9			102[4]
Water	Carbon, Inorganic Dissolved and Total (TIC)	Low	L-7	2 stations, 3–8 depths, 9 sampling trips	Triplicate sets 9 (18 samples)		9			102[4]

Matrix	Analytical Group	Concen-tration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	Inorganic No. of MS	No. of Field Blanks[3]	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Water	Chloride	Low	L-1	2 stations, 3–8 depths, 9 sampling trips	Triplicate sets 9 (18 samples)		9			102[4]
Water	Ferrous iron	Low	L-10	2 stations, variable depths and sampling trips	Triplicate sets 4 (8 samples)		4			78[5]
Water	Sulfide as S (Method 1)	Low	L-5	2 stations, variable depths and sampling trips	Triplicate sets 4 (8 samples)		4			78[5]
Water	Sulfide as S (Method 2)	Low	L-6	2 stations, variable depths and sampling trips; 10 ISUS gridding stations, 2 samples per station once	Triplicate sets 4 (8 samples)		4			123[5]

Matrix	Analytical Group	Concen-tration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	Inorganic No. of MS	No. of Field Blanks[3]	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Water	Dissolved methane	Low	L-9	2 stations, variable depths and sampling trips	Triplicate sets 4 (8 samples)		4			78[5]
Water	Dissolved nitrogen	Low	L-9	2 stations, variable depths and sampling trips	Triplicate sets 4 (8 samples)		4			78[5]
Gas	Ebullitive methane	Low	L-9	2[6]	0		0			20
Gas	Ebullitive nitrogen	Low	L-9	2[6]	0		0			20
Water	Total mercury	Low	L-11	1 station, 3–8 depths per month and a 2nd station 3–7 depths every other month over 8 months; 10 ISUS gridding stations, 2 samples per station once	11		11	14		131

Matrix	Analytical Group	Concen-tration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	Inorganic No. of MS/MSD	No. of Field Blanks[3]	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Water	Filtered mercury	Low	L-11	1 station, 1 depth per month and a 2nd station 1 depth every other month over 8 months; 10 ISUS gridding stations, 1 sample per station once						14
Water	Methyl mercury	Low	L-12	1 station, 3–8 depths per month and a 2nd station 3–7 depths every other month over 8 months; 10 ISUS gridding stations, 2 samples per station once	11	1 set per 10 samples	11	14		131

Matrix	Analytical Group	Concen-tration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	Inorganic	No. of Field Blanks[3]	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Water	Filtered Methyl mercury	Low	L-12	1 station, 3–8 depths per month and a 2nd station 3–7 depths every other month over 8 months; 10 ISUS gridding stations, 2 samples per station once						14
Zoo-plankton assemblages	Total and methyl mercury	Low	L-13, L14	1 station, 1 sample per month, and a 2nd station once	6	1 set per 10 samples	6			12
Zooplankton - Daphnia	Total and methyl mercury	Low	L-13, L-14	1 station, 1 sample per month, and a 2nd station once (if found in sufficient quantity)	6	1 set per 10 samples	6			

Notes on following page.

[1]From the Analytical SOP References table (Worksheet #23).
[2]Samples collected at different depths at the same location, are counted separately.
[3]A field blank for non-mercury analyses is termed a "field trip blank" by the laboratory (UFI) and, as defined in the work plan, will consist of sample bottles that are filled in the laboratory, transported to the field and then back to the laboratory for analysis. A field blank for total mercury and methyl mercury 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 field, and then poured into a second clean sample bottle for transport back to the laboratory.
[4]Samples will be collected at 2-m intervals at oxic depths and 1-m intervals at anoxic depths (total number of samples from water-column anoxic depths will depend on the time of year and extent of anoxia); table shows oxic depths only.
[5]Reduced species (CH_4, N_2, H_2S, Fe^{2+}) are collected at all anoxic depths, and 1 m above the uppermost anoxic depth (oxic sample); total number of samples will depend on the time of year and extent of anoxia.
[6] Ebullition volume will be measured weekly from each cone from April through October..

Reference Number	Title, Revision Date and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
S-1	UFI SOP 304 Water sample collection: submersible pump	UFI	Submersible pump with conduit, marine battery, collection bottles.	N	Includes descriptions and procedures for sampling with submersible pump
S-2	UFI SOP 306 Reduced species (H_2S, CH_4, and Fe^{2+}) sample collection	UFI	Submersible pump with conduit and a marine battery or a Kemmerer or Van Dorn, reduced species collection bottles, reagent cooler with bottles of zinc acetate solution and 6 N NaOH solution.	N	Includes descriptions and procedures for sampling and preservation of reduced species samples.
S-3	SU SOP AP # CESE-ENV-1669 Sampling stream and lake water for mercury at trace levels	SU	Peristaltic or submersible pump and precleaned fluoropolymer or styrene/ethylene/butylene/silicone (SEBS) tubing. A side arm filter apparatus is used for samples being analyzed for dissolved metals.	N	Includes descriptions and procedures for collecting low level mercury samples.

Reference Number	Title, Revision Date and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
S-4	SU SOP AP #CESE-ENV-310 Zooplankton sample collection and preservation and Secchi depth measurement field procedures	SU	A sampling net (diameter of 30 cm, length with cup 1m, and a mesh size of 64 µm) is slowly lowered to a depth.	N	Includes descriptions and procedures for sampling with mesh net. Note that zooplankton samples for this project are analyzed within 48 hours and are NOT preserved with AlkaSeltzer and ethanol.
S-5	UFI SOP 311 Gas cone deployment and collection	UFI	Gas cone (0.75 m diameter, concave polycarbonate plastic cone with stainless steel frame) with attached, inverted separatory funnel (500 ml or 1000 ml), cable or rope, marker buoy, tether rope, research (large white) marker buoy, cable or rope, and an anchor. For gas composition sampling, include a Pressure-Lok Series A Precision Analytical Syringe (Supelco brand).	N	Includes descriptions and procedures for collecting ebullient gas.

Field Equipment Calibration, Maintenance, Testing, and Inspection Table

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Submersible pump and tubing	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.		Check for physical damage and/or leaks	Weekly	Visual inspection	Repair as soon as possible (in field if possible or back at the lab)	B. Wagner	SOP 304
ISUS profiler	Calibrated at factory, Perform routine DI water check in field before and after each use, DI water check done weekly in the lab to verify instrument is operating correctly	Rinse all sensors with DI water, gently wipe all sensors dry using optical lens paper	DI 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)	A. Prestigiacomo	SOP 330

[1]Specify the appropriate reference letter or number from the Project Sampling SOP References table (Worksheet #21).

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-1	UFI SOP 104 - Chloride, high range (SM 18–20 4500 Cl^- C)	Definitive	Chloride	Titration	UFI	N
L-2	UFI SOP 106.1 - Nitrate/Nitrite (as N) (U.S. EPA Method 353.2)	Definitive	NO_x and NO_2	Segmented Flow Analysis (SFA) system (OI Analytical Flow Solution IV) – Model 502	UFI	N
L-3	UFI SOP 105.1 - Ammonia (as N) (U.S. EPA Method 350.1)	Definitive	T-NH_3	Segmented Flow Analysis (SFA) system (OI Analytical Flow Solution IV) – Model 502	UFI	N
L-4	UFI SOP 110 - Organic carbon, total/total dissolved (as C) (SM 18–20 5310C)	Definitive	DOC	Phoenix 8000 Carbon analyzer	UFI	N
L-5	UFI SOP 112 - Sulfide (as S), high range (SM 18 4500 S^{2-} E)	Definitive	Sulfide	Titration	UFI	N
L-6	UFI SOP 212 - Sulfide (as S), high range (SM 20 4500 S^- G)	Definitive	Sulfide	Ion-selective electrode	UFI	N
L-7	UFI SOP 203 - Carbon, inorganic dissolved and total (SM 18-20 5310C)	Definitive	DIC	Phoenix 8000 Carbon analyzer	UFI	N
L-8	UFI SOP 216 - Chlorophyll (U.S. EPA 445)	Definitive	Chlorophyll	Model TD-700 Fluorometer	UFI	N
L-9	UFI SOP 217 - Dissolved gas: methane, carbon dioxide, nitrogen (Addess 1990)	Definitive	Dissolved methane and nitrogen	GOW-MAC gas chromatograph	UFI	N
L-10	UFI SOP 218 - Ferrous iron (Heaney and Davidson 1977)	Definitive	Ferrous iron	Spectrophotometer	UFI	N

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-11	SU SOP AP #CESE-ENV-1631 - Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry (U.S. EPA Method 1631E)	Definitive	Total mercury	Tekran Series 2600 CVAFS	SU	N
L-12	SU SOP AP #CESE-ENV-1630 - Methyl mercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS (U.S. EPA Method 1630)	Definitive	Methyl mercury	Perkin Elmer Model Clarus 500 - Gas Chromatograph with Autodesorption 350 ATD by Perkin Elmer, Tekran Model 2357 CVAFS, Brooks-Rand Model III CVAFS, or equivalent	SU	N
L-13	SU SOP AP #CESE-ENV-7473 - Mercury in solids and solutions by Milestone thermal decomposition amalgamation and atomic absorption spectrophotometry	Definitive	Total mercury	DMA 80 automatic mercury analyzer (Milestone)	SU	
L-14	SU SOP AP #CESE-ENV-1630 - Methyl mercury in biomass by digestion, aqueous ethylation, purge and trap, and CVAFS (U.S. EPA Method 1630	Definitive	Methyl mercury	Perkin Elmer Model Clarus 500 - Gas Chromatograph with Autodesorption 350 ATD by Perkin Elmer, Tekran Model 2357 CVAFS, Brooks-Rand Model III CVAFS, or equivalent	SU	N

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-15	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

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
OI Analytical Flow Solution IV Model 502	See UFI SOP 106.1 See UFI SOP 105.1	Standards are placed at the start of every sample run.	The software calculates the standard curves and QC acceptance limits. The R^2 for the standards should be no less than 0.995.	Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.	Laboratory Staff	L-2 and L-3
		Calibration standards are run as the first sample, before running others, every 10 afterwards, and as the last sample of any run.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value based on a minimum of 10 values	Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary.	Laboratory Staff	L-4
Phoenix 8000 Carbon analyzer	See UFI SOP 110 See UFI SOP 203	Initial calibration after instrument set up. Calibration standards are run as the first sample, before running others, every 10 afterwards, and as the last sample of any run..	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a minimum of 10 values	Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary.	Laboratory Staff	L-4 and L-7

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
Ion-selective electrode (sulfide)	See UFI SOP 212.1	Check electrode performance and calibrate with each use. Check electrode potential in a sulfide standard every 2 hours.	Change in potential should be within ±2 mV	Follow troubleshooting procedure in the electrode manual.	Laboratory Staff	L-6
Model TD-700 Fluorometer	See UFI SOP 216	Initial calibration after instrument set up. The calibration can be checked with each use with the solid standard. The instrument will need to be recalibrated if ranges are changed (low to high or visa versa) or if lamps or filters are changed.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a minimum of 10 values	Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.	Laboratory Staff	L-8

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
GOW-MAC gas chromatograph	See UFI SOP 217	Initial calibration after instrument set up. Calibration standards are run as the first sample, before running others, every 10 afterwards, and as the last sample of any run. NOTE: If curve is not run daily, highest standard must be run as a continuing calibration verification sample (CCV).	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a minimum of 10 values	Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary.	Laboratory Staff	L-9
Spectrophotometer	See UFI SOP 218	Initial calibration after instrument set up. Calibration standards are run as the first sample, before running others, every 10 afterwards, and as the last sample of any run.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a minimum of 10 values	Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary.	Laboratory Staff	L-10

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
Tekran Series 2600 CVAFS	See SU SOP AP # CESE-ENV-1631	Daily prior to sample analysis	5 standards with the RSD ≤15%, or R2 ≥ 0.995 Low Std. Recovery 75–125%	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes	Laboratory Staff	L-11
		Immediately after Initial calibration	90–110% of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration		
		After every ten samples and at the end of the run	90–110 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCV must be reanalyzed		
Perkin Elmer Model Clarus 500 - Gas Chromatograph with Autodesorption 350 ATD by Perkin Elmer, Tekran Model 2357 CVAFS, Brooks-Rand Model III CVAFS, or equivalent	See SU SOP AP # CESE-ENV-1630	Initial calibration after instrument set up	5 standards with the RSD ≤15%, Low Std. or R2 ≥ 0.995 Recovery 75-125%	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes	Laboratory Staff	L-12
		ICV Immediately after Initial calibration	85–115% of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration		

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
Perkin Elmer Model Clarus 500 - Gas Chromatograph with Autodesorption 350 ATD by Perkin Elmer, Tekran Model 2357 CVAFS, Brooks-Rand Model III CVAFS, or equivalent *(continued)*	See SU SOP AP # CESE-ENV-1630 *(continued)*	CCV after every ten samples and at the end of the run	85-115 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCV must be reanalyzed	Laboratory Staff	L-12
Total Mercury Analyzer, Milestone D80, or LECO total mercury Analyzer	Mercury in solids and Solutions by Milestone Thermal Decomposition Amalgamation and Atomic Absorption Spectrophotometry SU SOP AP # CESE-ENV-7473	Daily prior to sample analysis	The software calculates the standard curves and QC acceptance limits. The R^2 for the standards should be no less than 0.995.	1. Reanalyze standards 2. Reweigh and reanalyze standards 3. Change catalytic seals	Laboratory Staff	L-13
		ICV Immediately after Initial calibration	90–110% of expected value	1. Reanalyze standards 2. Reweigh and reanalyze standards 3. Change catalytic seals		
		CCV after every ten samples and at the end of the run	90–110% of expected value	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 of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
Satlantic Inc., ISUS0095	See UFI SOP UFI-ISUS/Optical frame profiling and maintenance	Factory calibrated and maintained according to manufacturers instructions	DI water check, ±2 μM	Perform new DI water calibration; if that fails send back to manufacturer for recalibration	T. Prestigiacomo	L-15
SeaBird Elec, Inc., SBE 37-SI MicroCAT	See UFI SOP UFI-ISUS/Optical frame profiling and maintenance	Factory calibrated and maintained according to manufacturers instructions	Ensure data are consistent with ground-truth and other laboratory parameters	Annual recalibration	T. Prestigiacomo	L-15
WET Labs, C-Star	See UFI SOP UFI-ISUS/Optical frame profiling and maintenance	Factory calibrated and maintained according to manufacturers instructions	Ensure data are consistent with ground-truth and other laboratory parameters	Annual recalibration	T. Prestigiacomo	L-15
WET Labs, Eco Triplet-BB2 FL	See UFI SOP UFI-ISUS/Optical frame profiling and maintenance	Factory calibrated and maintained according to manufacturers instructions	Ensure data are consistent with values expected for this parameter	Annual recalibration	T. Prestigiacomo	L-15
Biospherical Instruments, QSP-2150	See UFI SOP UFI-ISUS/Optical frame profiling and maintenance	Factory calibrated and maintained according to manufacturers instructions	Ensure data are consistent values expected for this parameter	Annual recalibration	T. Prestigiacomo	L-15

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

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
OI Analytical Flow Solution IV – Model 502 Nitrogen Analyzer	Tubing and reagents routinely changed, system lines cleaned	Semi-annual PT samples	Visual inspection of hardware with each use	As required by NELAC or to maintain instrument in proper working order	Calibration curve should have a R2 ≥ 0.995	Remake standards, investigate and document any potential problems	Laboratory staff	L-2 and L-3
Phoenix 8000 Carbon Analyzer	Check connections, clean lines, change tubing, reagents and halogen scrubber	Semi-annual PT samples	Visual inspection of hardware with each use	As required by NELAC or to maintain instrument in proper working order	Calibration curve should have a R2 ≥ 0.995	Remake standards, investigate and document any potential problems	Laboratory staff	L-4
Ion Selective Electrode (Sulfide)	Maintain internal solution levels	Annual PT samples from independent supplier	Visual inspection of electrode with each use	As required by manufacturer or to maintain instrument in proper working order	Calibration curve should have a R2 ≥ 0.995	Remake standards, investigate and document any potential problems	Laboratory staff	L-6
TD-700 Fluorometer	Check lamps	Standardize with liquid chlorophyll standards every 3 months	Visual inspection of hardware with each use	As required to maintain instrument in proper working order	Standards have < 5% RSD	Re-run standards, investigate and document any potential problems	Laboratory staff	L-8

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
GOW-MAC GC	Keep lines clear, check/ change septum as needed	Compare current recoveries to previous/ historic recoveries	Visual inspection of hardware with each use	As required by NELAC or to maintain instrument in proper working order	Reproducible standards and a low blank	Re-run standards, investigate and document any potential problems	Laboratory staff	L-9
Spectrophotometer	Change bulb as needed, annual inspection by manufacturer		Visual inspection of hardware with each use	As required by NELAC or to maintain instrument in proper working order	Calibration curve should have a R2 ≥ 0.995	Remake standards, investigate and document any potential problems	Laboratory staff	L-10
Tekran Series 2600 CVAFS	Check pump tubing	Analyze blank , 2nd Source, Annual PT	Visual check sample used during an analysis, check drying trap	At start of an analysis run	Calibration curve should have a %RSD ≤15 % or R2 ≥ 0.995	Re-calibrate, compare against 2nd source, and OPR	Analyst	L-11
Perkin Elmer Model Clarus 500 - Gas Chromatograph, with Autosampler Turbomatrix Thermal Desorber, Tekran Model 2500 CVAFS, Brooks-Rand Model III CVAFS, or equivalent	Check ethylation agent and analytical system	Analyze primer and blank	Visual check shape of peak and response	At start of an analysis run	Calibration curve should have a %RSD ≤15 % or R2 ≥ 0.995	Re-calibrate, compare against 2nd source, and OPR	Analyst	L-12

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Total Mercury Analyzer, Milestone D80, or LECO total mercury Analyzer	Check response	Analyze primer and blank	Visual check shape of peak and response	At start of an analysis run	R2 $\geq$ 0.995	Re-calibrate, compare against 2nd source	Analyst	L-13
Satlantic Inc., ISUS0095	Rinse with deioinized water and gently wipe sensor dry with optical lens paper	Pre-cast and post-cast deionized water checks for the nitrate sensor are required each day the unit is deployed.	Visual inspection of hardware with each use	Daily	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.	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.		L-15
SeaBird Elec, Inc., SBE 37-SI MicroCAT	Rinse with deioinized water and		Visual inspection of hardware with	Daily	Assessment of results is done at UFI facilities	Identify data that fail QA/QC, record		L-15

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
WET Labs, C-Star WET Labs, Eco Triplet-BB2 FL Biospherical Instruments, QSP-2150	gently wipe sensor dry with optical lens paper		each use		(post collection). Acceptance criteria for quality control include consideration of field notation concerning interferences and presence of data points outside parameter detection range values.	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.		

[1]Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): MaryGail Perkins, UFI, Svetla Todorova, SU
Sample Packaging (Personnel/Organization): MaryGail Perkins, UFI, Svetla Todorova, SU
Coordination of Shipment (Personnel/Organization): MaryGail Perkins, UFI, Svetla Todorova, SU
Type of Shipment/Carrier: Samples delivered in person by field sampling team to the respective (UFI/SU) laboratories
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Upstate Freshwater Institute and Syracuse University
Sample Custody and Storage (Personnel/Organization): MaryGail Perkins (UFI)
Sample Preparation (Personnel/Organization): Laboratory staff (UFI), Laboratory staff (SU)
Sample Determinative Analysis (Personnel/Organization): Laboratory staff (UFI)
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): See Worksheet #19
Sample Extract/Digestate Storage (No. of days from extraction/digestion): See Worksheet #19
Biological Sample Storage (No. of days from sample collection): See Worksheet #19
SAMPLE DISPOSAL
Personnel/Organization: Laboratory staff (UFI)
Number of Days from Analysis: 60 days

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

Standard procedures for sample collection and shipping will be followed to ensure that samples are preserved and stored as required (Worksheet #19). All field measurements and sample collection activities will follow approved standard operating procedures as noted in UFI's "*Environmental Sample Collection Quality and Field Methods Manual*" and SU's SOPs. The general procedure is as follows:

- Water samples will be collected by UFI personnel for the purpose of determining chemical concentrations in the water column. All mercury samples will be collected using a continuous flow sampling device. The sampling device will consist of Teflon-lined tubing connected to a non-metallic submersible pump, consistent with EPA Method 1669 and SU's field sampling SOP.
- 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 (FSM) in the project work plan.
- Samples will be kept on ice and stored in the dark while in the field.
- Any sample-handling difficulties that are encountered in the field will be described in the field log.
- The samples will be delivered to the appropriate laboratory (UFI or SU) with a fully documented chain-of-custody form.
- Field personnel are responsible for making sure all documentation has been completed and turned over to the laboratory and/or other support personnel.
- The field log 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:

The laboratory will log in the samples, verify the sample containers/labels against the chain of custody, and assign a unique sample identification number to each sample, which will be attached to that sample throughout the life of the sample. Laboratory personnel are responsible for verifying that all required documentation has been completed by field personnel. Laboratory records related to sample handling and analysis are maintained through all stages of the analytical process. All laboratory processes, activities, and SOPs comply with NELAC standards and are fully documented in the UFI document "Environmental Testing Laboratory Quality Assurance Manual." and the CESE Laboratory Quality Manual.

Chain-of-custody Procedures:

A continuous record of the possession and proper handling of samples must 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.

Matrix	Water
Analytical Group	Chlorophyll a
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-8
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	1 station, 3–4 depths per month and a 2nd station, 3–4 depths every other month over 8 months

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample batch, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD 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 batch	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit

Matrix	Water
Analytical Group	NO_x
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-2
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	1 station, 3–8 depths per month and a 2nd station, 3–7 depths every other month over 8 months; 10 ISUS gridding stations, 2 samples per station

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
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.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Reference	Every sample run	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10–15 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 per sample run	Control limit recover 82 – 115 µg/L	Reanalyze and/or report LCS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	Control limit recover 65 – 127 µg/L	Reanalyze and/or report MS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	NO_2
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-2
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	1 station, 3–8 depths per month and a 2nd station, 3–7 depths every other month over 8 months; 10 ISUS gridding stations, 2 samples per station

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
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.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Reference	Every sample run	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10–15 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 per sample run	Control limit recover 83.5 – 107.5 µg/L	Reanalyze and/or report LCS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	Control limit recover 87.5 – 108.5 µg/L	Reanalyze and/or report MS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	$T\text{-}NH_3$
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-3
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	1 station, 3–8 depths per month and a 2nd station, 3–7 depths every other month over 8 months; 10 ISUS gridding stations, 2 samples per station

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
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.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Reference	Every sample run	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10–15 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 per sample run	Control limit recovery 51 – 143 µg/L	Reanalyze and/or report LCS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	Control limit recovery 66 – 121µg/L	Reanalyze and/or report MS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	DOC
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-4
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	1 station, 3–8 depths per month and a 2nd station, 3–7 depths every other month over 8 months

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
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.	Laboratory staff	Precision - Lab	RPD 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 Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) 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. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Laboratory control samples (LCS)	1 per sample batch	Control limit recovery 78.6 – 138.2 mg/L	Reanalyze and/or report LCS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	Control limit recover 58.7 – 134.9 mg/L	Reanalyze and/or report MS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

[1]Samples will be collected at 2-m intervals at oxic depths and 1-m intervals at anoxic depths (total number of samples from water-column anoxic depths will depend on the time of year and extent of anoxia).

Matrix	Water
Analytical Group	TIC
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-7
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	1 station, 3–8 depths per month and a 2nd station, 3–7 depths every other month over 8 months

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
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.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Reference	Every sample batch	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples following CCV	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit
Initial and continuing calibration verification (ICV/CCV)	1st sample and every 10 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	Chloride
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-1
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	1 station, 3–4 depths per month and a 2nd station, 3–4 depths every other month over 8 months

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample batch, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Reference	Every sample run	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Laboratory control samples (LCS)	1 per sample run	Control limit recover 78 – 130 mg/L	Reanalyze and/or report LCS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	Control limit recover 59.8 – 145.4 mg/L	Reanalyze and/or report MS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	Ferrous iron
Concentration Level	Low
Sampling SOP	S-1 and S-2
Analytical Method/ SOP Reference	L-10
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	2 stations, ~4 possible depths per month over 8 months[1]

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
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.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Reference	Every sample batch	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples, following CCV	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit
Initial and continuing calibration verification (ICV/CCV)	1st sample in a run and every 10 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

[1]Samples will be collected at 2-m intervals at oxic depths and 1-m intervals at anoxic depths (total number of samples from water-column anoxic depths will depend on the time of year and extent of anoxia).

Matrix	Water
Analytical Group	Sulfide (Method 1)
Concentration Level	Low
Sampling SOP	S-1 and S-2
Analytical Method/ SOP Reference	L-5
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	2 stations, ~4 possible depths per month over 8 months[1]

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%

[1]Samples will be collected at 2-m intervals at oxic depths and 1-m intervals at anoxic depths (total number of samples from water-column anoxic depths will depend on the time of year and extent of anoxia).

Matrix	Water
Analytical Group	NO_2
Concentration Level	Low
Sampling SOP	S-1 and S-2
Analytical Method/ SOP Reference	L-6
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	1 station, 3–8 depths per month and a 2nd station, 3–7 depths every other month over 8 months; 10 ISUS gridding stations, 2 samples per station

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample batch, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Reference	Every sample run	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples following the CCV	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	Warning Limit = LOD; Control Limit = LOQ
Initial and continuing calibration verification (ICV/CCV)	1st sample, one per sample run and every 10 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	Dissolved methane and nitrogen
Concentration Level	Low
Sampling SOP	S-1 and S-2
Analytical Method/ SOP Reference	L-9
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	2 stations, ~5 possible depths per month over 8 months[1]

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample batch, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration verification (ICV/CCV)	1st sample and every 10 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

[1]Samples will be collected at 2-m intervals at oxic depths and 1-m intervals at anoxic depths (total number of samples from water-column anoxic depths will depend on the time of year and extent of anoxia).

Matrix	Water
Analytical Group	Ebullitive methane and nitrogen
Concentration Level	Low
Sampling SOP	S-3
Analytical Method/ SOP Reference	L-9
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	2 stations

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample batch, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration verification (ICV/CCV)	1st sample and every 10 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	Total Mercury
Concentration Level	Ultra Low
Sampling SOP	S-4
Analytical Method/ SOP Reference	L-11
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	SU
No. of Sample Locations	Unfiltered: 1 station, 3–8 depths per month and a 2nd station, 3–7 depths every other month over 8 months; 10 ISUS gridding stations, 2 samples per station once Filtered: 1 sample per station per sampling

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	1 per sampling event	RPD 20%		Ed Mason	Precision - Field	RPD 20%

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	1 per sampling event	RSD 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.	Ed Mason	Precision - Field	RSD 35%
Equipment rinsate blank (Sampling equipment and filtering apparatus)	1 per sampling event		• Reanalyze • If criteria are still not met, repeat initial calibration	Ed Mason	Contamination	< MRL
Laboratory duplicate	1 every 20 samples	RPD 20%	• 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.	Ed Mason	Precision - Lab	RPD 20%
Ongoing Precision and Recover (OPR)	1 at the beginning and end of every batch	82-122%	• If initial is out, reanalyze. • If closing is out, reanalyze, if still out, review last CCV that was ran and follow CCV criteria.	Ed Mason	Precision - Lab	82–122%
Method blank	One per every batch of sample	Less than reporting limit	• Reanalyze • If criteria are still not met, repeat initial calibration	Ed Mason	Contamination	Less than reporting limit
Instrument blank	Immediately after initial calibration and after every CCV	Less than reporting limit	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCB must be reanalyzed • Change air bubble tubing	Ed Mason	Contamination	Less than reporting limit

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial calibration	Daily prior to sample analysis/as per method	5 standards with the RSD ≤15%, Low Std. Recovery 75–125%	• Reanalyze standards • Remake and reanalyze standards • Change all peristaltic pump tubes	Ed Mason	Accuracy/Bias	5 standards with the RSD ≤15%, Low Std. Recovery 75–125%
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% of expected value	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Ed Mason	Accuracy/Bias	90–110% of expected value
Quality control sample (QCS)	Immediately after initial calibration	82-122% of expected value	• Reanalyze • Remake and reanalyze ICV • If criteria are still not met, repeat initial calibration	Ed Mason	Accuracy/Bias	90–110% of expected value
Laboratory control samples (LCS)	1 with every batch of samples	82-122% of expected value	• 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	Ed Mason	Accuracy/Bias	Recovery within appropriate control limits (77–123%)
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	Recovery (76–128%) and RPD (<20%) or as specified in QAPP	• If Recovery is not within QC limits, and an RPD criterion is met document excursion. • If recover y is within QC limit, and RPD criterion is not met, reanalyze.	Ed Mason	Accuracy/Bias	Recovery 71–125%

Matrix	Water
Analytical Group	Methyl Mercury
Concentration Level	Ultra Low
Sampling SOP	S-4
Analytical Method/ SOP Reference	L-12
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	SU
No. of Sample Locations	1 station, 3–8 depths per events and a 2nd station, 3–7 depths every other event over 8 sampling events; 10 ISUS gridding stations, 2 samples per station once

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	1 per sampling event	RSD 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.	Ed Mason	Precision – Field	RSD 35%

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Equipment rinsate blank(Sampling equipment and filtering apparatus)	1 per sampling event	< MRL	• Reanalyze • If criteria are still not met, repeat initial calibration	Ed Mason	Contamination	< MRL
Laboratory duplicate	1 every 20 samples	RPD 20%	• 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.	Ed Mason	Precision – Lab	RPD 20%
Initial precision and recovery (IPR)	Set of four analyses	IPR within s (31%) and X (69–131%)	• Reanalyze	Ed Mason	Initial method implementation and Precision – Lab	IPR within s (31%) and X (69–131%)
Ethylation Blank	Immediately after initial calibration,	Less than reporting limit	• Reanalyze • If criteria are still not met, repeat initial calibration • Change air bubble tubing	Ed Mason		
Method blank	1 with every batch of samples	Less than reporting limit	• Reanalyze • If criteria are still not met, repeat initial calibration • If concentration is high and the analyte is not detected, document excursion	Ed Mason	Contamination	Less than reporting limit
Instrument blank	Immediately after initial calibration and after every CCV	Less than reporting limit	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCB must be reanalyzed • Change air bubble tubing	Ed Mason	Contamination	Less than reporting limit

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) 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 75-125%	• Reanalyze standards • Remake and reanalyze standards • Change all peristaltic pump tubes	Ed Mason	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	85–115% of expected value	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Ed Mason	Accuracy/Bias	85–115% of expected value
Laboratory control samples (LCS)	1 with every batch of samples	Recovery within appropriate control limits (53-125%) 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	Ed Mason	Accuracy/Bias	Recovery within appropriate control limits (67–133%)
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	Recovery (40-150%) and RPD (35%) or as specified in QAPP	• If Recovery is not within QC limits, and an RPD criterion is met document excursion. • If recover y is within QC limit, and RPD criterion is not met, reanalyze.	Ed Mason	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	Ed Mason	Accuracy/Bias	02 ng/L 0.05 ng/L

Matrix	Zooplankton
Analytical Group	Total and methyl mercury
Concentration Level	Low
Sampling SOP	S-4
Analytical Method/ SOP Reference	L-13, L-14
Sampler's Name	UFI
Field Sampling Organization	B. Wagner
Analytical Organization	SU
No. of Sample Locations	2 stations

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	Samples are collected in duplicate	RPD 35%		Ed Mason	Precision - Field	RPD 35%
Field triplicate	1 per month	RSD 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.	Ed Mason	Precision - Field	RSD 35%

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Equipment rinsate blank	1 per month	<MRL	• Reanalyze • If criteria are still not met, repeat initial calibration	Ed Mason	Contamination	< MRL
Laboratory duplicate	1 every 20 samples	RPD 20%	• 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.	Ed Mason	Precision - Lab	RPD 20%
Ongoing Precision and Recover (OPR)	1 at the beginning and end of every batch	82-122% (THg) 53-125% (MeHg)	• If initial is out, reanalyze. • If closing is out, reanalyze, if still out, review last CCV that was ran and follow CCV criteria.	Ed Mason	Precision - Lab	82-122% (THg) 53-125% (MeHg)
Method blank	Immediately after quality control sample and every 10 samples	Less than reporting limit	• Reanalyze • If criteria are still not met, repeat initial calibration	Ed Mason	Contamination	Less than reporting limit
Instrument blank	Immediately after initial calibration and after every CCV	Less than reporting limit	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCB must be reanalyzed • Change air bubble tubing	Ed Mason	Contamination	Less than reporting limit
Initial calibration	Calibrate prior to sample analysis/as per method	5 standards with the RSD $\leq$15%, Low Std. Recovery 75–125%(THg) 69-135% (MeHg)	• Reanalyze standards • Remake and reanalyze standards • Change all peristaltic pump tubes	Ed Mason	Accuracy/Bias	5 standards with the RSD $\leq$15%, Low Std. Recovery 75–125%(THg) 69-135% (MeHg)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
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 T Hg and 85-115% for MeHg of expected value	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Ed Mason	Accuracy/Bias	90–110% for T Hg and 85-115% for MeHg of expected value
Quality control sample (QCS)	Immediately after initial calibration	86-115% (THg) 69-110% (MeHg)	• Reanalyze • Remake and reanalyze ICV • If criteria are still not met, repeat initial calibration	Ed Mason	Accuracy/Bias	86-115% (THg) 69-110% (MeHg)
Laboratory control samples (LCS)	1 with every batch of samples	86-115% (THg) 69-110% (MeHg)	• 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	Ed Mason	Accuracy/Bias	86-115% (THg) 69-110% (MeHg)
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	75-125% (THg) 52-126% (MeHg)	• If Recovery is not within QC limits, and an RPD criterion is met document excursion. • If recover y is within QC limit, and RPD criterion is not met, reanalyze.	Ed Mason	Accuracy/Bias	75-125% (THg) 52-126% (MeHg)

Matrix	Water
Analytical Group	ISUS rapid profiling sensors: nitrate, bisulfide, temperature, specific conductance, transmissivity, chlorophyll, and light penetration
Concentration Level	Nitrate and bisulfide–Low Other parameters–N/A
Sampling SOP	NA
Analytical Method/ SOP Reference	L-15
Sampler's Name	UFI
Field Sampling Organization	B. Wagner
Analytical Organization	UFI
No. of Sample Locations	~ 25 samples will be collected outside the monthly sampling program

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) 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	T. Prestigiacomo	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	T. Prestigiacomo	N/A	Acceptable DI water checks (± 0.016 mg/L)

Sample Collection Documents and Records	On-site Analysis Documents and Records	Off-site Analysis Documents and Records	Data Assessment Documents and Records	Other
Field notes Chain-of-custody records Corrective action forms		Sample receipt, custody, and tracking records Standard traceability logs Equipment calibration logs Sample preparation logs Run logs 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)	Field sampling audit checklists Field analysis audit checklists Fixed laboratory audit checklists Data Usability Summary Report Corrective action forms	

Matrix	Analytical Group	Concen-tration Level	Sample Locations/ ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Water	Chlorophyll	Low	South Deep and North Deep	UFI SOP 216	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Nitrate/Nitrite as N (NO_x)	Low	South Deep, North Deep, and ISUS gridding stations	UFI SOP 106.1	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Nitrate as N (NO_2)	Low	South Deep, North Deep, and ISUS gridding stations	UFI SOP 106.1	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Ammonia as N ($T\text{-}NH_3$)	Low	South Deep, North Deep, and ISUS gridding stations	UFI SOP 105.1	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A

Matrix	Analytical Group	Concen-tration Level	Sample Locations/ ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Water	Organic Carbon, Total/Total Dissolved as C (DOC)	Low	South Deep and North Deep	UFI SOP 110	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Carbon, Inorganic Dissolved and Total (DIC)	Low	South Deep and North Deep	UFI SOP 203	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Chloride	Low	South Deep and North Deep	UFI SOP 104	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Ferrous iron	Low	South Deep and North Deep	UFI SOP 218	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Sulfide as S (Method 1)	Low	South Deep and North Deep	UFI SOP 112	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A

Matrix	Analytical Group	Concen-tration Level	Sample Locations/ ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Water	Sulfide as S (Method 2)	Low	South Deep, North Deep, and ISUS gridding stations	UFI SOP 212.1	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Dissolved methane	Low	South Deep and North Deep	UFI SOP 217	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Dissolved nitrogen	Low	South Deep and North Deep	UFI SOP 217	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Total mercury	Low	South Deep, North Deep, and ISUS gridding stations	SU SOP AP # CESE-ENV-1631	60 days	Syracuse University, Depart. Civil Environ. Eng. 151 Link Hall Syracuse, NY 13244 Edward Mason 315-443-1247	N/A

Matrix	Analytical Group	Concen-tration Level	Sample Locations/ ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Water	Methyl mercury	Low	South Deep, North Deep, and ISUS gridding stations	SU SOP AP # CESE-ENV-1630	60 days	Syracuse University, Depart. Civil Environ. Eng. 151 Link Hall Syracuse, NY 13244 Edward Mason 315-443-1247	N/A
Zooplankton	Total and methyl mercury	Low	South Deep and North Deep	CESE-ENV-1630, CESE-ENV-1631, CESE-ENV-7473	60 days	Syracuse University, Depart. Civil Environ. Eng. 151 Link Hall Syracuse, NY 13244 Edward Mason 315-443-1247	N/A
Water	ISUS rapid profiling sensors: nitrate, bisulfide, temperature, specific conductance, transmissivity, chlorophyll, and light penetration	Nitrate and bisulfide– Low Others– N/A	South Deep, North Deep, and ISUS gridding stations	UFI SOP UFI-ISUS/Optical frrame profiling and maintenance	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organizational Affiliation)	Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (CA) (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (Title and Organizational Affiliation)
Field sampling technical systems audit	2 times (at ~3 month intervals) during the field sampling season	Internal	UFI	David Matthews Technical Director, UFI	MaryGail Perkins, Field Team Leader, UFI	MaryGail Perkins Field Team Leader, UFI and Bruce Wagner Field staff, UFI	Bruce Wagner Field staff, UFI

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (Name, Title, Org.)	Timeframe for Response
Field sampling Technical Systems Audit (TSA)	Verbal communication or written audit report	MaryGail Perkins Field Team Leader, UFI Steven Effler, Project Manager, UFI Charles Driscoll, Project Manager, SU	48 hours	Written document (electronic or hardcopy)	David Matthews, Technical Director, UFI Steven Effler, Project Manager, UFI Charles Driscoll, Project Manager, SU	48 hours

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.

Type of Report	Frequency (daily, weekly monthly, quarterly, annually, etc.)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (Title and Organizational Affiliation)	Report Recipient(s) (Title and Organizational Affiliation)
Field sampling technical systems audit report	2 times (at ~3 month intervals) during the field sampling season	Deficiencies reported within 48 hours of audit and Corrective Action Response within 48 hours of audit report receipt	David Matthews, Technical Director, UFI	MaryGail Perkins, Field Team Leader, UFI Steven Effler, Project Manager, UFI Charles Driscoll, Project Manager, SU
Data usability assessment report	Annually	March 2008	Linda Cook, Exponent	Tim Larson, NYSDEC

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.	I	Laboratory Staff at UFI and SU
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.	I	Laboratory Staff at UFI and SU
Laboratory data	All laboratory data packages will be verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal. All received data packages will be verified externally according to the data validation procedures specified in Worksheet #36	E	Exponent

Each laboratory's QA officer 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	
UFI Field Manager/ UFI 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 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 Conduct field data collection audit to ensure that the proper field procedures are followed
UFI QA Officer/ SU QA Officer	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) Confirm that the analytical data meet specified detection limits in analytical SOPs
Correctness	
	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
UFI QA Officer SU QA Officer Scientific/Technical Manager	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)	
UFI 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	
UFI Field Manager	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
UFI Field Manager UFI QA Officer	Ensure that an accurate record was maintained during sample collection and analysis
UFI/SU Laboratory Personnel UFI/SU QA Officers	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
QA/QC - quality assurance and quality control
SOP - standard operating procedure

Step IIa/IIb	Validation Input	Description	Responsible for Validation (Name, Organization)
IIa	SOPs	Ensure that all sampling and analytical SOPs were followed.	MaryGail Perkins at UFI and Mario Montesdeoca at SU
IIa	Documentation of Method QC Results	Establish that all method required QC samples were run and met required limits.	Laboratory Staff at UFI and SU
IIb	Documentation of QAPP QC Sample Results	Establish that all QAPP required QC samples were run and met required limits	Laboratory Staff at UFI and SU
IIb	Project Quantitation Limits	Establish that all samples results met the project quantitation limits specified in the QAPP	Laboratory Staff at UFI and SU
IIa	Raw Data	Review 100% of raw data to confirm manual laboratory calculations and review 10% review of raw data to confirm automated laboratory calculations	Laboratory Staff at UFI and SU

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)
IIa	Aqueous	All Analyses	Low	QAPP Worksheets #12, #15, and #28	Exponent

Data verification and assessment will be completed by Exponent prior to finalization of the data and release of the data set to NYSDEC. EPA has not prepared national functional guidelines for any of the project-specific analytes included in this program (i.e., low-level total mercury, methyl mercury, and the conventional parameters). 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). 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 data assessment review will include evaluation of the results for method-specific quality control analyses (e.g., results of method blanks and applicable instrument blanks, results for all applicable MS/MSDs, and LCSs analyses, and the results of all applicable laboratory duplicate and/or triplicate sample analyses) with respect to method-specific and laboratory-established control limits, as may be applicable. Instrument calibrations, calculations, and transcriptions will not be checked because the laboratories will be responsible for 100-percent verification of these results and procedures as stated in the Work Plan.

Data qualifiers will be applied to the results according to procedures described in the EPA Contract Laboratory Program national functional guidelines for data review (U.S. EPA 2002), as applicable, with modifications as appropriate to accommodate method-specific quality control requirements or when specific MQOs and DQIs established for this project (e.g., control limits for bias and precision) are not achieved.

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:

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

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 minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte is greater than zero" (40 CFR 136B); 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 (Table 2), 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 Contract Laboratory Program National Functional Guidelines for Inorganic Data Review 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. Sample results less than 5 times the associated blank concentration will be qualified as estimated and potentially biased high (J+).

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: 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 Exponent on behalf of Honeywell. The report will meet the requirements for a NYSDEC data usability summary report (DUSR) as described in Appendix B of the 2002 Draft Voluntary Cleanup Guide (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 Exponent 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, and chain-of-custody documents.

ATTACHMENT 1

Sampling Standard Operating Procedures

Reference Number	Title of Standard Operating Procedure (SOP)	Originating Organization
S-1	UFI SOP 304 Water sample collection: submersible pump	UFI
S-2	UFI SOP 306 Reduced species (H_2S, CH_4, and Fe^{2+}) sample collection	UFI
S-5	UFI SOP 311 Gas cone deployment and collection	UFI
S-3	SU SOP AP # CESE-ENV-1669 Sampling stream and lake water for mercury at trace levels	SU
S-4	SU SOP AP #CESE-ENV-310 Zooplankton sample collection and preservation and secchi depth measurement field procedures	SU

4) The pump must flush for 90 seconds per sample depth before beginning to fill bottles. This allows water in the conduit to be completely flushed with sample water.

For Oxic sample collection

5) The bottles and caps are rinsed three times
6) The bottles can then be filled
7) Place bottles in a cooler and fill the cooler with ice and close
8) Fill out the chain of custody
9) Samples should be re-iced upon return to the lab to maintain a temperature of 4°C if samples will not be processed immediately

For anoxic sample collection:

1) Attach a small diameter sampling to the nozzle and turn the nozzle on so that water flows out at a slow rate.
2) 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.
3) Allow bottles to flush for three volumes, then cap and place in the cooler.
4) Bottles that need reagents added should be capped, then uncapped, the reagent(s) added, recapped and inverted several times, then placed in the cooler.
5) Remember – sulfide bottles initially have zinc acetate in them and cannot be flushed.
6) After all bottles from a cooler are filled, fill the cooler with ice and tightly close the lid.
7) Fill out the chain of custody sheet.
8) Samples should be re-iced upon return to the lab to maintain a temperature of 4°C if samples will not be processed immediately.

16) Calculations: none

17) Method performance: Under evaluation.

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: none

SOP No. 306: **Reduced Species (H_2S, CH_4 and Fe^{2+}) Sample Collection** ***(pp. 81-83)***

1) Test method: Reduced Species (H_2S, CH_4 and Fe^{2+}) Sample Collection

2) Applicable matrix or matrices: drinking, surface and saline waters

3) Detection limit: NA

4) Scope and application:

5) Summary of test method: The UFI reduced species sampled are hydrogen sulfide (H_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 (SOP 303, 304) with no preservatives. Hydrogen sulfide is collected as an anoxic sample, but requires the addition of zinc acetate and 6 N sodium hydroxide (NaOH). 2 ml of zinc acetate is placed into the bottom of a 300 ml BOD bottle. The sample is added via small tubing by filling the BOD underneath the zinc acetate. The BOD is filled almost to the (not overflowed!). 2 ml of 6N sodium hydroxide is then added.

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. Wear latex gloves when handling.

9) Equipment and supplies: Submersible pump with conduit and a marine battery or a Kemmer or Van Dorn, Reduced species collection bottles, 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

11) Reference Solution: none

12) Sample collection, preservation, shipment and storage:

1. 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. No preservatives added.

2. Hydrogen Sulfide

2 ml of zinc acetate are added to the bottom of a 300 ml BOD bottle. Sample is filled under the zinc acetate to near the BOD top. 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.

All samples will be stored on ice after collection, transported to UFI laboratories in secure coolers, and be accompanied by the necessary documentation (field sheets and chain of custodies) unless specifically noted.

13) Quality Control: Do not allow air to be introduced to the sample during any part of collection

14) Calibration and standardization: none

15) Procedure:

1. Methane and Ferrous Iron

1) Attach a small diameter sampling to the nozzle of either the submersible pump conduit or to the Kemmer or Van Dorn.
2) Place the tubing at the bottom of the BOD bottle.
3) Turn the nozzle on so that water flows out at a slow rate.
4) Fill BOD 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.
5) Allow bottles to flush for three volumes
6) 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.
7) Rinse the bottle to remove reagents on the outside of the bottle
8) Add a small amount of water onto the stopper. This acts as a water seal.
9) Place the protective plastic cap on the BOD
10) After all bottles from a cooler are filled, fill the cooler with ice and tightly close the lid.
11) Fill out the chain of custody sheet.
12) Samples should be re-iced upon return to the lab to maintain a temperature of 4°C if samples will not be processed immediately.

2. Hydrogen Sulfide

1) Attach a small diameter sampling to the nozzle of either the submersible pump conduit or to the Kemmer or Van Dorn.
2) Add 2 ml of zinc acetate to the bottom of the H_2S BOD bottle
3) Slowly fill the BOD with sample making sure to fill under the zinc acetate
4) Do not overflow sample!!
5) Fill to within ~ ½ inch of bottle height.
6) Add 2ml of azide 6 N sodium hydroxide

7) 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.
8) Rinse the bottle to remove reagents on the outside of the bottle
9) Add a small amount of water onto the stopper. This acts as a water seal.
10) Place the protective plastic cap on the BOD
11) After all bottles from a cooler are filled, fill the cooler with ice and tightly close the lid.
12) Fill out the chain of custody sheet.
13) Samples should be re-iced upon return to the lab to maintain a temperature of 4°C if samples will not be processed immediately.

16) Calculations: none

17) Method performance: Under evaluation.

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 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. 311: **Gas Cone Deployment and Collection** ***(pp. 96-98)***

1) Test method: Gas Cone 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 concave cone (~1m diameter) is placed at a depth of ~ 1m above the benthic sediment in a lake or reservoir. Gas bubbles released by the sediment are trapped in a 1000 ml seperatory funnel which can be read during the course of a routine sampling program. Volume of gas emitted per unit area of sediment per unit time (i.e., $ml/m^2/d$) can be estimated using data from the gas cone.

6) Definitions:

Ebullition – The evolution and release of gas bubbles from benthic sediment in a body of water

7) Interferences: Improper deployment will place the cone in the incorrect orientation (not vertical) and inaccurate gas collection will result.

8) Safety: Standard field procedures involving moderate lifting should be applied. Wear gloves during retrieval and deployment. Keep work area clean and clutter free.

9) Equipment and supplies: Gas cone (1m diameter, concave polycarbonate plastic cone with stainless steel frame) with attached, inverted seperatory funnel (1000 ml), cable or rope, marker buoy, tether rope, Research (large white) marker buoy, cable or rope, and an anchor

10) Reagents and standards: none

11) Reference Solution: none

12) Sample collection, preservation, shipment and storage: no water samples collected

13) Quality Control: During gas cone retrieval, pull the cone to the surface slowly as not to invert the cone. Bring seperatory funnel to the surface to the point that the volume of gas collected can be read. Be careful to keep the gas cone under the surface of the water so that air does not seep into the funnel. Deploy the gas cone downwind of the research buoy to avoid tangling. Record all information on the field sheet.

14) Calibration and standardization: none

15) Procedure:

1. Deployment

1) Lower the anchor to the large white research buoy to the bottom.
2) Place research buoy in the water
3) Attach tether line (~10m) from large white research buoy to gas cone marker buoy
4) Extend the tether line so that the gas cone line will be in the prevalent downwind direction from the research buoy (this should minimize tangling)
5) Attach the gas cone to the marker buoy with the correct length of cable or rope.
6) The gas cone should be deployed so that it is ~ 1 m from the bottom of the lake/reservoir.
7) Slowly lower gas cone to through the water column.
8) Place marker buoy

2. Collection

1) Pull the boat next to the marker buoy.
2) Pull the marker buoy into the boat.
3) Slowly pull the gas cone towards the surface
4) Use caution not to break the surface of the water with the gas cone
5) When in view, read the amount of gas collected by the gas cone in seperatory funnel.
6) Record the volume of gas collected on the field sheet
7) Fill the seperatory funnel with water by opening the spigot and submerging the collector.
8) With the gas cone still underwater, close spigot and slowly lower the gas cone to its proper depth
9) Be sure to lower the cone so that it is orientated properly (vertical with the seperatory funnel upwards)
10) Be sure that the tether line is fully extended with the gas cone in the prevalent downwind direction from the research buoy

16) Calculations: none

17) Method performance: Under evaluation.

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.

SOP No. 304: Water Sample Collection: Submersible Pump (pp. 76-77)

1) Test method: Water Sample Collection: 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: A submersible pump with attached conduit can be used to collect water chemistry samples from discrete depths in a lake, reservoir, or river of sufficient depth. The pump is fitting with conduit to push water from depth to the boat for sample collection. A 12 V marine battery powers the pump.

6) Definitions: none

7) Interferences: Allowing the pump to contact the benthos will pollute the sample

8) Safety: Electrical connects at the marine battery should be treated with caution

9) Equipment and supplies: Submersible pump with conduit, marine battery, collection bottles

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 secure coolers, and be accompanied by the necessary documentation (field sheets and chain of custodies) unless specifically noted.

13) Quality Control: Allow the pump to flush for at least 90 seconds prior to sample collection. Do not allow contact with the benthos. Record all information and complete the chain of custody.

14) Calibration and standardization: none

15) Procedure:

1) Place pump at conduit at depth of interest.
2) Do not power the pump on in the air! This will cavitate the conduit and result in sampling problems
3) Attach electrical hookups to the proper terminals on the marine battery.

23) References: none

Center for Environmental Systems and Engineering (CESE)

STANDARD OPERATING PROCEDURE

1. Title: Sampling Stream and Lake Water for Mercury at Trace Levels

AP # CESE-ENV-1669

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Prepared By: Joe Bushey

Approved By: _____ Date: December 21, 2007
Ed Mason-Technical Review

Approved By: _____ Date: December 21, 2007
Mario Montesdeoca-Laboratory Manager

Approved By: _____ Date: December 21, 2007
Charles T Driscoll-Primary Investigator

Effective Date: December 21, 2007

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2. Summary of Test Method

2.1 Before samples are collected, sampling equipment and sample containers are cleaned in a laboratory using mineral acids, and reagent water as described in the methods referenced in Table 1. The laboratory is responsible for generating acceptable equipment blank to demonstrate that the sampling equipment and containers are free from Mercury contamination before they are shipped to the field. An acceptable blank is one that is free from contamination below the Method Detection Limit (MDL) specified in the referenced analytical method (Section 5.0).

2.2 After cleaning, sample containers are filled with weak acid solution, individually double-bagged, and shipped/transported to the sampling site. All sampling equipment is also bagged for storage or shipment.

2.3 The laboratory prepares a large carboy or other appropriate clean container filled with reagent water (Section 10.1) for use with collection of field blanks during sampling activities. The reagent-water-filled container is ships/transports to the field site and handled as all other sample containers and sampling equipment. Field blank is processes according to QUAPP.

2.4 Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are

handled by the individual designated as "clean hands." "Dirty hands" is responsible for preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample.

2.5 Sampling equipment and sample containers used for metals determinations at or near the levels listed in Table 1 must be nonmetallic and free from any material that may contain metals.

2.6 Sampling personnel are required to wear clean, non-talc gloves at all times when handling sampling equipment and sample containers.

2.7 In addition to processing field blanks at each site, a field duplicate must be collected at each sampling site, or one field duplicate per sampling event, whichever is more frequent (Section 12.5). Section 12.0 gives a complete description of quality control requirements.

3. Scope and Application

3.1 This sampling procedure is based on Method 1669, Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels- a method for the collection and filtration of ambient water samples for subsequent determination of total and dissolved metals at the levels listed in Table 1.

3.2 This sampling procedure is applicable for determination of Hg (Chemical Abstract Service Registry Number (CASRN) 7439-97-6) and Hg species at trace levels.

3.3 This method is accompanied by the CESE- ENV- 1630 and CESE-ENV-1631. These methods include the sampling, handling, analysis, and quality control procedures necessary for reliable determination of mercury in aqueous samples.

3.4 This method is not intended for determination of mercury at concentrations found in untreated discharges from industrial facilities. Existing regulations typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metal concentrations are normally in the low part-per-trillion (ppt) to low ppb range. This method therefore directed at the collection of samples to be measured at or near the levels in Table 1. Actual concentration ranges to which this method is applicable will be dependent on the sample matrix, dilution levels, and other laboratory operation conditions.

3.5 The ease of contaminating ambient water samples with metal(s) of interest and interfering substances cannot be overemphasizing. This method includes sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination. These techniques are given in section 14.0 and are based on findings of researchers performing trace metal analysis (References 22.1-12).

3.6 Clean and ultraclean—the terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in mercury determinations.

3.7 This method is "performance based", i.e. an alternative sampling procedure or technique may be used, as long as neither samples nor blanks are contaminated when following the alternate procedure. Because the only way to measure the performance of the alternate procedure is through the collection and analysis of uncontaminated blank samples in accordance with the this method and the methods

referenced in Table 1, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected. Section 12.2 provides additional details on the tests and documentation required to support equivalent performance.

3.8 For dissolved metal determinations, samples must be filtered through a 0.45µm filter at the laboratory. The filtering procedures are described in this method. The samples are transported to the laboratory for preservation and/or filtering. Procedures for laboratory preservation are provided in the methods referenced in Table 1. Preservation requirements are summarized in Table 2.

3.9 The procedures in this Method are for use only by personnel thoroughly trained in the collection of samples for determination of metals at ambient water quality control levels.

4. Applicable Matrix or Matrices

4.1 This method is applicable for collection of stream and lake samples.

5. Method Detection Limit (MDL)

5.1 The target MDLs are 0.2 ng\L of Hg and 0.02 ng\L of MeHg, and they are used for purpose of determining cleanness of the system.

6. Definitions

6.1 Apparatus. Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis activities will be referred to collectively as the Apparatus.

6.2 Definitions of other terms are given in the Glossary Annex B.

7. Contamination and Interferences (References 22.1)

7.1 Contamination Problems in Trace Metals Analysis

7.1.1 Preventing ambient water samples from becoming contaminated during the sampling and analytical process is the greatest challenge faced in trace metals determinations. In recent years, it has been shown that much of the historical trace metals data collected in ambient water are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels (Reference 22.8). Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.

7.1.2 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, lab ware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, lab ware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam

fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation (Reference 22.4).

7.2 Contamination control

7.2.1 Philosophy. The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is nonmetallic and free from any material that may contain metals of concern.

7.2.2 The integrity of the results produced cannot be compromised by contamination of samples. Requirements and suggestions for controlling sample contamination are given in this sampling method and in the analytical methods referenced in Table 1.

7.2.2.1 Substances in a sample or in the surrounding environment cannot be allowed to contaminate the Apparatus used to collect samples for trace metals measurements.

7.2.2.2 While contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in Section 8 of this sampling method and in the methods referenced in Table 1.

7.2.3 Avoiding contamination. The best way to control contamination is to completely avoid exposure of the sample and apparatus to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being performed. Therefore, Personnel must be trained before performing this procedure. Documentation should be maintained by the sampling group.

7.2.4 Minimize exposure .When not being used, the sampling Apparatus should be covered with clean plastic wrap, stored in the clean bench or bagged in clean, colorless zip-type bags. Minimizing the time between cleaning and use will reduce contamination.

7.2.5 Wear gloves. Sampling personnel must wear clean, nontalc gloves (Section 9.5) during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

7.2.6 Use metal-free Apparatus—All Apparatus used for metals determinations at the levels listed in Table 1 must be nonmetallic and free of material that may contain metals. When it is not possible to obtain equipment that is completely free of the metal(s) of interest, the sample should not come into direct contact with the equipment.

7.2.7 Construction materials. Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE) or glass because mercury vapors can diffuse in or out of other materials, resulting either in contamination or low-biased results (Reference 22.4). PTFE is less

desirable than FEP because the sintered material in PTFE may contain contaminants and is susceptible to serious memory effects (Reference 22.8). Metal must not be used under any circumstance. Regardless of construction, all materials that will directly or indirectly contact the sample must be cleaned using the procedures described in the referenced analytical methods (see Table 1) and must be known to be clean and metal-free before proceeding.

7.2.7.1 Serialization—Serial numbers should be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the sampling process to shipment to the laboratory. Chain-of-custody procedures may also be used if warranted so that contamination can be traced to particular handling procedures or lab personnel.

7.2.7.1.1 The Apparatus should be clean when the sampling team receives it. If there are any indications that the Apparatus is not clean (e.g., a ripped storage bag), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory for proper cleaning before any sampling activity resumes.

7.2.7.1.2 Details for re-cleaning the Apparatus between collections of individual samples are provided in Section 14.0.

7.2.7.1.3 Avoid sources of contamination—Avoid contamination by being aware of potential sources and routes of contamination.

7.2.7.1.4 Contamination by carryover—Contamination may occur when a sample containing low concentrations of metals is processed immediately after a sample containing relatively high concentrations of these metals. At sites where more than one sample will be collected, the sample known or expected to contain the lowest concentration of metals should be collected first with the sample containing the highest levels collected last (Section 11.1.4). This will help minimize carryover of metals from high- concentration samples to low- concentration samples. If the sampling team does not have prior knowledge of the water body, or when necessary, the sample collection system should be rinsed with dilute acid and reagent water between samples and followed by collection of a field blank (Section 12.3).

7.2.7.1.5 Contamination by samples—significant contamination of the apparatus may result when untreated effluents, in-process waters, landfill leachates, and other samples containing mid- to high-level concentrations of inorganic substances are processed. As stated in Section 3.0, this sampling method is not intended for application to these samples, and samples containing high concentrations of metals must not be collected, processed, or shipped at the same time as samples being collected for trace metals determinations (Reference 22.1).

7.2.7.1.6 Contamination by indirect contact—apparatus that may not directly

contact samples may still is a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that the Apparatus that is directly or indirectly used in the collection of ambient water samples be cleaned as specified in the analytical method(s) referenced in Table 1.

7.2.7.1.7 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particulate matter, or vapors from automobile exhaust; cigarette smoke; nearby corroded or rusted bridges, pipes, poles, or wires; nearby roads; and even human breath (Section 7.1.2). Whenever possible, the sampling activity should occur as far as possible from sources of airborne contamination. Areas where nearby soil is bare and subject to wind erosion should be avoided (Reference 22.1).

7.2.8 Interferences—Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled. If a sample is suspected of containing substances that may interfere in the determination of trace metals, sufficient sample should be collected to allow the laboratory to identify and overcome interference problems.

7.2.8.1 The sampling group should assigned the sample for matrix spike and matrix spike duplicate that they deem necessary to test for possible matrix interference from a sample during analysis.

8. Safety

8.1 The toxicity or carcinogenicity of the chemicals used in this method has not been precisely determined; however, these chemicals should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Sampling teams are responsible for maintaining a current awareness of regulations for the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should also be made available to all personnel involved in sampling.

8.2 Operating in and around water body carries the inherent risk of drowning. The number of life jackets must be equal to the number of passengers operating the boat, when sampling in more than a few feet of water, or when sampling in swift currents.

8.3 Collecting samples in cold weather, especially around cold water bodies, carries the risk of hypothermia and collecting samples in extremely hot and humid weather carries the risk of dehydration and heat stroke. Sampling team members should wear adequate clothing for protection in cold weather and should carry an adequate supply of water or other liquids for protection against dehydration in hot weather.

8.4 When collecting samples from wetland sites, sampling team should have knowledge of the water level at the site. They should be equipped properly to walk through waterlogged soils, e.g. wearing boots.

9. Equipment and Supplies

9.1 All sampling equipment and sample containers must be cleaned in a laboratory before transporting to the field, as described in the methods referenced in Table 1. Performance criteria for equipment cleaning are described in the referenced methods. To minimize difficulties in sampling, the equipment is packaged in plastic containers and arranged to minimize field preparation.

9.2 Materials such as gloves (Section 9.5), storage bags (Section 9.6), and plastic wrap (Section 9.7), may be used new without additional cleaning unless the results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either a different supplier must be obtained or the materials must be cleaned.

9.3 Sample Bottles—Fluoropolymer (FEP, PTFE); 500 mL or 1 L with lids. Refer to the methods referenced in Table 1 for bottle cleaning procedures.

9.3.1 The Samples bottles are purchased from Fisher Scientific or Krackeler. Teflon Bottles are clean in the "TraceClean Instrument" by Milestone. Bottles are rinse three times with the DI water, and rinse twice with reagent water.

9.3.2 Cleaned sample bottles are filled with 0.4% HCl (v/v), individually double bagged and stored. In remote areas, it may be desirable to empty the weak acid solution from the sample bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 10.1).

9.3.3 Sampling devices are cleaned and prepared for field use in a mercury free clean room. Regardless of design, sampling devices are constructed of nonmetallic material and free from material that contains metals -fluoropolymer or other material that do not adsorb or contribute to mercury contamination. Commercially available sampling devices are used and any metallic, non-metallic-containing parts are replaced with parts constructed that are not source of mercury contamination.

9.4 Surface Sampling Devices—Surface samples are collected using a grab sampling technique. Samples may be collected manually by direct submersion of the bottle into the water or by using a grab sampling device. Examples of grab samplers are shown in Figures 1 and 2 and may be used at sites where depth profiling is neither practical nor necessary.

9.4.1 The grab sampler in Figure 1 consists of a heavy fluoropolymer collar fastened to the end of a 2-m-long polyethylene pole, which serves to remove the sampling personnel from the immediate vicinity of the sampling point. The collar holds the sample bottle. A fluoropolymer closing mechanism, threaded onto the bottle, enables the sampler to open and close the bottle under water, thereby avoiding surface microlayer contamination (Reference 22.11). Assembly of the cleaned sampling device is as follows (refer to Figure 1):

9.4.1.1 Thread the pull cord (with the closing mechanism attached) through the guides and secure the pull ring with a simple knot. Screw a sample bottle onto the closing device and insert the bottle into the collar. Cock the closing plate so that the plate is pushed away from the operator (Reference 22.1).

9.4.1.2 The cleaned and assembled sampling device should be stored in a double layer of

large, clean zip-type polyethylene bags or wrapped in two layers of clean polyethylene wrap if it will not be used immediately (reference 22.1).

9.4.1.3 An alternate grab sampler design is shown in Figure 2. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be submerged, the cap removed, sample collected, and bottle recapped at a selected depth. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination. Because a fresh bottle is used for each sample, carryover from previous samples is eliminated (Reference 22.12).

9.5 Subsurface Sampling Devices—Subsurface sample collection may be appropriate in lakes and sluggish deep river environments or where depth profiling is determined to be necessary. Subsurface samples are collected by pumping the sample into a sample bottle. Examples of subsurface collection systems include the jar system device shown in Figure 3 and described in Section 14.8 or the continuous-flow apparatus shown in Figure 4 and described in Section 14.9.

9.5.1 Jar sampler (Reference 22.1)—The jar sampler (Figure 3) is comprised of a heavy fluoropolymer 1-L jar with a fluoropolymer lid equipped with two 1/4 in. fluoropolymer fittings. Sample enters the jar through a short length of fluoropolymer tubing inserted into one fitting. Sample is pulled into the jar by pumping on fluoropolymer tubing attached to the other fitting. A thick fluoropolymer plate supports the jar and provides attachment points for a fluoropolymer safety line and fluoropolymer torpedo counterweight.

9.5.1.1 Advantages of the jar sampler for depth sampling are (1) all wetted surfaces are fluoropolymer and can be rigorously cleaned; (2) the sample is collected into a sample jar from which the sample is readily recovered, and the jar can be easily recleaned; (3) the suction device (a peristaltic or rotary vacuum pump) is located in the boat, isolated from the sampling jar; (4) the sampling jar can be continuously flushed with sample, at sampling depth, to equilibrate the system; and (5) the sample does not travel through long lengths of tubing that are more difficult to clean and keep clean (Reference 22.1). In addition, the device is designed to eliminate atmospheric contact with the sample during collection.

9.5.1.2 To assemble the cleaned jar sampler, screw the torpedo weight onto the machined bolt attached to the support plate of the jar sampler. Attach a section of the 1/4 in. o.d. tubing to the jar by inserting the tubing into the fitting on the lid and pushing down into the jar until approximately 8 cm from the bottom. Tighten the fitting nut securely. Attach the solid safety line to the jar sampler using a bowline knot to the loop affixed to the support plate.

9.5.1.3 For the tubing connecting the pump to the sampler, tubing lengths of up to 12 m have been used successfully (22.11).

9.5.2 Kemmerer is used to collect water chemistry samples from discrete depths in a lake, reservoir, or river of sufficient depth. A Kemmerer has a vertical orientation. The device is opened by attaching the covers to the release mechanism. Then the device is lowered to the depth of interest by the attached rope or cable. After arrival 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 can be collected.

9.5.2.1 Kemmerer is Constructed with an all Teflon® cylinder, Teflon® end seals and an all stainless steel trip head. For added strength, the center rod is solid Teflon®. The replaceable line has a Teflon® adapter for attaching it to the center rod. Samples touch only Teflon® allowing use for trace metals.1.2 L volume.

9.5.3 Continuous-flow sampler—This sampling system, shown in Figure 4, consists of a peristaltic or submersible pump (figure 6) and one or more lengths of precleaned fluoropolymer or styrene/ethylene/butylene/ silicone (SEBS) tubing. A filter is added to the sampling train when sampling for dissolved metals.

9.5.3.1 Advantages of this sampling system include (1) all wetted surfaces are fluoropolymer or SEBS and can be readily cleaned; (2) the suction device is located in the boat, isolated from the sample bottle; (3) the sample does not travel through long lengths of tubing that are difficult to clean and keep clean; and (4) in-line filtration is possible, minimizing field handling requirements for dissolved metals samples.

9.6 Gloves—Clean, nontalc polyethylene, latex, vinyl, or PVC; various lengths. Shoulder-length gloves are needed if samples are to be collected by direct submersion of the sample bottle into the water.

9.6.1 Gloves, shoulder-length polyethylene—Associated Bag Co., Milwaukee, WI, 66-3-301, or equivalent.

9.6.2 Gloves, PVC—Fisher Scientific Part No. 11-394-100B, or equivalent.

9.7 Storage Bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes).

9.8 Plastic Wrap—Clean, colorless polyethylene.

9.9 Cooler—Clean, nonmetallic, with white interior for shipping samples.

9.10 Ice or Chemical Refrigerant Packs—To keep samples chilled in the cooler during shipment.

9.11 Dupont Proshield

9.11.1 The garment is a coverall with front zipper closure. The garment was anti-static treated to act as a dry particular barrier and liquid repellent.

9.11.2 The garment is folded and stored in a plastic bag after every usage.

9.12 Boat

9.12.1 For most situations (e.g., most metals under most conditions), the use of an existing, available boat is acceptable. A flat-bottom, Boston Whaler-type boat is preferred because sampling materials can be stored with reduced chance of tipping.

9.12.2 If the boat I transported to the sampling site from another location, the boat should be washed with water from the sampling site away from any sampling points to remove any dust or dirt accumulation.

9.12.3 Samples should be collected upstream of boat movement.

9.12.4 For mercury, the following equipment and precautions may be necessary:

9.12.5 A metal-free (e.g., fiberglass) boat, along with wooden or fiberglass oars. Gasoline- or diesel-fueled boat motors should be avoided when possible because the exhaust can be a source of contamination. If the body of water is large enough to require use of a boat motor, the engine should be shut off at a distance far enough from the sampling point to avoid contamination, and the sampling team should manually propel the boat to the sampling point. Samples should be collected upstream of boat movement (reference 22.1).

9.12.6 Before first use, the boat should be cleaned and stored in an area that minimizes exposure to dust and atmospheric particles. For example, cleaned boats should not be stored in an area that would allow exposure to automobile exhaust or industrial pollution (Reference 22.1).

9.12.7 The boat should be frequently visually inspected for possible contamination.

9.13 Filtration Apparatus—Required when collecting samples for dissolved metals determinations.

9.13.1 Filter—0.45 µm, 15 mm diameter or larger, tortuous-path capsule filters (Reference 18), Gelman Supor 12175. Other vendors that can be used: PES™ membrane 47mm, 0.45µm from Delta Technical Products Co (deltatechprod.com).

9.13.2 Filter holder—For mounting filter to the gunwale of the boat. Rod or pipe made from plastic material and mounted with plastic clamps - Series 47 Filter Holder (cat No. 4N-47-4N) from Savillex.

9.14 Pump and Pump Apparatus—Required for use with the jar sampling system (Section 8.5.1) or the continuous-flow system (Section 14.9). Peristaltic pump; 115 V a.c., 12 V d.c., internal battery, variable-speed,single-head, Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent.

9.14.1 Cleaning—Peristaltic pump modules do not require cleaning. However, nearly all peristaltic pumps contain a metal head and metal controls. Touching the head or controls necessitates changing of gloves before touching the Apparatus. For the submersible pump is used, a large volume of sample should be pumped to clean the stainless steel shaft (hidden behind the impeller) that comes in contact with the sample. Pumps with metal impellers should not be used.

9.14.2 Tubing—For use with peristaltic pump. SEBS resin, approximately 3/8" ID by approximately 3 ft, Cole-Parmer size 18 (Cat. No. G-06464-18), or approximately ¼" ID, Cole-Parmer size 17, Catalog No. G-06464-17, C-flex tubing 3/16"ID x 5/16"OD (cat No.EW-06424-03), or equivalent. Tubing is cleaned by soaking in cold 5-10% HCl solution for 8-24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging

with mercury-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

9.14.3 Tubing—For connection to peristaltic pump tubing. Fluoropolymer, 3/8" or ¼" OD is used to reach the point of sampling. FEP tubing ¼"OD x 3/16"ID (cat No. EW-06406-66) from Cole Parmer required, or equivalent. If sampling will be at some depth from the end of a boom extended from a boat, sufficient tubing to extend to the end of the boom and to the depth will be required. Cleaning of the fluoropolymer can be the same as cleaning the tubing for the rotary vacuum pump (Section 8.15.1.2). If necessary, more aggressive cleaning (e.g., concentrated nitric acid) may be used.

9.14.4 Batteries to operate submersible pump—12 V, 2.6 amp, gel cell, YUASA NP2.6-12, or equivalent. A 2 amp fuse connected at the positive battery terminal is strongly recommended to prevent short circuits from overheating the battery. A 12 V, lead-acid automobile or marine battery may be more suitable for extensive pumping.

9.14.5 Tubing connectors—Appropriately sized PVC, clear polyethylene, or fluoropolymer "barbed" straight connectors cleaned as the tubing above. Used to connect multiple lengths of tubing.

9.15 Carboy—For collection and storage of dilute waste acids used to store bottles.

10. Reagents and Standards

10.1 Reagent Water—Water in which the analytes of interest and potentially interfering substances are not detected at the MDL of the analytical method used for analysis of samples. The laboratory prepared the reagent water by using a reverse osmosis, carbon tank and trace cartridge filtration polisher at the sink. A large carboy or other appropriate container filled with reagent water must be available for the collection of field blanks. The reagent water is prepared at Syracuse University.

10.2 Hydrochloric Acid—Dilute, trace-metal grade, shipped with sampling kit for cleaning equipment between samples.

11. Site selection, Sample Collection, Preservation, Holding Times

11.1 Site Selection

11.1.1 Selection of a representative site for surface water sampling is based on many factors including: study objectives, water use, point source discharges, non-point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, and the presence of structures (bridges, dams, etc.). When collecting samples to determine ambient levels of trace metals, the presence of potential sources of metal contamination are of extreme importance in site selection.

11.1.2 Ideally, the selected sampling site will exhibit a high degree of cross-sectional homogeneity. It may be possible to use previously collected data to identify locations for samples that are well mixed or are vertically or horizontally stratified. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing. Horizontal mixing occurs in constrictions in the channel. In

the absence of turbulent areas, the selection of a site that is clear of immediate point sources, such as industrial effluents, is preferred for the collection of ambient water samples (Reference 22.1 and 22.13).

11.1.3 To minimize contamination from trace metals in the atmosphere, ambient water samples should be collected from sites that are as far as possible (e.g., at least several hundred feet) from any metal supports, bridges, wires or poles. Similarly, samples should be collected as far as possible from regularly or heavily traveled roads. If it is not possible to avoid collection near roadways, it is advisable to study traffic patterns and plan sampling events during lowest traffic flow (Reference 22.6).

11.1.4 The sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of trace metals first, finishing with the samples known or suspected to contain the highest concentrations. For example, if samples are collected from a flowing river or stream near an industrial or municipal discharge, the upstream sample should be collected first, the downstream sample collected second, and the sample nearest the discharge collected last. If the concentrations of pollutants is not known and cannot be estimated, it is necessary to use precleaned sampling equipment at each sampling location.

11.2 Sample collection

11.2.1 See Section 14-Procedures

11.2.2 Re-Cleaning Apparatus between Samples

11.2.2.1 Sampling activity is planned so that samples known or suspected to contain the lowest concentrations of trace metals are collected first with the samples known or suspected to contain the highest concentrations of trace metals are collected last. In this manner, cleaning of the sampling equipment between samples in unnecessary. If it is not possible to plan sampling activity in this manner, dedicated sampling equipment is provided for each sampling event.

11.2.2.2 If samples are collected from adjacent sites (e.g., immediately upstream, downstream, or water column), rinsing of the sampling Apparatus with water that is to be sampled will be sufficient.

11.3 Preservation

11.3.1 In the laboratory, using a disposable, precleaned, plastic pipet, 4 mL of ultra-pure HCl is added per liter of sample. This will be sufficient to preserve a neutral sample to pH <2.

11.4 Holding Times

11.4.1 Preserved samples and in Teflon bottles and stored in 4 degrees C for 6 months or according to QUAPP requirement.

12. Quality Control and Documentation

12.1 The sampling team shall employ a quality assurance/ quality control (QA/QC) program. The minimum requirements of this program include the collection of equipment blanks, field blanks, and field replicates. It is also desirable to include blind QC samples as part of the program.

12.2 The sampling team is permitted to modify the sampling techniques described in this method to improve performance or reduce sampling costs, provided that reliable analyses of samples are obtained and that samples and blanks are not contaminated. Each time a modification is made to the procedures, the sampling team is required to demonstrate that the modification does not result in contamination of field and equipment blanks. The requirements for modification are given in Sections 12.3 and 12.4. Because the acceptability of a modification is based on the results obtained with the modification, the sampling team must work with the analytical laboratory to demonstrate equivalence. Final approval for the modification(s) is given by the project QA\QC coordinator.

12.3 Equipment Blanks

12.3.1 Before using any sampling equipment at a given site, the laboratory generates equipment blanks to demonstrate that the equipment is free from contamination. Two types of equipment blanks are generated: trip blanks/bottle blanks and sampling equipment blanks.

12.3.2 Equipment blanks are run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and the jar sampling device, then an equipment blank must be run on both pieces of equipment.

12.3.3 Equipment blanks are generated in the laboratory processing reagent water through the equipment using the same procedures that are used in the field. Therefore, the "clean hands/dirty hands" technique used during field sampling is followed when preparing equipment blanks at the laboratory. In addition, training is performed before performing on-site field activities.

12.3.4 Equipment Blank for Continuous-flow

12.3.4.1 The submersible pump is brought to the laboratory once a month. In the laboratory a 25 liters carboy or other container is filled with reagent water. An aliquot is taking for analysis, and the pump is run for 5-10 minutes and another sample is collected. The aliquots are analyzed using method cese-env-1631. The pump is dean clean, if the concentration is less than MDL.

12.3.5 The equipment blank must be analyzed using the procedures detailed in the referenced analytical method (see Table 1). If any metal(s) of interest or any potentially interfering substance is detected in the equipment blank at the minimum level specified in the cese-env-1631 method, the source of contamination/interference must be identified and removed. The equipment must be demonstrated to be free from the metal(s) of interest before the equipment may be used in the field.

12.4 Field Blank

12.4.1 To demonstrate that sample contamination has not occurred during field sampling and sample processing, Field sample is collected per QUAPP requirement or if possible one for every given

sampling event. Field blanks are collected before sample collection.

12.4.2 Field blanks are generated by filling a large carboy or other appropriate container with reagent water in the laboratory, transporting the filled container to the sampling site, processing the water through each of the sample processing steps and equipment (e.g., tubing, sampling devices, filters, etc.) that will be used in the field, collecting the field blank in one of the sample bottles, and shipping the bottle to the laboratory for analysis in accordance with the method(s) referenced in Table 1. For example, manual grab sampler field blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler field blanks are collected by immersing the tubing into the water and pumping water into a sample container.

12.4.3 Filter the field blanks using the procedures described in Section 14.10.

12.4.4 If it is necessary to acid clean the sampling equipment between samples, a field blank should be collected after the cleaning procedures for the last sample is performed.

12.5 Field Duplicate

12.5.1 To assess the precision of the field sampling and analytical processes, at least one field duplicate sample must be collected for every 20 samples that are collected at a given site.

12.5.2 The field duplicate is collected either by splitting a larger volume into two aliquots, by using a sampler with dual inlets that allows simultaneous collection of two samples, or by collecting two samples in rapid succession.

12.5.3 Field duplicates for dissolved metals determinations must be processed using the procedures in Section 14.10.

12.5.4 Field duplicate are submitted as blind samples to the laboratory.

12.6 Field Triplicate

12.6.1 Triplicates are performed specifically per Quality Assurance Project Plan.

12.6.2 To additional assess the precision of the field sampling and analytical processes, at least one field triplicate samples will be collected per month or per 250 samples.

12.6.3 The field triplicate are collected either by splitting a larger volume into three aliquots, by using a sampler with dual inlets that allows simultaneous collection of two samples, or by collecting two samples in rapid succession.

12.6.4 Field triplicates for dissolved metals determinations must be processed using the procedures in Section 14.10.

12.6.5 Field triplicates are submitted as blind samples to the laboratory.

12.7 Matrix Spike and Matrix Spike Duplicate (MS\MSD)

12.7.1 MS\MSD are field QC samples assigned by field crew during sampling.

12.7.2 The frequency of the MS\MSD is determined by the possible matrix interference, QAPP and the analytical method. The standard frequency is 10%.

13. Calibration and Standardization

13.1 N/A

14. Procedure

14.1 Sample Collection Procedure—Before collecting ambient water samples, consideration is given to the type of sample to be collected, the amount of sample needed, and the devices to be used (grab, surface, or subsurface samplers). Sufficient sample volume is collected to allow for necessary quality control analyses, such as matrix spike/matrix spike duplicate analyses.

14.2 Five sampling procedures are described:

14.2.1 Section 14.6 describes a procedure for collecting samples directly into the sample container. This procedure is the simplest and provides the least potential for contamination because it requires the least amount of equipment and handling.

14.2.2 Section 14.7 describes a procedure for using a grab sampling device to collect samples.

14.2.3 Section 14.8 describes a procedure for depth sampling with a jar sampler. The size of sample container used is dependent on the amount of sample needed by the analytical laboratory.

14.2.4 Section 14.9 describes a procedure for continuous-flow sampling using a submersible or peristaltic pump.

14.2.5 Section 14.10 describes a procedure for using a Kemmerer sampling device to collect water column samples.

14.3 The sampling team should ideally approach the site from down current and downwind to prevent contamination of the sample by particles sloughing off the boat or equipment. If it is not possible to approach from both, the site should be approached from down current if sampling from a boat or approached from downwind if sampling on foot. When sampling from a boat, the bow of the boat should be oriented into the current (the boat will be pointed upstream). All sampling activity should occur from the middle of the boat.. If the samples are being collected from a boat, it is recommended that the sampling team create a stable workstation by arranging the cooler or shipping container as a work table on the upwind side of the boat, covering this worktable (Reference 22.1).

14.4 All operations involving contact with the sample bottle and with transfer of the sample from the sample collection device to the sample bottle (if the sample is not directly collected in the bottle) are handled by the individual designated as "clean hands." "Dirty hands" is responsible for all activities that do not involve direct contact with the sample. Although the duties of "clean hands" and "dirty hands" would appear to be a logical separation of responsibilities, in fact, the completion of the entire protocol may

require a good deal of coordination and practice. For example, "dirty hands" must open the box or cooler containing the sample bottle and unzip the outer bag; clean hands must reach into the outer bag, open the inner bag, remove the bottle, collect the sample, replace the bottle lid, put the bottle back into the inner bag, and zip the inner bag. "Dirty hands" must close the outer bag and place it in a cooler. To minimize unnecessary confusion, it is recommended that a third team member be available to complete the necessary sample documentation (e.g., to document sampling location, time, sample number, etc). Otherwise, "dirty hands" must perform the sample documentation activity (Reference 22.1).

14.5 Extreme care must be taken during all sampling operations to minimize exposure of the sample to human, atmospheric, and other sources of contamination. Care must be taken to avoid breathing directly on the sample, and whenever possible, the sample bottle should be opened, filled, and closed while submerged.

14.6 Manual collection of surface samples directly into the sample bottle.

14.6.1 At the site, all sampling personnel must put on clean gloves before commencing sample collection activity, with "clean hands" donning shoulder-length gloves. Note that "clean hands" should put on the shoulder-length polyethylene gloves and both "clean hands" and "dirty hands" should put on the PVC gloves.

14.6.2 "Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.

14.6.3 Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.

14.6.4 "Clean hands" unscrews the cap and, while holding the cap upside down, discards the diluted acid solution from the bottle into a carboy for wastes (Section 9.14) or discards the reagent water directly into the water body.

14.6.5 "Clean hands" then submerges the sample bottle, and allows the bottle to partially fill with sample. "Clean hands" screws the cap on the bottle, shakes the bottle several times, and empties the rinsate away from the site. After two more rinsings, "clean hands" holds the bottle under water and allows bottle to fill with sample. After the bottle has filled (i.e., when no more bubbles appear), and while the bottle is still inverted so that the mouth of the bottle is underwater, "clean hands" replaces the cap of the bottle. In this way, the sample has never contacted the air.

14.6.6 Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.

14.6.7 "Dirty hands" zips the outer bag.

14.6.8 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

14.6.9 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the

procedure described in Section 14.10.

14.7 Sample collection with grab sampling device.

14.7.1 The following steps detail sample collection using the grab sampling device shown in Figure 1 and described in Section 9.4.1. The procedure is indicative of the "clean hands/dirty hands" technique that must be used with alternative grab sampling devices such as that shown in Figure 2 and described in Section 9.4.2.

14.7.2 The sampling team puts on gloves. Ideally, a sample bottle will have been pre-attached to the sampling device in the class 100 clean room at the laboratory. If it is necessary to attach a bottle to the device in the field, "clean hands" performs this operation,

14.7.3 "Dirty hands" removes the sampling device from its storage container and opens the outer polyethylene bag.

14.7.4 "Clean hands" opens the inside polyethylene bag and removes the sampling device.

14.7.5 "Clean hands" changes gloves.

14.7.6 "Dirty hands" submerges the sampling device to the desired depth and pulls the fluoropolymer pull cord to bring the seal plate into the middle position so that water can enter the bottle.

14.7.7 When the bottle is full (i.e., when no more bubbles appear), "dirty hands" pulls the fluoropolymer cord to the final stop position to seal off the sample and removes the sampling device from the water.

14.7.8 "Dirty hands" returns the sampling device to its large inner plastic bag, "Clean hands" pulls the bottle out of the collar, unscrews the bottle from the sealing device, and caps the bottle. "Clean hands" and "dirty hands" then return the bottle to its double-bagged storage as described in Sections 14.5.6 through 14.5.7.

14.7.9 Closing mechanism—"Clean hands" removes the closing mechanism from the body of the grab sampler, rinses the device with reagent water, places it inside a new clean plastic bag, zips the bag, and places the bag inside an outer bag held by "dirty hands." "Dirty hands" zips the outer bag and places the double-bagged closing mechanism in the equipment storage box.

14.7.10 Sampling device "Clean hands" seals the large inside bag containing the collar, pole, and cord and places the bag into a large outer bag held by "dirty hands." "Dirty hands" seals the outside bag and places the double-bagged sampling device into the equipment storage box.

14.7.11 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

14.7.12 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedures described in Section 14.9.

14.8 Depth sampling using a jar sampling device (Figure 3 and Section 9.5.1)

14.8.1 The sampling team puts on gloves (and wind suits, if applicable) and handles bottles as with manual collection (Sections 14.6.1 through 14.6.4 and 14.6.6 through 14.6.7).

14.8.2 "Dirty hands" removes the jar sampling device from its storage container and opens the outer polyethylene bag.

14.8.3 "Clean hands" opens the inside polyethylene bag and removes the jar sampling apparatus. Ideally, the sampling device will have been preassembled in a class 100 clean room at the laboratory. If, however, it is necessary to assemble the device in the field, "clean hands" must perform this operation, described in Section 9.5.2, inside a field-portable glove bag (Section 9.6).

14.8.4 While "dirty hands" is holding the jar sampling apparatus, "clean hands" connects the pump to the to the 1/4 in. o.d. flush line.

14.8.5 "Dirty hands" lowers the weighted sampler to the desired depth.

14.8.6 "Dirty hands" turns on the pump allowing a large volume (>2 L) of water to pass through the system.

14.8.7 After stopping the pump, "dirty hands" pulls up the line, tubing, and device and places them into either a field-portable glove bag or a large, clean plastic bag as they emerge.

14.8.8 Both "clean hands" and "dirty hands" change gloves.

14.8.9 Using the technique described in Sections 14.6.2 through 14.6.4, the sampling team removes a sample bottle from storage, and "clean hands" places the bottle into the glove bag.

14.8.10 "Clean hands" tips the sampling jar and dispenses the sample through the short length of fluoropolymer tubing into the sample bottle.

14.8.11 Once the bottle is filled, "clean hands" replaces the cap of the bottle, returns the bottle to the inside polyethylene bag, and zips the bag. "Clean hands" returns the zipped bag to the outside polyethylene bag held by "dirty hands."

14.8.12 "Dirty hands" zips the outside bag. If the sample is to be analyzed for dissolved metals, it is filtered as described in Section 14.9.

14.8.13 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

14.9 Continuous-flow sampling (Figure 4 and Section 9.5.3)

14.9.1 The continuous-flow sampling system uses submersible (figure 6) or peristaltic pump (Section 9.13) to pump sample to the boat or to shore through the SEBS-resin or PTFE tubing.

14.9.2 Before putting on gloves, the sampling team removes the bags containing the pump (Section 9.13), SEBS-resin tubing (Section 9.13.2), batteries (Section 9.13.4), gloves (Section 9.5), plastic wrap (Section 9.7), wind suits (Section 9.10), and, if samples are to be filtered, the filtration apparatus (Section 9.12) from the coolers or storage containers in which they are packed.

14.9.3 "Clean hands" and "dirty hands" put on the wind suits and PVC gloves (Section 9.5).

14.9.4 "Dirty hands" removes the pump from its storage bag, and opens the bag containing the SEBS-resin tubing.

14.9.5 "Clean hands" installs the tubing while "dirty hands" holds the pump. "Clean hands" immerses the inlet end of the tubing in the sample stream.

14.9.6 Both "clean hands" and "dirty hands" change gloves. "Clean hands" also puts on shoulder length polyethylene gloves (Section 9.5).

14.9.7 "Dirty hands" turns the pump on and allows the pump to run for 5-10 minutes or longer to purge the pump and tubing.

14.9.8 If the sample is to be filtered, "clean hands" installs the filter at the end of the tubing, and "dirty hands" sets up the filter holder on the gunwale as shown in Figure 4.

14.9.9 The sample is collected by rinsing the sample bottle and cap three times and collecting the sample from the flowing stream.

14.9.10 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

14.10 Sampling Collection with Kemmerer sampling device (Annex A for quick reference):

14.10.1 The following steps detail sample collection using the Kemmerer sampling device shown in Figure 5 and described in Section 9.5.3.

14.10.2 The sampling team puts on gloves.

14.10.3 "Dirty hands" removes the sampling device from its storage container and opens the outer polyethylene bag.

14.10.4 "Clean hands" opens the inside polyethylene bag and removes the sampling device.

14.10.5 "Clean hands" changes gloves.

14.10.6 "Dirty hands" performs the sampling as follow:

14.10.6.1 Device is opened by attaching the covers to the release mechanism.

14.10.6.2 Then the device is lowered to the depth of interest.

14.10.6.3 When at the depth of interest a weighted messenger is sent down the line to the release mechanism which triggers device closure.

14.10.7 The device is then raised to the surface.

14.10.8 For Oxic sample collection:

14.10.8.1 Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.

14.10.8.2 Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.

14.10.8.3 "Clean hands" unscrews the cap and, while holding the cap upside down, discards the diluted acid solution from the bottle into a carboy for wastes (Section 9.14).

14.10.8.4 The water sample can then be poured out into the bottles.

14.10.8.5 After the bottle is filled (i.e., when no more bubbles appear)."Clean hands" replaces the cap of the bottle.

14.10.8.6 Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.

14.10.8.7 "Dirty hands" zips the outer bag Place bottles in a cooler and fill the cooler with ice and close.

14.10.8.8 Fill out the chain of custody.

14.10.8.9 Samples should be re-iced upon return to the lab to maintain a temperature of 4°C if samples will not be processed immediately.

14.10.8.10 Samples are filtered if needed and preserved by adding 4 mL/L of pretested 11.6 M HCl at the lab.

14.10.9 For anoxic sample collection:

14.10.9.1 Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.

14.10.9.2 Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.

14.10.9.3 "Clean hands" unscrews the cap and, while holding the cap upside down, discards

the diluted acid solution from the bottle into a carboy for wastes (Section 9.14).

14.10.9.4 After the sampling tubing has been attached to the device, turn on the pump nozzle so that water flows out at a slow rate.

14.10.9.5 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.

14.10.9.6 Allow bottles to flush for three volumes, then cap and place in the cooler.

14.10.9.7 Bottles that need reagents added should be capped, then uncapped, the reagent(s) added, recapped and inverted several times, then placed in the cooler.

14.10.9.8 After the bottle is filled (i.e., when no more bubbles appear)."Clean hands" replaces the cap of the bottle.

14.10.9.9 Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.

14.10.9.10 "Dirty hands" zips the outer bag Place bottles in a cooler and fill the cooler with ice and close.

14.10.9.11 After all bottles from a cooler are filled, fill the cooler with ice and tightly close the lid.

14.10.9.12 Fill out the chain of custody sheet.

14.10.10 Samples should be re-iced upon return to the lab to maintain a temperature of 4°C if samples will not be processed immediately.

14.10.10.1 Samples are filtered if needed and preserved by adding 4 mL/L of pretested 11.6 M HCl at the lab.

14.10.11 Closing mechanism—"Clean hands" removes the closing mechanism from the body of the kemmerer sampler, rinses the device with 0.4% HCl, places it inside a new clean plastic bag, zips the bag, and places the bag inside an outer bag held by "dirty hands." "Dirty hands" zips the outer bag and places the double-bagged closing mechanism in the equipment storage box.

14.10.12 Sampling device "Clean hands" seals the large inside bag containing the collar, pole, and cord and places the bag into a large outer bag held by "dirty hands." "Dirty hands" seals the outside bag and places the double-bagged sampling device into the equipment storage box.

14.10.13 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

14.11 Sample Filtration

14.11.1 The filtration procedure described below is used for samples collected using the manual (Section 14.6), grab (Section 14.7), or jar (Section 14.8) collection systems (Reference 7). In-line filtration using the continuous-flow approach is described in Section 14.8.8. Because of the risk of contamination, it is recommended that samples for mercury be shipped unfiltered by overnight courier and filtered when received at the laboratory.

14.11.2 Set up the filtration system inside the glove bag, using the shortest piece of pump tubing as is practicable. Place the peristaltic pump immediately outside of the glove bag and poke a small hole in the glove bag for passage of the tubing. Also, attach a short length of tubing to the outlet of the capsule filter.

14.11.3 “Clean hands" removes the water sample from the inner storage bag using the technique described in Sections 14.6.2 through 14.6.4 and places the sample inside the glove bag. "Clean hands" also places two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.

14.11.4 "Clean hands" removes the lid of the reagent water bottle and places the end of the pump tubing in the bottle.

14.11.5 "Dirty hands" starts the pump and passes approximately 200 mL of reagent water through the tubing and filter into the waste bottle. "Clean hands" then moves the outlet tubing to a clean bottle and collects the remaining reagent water as a blank. "Dirty hands" stops the pump.

14.11.6 "Clean hands" removes the lid of the sample bottle and places the intake end of the tubing in the bottle.

14.11.7 "Dirty hands" starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump. "Clean hands" uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.

14.11.8 "Dirty hands" starts the pump and the remaining sample is processed through the filter and collected in the sample bottle. If preservation is required, the sample is acidified at this point (Section 10.3).

14.11.9 "Clean hands" replaces the lid on the bottle, returns the bottle to the inside bag, and zips the bag. "Clean hands" then places the zipped bag into the outer bag held by "dirty hands."

14.11.10 "Dirty hands" zips the outer bag, and places the double-bagged sample bottle into a clean, ice-filled cooler for immediate shipment to the laboratory.

15. Calculations

15.1 N/A

16. Method Performance

16.1 New equipment that will come into contact with samples is cleaned prior to use, and equipment blank is tested for contamination.

16.2 Equipment Blank Test-10 gallons container was filled with reagent water and the pump was run for 4 minutes. Three aliquots were collected and analyzed.

16.3 The submerge pump test samples' results were below the MDL. The results ranged from 0.131 ng/L - 0.147 ng/L.

17. Pollution Prevention

17.1 The only materials used in this method that could be considered pollutants are the acids used in the cleaning of the Apparatus, the boat, and related materials. These acids are used in dilute solutions in small amounts and pose little threat to the environment when managed properly.

17.2 Cleaning solutions containing acids should be prepared in volumes consistent with use to minimize the disposal of excessive volumes of acid.

17.3 To the extent possible, the Apparatus used to collect samples should be cleaned and reused to minimize the generation of solid waste.

18. Data Assessment, Review and Acceptance Criteria of QC Measures

18.1 N/A

19. Corrective Actions for Out-of-Control Data

19.1 N/A

20. Contingencies for Handling Out-of-Control or Unacceptable Data

20.1 N/A

21. Waste Management

21.1 It is the sampling team's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the discharge regulations, hazardous waste identification rules, and land disposal restrictions; and to protect the air, water, and land by minimizing and controlling all releases from field operations.

21.2 Storing solutions must be neutralized before being disposed of, or must be handled as hazardous waste.

21.3 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better—Laboratory Chemical Management for Waste Reduction,* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

21.4 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

22. References

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22.13 Hunt, C.D. In *Manual of Biological and Geochemical Techniques in Coastal Areas*, 2nd ed.; Lambert, C.E. and Oviatt, C.A., Eds.; Marine Ecosystems Research Laboratory; Graduate School of Oceanography; The University of Rhode Island: Narragansett, RI, MERL Series, Report No. 1, Chapter IV.

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22.15 Horowitz, A.J., Kent A.E., and Colberg, M.R. "The Effect of Membrane Filtration Artifacts on Dissolved Trace Element Concentrations," *Wat. Res.* **1992**, *26*, 53.

22.16 Methods 1624 and 1625, 40 *CFR* Part 136, Appendix A.

23. Tables, Diagrams, Figures, Flowcharts and Validation Data

23.1 Table 1-MDLs

23.2 Figure 1: Grab Sampling Device I

23.3 Figure 2: Grab Sampling Device II

23.4 Figure 3: Jar sampling Device

23.5 Figure 4: Sample Pumping System

23.6 Figure 5: Kemmerer Sampling Device

23.7 Figure 6: Submersible Pump

23.8 Annex A: Quick Reference for Kemmerer Sampling Device.

23.9 Annex B: Glossary

Table 1
Target analyte list, methods, method detection limits, and method reporting limits

		Water	
Analyte	Method	Method Detection Limit	Method Reporting Limit
Mercury	EPA Method 1631E (U.S. EPA 2002)	0.2 ng/L	0.5 ng/L
Methyl Mercury	EPA Method 1630 (U.S. EPA 2001)	0.02 ng/L	0.05 ng/L

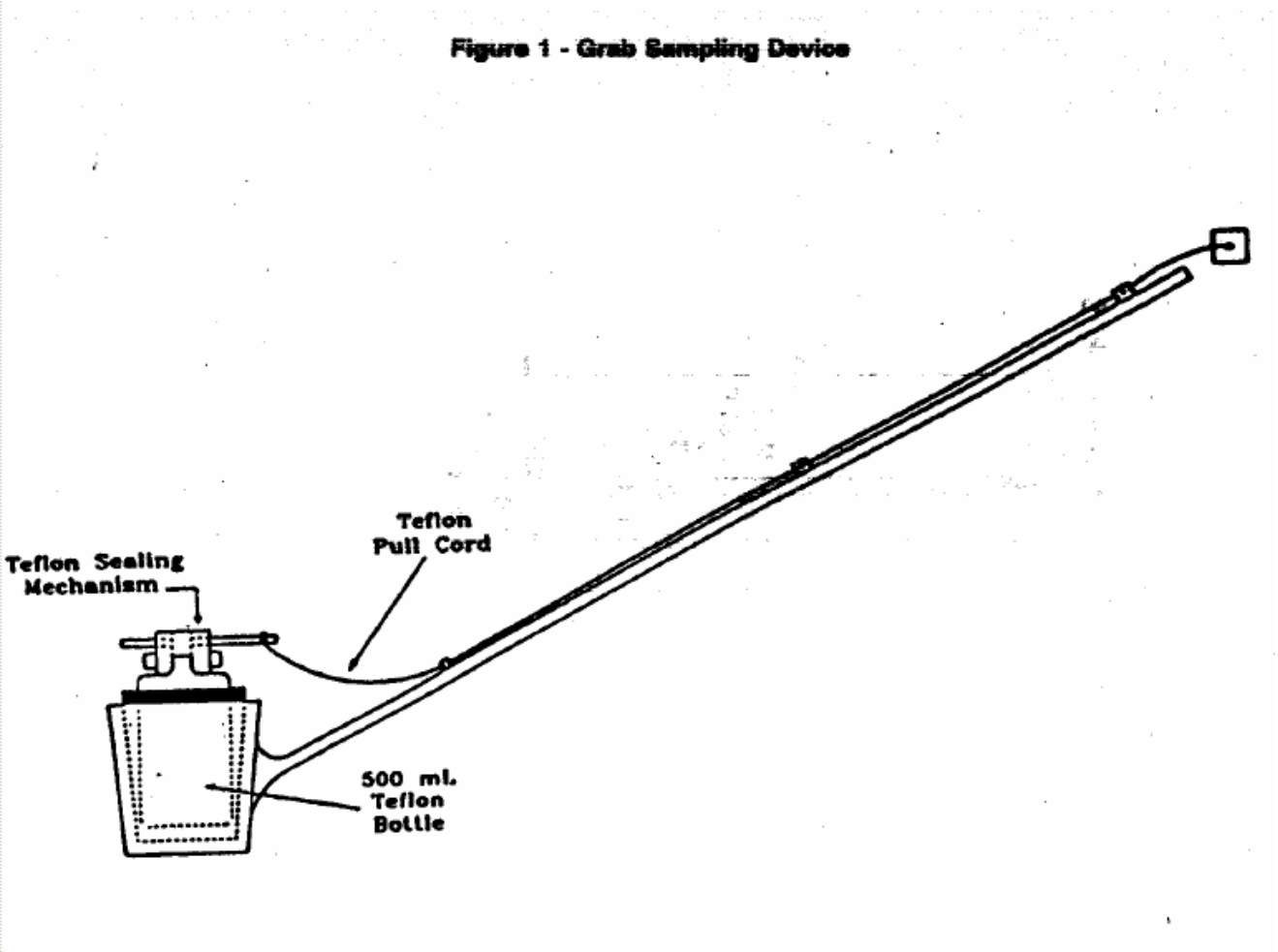

Figure from EPA Method 1699

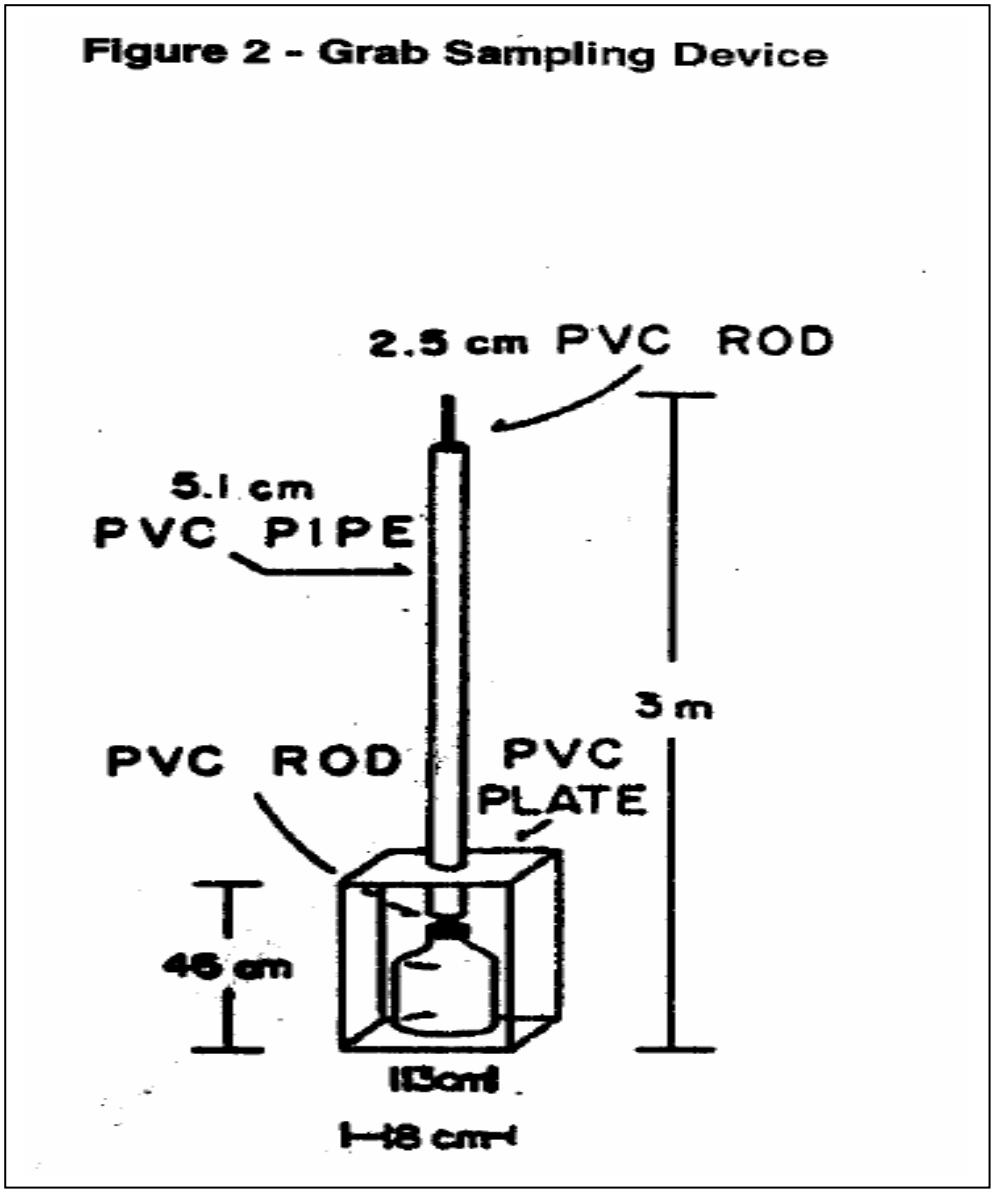

Figure from EPA Method 1699

Figure 3 - Jar Sampling Device

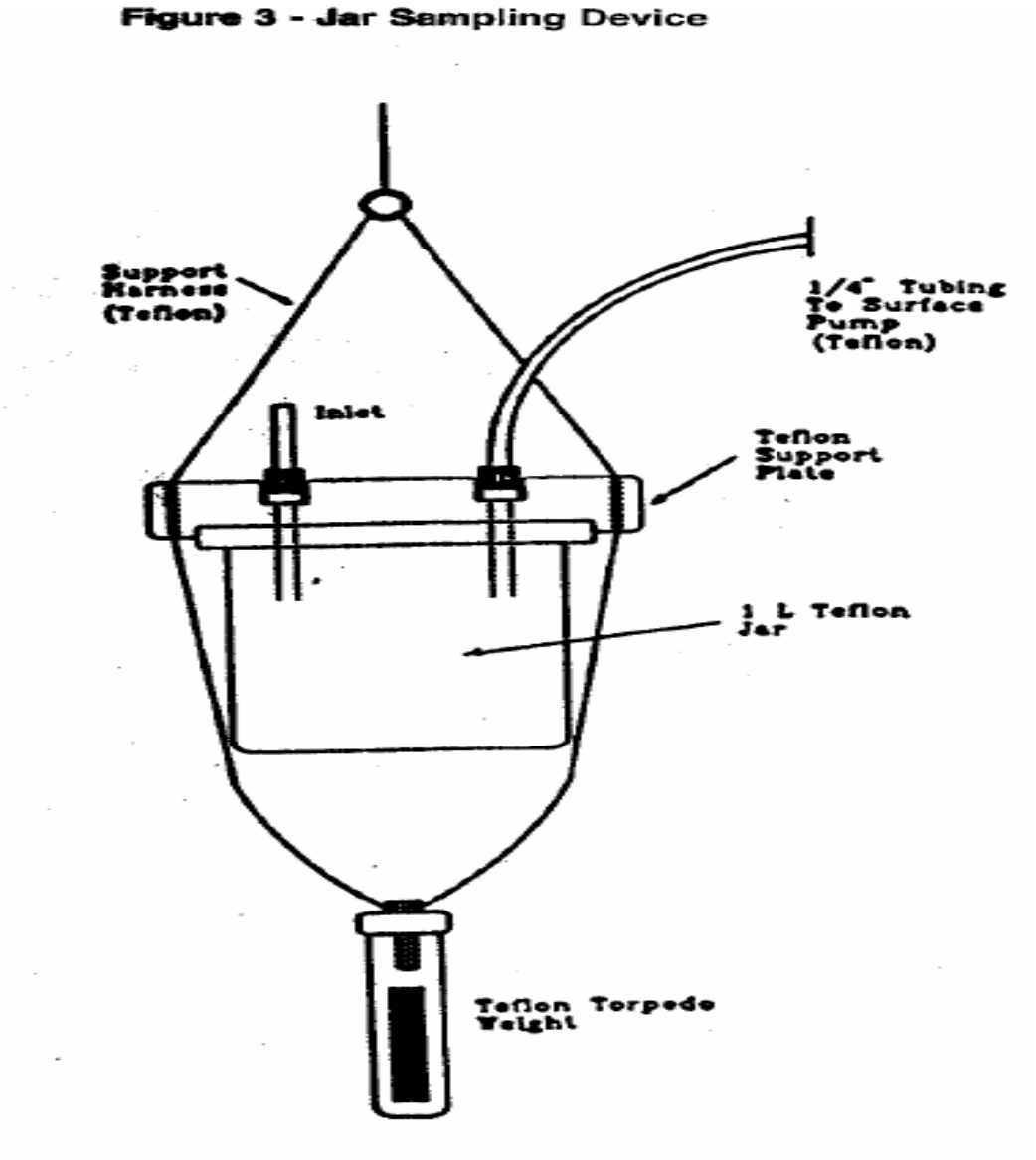

Figure from EPA Method 1699

Figure 4 - Sample Pumping System

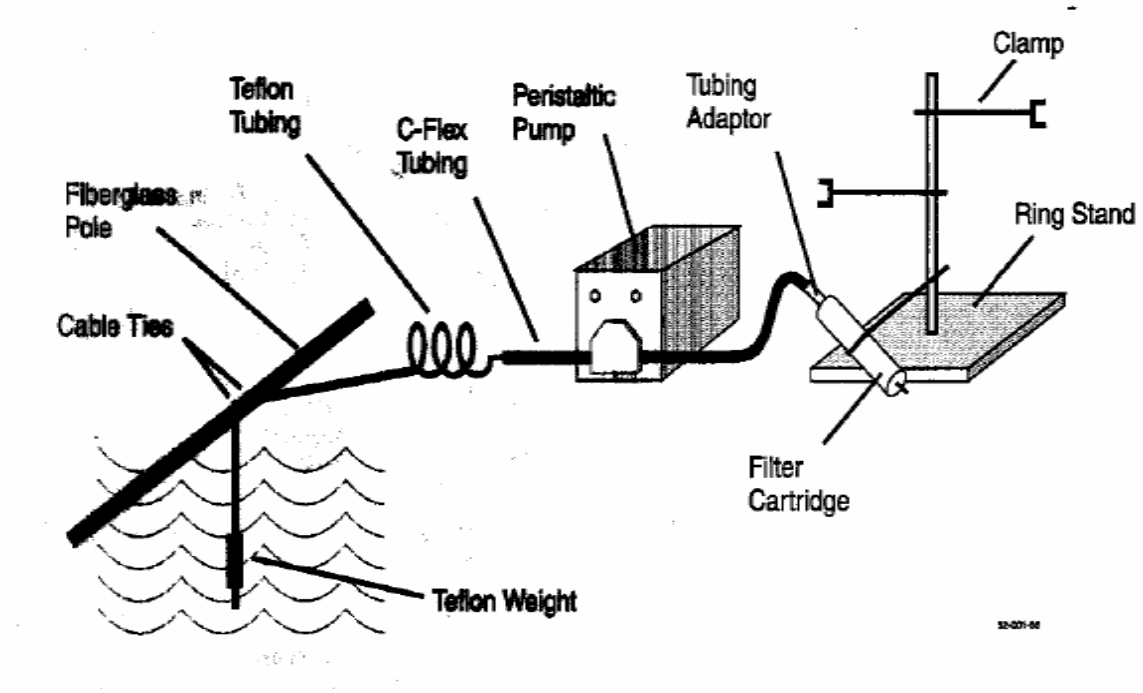

Figure from EPA Method 1699

Figure 5. Kemmerer Sampling Device.

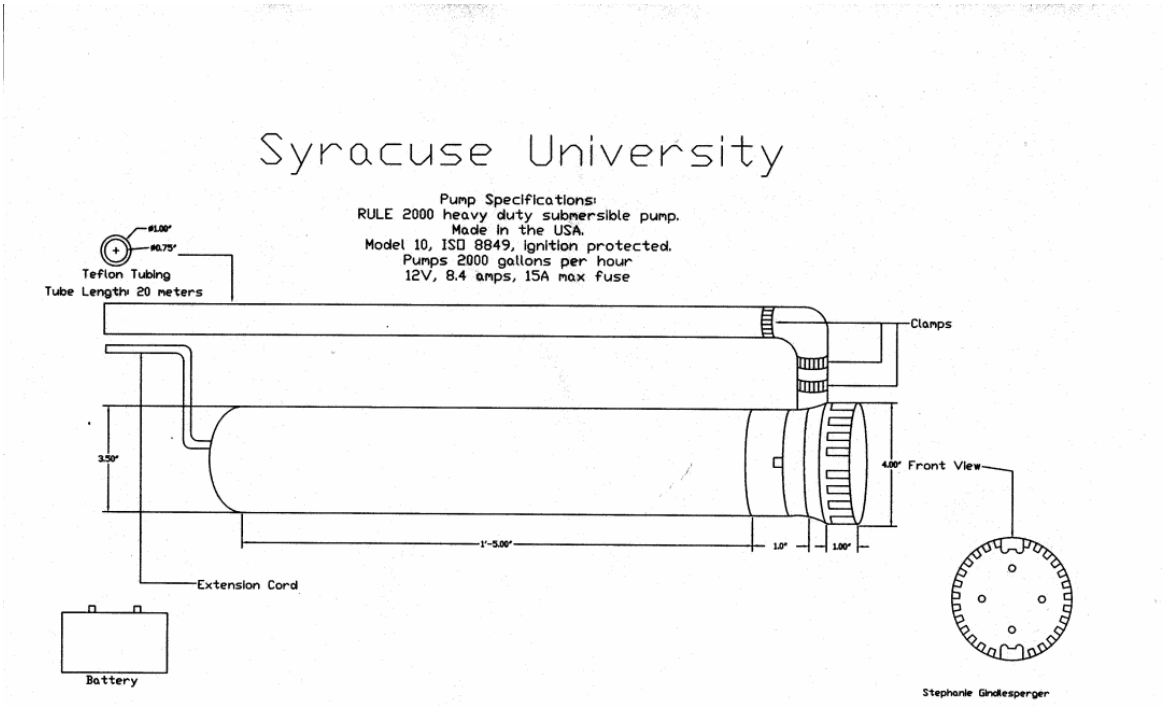

Figure 6. Submersible pump

Annex A
Quick Reference for Kemmerer Sampling Device:

A. Sampling Collection with Kemmerer sampling device:

1. The following steps detail sample collection using the Kemmerer sampling device shown in Figure 5 and described in Section 9.5.3.
2. The sampling team puts on gloves.
3. "Dirty hands" removes the sampling device from its storage container and opens the outer polyethylene bag.
4. "Clean hands" opens the inside polyethylene bag and removes the sampling device.
5. "Clean hands" changes gloves.
6. "Dirty hands" performs the sampling as follow:
    a. Device is opened by attaching the covers to the release mechanism.
    b. Then the device is lowered to the depth of interest.
    c. When at the depth of interest a weighted messenger is sent down the line to the release mechanism which triggers device closure.
7. The device is then raised to the surface.
8. For Oxic sample collection:
    a. Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.
    b. Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.
    c. "Clean hands" unscrews the cap and, while holding the cap upside down, discards the diluted acid solution from the bottle into a carboy for wastes (Section 9.14).
    d. The water sample can then be poured out into the bottles.
    e. After the bottle is filled (i.e., when no more bubbles appear)."Clean hands" replaces the cap of the bottle.
    f. Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.
    g. "Dirty hands" zips the outer bag Place bottles in a cooler and fill the cooler with ice and close.
    h. Fill out the chain of custody.
    i. Samples should be re-iced upon return to the lab to maintain a temperature of 4°C if samples will not be processed immediately.
    j. Samples are filtered if needed and preserved by adding 4 mL/L of pretested 11.6 M HCl at the lab.

9. For anoxic sample collection:
    a. Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.
    b. Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.
    c. "Clean hands" unscrews the cap and, while holding the cap upside down, discards the diluted acid solution from the bottle into a carboy for wastes (Section 9.14).
    d. After the sampling tubing has been attached to the device, turn on the pump nozzle so that water flows out at a slow rate.
    e. 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.
    f. Allow bottles to flush for three volumes, then cap and place in the cooler.
    g. Bottles that need reagents added should be capped, then uncapped, the reagent(s) added, recapped and inverted several times, then placed in the cooler.
    h. After the bottle is filled (i.e., when no more bubbles appear)."Clean hands" replaces the cap of the bottle.
    i. Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.
    j. "Dirty hands" zips the outer bag Place bottles in a cooler and fill the cooler with ice and close.
    k. After all bottles from a cooler are filled, fill the cooler with ice and tightly close the lid.
    l. Fill out the chain of custody sheet.
10. Samples should be re-iced upon return to the lab to maintain a temperature of 4°C if samples will not be processed immediately.
11. Samples are filtered if needed and preserved by adding 4 mL/L of pretested 11.6 M HCl at the lab.
12. Closing mechanism—"Clean hands" removes the closing mechanism from the body of the kemmerer sampler, rinses the device with 0.4% HCl, places it inside a new clean plastic bag, zips the bag, and places the bag inside an outer bag held by "dirty hands." "Dirty hands" zips the outer bag and places the double-bagged closing mechanism in the equipment storage box.
13. Sampling device "Clean hands" seals the large inside bag containing the collar, pole, and cord and places the bag into a large outer bag held by "dirty hands." "Dirty hands" seals the outside bag and places the double-bagged sampling device into the equipment storage box.
14. Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

Annex B
Glossary of Definitions

These definitions and purposes are specific to this sampling method but have been conformed to common usage as much as possible.

1. Ambient Water—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

2. Apparatus—The sample container and other containers, filters, filter holders, labware, tubing, pipets, and other materials and devices used for sample collection or sample preparation, and that will contact samples, blanks, or analytical standards.

3. Equipment Blank—An aliquot of reagent water that is subjected in the laboratory to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. The purpose of the equipment blank is to determine if the sampling devices and apparatus for sample collection have been adequately cleaned before they are shipped to the field site. An acceptable equipment blank must be achieved before the sampling devices and Apparatus are used for sample collection.

4. Trip blank/Bottle Blank-A 0.4% HCl solution is placed in a sample container in the laboratory, shipped to the field, exposed to sampling site conditions, and opened and closed in the field. The purpose of the Trip Blank/Bottle Blank is to determine whether the transportation to or the sampling site, or cleaning and storage and have contaminated the sample.

5. Field Blank—A 0.4% HCl solution is placed in a sample container in the laboratory, shipped to the field, and treated as a sample in all respects, including contact with the sampling devices and exposure to sampling site conditions, filtration, storage, preservation, and all analytical procedures. The purpose of the field blank is necessary when you cross a gradient collecting a second site (i.e., going from a high-concentration sample to a low concentration sample). A field blank may be to determine whether the field or sample transporting procedures and environments have contaminated the sample.

6. Field Duplicates (FD1 and FD2)—Two identical aliquots of a sample collected in separate sample bottles at the same time and place under identical circumstances using a duel inlet sampler or by splitting a larger aliquot and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

7. Matrix Spike (MS) and Matrix Spike Duplicate (MSD)—Aliquots of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.

8. Method detection limit—To establish the ability to detect an analyte, the analyst will determine the MDL according to the procedure at 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The MDL will be determined when a new operator begins work or whenever, in the judgment of the analyst, a change in instrument hardware or operating conditions would dictate that the MDL be re-determined.

9. Reagent Water—Water demonstrated to be free from the metal(s) of interest and potentially interfering substances at the MDL for that metal in the referenced method or additional method.

10. Trace-Metal Grade—Reagents that have been demonstrated to be free from the metal(s) of interest at the method detection limit (MDL) of the analytical method to be used for determination of this metal(s). The term "trace-metal grade" has been used in place of "reagent grade" or "reagent" because acids and other materials labeled "reagent grade" have been shown to contain concentrations of metals that will interfere in the determination of trace metals at levels listed in Table 1.

11. Field Triplicates (FT1 , FT2, and FT3)—Two identical aliquots of a sample collected in separate sample bottles at the same time and place under identical circumstances using a duel inlet sampler or by splitting a larger aliquot and treated exactly the same throughout field and laboratory procedures. Analyses of FT1, FT2 and FT3 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Center for Environmental Systems and Engineering (CESE)

STANDARD OPERATING PROCEDURE

1. Standard Operating Procedure for Zooplankton Sample Collection and Preservation and Secchi Depth Measurement Field Procedures

AP #CESE-ENV-310

Rev # 3-December 21, 2007 1 of 8

Prepared By: Ed Mason

Approved By: _____ Date: December 21, 2007
Edward Mason-Technical Review

Approved By: _____ Date: December 21, 2007
Mario Montesdeoca-Laboratory Manager

Approved By: _____ Date: December 21, 2007
Charles T Driscoll-Primary Investigator

Effective Date: December 21, 2007

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2. Summary of Test Method

2.1 Two sampling tows are performed at each station. One tow is from 20 meters below the water surface to the surface using a 63 microns net. The other tow is from 100 meters below the surface to the surface using a 153 microns net. If the station depth is less than the specified depth, the tow is taken from two meters above the bottom to the surface. The tow net, with a screened sample bucket attached at the bottom, is lowered to the desired depth, and raised at 0.5 meters/second to collect zooplankton from the water column. After lifting the net from the water it is sprayed with a garden hose to wash the organisms down into the bucket. The sample is concentrated into the sample bucket.

2.2 The sample is treated with Alka-Seltzer and then washed and preserved with ethanol to prevent decomposition of the zooplankton for long-term storage.

2.3 For regulated and contracted work, the samples are maintained at 3-5^0 C, centrifuge, and freeze-dry within 48 hours. Samples are analyzed within 6 months.

3. Scope and Application

3.1 This Standard Operating Procedure describes the field sampling and preservation of zooplankton samples and the measurement of Secchi depth for streams and lakes.

4. Applicable Matrix or Matrices

4.1 This method is applicable to Zooplankton samples.

5. Method Detection Limit

5.1 N/A

6. Definitions

6.1 N/A

7. Interferences

7.1 Weather conditions that create current or mixing will interfere or will stop the sampling event.

8. Safety

8.1 All analysts will attend the "Chemical Hygiene Plan" training provided by the Environmental Health Office (EHO).

8.2 It is strongly advised that the analyst check the material Safety Data Sheets for any reagent he/she is not familiar with. Product handling and protective measures should always be observed.

8.3 The analyst shall practice standard laboratory safety procedures as specified in the Chemical Hygiene Plan prepared by the EHO.

8.4 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

8.5 During sampling, caution, common sense, and good judgment should dictate appropriate safety gear to be worn in any given situation on deck. Hard hats, gloves, and steel-toed shoes must be worn in working conditions where there is a possibility of injury to the head, hands, or feet; however, if in doubt, please ask the Chemical Hygiene Officer.

8.6 Collecting samples in cold weather, especially around cold water bodies, carries the risk of hypothermia and frostbite. Make sure that the sampling team is dressed appropriately for sampling on cold weather. Dressing on layers allows trapping air, which helps to keep you warm, tightly woven, waterproof clothes are best, and because most body heat is lost through the head, a head gear should be worn. Also it is important to know your team members background to make sure that they know how to take care of themselves. During the sampling events, team members should watch each other for symptoms of hypothermia and frostbite. Dehydration is also a possibility on cold weather, and make sure that all team members are drinking water.

8.7 Collecting samples in extremely hot and humid weather carries the risk of dehydration and heat stroke. Sampling team members should carry an adequate supply of water or other liquids for protection against dehydration in hot weather.

9. Equipment and Supplies

Plankton tow net, 63 microns pore size, 0.5-m diameter (D:L=1:3)
Plankton tow net, 153 microns pore size, 0.5-m diameter (D:L=1:3)
Tow net sample bucket with a 61 microns pore size metal screen
Tow net sample bucket with a 151 microns pore size metal screen
Flowmeters - Kahl Scientific Company, 005WA200
Weights, 10-20 lbs.
Safety line for sample bucket
Garden hose
500-mL Teflon sample bottles
Repipettor with 20-mL delivery capability
Graduated cylinder with 50 - 100 mL capacity
Waterproof notebook
Gloves (rubber, vinyl or nitrile)
Winch with metering sheave and hydrographic line
50 mL centrifuge tube (Catalogue #: Corning 430828)
Freeze Dryer (Lanconco Freezone 6plus)

10. Reagents and Standards

10.1 Milli-Q water

10.2 95% Ethanol -95% un-denatured ethyl alcohol.

10.3 Alka-seltzer-Over the counter medication tablet manufacture by Bayer corporation

11. Sample Collection, Preservation, Holding Times, Shipment, and Storage.

11.1 The preservation type and the holding times depend on the resources available and the required time for the results. All samples are collected in a 500 ml Teflon bottles.

11.2 For long-term storage and delay processing for analysis, the samples are treated with Alka-Selzer, and then, washed with ethanol and preserved with 95% un-denatured ethanol. After preservation, the samples are store on the dark and on a cool environment.

11.3 Samples that are from regulated (for Honeywell Onondaga Lake Program) or contracted work that require immediate processing have a holding time of six month after freeze-dried. For freeze-drying, the samples are placed in a cooler with ice, transferred to the laboratory, and placed in a refrigerator. Within 48 hours, the samples are centrifuged and freeze-dried.

12. Quality Control and Documentation

12.1 Quality Control

12.1.1 Field QC samples

12.1.1.1 Duplicate and split field samples will be taken for every 10 samples, and Duplicate samples are also collected for each net mesh.

12.1.1.2 Field triplicate samples are collected as per QAPP requirements.

12.1.1.3 The field duplicates, split and triplicate are collected from an anchored vessel 5 minutes after the original sample was collected from the same location.

12.1.1.4 Field blank (net blank) is collected one per sampling event.

12.1.2 If the initial and final metering sheave readings do not correspond to within a meter, corrective action such as using a heavier weight, and/or lubricating the sheave is taken prior to rerunning the tow.

12.2 Documentation

12.2.1 All bottles are labeled with the following information:

12.2.1.1 Sampling site

12.2.1.2 Sampling Date

12.2.1.3 Person performing the sampling

12.2.1.4 Analysis requested

12.2.2 The proper chain of custody is filled and signed with the same information.

13. Calibration and Standardization

13.1 Flow meter Calibration

13.1.1 During each survey season, when calm weather permits, the flow meter is calibrated. This should be done at the beginning of each cruise if possible. This is accomplished by lowering the rim of the net with flow meter (without the net cloth) to the 20 meters depth, raising it at 0.5 meter/second, and recording the resulting flow meter reading. This is repeated 20 times. Readings are recorded on the appropriate data sheet and entered into the computer database. The mean flow meter value of these 20 readings is then used along with the reading during sampling to calculate the net efficiency.

13.1.2 If the meters begin to give erratic readings that do not correlate with changes in tow depth, line angle, or evidence of net clogging, the chief scientist should be consulted. The meters may need to be cleaned or replaced. Meters should be recalibrated after servicing.

13.2 Cable angle

13.2.1 The cable line of the winch should be nearly vertical to obtain reproducible results. If the angle between the cable line and a vertical line drawn from the top of the cable line to the

water surface exceeds 30° during retrieval the sample is discarded, the net is washed and the tow is repeated. If weather conditions continually produce drifting of the tow net such that the less than 30° requirement can not be met, the sampling event is stopped until proper sampling can be performed.

13.3 Uninterrupted towing

13.3.1 If the tow is interrupted by stopping or changing the winch speed, the sample is discarded, the net is washed, and the tow repeated.

14. Procedure

14.1 Zooplankton Sampling

14.1.1 The appropriate sample bucket is attached to the net and the net is attached to the winch cable. A rope bridle is clipped to the net frame and extended to the cod end of the net where it is attached to the sample bucket. A weight is added to the lower end of the rope and the bridle is adjusted so that the frame of the net (not the mesh netting) supports the weight.

14.1.2 The protective cover is removed from the flow meter which has been mounted slightly off-center in the mouth of the net. The flow meter to set to zero.

14.1.3 Field Blank (Net blank)- the field blank is taken at the beginning of the sampling event. 'Clean hands' will fill the ½ liter vessel with lake water and pour through the filtering apparatus into the large beaker. 'Clean hands' will remove the dirty gloves and put on a new pair of gloves to pour the beaker contents into a blank sampling vessel. The blank will be placed on ice.

14.1.4 In Lakes, with few organisms, two tows must be done for each sample collected with the 63 microns mesh net. The two tows are combined into one sample bottle. Flowmeter readings from both tows are added up and reported as one reading for the combined sample

14.1.5 The winch operator deploys the net so that the rim is at the surface of the water and then sets the cable sheave to zero.

14.1.6 The cable is deployed until the sheave reads 20 meters (63 microns net) or 100 meters (153 microns net).If the total water depth is less than the specified sample depth, then the rim is only lowered to two meters above the bottom. The net is retrieved at 0.5 meter/second. The sheave reading is checked to be sure that it again reads zero as the net rim clears the water surface. If the cable is slipping or the sheave is not functioning properly, adjustments must be made to the cable metering system.

14.1.7 The flowmeter number, final reading, and average net angle off of vertical during retrieval are recorded.

14.1.8 The net is rinsed down gently from the outside with ambient temperature lake water to wash all of the organisms off the net cloth and into the sample bucket.

14.1.9 The collection bucket is swirled gently to concentrate the sample. The bucket is detached and the contents transferred to the sample storage bottle. The bucket is gently rinsed from the outside at least three times.

14.1.10 Once the sample is condensed into the bucket, the person designated as dirty hands will pour the contents into the modified filtering apparatus, which has been placed in a large plastic beaker. Dirty hands will use the squeeze bottle still contained in the Ziploc bag to rinse out all contents from the bucket. Clean hands will pour the filtered contents into the THg sample vessel and make sure all zooplankton are removed from the filtering apparatus. Clean hands will fill the vessel with water up to the 50mL mark and place back into the clean bag, which is then placed back into the dirty bag. This sample is placed on ice. All clean THg sampling apparatus will be put away for the next step.

14.1.11 A final check is made to assure that the sample ID, flow meter ID, flow meter reading, cable angle, station code, total depth, depth of tow, date, time, net mesh, and operator code are recorded. The cover is placed over the flow meter and the net is brought inside for storage.

14.2 Secchi depth measurements

14.2.1 After completion of the zooplankton tows, a Secchi disk transparency measurement should be taken, if it is more than one hour after sunrise and one hour before sunset.

14.2.2 Unwind an amount of rope from the 30-cm diameter white Secchi disk equivalent to the estimated Secchi depth, plus about five meters.

14.2.3 Lower the Secchi disk from the shady side of the boat out of direct sunlight, until it is no longer visible.

14.2.4 Raise the disk slowly until it is just visible again.

14.2.5 Lower the disk once more until it disappears again. Make sure that you cannot see the disk. Secchi depths in the Great Lakes can be quite deep, and as a result, perspective effects can make the disk appear very small and difficult to see.

14.2.6 Keeping your eye on the spot on the rope that was just at the surface of the water as the disk disappeared, raise the rope just enough to grab the rope at that spot, and then tow in the disk.

14.2.7 Measure the length of rope from the disk to the spot you grabbed. This is the Secchi depth. The rope should be marked in meters; estimate the length to the nearest decimeter.

14.2.8 Field duplicates are taken for Secchi disk measurements each time a field duplicate is scheduled for collection for the Surface sample of a lake (the sample collected at 1 meter below the surface).Two different analysts should take the duplicate measurements and the acceptance criteria for these duplicates is less than or equal to 0.5 meters.

14.3 Sample Processing

14.3.1 The zooplankton samples should be refrigerated as soon as possible after collection.

14.3.2 The sample then stands for 30 minutes in the refrigerator.

14.3.3 Put the sample bottles in the centrifuge machine, four samples at a time, at an RPM of 1500 for five minutes. Decant water. Transfer remaining sample to a 50 mL centrifuge vial. Repeat this process until vials have a small volume of water remains. If any vials still have zooplankton close to the top of the vial after being run, put them into the centrifuge for a second time.

14.3.4 Decant as much clear liquid from the vial as possible without losing any zooplankton.

14.3.5 Filled the vial with DI water, and then centrifuge the vials once again (make sure you put vials with similar levels of liquid in the machine at the same time). Dump as much clear liquid as possible again. Ideally, you want the liquid level to be under 7.5 mL without losing any of the zooplankton at the bottom.

14.3.6 Place in freezer overnight.

14.3.7 Remove samples from freezer and remove the caps of the vials and tightly parafilm the tops of the vials. Poke 4-6 small holes in the parafilm. Then place as many vials as possible straight up in a freeze-dry glass container. Place the rubber stopper on top of the container and place a bent glass tube with a piece of freeze-dry filter paper at the end into the hole in the rubber stopper. Connect the other end of the tube to the freeze-dry apparatus. Then, turn the knob so that the notch in the knob faces the opposite direction of the hole on the knob. Suction should be visible inside the container. Leave the samples on the freeze-dryer for at least 48 hours. When adding samples to the freeze dryer, only turn one knob at a time. Wait for vacuum to reach the green light level.

14.4 The samples are now ready for analysis and for long term storage.

15. Calculations

15.1 N/A

16. Method Performance

16.1 N/A

17. Pollution Prevention

17.1 Any waste created during the sampling event will be brought back to the laboratory for proper disposal.

18. Data Assessment, Review, and Acceptance Criteria of QC Measures

18.1 N/A

19. Corrective Actions for Out-of-Control Data

19.1 N/A

20. Contingencies for Handling Out-of-Control or Unacceptable Data

20.1 N/A

21. Waste Management

21.1 Guidelines for managing laboratory wastes are addressed in the "Hazardous Waste Management" manual.

21.2 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

22. References:

22.1 EPA- Method LG402-Revision 10, "Standard Operating Procedure for Zooplankton Sample Collection and Preservation and Secchi Depth Measurement Field Procedures", March 2005.

22.2 Haney, J.F., and D.J. Hall. 1973. Sugar - coated *Daphnia*: A preservation technique for Cladocera. Limnol. Oceanogr. 18: 331-333.

22.3 Prepas, E. 1978. Sugar frosted *Daphnia*: An improved fixation technique for Cladocera. Limnol. Oceanogr. 23: 557-559.

23. Tables, Diagrams, and Flowcharts

23.1 N/A

ATTACHMENT 2

Analytical Standard Operating Procedures

Reference Number	Title of Standard Operating Procedure (SOP)	Originating Organization
L-1	UFI SOP 104 - Chloride, high range (SM 18–20 4500 Cl^- C)	UFI
L-3	UFI SOP 105 - Ammonia (as N) (U.S. EPA Method 350.1)	UFI
L-2	UFI SOP 106 - Nitrate/nitrite (as N) (U.S. EPA Method 353.2)	UFI
L-4	UFI SOP 110 - Organic carbon, total/total dissolved (as C) (SM 18–20 5310C)	UFI
L-5	UFI SOP 112 - Sulfide (as S), high range (SM 18 4500 S^{2-} E)	UFI
L-7	UFI SOP 203 - Carbon, inorganic dissolved and total (SM 18-20 5310C)	UFI
L-6	UFI SOP 212.1 - Sulfide (as S), high range (SM 20 4500 S^- G)	UFI
L-8	UFI SOP 216 - Chlorophyll (U.S. EPA 445)	UFI
L-9	UFI SOP 217 - Dissolved gas: methane, carbon dioxide, nitrogen (Addess 1990)	UFI
L-10	UFI SOP 218 - Ferrous iron (Heaney and Davidson 1977)	UFI
L-11	SU SOP AP #CESE-ENV-1631 - Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry (U.S. EPA Method 1631E)	SU

L-12	SU SOP AP #CESE-ENV-1630 - Methyl mercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS (U.S. EPA Method 1630)	SU
L-13	SU SOP AP #CESE-ENV-7473M - Mercury in solids and solutions by Milestone thermal decomposition amalgamation and atomic absorption spectrophotometry	SU
L-14	SU SOP AP #CESE-ENV-Z-V1630 - Methyl mercury in biomass by digestion, aqueous ethylation, purge and trap, and CVAFS (U.S. EPA Method 1630	SU
L-15	UFI SOP UFI-ISUS/Optical frame	UFI

Upstate Freshwater Institute Inc.

Environmental Testing Laboratory
Methods Manual

Revision 1.0
Effective: March 15, 2007

Approvals:

Approved: MaryGail Perkins 1/30/08
Laboratory Director MaryGail Perkins Date
Phone Number: (315)431-4962 ext. 115

Approved: MaryGail Perkins 1/30/08
Quality Assurance Officer MaryGail Perkins Date
Phone Number: (315)431-

Approved: Steven W. Effler 1/30/08
Director of Research Steven W. Effler Date
Phone Number: (315)431-4962 ext. 102

Prepared by:
M.G. Perkins, Laboratory Director
Upstate Freshwater Institute, Inc.
224 Midler Park Drive
Syracuse, NY 13206
Website: www.upstatefreshwater.org
Email: ufilab@upstatefreshwater.org
Phone: (315)431-4962
Fax: (315)431-4969

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Standard Operating Procedures – Methods

Alphabetical List of Methods

Chloride (High Range)……SOP 104

1) Test Method: <u>CHLORIDE, HIGH RANGE > 100 mg/L SM 4500 Cl- C.</u>

2) Applicable Matrix or Matrices: drinking, surface and saline waters, domestic and industrial wastes.

3) Detection Limit: See UFI Controlled Document No. 12.

4) Scope and Application: drinking, surface, and saline waters, domestic and industrial wastes

5) Summary of Test Method: Chloride can be titrated with mercuric nitrate $Hg(NO_3)_2$, because of the formation of soluble, slightly dissociated mercuric chloride. In the pH range 2.3 to 2.8, diphenylcarbazone indicates the titration endpoint by formation of a purple complex with excess mercuric ions. Increasing the strength of the titrant and modifying the indicator mixtures extends the range of measurable concentrations.

6) Definitions:

Chloride- One of the major inorganic anions found in water and wastewater.
Soluble- Capable of being easily dissolved.

7) Interferences: Chromate, ferric and sulfide ions in excess of 10 mg/L

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:

- titration burette (25ml)
- stir plate
- stir bars
- beakers (250ml)
- class A pipette: 25ml, 50ml.
- 100ml Graduated Cylinder

10) Reagents and Standards:

Standard sodium chloride 500 $mgCl^-/L$ – Currently use purchased 0.0141N=0.0141M. Sodium Chloride, or make by dissolving 1.648g NaCl (dried @ 105^0 C for 1 hour) in Type II water, dilute to 1 liter.

Mixed indicator reagent (high range) - Use purchased prepared LabChem reagent Diphenylcarbazone Bromophenol Blue Mixed Indicator.

Mercuric Nitrate Titrant 0.141N – Use purchased prepared LabChem reagent

Nitric Acid 0.1N – Dilute 6.4 ml conc. HNO_3 to1 liter.

Reference Solution (1000 mg Cl^-/L)-Take 100mls of 10,000 mg Cl^-/L and dilute with DI in a 1000ml volumetric flask (see below for preparation of 10,000mg Cl^-/L).

High Range Spike Solution (10,000 mg Cl^-/L)- Dissolve 16.48g NaCl in one Liter of Type II water.

11) Sample Collection, Preservation, Shipment and Storage: chloride is a very conservative constituent. Samples can be collected in plastic or glass**,** no special storage is required. Holding time is 28 days.

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: Standardize the titrant with each use in the following manner:

1) Measure 50mls of the purchased 500mgCl^-/L of Sodium Chloride using a class A 50ml glass pipette into a clean beaker.
2) Add 50mls of Type II waterto bring the total volume to 100mls. The 50 ml of water is only to make endpoint determination comparable with the samples.
3) To beaker add approximately 0.5 ml mixed indicator reagent (high range) to the sample, the color should be reddish purple.
4) Add 0.1N drop wise until the color just turns yellow (about 8 drops)
5) Place beaker with stir bar on stir plate and Titrate with mercuric nitrate titrant (0.141N) to first permanent dark purple, record volume titrated in appropriate laboratory worksheet.
6) Repeat three times

Calculation of Titrant Standardization

$$\text{Concentration of Titrant mg Cl/ml} = \frac{\text{mg Cl in standard* vol. of Std/1000}}{\text{ml titrant to endpoint}}$$

Example:

25 mls of the 500mgCl^-/L standard takes 2.5ml titrant to endpoint

$$\frac{(500\text{mg/l})(.025\text{L})}{2.5} = 5.0 \text{ mg Cl/ml titrant}$$

14) Procedure: After standardizing your Titrant,
1) Prepare a Method Blank by measuring 100mls Type II water and titrate by repeating steps 1-5 and record result.
2) Next prepare a Reference by measuring 25mls of the 1000mgCl^-/L Reference Solution with a 25ml glass pipette, place in a clean beaker. Add 75 ml of Type II water into the beaker to bring volume up to 100mls. Titrate by repeating steps 1-5 and record the results.
3) Next, using a graduated cylinder, measure out 100mls of Type II water into a beaker using an Eppendorf pipette, add 0.5ml of prepared spike solution (10,000mgCl^-/L), repeat steps 1-5. Record this result as the LCS.
Analyze all samples by repeating steps 1-5, and recording the results on an appropriate laboratory worksheet.

Sample Volume: Generally 50 ml of sample plus 50 ml of Type II water for a total volume of 100mls. However, if increasing the sample volume provides for a better and more accurate endpoint; omit the Type II water and record the sample volume in the appropriate laboratory worksheet.

15) Calculations:

$$Cl^- = \frac{(\text{Average of Titrant std} * \text{Volume of Titrant})}{(\text{Sample volume}/1000)}$$

16) Method Performance: According to Standard Methods, using a synthetic sample containing multiple ions; 241 mg Cl^-/L, the method has a relative standard deviation of 3.3% and a relative error of 2.9%.

UFI laboratory follows the following chart for identifying and running QC samples. Each type of sample may not be applicable to every analysis. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Method Blank	A sample of Deionized water.	One every batch	MB
Reference (100mgCl/L)	A standard sample, made from either a different lot # solution, a different manufacturer, or another method (dissolving a solid)	Every sample batch	REF
Laboratory Control Sample or Blank Spike (100mgCl/L)	A spike of unknown concentration to Type II water	One per sample batch	LCS

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
Matrix spike	A spike of known concentration 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

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 there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper control line and a lower control line. The upper and lower warning lines are 2 standard deviations from the mean. The upper and lower control lines are three standard deviations from the mean. The process should be shut down for trouble shooting if the following occur:

- A single action outside the action line.
- 2 out of 3 consecutive measurements between the warning and action lines
- 7 consecutive measurements above or below the center line
- 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 non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. Flags are located in UFI Controlled Document No. 12.

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. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

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. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. Wastes from this test can be washed down the sink with the tap running.

22) References:

1) Standard Methods 20th Edition 4500-Cl^- C. pp 4-68-69

2) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data:

Ammonia (as N)……..……SOP 105

1) Test Method: **NITROGEN, AMMONIA** USEPA method 350.1

2) Applicable Matrix or Matrices: drinking, surface and saline waters, domestic and industrial wastes.

3) Detection Limit: Published: 10 ug/L
Working: 5 ug/L

4) Scope and Application: This method covers the determination of ammonia in drinking, surface, and saline waters, domestic and industrial wastes in the range 10 – 5000 ug/L NH_4 as N.

5) Summary of Test Method: Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside.

6) Definitions: Ammonia is naturally present in ground waters and other systems as it is produced mostly by the hydrolysis of urea and the deamination of organic-nitrogen containing compounds. Its levels in natural systems should be low, as it adsorbs to soil and clay particles.

7) Interferences: Calcium and magnesium ions may be present in concentrations sufficient to cause precipitation problems during analysis. A 5% EDTA solution is used to prevent the precipitation of calcium and sodium ions in river water

8) Safety: Always wear safety goggles, gloves and lab coats when handling acids or other toxic substances. Use caution when handling phenol, skin contact can cause burns. 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:

- 0.45 um mixed cellulose ester filters
- Technicon Autoanalyzer (AAII) System – sampler, analytical cartridge, pump, heating bath, colorimeter
- Fisherbrand sampling vials (4.0mL)
- At least 8 100mL volumetric flasks
- Transfer pipets covering the desired standard range (1ml-20ml)
- Fisherbrand pump tubes of various size described on attached instrument setup sheet.
- Eppendorf pipettes

10) Reagents and Standards:

1) Sulfuric acid 5N (air scrubber sol'n) - Carefully add 139 ml conc. sulfuric acid to Type II water, cool, dilute to 1 liter.

Hold time: two months

2) Sodium phenolate (nPHEN+JD) – Add 32g of NaOH into a flask, then add Type II water to fill it halfway. The reaction is exothermic, so cool the outside of flask with running water. Pour 93mL of liquefied phenol into the 1L flask while under the hood. Allow to stand 24 hours before use.
   Hold Time: two weeks

3) Sodium hypochlorite sol'n (nBL+JD) – Dilute 250 ml bleach containing 5.25% NAOCL (Clorox) to 500 ml with Type II water. Due to instability of the bleach, this reagent should be remade weekly with fresh bleach. If bought from Labchem, add 0.5 mL of Brij solution for every 1L.
   Hold Time: one month or on Labchem bottle.

4) EDTA 5% (disodium ethylenediamin-tetraacetate) – Dissolve 50g of EDTA (disodium salt) and approximately 6 pellets of NaOH in 1 liter of Type II water. Used to remove cation interference from samples with high cation concentration. Add 0.5 ml Brij-35 solution. This may be used at operator's discretion.

5) EDTA 0.5% (nEDTA+JD) - Dissolve 5g of EDTA (disodium salt) and approximately 6 pellets of NaOH in 1 liter of Type II water. Add 0.5 ml Brij-35 solution.
   Hold Time: one month

6) Sodium nitroprusside 0.05% (nNitro+JD) - Dissolve 0.5g of sodium nitroprusside (sodium nitroferricyanide) in 1 liter Type II water.
   Hold Time: one month

7) Stock Ammonia Solution 10 mgN/L (nNHSTOCK+JD) – Dilute 5 ml of prepared (LabChem Catalog# LC17940-1) 1000mgN/L to 500 ml with Type II water in a volumetric flask.
   Hold time: one month

8) Ammonia Spike - 1:1 ratio of working ammonia stock and Type II water. Ammonia and Nitrate are often run at the same time, so the spike can be prepared as 1:1 ratio of ammonia working stock to nitrate working stock.
   Hold Time: one month

9) Ammonia reference (nNHXREF+JD) – Add 5.71g of ammonium Nitrate (MW – 80.4) to a 1L volumetric flask.
   Hold Time: three months

10) Ammonia working reference (nNHXWORKREF+JD) – Pipette 5mL of the reference solution into a 500ml flask and dilute with Type II water
    Hold Time: one month

11) Ammonia reference used – Should be at a concentration similar to samples, made like a standard.
Hold time: Prepare daily

Standards:

Prepare standards as required by sample conc. range from the table below; prepare a minimum of 6 standards which bracket expected sample concentrations.

mls. 10mgN/L stock/100 mls	conc. ug/L
LOW RANGE	
0.1	10
0.3	30
0.5	50
1.0	100
2.0	200
3.0	300
HIGH RANGE	
0.1	10
0.3	30
0.5	50
1.0	100
5.0	500

Pipettes that are used should be to the highest accuracy possible. Pipette at ~ room temperature if possible.

11) Sample Collection, Preservation, Shipment and Storage: Filter samples**,** then refrigerate at 4°C. Holding time for preserved samples is 28 days. Freeze unacidified samples if hold time will be longer than 7 days.

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: Standards are placed at the start of every sample run. The software which is used for data collection from the AAII calculates and plots the calibration data. See instructions for AA and software use in the manual. The R^2 for the standards should be no less than 0.995.

14) Procedure:
Startup:

Replace tubes that look warn or flattened. Usually air tubes are replaced most often. Replace all tubes at one time for best results.
Wash door with isopropyl alcohol before placing over rollers.
Place tubing ends into appropriate Type II water reservoirs (chemicals harmful if mixed improperly). Be sure sampling arm is in DI reservoir, to do so rotate the cam to a notch section while the power button is on. Turn pump switch on. All Type II water to flush system for ~10 minutes.
*Note Type II water Reservoirs should be refilled periodically throughout entire day of sampling.
Check chemical bottles. Replace those that are too low to use. Turn off, place labeled tubes into corresponding reagent bottle, turn pump back on. Cover the reagents with parafilm.
Allow reagents to run through system for ~10 minutes.
Watch the real time screen to see when base line levels out start calibration.

Setting Baseline:
There are two channels attached to the AA, the ammonia channel is channel one. There are several knobs on the detector box for the ammonia channel. In the middle of the detector box are two knobs labeled A and B. Knob A controls the aperture that allows light to hit the sample cell. Knob B controls the aperture for the reference cell. Rotate knob A counterclockwise to increase the absorbance or to decrease the light transmitted. Turn clockwise to decrease absorbance or increase the light transmitted. In the New Analyzer program (NAP) click on "control" and select "real time". The baseline should fall between 5-7%. Rotate knob A accordingly to acquire the desired baseline. Large jumps in the baseline are normally due to air peaks. The bubbles may be too numerous or too long. To reduce the length of the bubbles tighten the tubing running underneath the plate by pulling on the tube in a direction away from the door.

Setting High Point:
Place sampling tray to position 37. Use a disposable glove (to avoid contamination) to take sample vials from the bag and place onto the center of the sampling tray. Pour 4 vials of highest standard solution into vials (rinsing once) and place on positions 37-40. Place pick into the large hole of the last sample of the sampling tray in order to stop the tray when that sample is analyzed. Push the power button to begin sampling. It takes approximately 10 minutes for the samples to reach the detector. When the samples arrive at the detector the absorbance should increase. When the sample seems to flatten use the black knob at the top end of the detector to adjust the absorbance. The desired absorbance falls between 95-97%. Final sample should not need adjustment. Allow the baseline to drop back to 5-7%. If the baseline is not correct, then reset the baseline and the high point.

Sampling:
1) Close the real time box and click "sample table" select "load"

2) Click the last table recorded from the main file menu and click "OK"

3) Click "file" select "save as" and same in that seasons folder the file renamed with the correct date.

4) Close the sample table.

5) Click on the black arrow next to sample table or go to the control dialog box to retrieve the saved table.

6) In the method box for channel one choose the NH3WQC file from the previous day. Type in the new date. Channel 2 will most likely be a nitrate method if nitrate is run at the same time. If not, then choose a dummy method and write the date+junk as the filename.

7) Obtain a sampling sheet and reagent sheet from the AA binder. Fill out the Reagent sheet with the reagents used that day.

8) The standard curve must be run first. The NH3WQC method file is programmed for the first sample to be the high standard, the next 6 samples are your standards in descending order. The sample sheet and the sample table should be labeled in a similar way. On the sample sheet write high STD, S6 for your high standard followed by S5, S4, etc. These should then be followed by a blank. References should now be run to check if the standards were made at the correct concentration. Run a duplicate of your reference solution followed by an internal standard such as S3 or S4. This series is followed by a blank. Sample vials should be rinsed with a little sample before filling on the sample tray. The Tray should be loaded and oriented, so that the first vial (high std) will be the first one the sampling arm takes from.

9) Make sure the pick is removed before turning on the power. At this point the pump should be on, the sampling button may need to be turned off and turned on again to begin.

10) Turn the control panel to the "on" position so the data is recorded on the computer.

11) Select "view" from the menu.

12) Double click channel one in the new window that appears.

13) In this magnified window of channel one click "sample table" from the menu. Fill out the sample table the same as the sample sheet with UFI ID numbers, saving often.

14) When the standards are all flagged by the computer, then check to be sure the $R^2>0.995$, and the curves appear linear.

15) Watch to make sure samples do not reach 100% absorbance. If samples reach 100% absorbance, then they will need to be diluted. Keep in mind that sample vials are ~4mL, so make dilutions based on 4mL total volumes. Contamination may occur in the next sample so rerun if suspect. If a sample is expected to be high, then follow it by a blank and dilute accordingly. Dilution factors are recorded in the dilution column on the sample table on NAP and on the worksheet. The sample that went over 100% absorbance should get a slash on the column marked NH3 on the worksheet. Samples that are acceptable (not over 100% and not contaminated) get a y.
*NOTE - If a standard goes over 100% there was a baseline shift and the system will need to have the baseline reset as well as the high concentration point.

Shut down:

1) The pick should be placed in the large hole of the last sample.

2) Allow time for the final sample and the baseline flag to be calculated. When the run is complete a blue baseline should appear across the bottom of the screen.

3) Turn off data collection on the computer.

4) Remove the tubes from the Type II water and flush system with air until water is removed, or, at the operator's discretion, leave with Type II water in tubes, if used on a routine basis.

5) Turn off pump when all water is removed, or when done rinsing.

6) Take off the door and release tube tension by removing one of the tube holders.

7) Pour waste down the drain flushing with water. All waste from channel two should be in one container. DO NOT MIX WASTE BETWEEN CHANNEL ONE AND TWO. A HARMFUL REACTION OCCURS.

8) Turn off the power strip to the auto-analyzer.

Reporting Data:

1) Edit all peaks to ensure they were flagged at the pure sample point and not on air bubbles

2) Check to ensure no peaks were missed and flags line up with the sample name. Use the "Edit peaks" function to delete or add peaks.

3) Print the standard curve on the "standards" window.

4) Print the data points from the channel one window.

Maintenance (Routine):

All Maintenance is to be logged in the maintenance and repairs logbook.

1) Bulbs are to be replaced at the beginning of each field season or when needed.

2) Tubes are to be replaced biweekly or as needed. Tubes will be flattened or gray if needed to be changed.

3) The tubes are to be cleaned with the following procedure once a month or as needed.
   a) Attach 5N sulfuric acid through all lines. Run for 15 minutes with the Cd column off.
   b) Rinse with Type II water for 15 minutes
   c) Run 1N NaOH for 15 minutes with the Cd column off.
   d) Rinse with Type II water for 15 minutes

4) Pour 3mL of concentrated sulphuric acid in volumetric flasks and dilute with DI until full in order to destroy algae. Performed each week and left on weekends to stand.

15) Calculations: The software associated with AAII does all necessary calculations.

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. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
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
Reference	A standard sample, made from either a different lot # solution, a different manufacturer, or another method (dissolving a solid)	Every sample batch	Ref
Continuing Calibration Verification	A standard sample, run throughout the course of the run, generally of varying concentration, and near the expected sample concentration range(s)	First sample, before running others, every 10-15 afterwards, and the last sample of any run NOTE: If curve is not run daily, highest standard must be run as a CCV	CCV
Initial Calibration Verification	A CCV done at the beginning of the run	1st sample	ICV

Laboratory Control Sample or Blank Spike	A spike of unknown concentration to Type II water	One per sample batch	LCS or BS
Matrix spike	A spike of known concentration to sample matrix	Every 20 samples or one per batch if less than 20 samples	SPK
Matrix Spike Duplicate	Same as above, repeated	One per month or ~250 samples	SPKDUP
Continuing Calibration Blank	Blank Sample	Every ten, or one per batch, following CCV	CCB
Dilution Duplicate	Dilution of original sample, diluted to ½ of dilution concentration	One per sample batch, if samples diluted	DILDUP
Triplicate	An identical sample to two others, from the same container as the duplicate	One per month or ~250 samples	TRIP

17) Pollution Prevention: Dispose of the wastes in accordance with proper laboratory procedures. This procedure has no discernible negative impact on the environment.

18) Data Assessment and Acceptance Criteria for Quality Control Measures:
Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. The following table charts the flags utilized, and their meanings.

Data Flag ID	Meaning of Flag
F1	Sample analyzed/received past holding time
F2	Sample diluted to run within calibration curve
F3	Sample outside calibration curve
F4	Lower than normal volume of sample analyzed
F5	Sample not digested/prepared properly
F6	Sample not preserved properly
F7	Sample received outside “normal” temperature limits
F8	Sample container inappropriate
F9	Sample container broken/cracked/leaked
F10	Sample taken from container other than specified analyte

F11	Data associated with failed spike/LCS
F12	Data associated with failed CCV/CCB
F13	Data associated with failed duplicate

Detection limits are determined semi-annually and filed in the instrument log book.

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. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

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. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. Wastes from this test can be washed down the sink with the tap running.

22) References:

1) Methods for Chemical Analysis of Water and Wastes. 1983. USEPA method 350.1 pp. 350.1.1

2) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data:

Nitrate/Nitrite (as N)…….……SOP 106

1) Test Method: **NITROGEN, NITRATE-NITRITE-** USEPA method 353.2

2) Applicable Matrix or Matrices: drinking, surface and saline waters, domestic and industrial wastes.

3) Detection Limit: Published: 10 ug/L
Working: 5 ug/L

4) Scope and Application: This method pertains to the determination of nitrite singly, or nitrate + nitrite in surface and saline waters and domestic and industrial wastes.

5) Summary of Test Method: A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by deionizing with sulfanilamide and coupling with N-(1-naphyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colormeterically. Separate, rather than combined nitrate + nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.

6) Definitions:

Chelate- To combine (a metal ion) with a chemical compound to form a ring compound, or to remove (a heavy metal, such as lead or mercury) by means of a chelate, such as EDTA.

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; smelt.

7) Interferences: Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrite is found in a soluble state, the sample may be pre-filtered. Low results might be obtained for samples which contain high concentrations of iron, copper, or other metals. EDTA is added to the samples to eliminate this interference.

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:

- 0.45 um mixed cellulose ester filters, Technicon Autoanalyzer (AAII) System – sampler, analytical cartridge, pump, and colorimeter
- Fisherbrand sampling vials (4.0mL)
- At least 8 100mL volumetric flasks

- Transfer pipets covering the desired standard range (1ml-20ml)
- Fisherbrand pump tubes of various size described on attached instrument setup sheet
- Eppendorf pipets

10) Reagents and Standards:

1) Color reagent – nCOLOR+JD
To approximately 800 ml of Type II water, add, while stirring 100 ml conc. phosphoric acid, 40g sulfanilamide, and 2g N-1-napthylethlenediamine dihydrochloride. Stir until dissolved and dilute to 1 liter. Store in a brown bottle and keep refrigerated.
Hold Time: 3 Months, but discard if the solution becomes discolored.

2) Hydrochloric acid 6N – Prepare using a 1:1 ratio of concentrated HCl and Type II water.
Holding time: six months

3) Copper sulfate solution 2% (n10CS+JD) - Dissolve 20g $CuSO_4 \cdot 5H_2O$ in 500 ml Type II water, dilute to 1 liter.
Holding Time: 1 year

4) Ammonium chloride-EDTA solution – nAMC+JD
Dissolve 85g of reagent grade ammonium chloride and 0.1g of disodium ethylenediamin-tetraacetate in 900 ml of Type II water. Adjust the pH to 8.5 with concentrated ammonium hydroxide and dilute to 1 liter. Add 0.5 ml Brij-35. Alternately use prepared (Lab Chem) solution, add 0.5 ml Brij-35/L.
Holding Time: one month

5) Nitrate Reference Stock 1000ppm or 1ml=1mg N (nNHXREFStock+JD) - Add 5.71g of ammonium Nitrate to a 1L volumetric flask.
Holding Time: three months

6) Nitrate working reference (nNHXWORKREF+JD) – Pipette 5mL of the reference stock solution into a 500ml flask and dilute with Type II water
Holding Time: one month

7) Nitrate reference used – minimum of two reference solutions are prepared to encompass each range. Concentrations of 30 and 100ug/L are used to demonstrate the low range NOx and high range NH_3. While concentrations of 100 and 1000ug/L are prepared to demonstrate the low range of NH_3 and high range of NOx.
Holding Time: Prepared Daily

8) Nitrite Reference Stock 1000ppm or 1ml=1mg N – nNO2REFStock+JD
Add 4.93g of sodium Nitrite to a 1L volumetric flask.

Holding Time: three months

9) Nitrite working reference (nNO2WORKREF+JD) – Pipette 5mL of the reference stock solution into a 500ml flask and dilute with Type II water
Holding Time: one month

10) Nitrite reference used – minimum of two reference solutions are prepared to encompass each range. Concentrations of 30 and 100ug/L are used to demonstrate the low range NOx and high range NH_3. While concentrations of 100 and 1000ug/L are prepared to demonstrate the low range of NH_3 and high range of NOx.
Holding Time: Prepared Daily

11) Nitrate Spike Solution - (nNHXSPK+JD) – 1:1 ratio of working Nitrate stock with Type II water. Ammonia and Nitrate are often run at the same time, so the spike can be prepared as 1:1 ratio of Nitrate working stock with ammonia working stock.
Holding time: one month

12) Nitrite Spike Solution - (nN02SPK+JD) –.1mL of Nitrite working stock to 10mL of Type II water.
Holding time: one month

NITRATE Standards:

Nitrate Working Stock Solution – nNO3STOCK+JD
10 mgN/L – Dilute 5 ml of commercial standard (Lab Chem) 1000ppm or 1mL=1 mgN to 500 ml with Type II water.
Holding Time: one month

Prepare standards as required by sample conc. range. An example table is below. Prepare a minimum of 6 standards which bracket expected sample concentrations.

mls. 10mgN/L stock/100 mls	conc. ug/L
LOW RANGE	
0.1	10
0.3	30
0.5	50
1.0	100
3.0	300
5.0	500
HIGH RANGE	
1.0	100
3.0	300

5.0	500
7.0	700
10.0	1000
15.0	1500
20.0	2000

NITRITE Standards:

Working Nitrite Stock Solution 10 mgN/L – nNO2STOCK+JD
Dilute 5 ml of prepared commercial standard (Lab Chem) 1000mgN/L to 500 ml with Type II water. Prepare daily as needed.
Hold time: one month

Prepare standards as required by sample conc. range. An example table is below. Prepare a minimum of 6 standards which bracket expected sample concentrations.

mls. 10mgN/L stock/100 mls	conc. ug/L
RANGE	
0.1	10
0.3	30
0.5	50
1.0	100
2.0	200
5.0	500

TO PREPARE THE CADMIUM REDUCTION COLUMN:

To wash cadmium granules (new or used): Place granules into beaker add 6N HCL (1:1) swirl and drain HCl from beaker. Then rinse with Type II water three times. The color of the cadmium should be silver. Place enough 2% copper sulfate solution to thoroughly cover granules, let stand for five minutes or until the blue color partially fades (granules will fade to black). Gently bath the cadmium-copper with Type II water (at least 5times) to remove all the precipitated copper, be sure granules are always immersed in liquid to avoid aeration.

To fill column: Make sure tubing is clean by inserting a 6N HCL dipped pipe cleaner into tube. While holding the tubing in a U shape, fill with Type II water to prevent entrapment of air bubbles. Insert a small tuft of aquarium filter wool into one end of the tube, place in plastic plug. Transfer the copper-cadmium granules into the tubing using a reagent spatula being careful to exclude air bubbles. Cadmium will settle, so flick tubing occasionally to ensure tight packing of granules. Insert aquarium wool in the other end when column is packed. Making sure column knob is in the "on" position and reagents are running through system (do not allow air bubbles to enter line), attach the new column at one end, (closest to you) wait for bubbles to move through the system. Connect the other end of the column once there is obvious flow through the column.

To condition new column: Turn column knob to "off" position and disconnect the NO_2/NO_x line from analyzer and place into a 100 mL graduated cylinder. Fill cylinder with 10mL of Nitrate working stock solution and dilute with Type II water to 100mL. Turn column knob to "on" position making sure no air bubbles enter column (may need to remove column). Allow conditioning solution to flow through system for 15minutes or until a dark pink is present for 10 minutes. Once conditioned shut knob off and reconnect NO_2/NO_x tube to sampler. DO NOT ALLOW AIR BUBBLES TO ENTER COLUMN. Before calibration, make sure pink color is no longer visible in system

11) Sample Collection, Preservation, Shipment and Storage: Filter samples (0.45 um). Samples can be collected in clean glass or plastic bottles. If samples cannot be run within 24 hrs. preserve with 2ml conc. H_2SO_4/L and refrigerate at 4°C. Holding time for preserved samples is 28 days.

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: Standards are placed at the start of every sample run. The software which is used for data collection from the AAII calculates and plots the calibration data. See instructions for AA and software use in the Appendix. The R^2 for the standards should be no less than 0.995.

14) Procedure:

Startup:

1) Replace tubes that look warn or flattened. Usually air tubes are replaced most often.

2) Wash Door with isopropyl alcohol before placing over rollers.

3) Place tubing ends into appropriate Type II water reservoirs (chemicals harmful if mixed improperly). Be sure sampling arm is in DI reservoir, to do so rotate the cam to a notch section while the power button is on. Turn pump switch on. All Type II water to flush system for ~10 minutes.

4) *Note Type II water Reservoirs should be refilled periodically throughout entire day of sampling.

5) Check chemical bottles. Replace those that are too low to use. Place labeled tubes into corresponding reagent bottle. Cover the reagents with parafilm.

6) NITRATE ONLY – when the black knob near the column is turned so that the yellow dot is facing away from the column it is in the off position. Allowing any

bubbles coming toward the cadmium column tube to be pushed through the system with out damning the column. Before you turn the black know to the on position remove the cadmium column, the end that is the start of the flow (the side that is closest to you). Then turn the black knob on by turning it so the yellow dot is near the area where the column is when it is attached. Put a paper towel under the open end to catch the draining solution and let all the bubbles flow out. When reattaching the column spay Type II water into each end of the column to avoid introducing air into column. Remember to attach the end closest to you first (always make sure to you attach the column the same way ever time by remembering what end of the tub you started with before you removed it in the beginning).

7) watch the real time screen to see when the base line levels out and then start the calibration

Setting Baseline:

There are two channels attached to the AA, the NOX channel is channel two. There are several knobs on the detector box for the channel. In the middle of the detector box are two knobs labeled A and B. Knob A controls the aperture that allows light to hit the sample cell. Knob B controls the aperture for the reference cell. Rotate knob A counterclockwise to increase the absorbance or to decrease the light transmitted. Turn clockwise to decrease absorbance or increase the light transmitted. In the New Analyzer program (NAP) click on "control" and select "real time". The baseline should fall between 5-7%. Rotate knob A accordingly to acquire the desired baseline. Large jumps in the baseline are normally due to air peaks. The bubbles may be too numerous or too long. To reduce the length of the bubbles tighten the tubing running underneath the door by pulling on the tube in a direction away from the door.

Setting High Point:

Place sampling tray to position 37. Use a disposable glove (to avoid contamination) to take sample vials from the bag and place onto the center of the sampling tray. Pour 4 vials of highest standard solution into vials (rinsing once) and place on positions 37-40. Place pick into the large hole of the last sample of the sampling tray in order to stop the tray when that sample is analyzed. Push the power button to begin sampling. It takes approximately 10 minutes for the samples to reach the detector. You can see this by watching the real time screen. When the samples arrive at the detector the absorbance should increase. When the sample seems to flatten use the black knob at the top end of the detector to adjust the absorbance. The desired absorbance falls between 95-97%. Final sample should not need adjustment. Allow the baseline to drop back to 5-7%. If the baseline is not correct, then reset the baseline and the high point.

Sampling:

1) Close the real time box and click "sample table" select "load"

2) Click the most recent table recorded from the main file menu and click "OK"

3) Click “file” “save as” and same in that seasons folder the file renamed with the correct date.

4) Close the sample table

5) Click on the black arrow next to sample table or go to the control dialog box to retrieve the saved table.

6) In the method box for channel one choose the DFGNO3 for nitrate (DFGNO2L for nitrite) file from the previous day. Type in the new date. Channel 1 will most likely be an ammonia method if both channels are run at the same time. If not, then choose a dummy method and write the date+junk as the filename for channel one.

7) Obtain a sampling sheet and reagent sheet from the AA binder. Fill out the Reagent sheet with the reagents used that day.

8) The standard curve must be run first. The DFGNO3 and the DFGNO2L method file is programmed for the first sample to be the high standard, the next 6 samples are your standards in descending order. The sample sheet and the sample table should be labeled in a similar way. On the sample sheet write high STD, S6 for your high standard followed by S5, S4, etc. These should then be followed by a blank. References should now be run to check if the standards were made at the correct concentration. Run a duplicate of your reference solution followed by an internal standard such as S3 or S4. This series is followed by a blank and the LCS. Sample vials should be rinsed with a little sample before filling on the sample tray. The tray should be loaded and oriented, so that the first vial (high std) will be the first one the sampling arm takes from.

9) Make sure the pick is removed before turning on the power. At this point the pump should be on, the power button may need to be turned off and turned on again to begin.

10) Turn the control panel to the “on” position so the data is recorded on the computer.

11) Select “view” from the menu

12) Double click channel two in the new window that appears.

13) In this magnified window of channel two click “sample table” from the menu. Fill out the sample table the same as the sample sheet with UFI ID numbers, saving often.

14) When the standards are all flagged by the computer, then check to be sure the R^2>0.995, with a linear curve.

15) Watch to make sure samples do not reach 100% absorbance. If samples reach 100% absorbance, then they will need to be diluted. Keep in mind that sample vials are ~4mL, so make dilutions based on 4mL total volumes. Contamination may occur in the next sample so rerun if suspect. If a sample is expected to be high, then follow it by a blank and dilute accordingly. Dilution factors are recorded in the dilution column on the sample table on NAP and on the worksheet. The sample that went over 100% absorbance should get a slash on the column marked NOx on the worksheet. Samples that are acceptable (not over 100% and not contaminated) get a y.
*NOTE - If a standard goes over 100% there was a baseline shift, requiring the system to have the baseline reset as well as the high concentration point.

Shut down:

1) The pick should be placed in the large hole of the last sample.

2) Allow time for the final sample and the baseline flag to be calculated. When the run is complete a blue baseline should appear across the bottom of the screen.

3) Turn off data collection on the computer.

4) NITRATE ONLY - Turn off the column by rotating the knob to the original position, facing the sampling tray.

5) Remove tubes from reagents and allow Type II water to flush the system for ~10 minutes.

6) Remove the tubes from the Type II water and flush system with air until water is removed, or, at the operator's discretion, leave with Type II water in tubes, if used on a routine basis.

7) Turn off pump when all water is removed, or when done rinsing.

8) Take off the door and release tube tension by removing one of the tube holders.

9) Pour waste down the drain flushing with water. All waste from channel two should be in one container. DO NOT MIX WASTE BETWEEN CHANNEL ONE AND TWO. A HARMFUL REACTION OCCURS.

10) Turn off the power strip to the auto-analyzer.

Reporting Data:

5) Edit all peaks to ensure they were flagged at the pure sample point and not on air bubbles

6) Check to ensure no peaks were missed and flags line up with the sample name. Use the "Edit peaks" function to delete or add peaks.

7) Print the standard curve on the "standards" window.

8) Print the data points from the channel one window.

Maintenance (Routine):
All Maintenance is logged in the maintenance and repairs logbook.

1) Bulbs are to be replaced at the beginning of each field season or when needed.

2) Tubes are to be replaced biweekly or as needed. Tubes will be flattened or gray if needed to be changed.

3) The tubes are to be cleaned with the following procedure once a month or as needed.
    a. Attach 5N sulfuric acid through all lines. Run for 15 minutes with the Cd column off.
    b. Rinse with Type II water for 15 minutes
    c. Run 1N Noah for 15 minutes with the Cd column off.
    d. Rinse with Type II water for 15 minutes
4) Pour 3mL of concentrated sulphuric acid in volumetric flasks and dilute with DI until full in order to destroy algae. Performed each week and left on weekends to stand.

5) The Column should be repacked each week or when needed. The column will go from black to gray when capacity to reduce NO3 is eliminated. Excessive air entering the column will also force the column to be repacked.

Nitrate Data Entry:

Follow the instructions for ammonia.

15) Calculations: Dilution factors entered multiply the concentration by the number entered.

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. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
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
Reference	A standard sample, made from either a	Every sample batch	Ref

	different lot # solution, a different manufacturer, or another method (dissolving a solid)		
Continuing Calibration Verification	A standard sample, run throughout the course of the run, generally of varying concentration, and near the expected sample concentration range(s)	First sample, before running others, every 10-15 afterwards, and the last sample of any run NOTE: If curve is not run daily, highest standard must be run as a CCV	CCV
Initial Calibration Verification	A CCV done at the beginning of the run	1st sample	ICV
Laboratory Control Sample or Blank Spike	A spike of unknown concentration to Type II water	One per sample batch	LCS or BS
Matrix spike	A spike of known concentration to sample matrix	Every 20 samples or one per batch if less than 20 samples	SPK
Matrix Spike Duplicate	Same as above, repeated	One per month or ~250 samples	SPKDUP
Continuing Calibration Blank	Blank Sample	Every ten, or one per batch, following CCV	CCB
Dilution Duplicate	Dilution of original sample, diluted to ½ of dilution concentration	One per sample batch, if samples diluted	DILDUP
Triplicate	An identical sample to two others, from the same container as the duplicate	One per month or ~250 samples	TRIP

17) Pollution Prevention: Dispose of reagents in accordance with proper laboratory procedures. This procedure has no discernible 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 there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper action line and a lower action line. The upper and lower warning lines are 2 standard deviations from the mean. The upper and lower action lines are three standard deviations from the mean. The process should be shut down for trouble shooting if the following occur:

- A single action outside the action line.
- 2 out of 3 consecutive measurements between the warning and action lines

- 7 consecutive measurements above or below the center line
- 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 non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. The following table charts the flags utilized, and their meanings.

Data Flag ID	Meaning of Flag
F1	Sample analyzed/received past holding time
F2	Sample diluted to run within calibration curve
F3	Sample outside calibration curve
F4	Lower than normal volume of sample analyzed
F5	Sample not digested/prepared properly
F6	Sample not preserved properly
F7	Sample received outside “normal” temperature limits
F8	Sample container inappropriate
F9	Sample container broken/cracked/leaked
F10	Sample taken from container other than specified analyte
F11	Data associated with failed spike/LCS
F12	Data associated with failed CCV/CCB
F13	Data associated with failed duplicate

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. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

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. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. Wastes from this test can be washed down the sink with the tap running.

22) References:

1) Methods for Chemical Analysis of Water and Wastes. 1983. USEPA method 353.2 pp. 353.2-1

2) www.dictionary.com Online dictionary

3) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data:

Organic Carbon, Total/Total Dissolved (as C)……SOP 110

1) Test Method: CARBON, DISSOLVED TOTAL ORGANIC (DOC/TOC), USING Phoenix 8000 SM 18th 5310 C

2) Applicable Matrix or Matrices: drinking, surface and saline waters, domestic and industrial wastes.

3) Detection Limit: See UFI Controlled Document No. 12

4) Scope and Application: Extreme care should be exercised when running samples with concentrations less than 1 mg/l, scrupulous attention should be given to cleanliness to avoid contamination. Ground and surface waters, waters high in particulate matter can be sampled using this instrument due to the large bore size of the instrument tubing (for TOC/DOC).

5) Summary of Test Method: In the TOC mode, inorganic carbon is removed by acidification and sparging. TOC measurement involves the oxidation of organic carbon in a sample. In the Phoenix 8000 it occurs by first oxidation of persulfate. The sample is exposed to simultaneous exposure of persulfate ions and to UV radiation. Carrier gas is swept through UV reactor to carry CO2 out of the UV chamber. The remaining carbon in the sample is measured as TOC by an infrared detector NDIR in parts per million. UFI measures DOC, as samples are filtered before being analyzed.

6) Definitions:

DOC - Dissolved organic carbon, organic carbon remaining in a sample after the sample has been filtered through a 0.7 micron glass fiber filter.

TOC - Total organic carbon.

7) Interferences: Water with high alkalinity level may require additional acid. High levels of sulfate may require the use of a sulfide scrubber.

8) Safety: Always wear safety glasses, 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 laboratory director immediately.

9) Equipment and Supplies:

- Carbon analyzer (Phoenix 8000)
- Standards
- Glass vials for analyzer
- Pre-ashed (500°C 15 min) GF/F glass fiber filters.
- Copper and Tin
- Ultra High Purity Nitrogen Gas

10) Reagents and Standards:

1. Phosphoric acid 21%.
   - Measure 37 ml of 85% phosphoric acid (H3PO4) into rinsed bottle.
   - Add 188 ml of ultra pure Type II water.

2. 10% Persulfate and 55 Phosphoric Acid Reagent Mixture:
   - Measure 25 g 98% sodium persulfate ($Na_2S_2O_8$) into rinsed bottle.
   - Add 9 ml 85% phosphoric acid (H3PO4).
   - Add 213 ml of ultra pure Type II water.

     ✓ Prepared persulfate stock must be used within one week and acid reagent within one month.

3. Organic carbon standard 1000ppm obtained from commercial vendor and use to prepare standard.

4. Reference solution (generally 1000ppm) obtained from a different lot number (may also be a different vendor)

11) Sample Collection, Preservation, Shipment and Storage: Samples should be collected in acid washed bottles and kept cool and in the dark. For DOC filter sample through an ashed (500°C) 0.7 micron glass fiber filter. If sample is to be run within seven days, refrigerate. Otherwise acidify to pH < 2 with H_2SO_4 and refrigerate.

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: Standard preparation is recorded on standard sheet. The signed and dated standard sheet is filed with the data set.
Range TOC 0.2ppm-20ppm.
Preparing the standards, use the purchased 1000ppm organic carbon solution to create different concentrations of standards. All standards prepared in 250ml volumetric cylinders.

	Concentration (mg/L)	**ml of 1000ppm/250 ml**
1	0.0	0.0
2.	0.5	0.125
3.	1.0	0.25
4.	5.0	1.25
5.	10.0	2.5
6	15.0	3.75
7.	20.0	5.0

To prepare standards:

20.0mg/l: In a 250ml volumetric cylinder, add 5ml of 1000ppm organic carbon standard, and bring to volume (250ml) using Type II water
15.0mg/l: In a 250ml volumetric cylinder, add 3.75ml of 1000ppm organic carbon standard, and bring to volume (250ml) using Type II water
10.0mg/l: In a 250ml volumetric cylinder, add 2.5ml of 1000ppm organic carbon standard, and bring to volume (250ml) using Type II water
5.0mg/l: In a 250ml volumetric cylinder, add 1.25ml of 1000ppm organic carbon standard, and bring to volume (250ml) using Type II water
1.0mg/l: In a 250ml volumetric cylinder, add 0.25ml of 1000ppm organic carbon standard, and bring to volume (250ml) using Type II water
0.5mg/l: In a 250ml volumetric cylinder, add 0.125ml of 1000ppm organic carbon standard, and bring to volume (250ml) using Type II water
0.0mg/l: Fill 40ml vial with Type II water.
*If the samples being analyzed are acidified, then the standards are acidified using H_2SO_4

14) Procedure:

a. This procedure is intended for those familiar with the instrument and software, it is not a substitute for familiarization with the instrument manual.

- Make sure gas (UHP N_2) is turned on at the tank; check to see that there is more than 500 psi in the tank and pressure less then 35psi
- Make sure you empty old Type II water from the labeled container and refill it with fresh Type II water. Check to make sure you have adequate volume of the reagents (the persulfate, and the phosphoric acid). Make sure the reagents have not expired.
- Start the TIC software by clicking on the "short cut to Phoenix" icon.
- Choose setup, instrument. On the system status screen choose ready (the UV light should come on). Within the Instrument Setup Preferences box you are given the option to check the "Turn off system after auto sampler is done" on or off, as well as "Print data report after each sample set". If it is the last run of the day you will have to check the "Turn off system… etc" box and the "Print data report… etc" should always be checked, afterwards, click OK. Wait approximately 15-20 minutes fort the UV lamp to warm –up and for the baseline to stabilize (baseline should read appx. 3-6)
- Run the cleaning procedure from sample setup; choose file; open and choose clean.set
- Remember to reset the status of all lines in the file to ready: edit, reset status, OK, save/use, exit, save changes? Yes, start
- Follow the same procedure to run blanks; from sample setup – choose file blktcr2.set -- edit, reset status, OK, save/use, exit, save changes? Yes, start

- Blank values should be TOC Range 2 ≈ 80,000 to 150,000.

✓ Make sure if a blank method is chosen that the same blank type is chosen.

✓ Do not choose any methods that are not meant for that sample analysis, such as the sample blanks or cleaning procedure.

b. To calibrate using an existing file:
From standards run screen choose sample setup, file, open choose the existing file name (TOCSTD.set), OK; remember to reset the status of all lines in the file to ready (edit, reset status, OK). Make sure the vial ID's in the file coincide with the vial placement in the sample tray. When putting the sample rack in position, be sure that it is flush and securely placed. Choose save/use, save changes? Yes, and start to calibrate instrument. When the calibration is complete, the data will print out, and the computer screen will show a graph with an r-square value. Below it there is data on the standards that have been run.

- Click on the standard data that was run on the present day – all six values, and uncheck the previous data.
- Click the button "Re-calc." A new standard curve will appear with a new r-square value.
- Click File click Print selected graph. Click "Print" to print calibration report.
- View the curve, and if r^2 >0.9992, Click "OK" and run samples.

✓ To run standards use custom method **TOC Range 0.1ppm-20ppm C**.

c. To calibrate by creating a new calibration file:
To set up a new file or edit an old one: start at sample setup, calibration, standards, file, open, choose an existing file or choose cancel and create a new one. Be sure to indicate conc. and method ID, if this file is set up incorrectly the instrument will not calibrate properly!! Choose OK to exit back to sample run screen.

d. Running samples:
Autosampler run order is recorded on autosampler sequence sheet.

To set up a new file or use an old run samples file: start at sample setup, file, open, choose an existing file or create a new one. Be sure to indicate method ID, if this file is set up incorrectly the instrument will not run samples properly!! In addition, you must type in proper sample ID numbers on the file and ensure the sample vials manually placed in the rack correspond to the template file. The sample vials should be filled so that it is enough for a single sampling and a duplicate. Make sure the first sample is just Type II water, label it "blank." Once this is completed, choose OK to exit back to sample run screen.

When Data is taken and run is finished:

Click Results, click Multiple Analysis, click View in Excel
Save that data which appears in the RAW DATA folder in DOC. A message will pop up saying you haven't saved it as an excel file but click No.

e. Calibration verification:
Select Calibration Verification as the Sample Type in the Open - File window. A window pops up that list the previously entered Calibration Verification; select one suitable for the selected run.
The results for a Calibration Verification are processed differently than sample because of the difference in blank between samples and standards, and it is very important that the Calibration Verification be analyzed using the same mode and range

15) Calculation: Calculations are performed using the instrument software.

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. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Initial Calibration Verification	A standard sample	2nd sample	ICV
Initial Calibration Blank	Blank Sample	3rd sample	ICB
Laboratory Control Sample	A spike of unknown concentration to Type II water	One per sample batch	LCS
Reference	A standard sample, made from either a different lot # solution, a different manufacturer	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 sample, run throughout the course of the run, generally of varying concentration, and near the expected sample concentration range(s)	Every 10 samples	CCV
Continuing	A blank sample, run	Every 10 samples	CCB

Calibration Blank	throughout the course of the run		
Matrix Spike Duplicate	Same as above, repeated	One per month or ~250 samples	MSD

17) Pollution Prevention: Dispose of the reagents in accordance with proper laboratory procedure and the Chemical Hygiene Plan. This procedure has no discernible 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 there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper action line and a lower action line. The upper and lower warning lines are 2 standard deviations from the mean. The upper and lower action lines are three standard deviations from the mean. These specific standard deviations are calculated annually from the previous year's data. Data is automatically flagged. To see up to date flags and control limits, see UFI Controlled Document No. 12. All Q and F flags can be found in UFI Controlled Document No. 12. The process should be shut down for trouble shooting if the following occur:

- A single action outside the action line.
- 2 out of 3 consecutive measurements between the warning and action lines
- 7 consecutive measurements above or below the center line
- 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 non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. The following table charts the flags utilized, and their meanings.

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. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

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. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. Wastes from this test can be washed down the sink with the tap running.

22) References:

1) Standard Methods 20th Edition, method, 5310 C., pp5-22,

2) Teckmar-Dohrmann Manual Sections 1 and 6.

3) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data:

Sulfide (as S), high range …….SOP 112

1) Test Method: HYDROGEN SULFIDE > 1.0 mg/L SM 18th ed 4500 S 2- E

2) Applicable Matrix or Matrices: drinking, surface and saline waters, domestic and industrial wastes.

3) Detection Limit: See UFI Controlled Document No. 12.

4) Scope and Application: Hydrogen sulfide can be measured in natural waters.

5) Summary of Test Method: Excess iodine is added to a sample that has been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfate under acidic conditions. The excess iodine is back titrated with sodium thiosulfate.

6) Definitions:

Hydrogen sulfide- in sufficient quantities, it is toxic to a number of organisms. It attacks olfactory systems of humans. It has natural and anthropogenic sources.

7) Interferences: The iodometric method suffers interference from reducing substances that react with iodine such as thiosulfate, sulfite, and various organic compounds, both solid and dissolved. Pre-treatment with zinc acetate to precipitate the sulfide as zinc sulfate will eliminate this interference.

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:

- glass stoppered BOD bottles
- titration burette (25ml)
- siphon
- beaker (250ml)
- stir plate
- stir bars
- 2ml preset volume squeeze bottles for field.

10) Reagents and Standards:

Zinc acetate solution – Dissolve 220g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 870 ml Type II water; this makes 1 liter.

Sodium hydroxide solution 6N – Dissolve 240g NaOH in approximately 900 mls of Type II water, cool dilute to 1 liter.

Hydrochloric acid 6N – Carefully, in a hood following all safety procedures, add 500 ml conc. hydrochloric acid to 400 ml Type II water, cool and dilute to 1 liter. Standard iodine solution 0.025N – Dissolve 20 to 25g potassium iodide (KI) in a little Type II water and add 3.2g iodine. After iodine has dissolved, dilute to 1 liter. Standardize as per procedure below.

Stock sodium thiosulfate solution 0.25N – Dissolve 62.05g $Na_2S_2O_3 \bullet 5H_2O$ in Type II water. Add 0.4g solid NaOH and dilute to 1 liter.

Sodium thiosulfate titrant 0.025N – Dilute 100 ml of stock sodium thiosulfate (0.25N) to 1 liter with Type II water. Standardize with bi-iodate solution as per procedure below.

Standard potassium bi-iodate solution 0.0021M - Dissolve 0.8124Gg $KH(IO_3)_2$ in Type II water, dilute to 1 liter.

Starch solution – Dissolve 20g laboratory grade soluble starch and 2g salicylic acid, as a preservative, in 1 liter hot Type II water or use purchased reagent.

11) Sample Collection, Preservation, Shipment and Storage: Place 2 ml of zinc acetate solution into the bottom of a 300 ml BOD bottle. Fill bottle with sample taking care to fill bottle under the zinc acetate. Add 2 ml 6 NaOH. Stopper bottle with no air bubbles and invert bottle rapidly to mix. Let precipitate settle for 30 min. The treated sample is stable for 7 days. Store samples in a cool and dark area.

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:

Standardization of thiosulfate – Dissolve approximately 2g KI in a beaker with 100 to 150 ml Type II water. Add a few drops of conc. H_2SO_4 and 20 mls standard bi-iodate solution. Dilute to 200 ml and titrate liberated iodine with thiosulfate titrant, adding starch toward the end of the titration, when a straw yellow color is reached. Continue titration to a clear end point. When the solutions are of equal strength 20 ml of bi-iodate should require 20 ml of thiosulfate titrant to reach the endpoint.

Standardization of Iodine - Using a volumetric pipette measure 10 ml of standard iodine solution into beaker and dilute to 50 or 100 mls. Titrate with sodium thiosulfate titrant, until a pale yellow color is reached, add starch toward the end of the titration to create a blue color. Continue titration to a clear end point.

14) Procedure: Decant clear supernatant, being careful not to loose any of the precipitate. To the precipitated sample an amount of iodine estimated to be in excess of the sulfide present (5 or 10 mls is usually sufficient, for some systems like Onondaga more may be required in the latter part of the summer). Add 2ml 6N HCL and mix sample by inversion until the precipitate dissolves. Titrate with sodium hydroxide titrant to a light pale straw yellow color, add a few drops of starch and titrate until the color disappears.

15) Calculations:

$$\text{mg } S^{2-}/L = \frac{[A \times B - C \times D] \times 16000}{250 \text{ ml}}$$

where:

A = volume of iodine added to sample
B = mls thiosulfate needed to titrate iodine (C)
C = mls iodine standardized
D = mls thiosulfate needed to titrate sample
E = mls bi-iodate used for standardization
F = mls thiosulfate needed to titrate bi-iodate (E)

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. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
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

The precision of the end point varies with the sample. In clean waters it should be determinable within 1 drop, which is equivalent to 0.1 mg/L in a 200-ml sample.

17) Pollution Prevention: Dispose of reagents in accordance with proper laboratory procedure.

18) Data Assessment and Acceptance Criteria for Quality Control Measures:
Instrumentation profiles of dissolved oxygen should be checked, no sulfite should be present in oxygenated waters.
Record results from all quality control samples onto the QC file. The control charts are designed so that there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper action line and a lower action line. The process should be shut down for trouble shooting if the following occur:

- A single action outside the action line
- 2 out of 3 consecutive measurements between the warning and action lines
- 7 consecutive measurements above or below the center line
- 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 non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. **Data flags and their meaning may be found in UFI control document number 12.**

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. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

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 sufficient sample data, the data should be flagged with an explanation of the circumstances. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. Wastes from this test can be washed down the sink with the tap running.

22) References:

1) Standard Methods 20th edition 4500-S^{2-} F. pp 4-167

2) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data:

Carbon, Inorganic Dissolved and Total…….SOP 203

1) Test Method: <u>CARBON, DISSOLVED/ TOTAL INORGANIC (DIC/TIC),</u> USING DOHRMAN PHOENIX 8000 SM 4500 18th edition 5310C

2) Applicable Matrix or Matrices: This method includes the measurement of carbon in drinking, surface and saline waters, domestic and industrial wastes.

3) Detection Limit: See UFI Controlled Document No. 12

4) Scope and Application: Ground and surface waters, waters high in particulate matter can be sampled using this instrument due to the large bore size of the instrument tubing.

5) Summary of Test Method: The sample is injected into an acid filled reaction chamber. Under acidic conditions, all inorganic carbon is converted to CO_2. The CO_2 is removed, along with dissolved CO_2, by a stream of inert gas (Nitrogen). The CO_2 levels are measured by an infrared detector (NDIR). Under these conditions organic carbon is not oxidized and only IC is measured.

6) Definitions:

Inorganic carbon (IC) – includes carbonate, bicarbonate, and dissolved carbon dioxide.

7) Interferences:

Water with high alkalinity level may require additional acid.
High level of sulfate may require the use of a sulfide scrubber.

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:

- Standards
- Carbon Analyzer (Phoenix 8000)
- Glass vials for analyzer
- Volumetric Flasks
- Ultra High Purity Nitrogen Gas
- Copper and Tin
- Glass Woal

10) Reagents and Standards:

Phosphoric acid 21%.

- Measure 37 ml of 85% phosphoric acid (H3PO4) into rinsed bottle.
- Add 188 ml of ultra pure Type II water.

10% Persulfate and 55 Phosphoric Acid Reagent Mixture:

- Measure 25 g 98% sodium persulfate ($Na_2S_2O_8$) into rinsed bottle.
- Add 9 ml 85% phosphoric acid (H3PO4).
- Add 213 ml of ultra pure Type II water.
  - ✓ Prepared persulfate stock must be used within 7 days and acid reagent within one month.

Inorganic carbon standard (1000ppm) obtained from commercial vendor and can be used for spikes or to make high range standards.

Low Range DIC Stock standard, 100 mg/L – dry Na_2CO_3 @ 105°C for at least 1 hr. Weigh 0.4415mg, dilute to 500 milliliters with DDI.

High Range DIC Stock standard, 1000 mg/L – dry Na_2CO_3 @ 105°C for at least 1 hr. Weigh 4.415g, dilute to 500 milliliters with DDI

Reference solution obtained from a different lot number (may also be a different vendor)

11) Sample Collection, Preservation, Shipment and Storage: Collect samples in VOC vials (40ml) with proper septa filling with minimal agitation and with no head space to prevent de-gassing. Keep cool until analysis. Samples should be run as soon as possible.

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: Standard preparation is recorded on standard sheet. The signed and dated standard sheet is filed with the data set. Choose the proper sample range for the samples. A series of 6 or 7 standards should be prepared:

Low range (most lakes, reservoirs, streams):

Conc. mg/l	ml of 100 mg/l stock in 250 ml	expected ugC (for use in software)
0.0	0	.004
0.5	1.25	2.0
1.0	2.5	4.0
5.0	12.5	20.0
10	25.0	40.0
15	37.5	60.0
20	50.0	80.0

High range (Onondaga Lake):

Conc. mg/l	ml of 1000 mg/l stock in 250 ml	expected ugC (for use in software)
0	0	.004
10	2.5	5.0
20	5.0	10.0
30	12.5	15.0
40	25.0	20.0
50	50.0	25.0

14) Procedure –

This procedure is intended for those familiar with the instrument and software, it is not a substitute for familiarization with the instrument manual.

-Make sure gas (UHP N_2) is turned on at the tank, check to see that there is more than 500 psi in the tank. Make sure you empty old Type II water from the labeled container and refill it with fresh Type II water. Check to make sure you have adequate volume of the reagents (the persulfate, and the phosphoric acid). Make sure the reagents have not expired.

-Start the TOC software by clicking on the "short cut to Phoenix" icon. Phoenix will initialize.

- -Choose setup, instrument on system status screen choose ready (the UV light should come on). Within the Instrument Setup Preferences box you are given the option to check the "Turn off system after auto sampler is done" on or off, as well as "Print data report after each sample set". If it is the last run of the day you will have to check the "Turn off system… etc" box and the "Print data report… etc" should always be checked, afterwards, click OK. Click "Run." Wait approximately 15-20 minutes for the UV lamp to warm–up and for the baseline to stabilize (baseline should read appx. 3-6)

-run the cleaning procedure (from sample set-up – choose file, open clean.set OK) remember to reset the status of all lines in the file to "ready" (edit, reset status, OK, save/use, exit, save changes? Yes, start

-run blanks (from sample set-up – choose file blkicr2.set or blkicr3.set or blkicr4.set or blkicr5.set

blank values should be IC range 2 ≈ 20,000 for ranges 3,4,5 ≈ 150,000 different conc. ranges are as follows :

range	conc
1	0.002 – 0.1 ppm
2	0.1 – 20 ppm
3	20 – 200 ppm
4	200 – 1000 ppm
5	1000 – 10,000 ppm

-run a calibration file based on the concentration range of the samples.

To calibrate using an existing file:
From the sample run screen choose sample set-up, file, open choose the existing file name, OK). The DIC sample files included HIDICSTD.set and DICSTD.set remember to reset the status of all lines in the file to ready (edit, reset status, OK, Make sure the vial ID's in the file coincide with the vial placement in the sample tray. When putting the sample rack in position, be sure that it is flush and securely placed. Choose save/use, save changes? Yes, exit, and start to calibrate instrument.

When the calibration is complete, the data will print out, and the computer screen will show a graph with an r-square value. Below it there is data on the standards that have been run.

- Click on the standard data that was run on the present day – all six values, and uncheck the previous data.
- Click the button "Re-calc." A new standard curve will appear with a new r-square value.
- Click File click Print selected graph. Click "Print" to print calibration report.
- view the curve, and if r^2 >0.9992, Click "OK" and run samples.

To calibrate by creating a new calibration file: To set up a new file or edit an old one: start at sample set-up, calibration, standards, file, open, choose an existing file or choose cancel and create a new one. Be sure to indicate conc. and method ID, if this file is set up incorrectly the instrument will not calibrate properly!! Choose OK to exit back to sample run screen.

Running samples: choose an existing sample file or create a new one.

To run samples using an existing file: from the sample run screen choose sample set-up, file, open choose the existing file name, OK) remember to reset the status of all lines in the file to ready (edit, reset status, OK, Make sure the vial ID's in the file coincide with the vial placement in the sample tray. Edit the file to suit the samples you are running, you can change identification numbers, or add/delete samples. Choose save/use, save changes? Yes, exit, and start. Continuing Calibration verification samples should be run every ten samples, and at the beginning and end of the sample run (for how to see below)

To run samples by creating a new sample run file: this is accomplished easiest by pulling up an existing file and editing it then saving the file under a new name.

Calibration verification:

Select Calibration Verification in the sample set-up window, as the Sample Type. A window pops up that list the previously entered Calibration Verification; select one suitable for the selected run. The results for a Calibration Verification are processed differently than sample because of the difference in blank between samples and standards, and it is very important that the Calibration Verification be analyzed using the same mode and range

When Data is taken and run is finished:

Click Results, click Multiple Analysis, click View in Excel

Save that data (File, Save As) which appears in the RAW DATA folder in DIC. A message will pop up saying you haven't saved it as an excel file but click No.

15) Calculation: Calculations are performed automatically using the instrument software.

16) Method Performance: UFI laboratory follows the following chart for identifying and running QC samples. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Initial Calibration Verification	A standard sample	2nd sample	ICV
Initial Calibration Blank	Blank Sample	3rd sample	ICB
Laboratory Control Sample	A spike of unknown concentration to Type II water	One per sample batch	LCS
Reference	A standard sample, made from either a different lot # solution, a different manufacturer	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 sample, run throughout the course of the run, generally of varying concentration, and near the expected sample concentration range(s)	Every 10 samples	CCV
Continuing Calibration Blank	A blank sample, run throughout the course of the run	Every 10 samples	CCB

17) Pollution Prevention: Dispose of the reagents in the combustion tubes in the proper manner. This procedure has no discernible 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 there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper action line and a lower action line. The upper and lower warning lines are 2 standard deviations from the mean. The upper and lower action lines are three standard deviations from the mean. These specific standard deviations are calculated annually from the previous year's data. Data is automatically flagged. To see

up to date flags and control limits, see UFI Controlled Document No. 12. All Q and F flags can be found in UFI Controlled Document No. 12. The process should be shut down for trouble shooting if the following occur:

- A single action outside the action line.
- 2 out of 3 consecutive measurements between the warning and action lines
- 7 consecutive measurements above or below the center line
- 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 non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. The following table charts the flags utilized, and their meanings.

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. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

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. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. Wastes from this test can be washed down the sink with the tap running.

22) References:

1) Standard Methods 18th Edition, method 5310 C pg 5-13,5-14,

2) Standard Methods 20th Edition, method 5310 C, 5-22 to 5-24

3) Teckmar-Dohrmann Manual Sections 1 and 6.

4) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data:

Sulfide (as S), low range(B)……..……SOP 212.1

1) Test Method: **SULFIDE Low Range** SM 20th Edition 4500-Si^- G. Ion-Selective Electrode Method. pp. 4-168-172.

2) Applicable Matrix or Matrices: wastewater, effluent, and stream samples

3) Detection Limit: See UFI Controlled Document No. 12.

4) Scope and Application: This method is applicable for use with most waters and wastewaters.

5) Summary of Test Method: The potential of a silver/sulfide ion-selective electrode (ISE) is related to the sulfide ion activity. An alkaline antioxidant reagent (AAR or SAOB) is added to samples and standards to inhibit oxidation of sulfide by oxygen and to provide a constant ionic strength and pH. Use of the AAR allows calibration in terms of total dissolved sulfide concentration. All samples and standards must be at the same temperature. Sulfide concentrations between 0.032 mg/l and 100 mg/l can be measured directly.

6) Definitions:

Nernst equation—

$$E_{cell} = E^0_{cell} - \frac{RT}{NF} \ln \frac{(a_{H+})^2_i (a_{Cl-})^2_i}{(p_{H2})_i}$$

Hypolimnion—the portion of a lake that is below the thermocline. This may become anoxic when the lake becomes stratified.

7) Interferences: Sulfide oxidation may cause potential readings to drift in the direction of decreasing concentration. Flush surface of samples with nitrogen to minimize contact with atmospheric oxygen for low-level measurements. Temperature changes may also cause upward or downward drift. Allow samples to come to the same temperature.

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 and begin clean up.

9) Equipment and Supplies:

- Ion-specific sulfide electrode
- double-junction reference electrode
- pH meter
- stir plate
- electrochemical cell
- gas dispersion tube

- BOD or other gas tight sample containers
- Plastic syringes
- 100ml graduated cylinder
- 1L volumetric flasks
- Dark Nalgene storage bottle for buffer

10) Reagents and Standards:

Alkaline antioxidant reagent or SAOB (AAR)- Only make 300-600 ml at a time for best results. The color should be between colorless and yellow. Store in a dark, capped bottle. Equal parts of Sodium Hydroxide, EDTA, and Ascorbic Acid; which need to be combined in that order, in order to work effectively. Soultion concentrations are given below.

NaOH to 50mL Type II water add 80g NaOH, bring to 1 liter in a volumetric flask.

EDTA to ~500 mL Type II water in a 1 liter flask, add 67g Na_2H_2EDTA and bring to volume.

Ascorbic acid to ~650 mL, add 35g ascorbic acid in a 1000ml flask. Gently mix to dissolve, fill to volume with Type II water.

Lead perchlorate(0.1M)-In 100mL Type II water, dissolve 4.6g of $Pb(ClO_4)_2$. $3H_2O$. Standardize with Na_2H_2EDTA or use $Pb(ClO_4)_2$. $3H_2O$ from a commercial vendor.

Sulfide Reference Stock Solution (130mg/L)-Dilute 13.0mL of 1.00mg S^{2-}/mL with AAR.

In a 1L flask add 500ml of AAR and 10g $Na_2S.9H_2O$ mixed until dissolved. Dilute to 1L with Type II water.

Sulfide Stock- Currently purchased from Fisher in 1000ppm concentration. Be careful, as solution is only good for a few weeks.

Degassed Type II water.

11) Sample Collection, Preservation, Shipment and Storage: Samples should be collected in 300 ml BOD bottles without exposure to air. Sampled from the bottom depths-up, flushing the bottle at least 3 times its volume, and being careful to exclude air bubbles. Stopper carefully to exclude air bubbles and mix by inverting bottles several times. Keep bottle cool and return to the lab as soon as possible.

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: Check electrode performance and calibrate daily. Check electrode potential in a sulfide standard every 2 hours, or every ten samples, whichever is briefer.

Check electrode performance: Pipette 50ml AAR, 50ml Type II water, and 1ml sulfide stock solution into a measurement cell. Place Ag/S and reference electrodes in the solution and read potential. Add 10ml stock solution and read potential. The change in potential should be –28 plus or minus 2 mV. If it is not, follow the troubleshooting procedure in the electrode manual. Alternatively, run a known CCV standard.

Calibration: Place electrodes in the most dilute standard but use calibration standards that bracket the sulfide concentrations of the samples. Record the potential when the instrument indicates it's ready or is output to the printer. This may take more then 30 minutes for very low sulfide concentrations (less than 0.03mg/l). Rinse the electrodes, blot dry with a Kimwipe, and read potential of the next highest standard. Repeat this procedure for all standards, working from lowest concentration to highest. The meter will develop a calibration curve from these standards. When finished, rinse the electrodes with Type II water and blot dry with a Kimwipe. Thoroughly rinse and dry electrochemical cell between uses.

14) Procedure: For samples with concentrations greater than 0.03mg/l the following procedure can be used.

1) Add 40ml AAR, 0.15ml (three drops) zinc acetate, and 50ml of sample to a 100ml volumetric flask. Dilute to 100ml with AAR.
2) Pour into the electrochemical cell and insert the electrodes.
3) Record the potential when the instrument indicates it's ready or is output to the printer.
4) Enter sulfide concentration into spreadsheet to check concentration.

15) Calculations:

$$C_0 = \frac{fC_s}{(1+f)10^{E_s - E_o/m} - 1}$$

C_o and C_s = sulfide concentrations in sample and known addition
E_0 and E_s = potential measured for sample and known addition
m= slope of calibration curve (~28mV/log S^{2-})
f= ratio of known addition volume to sample volume

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. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
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
Reference	A standard sample, made from either a different lot # solution, a different manufacturer, or another method (dissolving a solid)	Every sample batch	Ref
Continuing Calibration Verification	A standard sample, run throughout the course of the run, generally of varying concentration, and near the expected sample concentration range(s)	First sample, before running others, every 10-15 afterwards, and the last sample of any run NOTE: If curve is not run daily, highest standard must be run as a CCV	CCV
Initial Calibration Verification	A CCV done at the beginning of the run	1st sample	ICV
Laboratory Control Sample or Blank Spike	A spike of unknown concentration to Type II water	One per sample batch	LCS or BS
Matrix spike	A spike of known concentration to sample matrix	Every 20 samples or one per batch if less than 20 samples	SPK
Matrix Spike Duplicate	Same as above, repeated	One per month or ~250 samples	SPKDUP
Continuing Calibration Blank	Blank Sample	Every ten, or one per batch, following CCV	CCB

17) Pollution Prevention: This procedure has no discernible 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 there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper action line and a lower action line. The upper and lower warning lines are 2 standard deviations from the mean. The upper and lower action lines are three standard deviations from the mean. The process should be shut down for trouble shooting if the following occur:

- A single action outside the action line.
- 2 out of 3 consecutive measurements between the warning and action lines

- 7 consecutive measurements above or below the center line
- 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 non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. For flags and their meanings see UFI Controlled Document No. 12..

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. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

20) Contingencies for Handling Out-of-Control or Unacceptable Data: Samples are not to be run on equipment not meeting control criteria. If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is sufficient sample data, the data should be flagged with an explanation of the circumstances. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: wastes from this test can be washed down the sink with the tap running.

22) References:

1) Standard Methods 20th Edition 4500-S G. Ion-Selective Electrode Method. pp. 4.168-169

2) Orion Silver/Sulfide Electrode Instruction Manual: Thermo Electron Corp., 2003

3) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data:

Chlorophyll, EPA 445……..……SOP 216

1) Test Method: CHLOROPHYLL EPA 445.0

2) Applicable Matrix or Matrices: drinking, surface and saline waters, domestic and industrial wastes.

3) Detection Limit: Method detection limits using mixed assemblages of algae provide little information because of interference of other pigments in the fluorescence of chlorophyll a. An estimated detection limit (by EPA) is 0.10 ug/L in 10ml of final extract solution. The detection limit is also effected by the volume of water initially filtered. Filtering 500 ml of sample versus 50 ml will increase the detection limit by 10 fold.

4) Scope and Application: This method is suitable for the determination of chlorophyll in surface waters. The upper limit of linear dynamic range for the instrumentation is 250 ug/L.

5) Summary of Test Method: Chlorophyll containing particulate matter is concentrated by filtering samples through membrane filters. Pigments are extracted from the filter using acetone and their concentration is measured spectrophotometrically.

6) Definitions:

> **Fluorescence -** the emission of electromagnetic radiation, especially of visible light, stimulated in a substance by the absorption of incident radiation and persisting only as long as the stimulating radiation is continued

7) Interferences: Any substance extracted from the filter that fluoresces in the red region of the spectrum may interfere in the accurate measurement of chlorophyll *a*. Chlorophylls *a* and b may significantly interfere with chlorophyll a measurements depending on the amount present. Due to the spectral overlap of chlorophyll *b* and pheophytin *a* and chlorophyll *a* , underestimation of chlorophyll *a* occurs accompanied by overestimation of pheophytin *a* when chlorophyll *b* is present in the sample. The degree of interference depends on the ratio of a:b. Specific details and correction can be found in the method. Knowledge of the taxonomy of the algae under consideration will aid in determining if the spectrophotometric method using trichromatic equations to determine chlorophyll a, b, and c or an HPLC method would be more appropriate.

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:

- cellulose acetate filters 0.45 um (other types won't dissolve in the acetone)
- vacuum filtering apparatus

- glass vials
- fluorometer
- fluorometer cells
- pencil to record raw data, not pen

Model TD-700 Fluorometer equipped with:

- 13 mm cuvette holder (included with the TD-700 Fluorometer)
- Standard-solid, Red TD700 P/N 7000-994
- Optical Filter Kit PN 7000-962, which includes:
    - PN 10-113 (436 nm) Excitation Filter
    - PN 10-115 (680 nm) Emission Filter;
- PN 10-089 Blue Lamp (F4T4.5B2 equivalent).
- Filter Retainer 7000-949, set of four.
- Turner Designs power supply.

The TD-700 must have two different optical filters to operate correctly: an excitation filter and an emission filter.

To remove or to install optical filters in the Filter Cylinder:

1) Remove any test tubes or cuvettes and sample adaptors from the instrument. Then, grasp the Filter Cylinder by the rim and pull straight up and out of the unit.
2) Locate the filters (excitation and emission filters) from the chlorophyll A filter kit; the filters are marked on their rim with an identification number.
3) The Filter Cylinder has eight opening for four different filter sets, the opening for filter **set A** are marked, **" A/EX "** and **" A/EM "**.
4) Handle the filter on the edges so as to avoid leaving fingerprints on the filter, or wipe the filter before installing. If the filter has one side that is " mirrored " or highly reflective, it must be installed so the mirrored side faces outward from the cylinder (toward the lamp). Insert the excitation filter in the opening marked with the set letter **" A/EX ".** Push the filter in so it rests flush with the back of the opening. Then insert the O-ring and press it in until it is flush against the filter.
5) Locate the emission filter to be installed. Handle the filter at the edges; insert it (mirror side in) in the opening marked with the appropriate set **"A/EM"**. Push the filter in, then insert O-ring and press it in.
6) Position the Filter Cylinder in the sample chamber so that the alignment mark for the filter set, we are using **"A"**, is aligned with the silver alignment mark on the inside rim of the sample chamber.
7) To remove a filter, take out the flexible rubber O-ring holding the filter in place. Use a tool such as a plastic pen cap r plastic-nosed forceps to do this. Be careful not to scratch the surface of the filter. Place your hand over the opening and tilt the cylinder so the filter drops out into your hand. **Be careful, the filters are glass and may break if dropped**.
8) Install the proper lamp to line up the lamp prongs with the slots on the lamp sockets, push the lamp in and turn it about 90 degrees so that it is firmly seated.
9) Replace cover.

10) Reagents and Standards:

Acetone 90% - dilute 900 ml spectral grade acetone to 1 liter with Type II water.

Magnesium carbonate – Dissolve 1g in Type II water, dilute to 100 ml. Shake vigorously before use.

Liquid standards are obtained from Turner Designs via overnight mail. Ampules should be stored in the freezer until use. Once the ampule is opened it must be used immediately.

11) Sample Collection, Preservation, Shipment and Storage: Samples should be collected in clean bottles. They should be kept cool and in the dark until processing, which should occur as soon as possible.

Samples are filtered onto a .45nm cellulose nitrate filters, care should be taken to wash the sides of the filtering apparatus onto the filter within ten minutes. Pump pressure should not exceed 7 psi. Filter as much sample as practical, the filter should look colored and the flow should be significantly diminished. Several (2-3) drops of $MgCO_3$ should be added to the first volume of water filtered as a preservative. The filters can then be placed into a labeled glass vial and frozen until analysis. Record volume filtered as well as filter lot number in the appropriate laboratory notebook. Holding time is three weeks from filtering date.

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: Calibrate the instrument according to the following procedure:
Have ready a blank of 90% acetone and a standard of known pure chlorophyll a in 90% acetone (from Turner Design),

- turn on the fluorometer and allow it to warm up for at least 10 min, temperature affects the fluoroscence – DO NOT allow any sample to remain in the instrument for any longer than necessary for a stable reading.

Prepare a pure chlorophyll A and the blank of 90% acetone in a 13 mm test tube. The Direct concentration procedure should be used and the TD-700 will display actual concentration in the units chosen during setup.

- To choose the Direct Concentration Mode, press <**ENT**> from the HOME Screen and then press <**1**> for SETUP and <**1**> again for MODE. Use <**↔**> to choose the MULTI-OPTIONAL MODE.

- Press <**ESC** > to return to the previous screen, the press <**2**> to choose the calibration procedure. Use the<↔> key to choose " DIRECT CONC ".

- Press <**ESC**> to return to the previous screen and press < **3**> to choose the units of measure. Use the < ↔> key to choose the ug/l.

- Press < **ESC**> twice to return to the SETUP/CAL screen.

- To access the calibration sequence, press <**2**> from SETUP/CAL screen. The Direct concentration calibration sequence will appear.

  When the TD- 700 calls for the maximum range (the maximum concentration you want to read and it has to be about 20% higher than Hi STD). Press < **1**> to accept value or < **9**> to enter a new value and press <**ENT**> key.

  Key in the number of standards you will be using and press <**ENT**>.

  When the TD-700 calls for the "HiSDT Conc", press <**1**> to accept the current value or to press < **9**> to change the value. Key in the actual concentration of the highest concentration Standard (Hi STD), which you can find on the label of the ampule and press <**ENT**>. Your Hi STD must be about 80% of the Max Range you entered. We use two standards for calibration. Calibrate using the highest concentration standard first.

  Fill a clean test tube with the Hi STD, wipe the outside of the tube dry and insert it into the sample chamber. Press <*****>. The unit will adjust sensitivity (SENS FACTOR), to the level appropriate for that standard then read the standard (the ideal sensitivity is between 25%-30%).

  The unit will prompt you enter the actual concentration of the second standard, which you can find on the label of the ampule, enter the conc. and insert the second standard. Press <*****> and then <**ENT**> when you are finished.

  When all the standards have been run, the TD-700 will prompt you to insert the BLANK. Fill a clean test tube with the BLANK (90% of acetone), wipe the outside dry and insert it into the sample adapter in the sample chamber. Press <**ENT**>.

  Wait for the BLANK reading to stabilize, then press <**O**>. The TD-700 will read the BLANK, and then automatically return to the HOME screen. When finished, remove the BLANK. Remove the filter cylinder as described previously and set aside. Insert the solid standard. with the H (located on top of handle) to the left of the instrument. After number stabilizes, press the * key, record value. Remove the solid standard and turn 180 degrees so the L is facing the left of the instrument. After number stabilizes, press the * key, record value. These high and low values will be the referenced values for all calibration checks during sample

runs performed in between liquid calibrations. Record date of calibration, analyst and high and low values on solid standard box.

Calibration data will printout automatically.

Once the instrument is calibrated the calibration should remain stable for some time, the calibration is checked with each use at the beginning, end and in-between every 20 samples with the solid standard. The instrument will need to be recalibrated monthly or if ranges are changed (low to high or visa versa)or if lamps or filters are changed as well as if the instrument is relocated.

14) Procedure:

Add to each sample 20 ml prepared 90% acetone. Cap vial and mix vigorously to dissolve filter. Allow to stand overnight in a dark freezer to extract. A filter blank should be prepared by placing a clean filter into a vial and adding 20 ml of acetone, a filter blank must be run with each batch of samples. The next day, remove samples from refrigerator and mix again. Allow samples to come to room temperature to prevent condensation on the spec cells. Turn on the fluorometer to warm up during this time. At the start of every run instrument must be calibrated to the solid standards using the same procedure as described in section 13 and the referenced values that were assigned at the time of the liquid standard calibration. Pour or pipette samples into a clean cuvette and measure the fluorescence. Remember to record all of the sample information including the vol. filtered on the fluorometer data sheet. Rinse the cuvette with a 90% acetone three times as well as some of the next sample between samples, wiping cuvette with Kim Wipes before analysis.

Fluorescence is very temperature sensitive; therefore temperature is recorded throughout sample runs. If temperature drifts more then three degrees during a run instrument should be recalibrated using the solid standards.

During the sample run if the solid standards drift more then 10 percent, the instrument must be recalibrated using the liquid standards from Turner Design.

15) Calculations:

If the instrument was calibrated using the direct concentration procedure, the concentrations readings are the actual concentration of chlorophyll *a* in the extract. To calculate the concentration for the actual sample the extract conc. must be normalized for the sample volume filtered and the volume of acetone used for extraction. Use the following equation:

$$\text{Chlorophyll mg/m}^3 \text{ or ug/L} = \frac{(1)\,(F_x)(v)}{(V)}$$

where:

v = volume of acetone (mls)
V = volume of water filtered (L)
F_x = fluoroscence of the extract (ug/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. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Method Blank	Filtered 100 ml of Type II water.	One per sample batch	MB
Initial Calibration Verification (solid stds)	A CCV done at the beginning of the run	1st sample	ICV
Continuing Calibration Verification (solid stds)	A standard sample, run throughout the course of the run, generally of varying concentration, and near the expected sample concentration range(s)	First sample, before running others, every 10-15 afterwards, and the last sample of any run NOTE: If curve is not run daily, highest standard must be run as a CCV	CCV
Continuing Calibration Blank (90% Acetone)	Blank Sample	Every ten, or one per batch, following CCV	CCB
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

The estimated detection limit (EDL) for the evaluation of this method by EPA was 0.05 ug/L. The precision for chlorophyll a for a 24 hr extraction time was < 3.0 ug/L with a relative standard deviation of between 3.5 and 5% depending on sample volume filtered (100ml and 300ml respectively).

17) Pollution Prevention: This procedure has no discernible 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 there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper control line and a lower control line. The upper and lower warning lines are two standard deviations from the mean. The upper and lower control lines are three standard deviations from the mean. The process should be shut down for trouble shooting if the following occur:

- A single action outside the action line.
- 2 out of 3 consecutive measurements between the warning and action lines
- 7 consecutive measurements above or below the center line
- 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 non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. For flags and their meaning refer to UFI control document number 12.

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. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

20) Contingencies for Handling Out-of-Control or Unacceptable Data: Samples are not to be run on equipment not meeting control criteria. If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is sufficient sample data, the data should be flagged with an explanation of the circumstances. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. Wastes from this test can be washed down the sink with the tap running. Acetone should be disposed of properly.

22) References:

1) EPA Method 445.0 "In Vitro Determination of Chlorophyll a and Phaeophytin a In Marine and freshwater Phytoplankton by Fluorescence' Adapted by Elizabeth J. Arar and Gary B. Collins November 1992. In USEPA Methods for the Determination of CHEMICAL Substances in marine and Estuarine Environmental Samples. Environmental Monitoring Systems Laboratory Office of research and Development US Environmental Protection Agency, Cincinnati OH 45268

2) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data:

Dissolved Gas; Methane, Carbon Dioxide, Nitrogen ……SOP 217

1) Test Method: <u>DISSOLVED GAS (METHANE, CARBON DIOXIDE, NITROGEN)</u>

2) Applicable Matrix or Matrices: drinking, surface and saline waters, domestic and industrial wastes.

3) Detection Limit: See UFI Controlled Document No. 12.

4) Scope and Application: natural water systems

5) Summary of Test Method: Gas chromatography is commonly used for the isolation and quantification of dissolved gases in water. The low solubility of CH_4, CO_2, N_2 allows for an efficient partitioning of the species from the dissolved phase to an overlying gaseous headspace in the gas of interest. Helium is used as both the headspace and carrier gas. Dissolved gases are partitioned from the liquid phase to the gas phase using a modified syringe stripping technique. The gas phase is the injected into a gas chromatograph for quantification.

6) Definitions:

Extract- to obtain from a substance by chemical or mechanical action, as by pressure, distillation, or evaporation

Solubility- the amount of a substance that can be dissolved in a given amount of solvent

7) Interferences: Samples must be kept in BOD bottles, with water tight seals so that the integrity of the sample is not compromised

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:

- BOD or other gas tight bottles
- 10 ml gas tight syringe
- Wide-bore pipette more ~ 10 mL

10) Reagents and Standards:

Standard ~5% CH_4, CO_2, N_2 – pre-made from Empire Gas, exact %s available from manufacturer..

11) Sample Collection, Preservation, Shipment and Storage: Sample should be collected in a gas tight bottle (i.e. BOD). The bottles should be flushed several times

their volume, sealed and kept cool until analysis. If samples cannot be analyzed within several hours a few drops of conc. H_2SO_4 can be added to prevent bacterial action.

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: inject at least 3 aliquots of standard gas into the GC. When three successive injections of standard have reproducible results continue with samples.

14) Procedure:

Analysis is performed with a GOW-MAC gas chromatograph equipped with a thermal conductivity detector. The GC is equipped with a six port sample valve fitted with a 0.25 ml gas sampling loop (Valco). The column is a 6 ft. 1/8" O>D> s.s. carbosieve S-II (Supelco).

The gas chromatograph should be set up as follows:

carrier gas = UHP helium
column temperature = 160°C
detector temperature = 190 °C
bridge current = 174 ma
flow rate = 30 ml/min. (about 26 psig on regulator)
sample loop temperature = 104°C

Overfill a 10 ml gas tight syringe with sample, use a wide bore glass pipette to reduce aeration. Seal syringe and expel sample until the syringe is only half full, fill empty half of the syringe with UHP helium at atmospheric pressure. Equilibrate the two phases by vigorously shaking for 1 minute. This method has been shown to strip 97-98% of the dissolved gas in the liquid. Inject the gas phase into the GC, be careful not to inject the liquid into the GC.

15) Calculations:

Concentration in the standard:

$$pv = nrt$$

under atmospheric conditions v = nrt
therefore:

$$v = (n)(0.08205)(293.15) \text{ lit atm/K mol}$$

n = # of moles
v = volume % of constituent (3/99 std. 5.15% for methane, 5.02% for CO2, 4.9% for N2)

$$n = \frac{0.0515 \text{ or } 0.0502 \text{ or } 0.049}{(0.08205)(293.15)}$$

$$= 0.0021, 0.0022, 0.0020 \text{ moles/L}$$

for CH_4

$$\frac{0.0021 \text{ mol}}{\text{L}} \cdot \frac{16\text{g}}{\text{mol}} = 33.39 \text{ mg/L}$$

for CO_2

$$\frac{0.00209 \text{ mol}}{\text{L}} \cdot \frac{44\text{g}}{\text{mol}} = 91.82 \text{ mg/L}$$

for N_2

$$\frac{0.00204 \text{ mol}}{\text{L}} \cdot \frac{28\text{g}}{\text{mol}} = 57.04 \text{ mg/L}$$

To calculate concentration in sample:

$$\text{slope} = \frac{\text{area of std.}}{\text{conc. std.}}$$

$$\text{mg/L} = \frac{\text{area of sample}}{\text{slope}}$$

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. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation

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
Reference	A standard sample, made from either a different lot # solution, a different manufacturer, or another method (dissolving a solid)	Every sample batch	Ref
Continuing Calibration Verification	A standard sample, run throughout the course of the run, generally of varying concentration, and near the expected sample concentration range(s)	First sample, before running others, every 10-15 afterwards, and the last sample of any run NOTE: If curve is not run daily, highest standard must be run as a CCV	CCV
Initial Calibration Verification	A CCV done at the beginning of the run	1st sample	ICV
Continuing Calibration Blank	Blank Sample	Every ten, or one per batch, following CCV	CCB

17) Pollution Prevention: This procedure has no discernible 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 there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper action line and a lower action line. The upper and lower warning lines are 2 standard deviations from the mean. The upper and lower action lines are three standard deviations from the mean. The process should be shut down for trouble shooting if the following occur:

- A single action outside the action line.
- 2 out of 3 consecutive measurements between the warning and action lines
- 7 consecutive measurements above or below the center line
- 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 non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. Flags and their associated meanings can be found in UFI controlled document No. 12

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. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

20) Contingencies for Handling Out-of-Control or Unacceptable Data: Samples are not to be run on equipment not meeting control criteria. If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is sufficient sample data, the data should be flagged with an explanation of the circumstances. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: There are no wastes produced from this analysis

22) References:

1) Addess, J.A. 1990. Methane Cycling in Onondaga Lake, New York, Master Thesis, State University of New York, College of Environmental Science and Forestry, Syracuse, NY

2) Fendinger, N.J. and Adams, D.D. 1986. A Headspace Equilibrium Technique for Measurement of Dissolved Gases in Sediment Pore Water. Inter. J. Anal. Chem. Vol. 23 pp 253-265.

3) Rudd, J.W.M., Hamilton, R.D., and Campbell, N.E.R. 1974. Measurement of Microbial Oxidation of Methane in Lake Water. Limnology and Oceanography. Vol. 19(3) pp 519-524.

4) Stainton, M.P. 1973. A Syringe Gas-Stripping Procedure for Gas-Chromatographic Determination of Dissolved Inorganic and Organic Carbon in Fresh Water and Carbonates in Sediments. J. Fish. Res. Board Ca. Vol. 30 pp 1441-1445.

5) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

6) www.dictionary.com Online reference dictionary

23) Tables, Diagrams, Flowcharts and Validation Data:

Ferrous Iron …….……..……SOP 218

1) Test Method: FERROUS IRON

2) Applicable Matrix or Matrices: drinking, surface and saline waters, domestic and industrial wastes.

3) Detection Limit: Located in UFI controlled document No. 12.

4) Scope and Application: natural water systems

5) Summary of Test Method: Bipyridyl reacts with ferrous iron in an acid media to form a ferrous-bipyridyl complex that is pink in color and can be measured with a spectrophotometer.

6) Definitions:

Ferrous iron: iron cation having a +2 charge. It is a soluble form that has not yet been oxidized.

7) Interferences: turbidity, sample blanks are used as a correction.

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:

- Test tubes (labeled sample and blank)
- Spectrophotometer
- Appropriate cells for expected conc. (generally 10cm cell)
- Pippettes
- Volumetric flasks
- Dark BOD bottles for sampling

10) Reagents and Standards:

Hydrochloric acid 0.1M – Add 8ml conc. HCL to Type II water, dilute to 1 liter.

Acetic acid 4M – add 230 ml of conc. Glacial acetic acid to Type II water, dilute to 1000 ml in volumetric flask

Sodium acetate trihydrate 4M – Dissolve 544.32g sodium acetate trihydrate in Type II water, dilute to 1 liter in volumetric flask.

Reagent A - 2,2’ bipyridyl (a,a bipyridyl) or Dipyridyl – Dissolve 0.5g 2,2’ bipyridyl or Dipyridyl in liter of 0.1M HCL in volumetric flask.

Reagent B – pH 4.75 buffer sol'n – Mix equal volumes of 4M acetic acid and 4M sodium acetate.

11) Sample Collection, Preservation, Shipment and Storage: Samples should be collected in dark BOD bottles, being careful to exclude any air. Samples should be kept cool and in the dark and should be analyzed as soon as possible. Holding time for ferrous iron is 8 hours from collection.

12) Quality Control: UFI's QC parameters are outlined in the UFI control document number 12. 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:

1) Prepare a **Standard Fe2+ Stock Solution** by dissolving 0.315g Ferrous Ammonium Sulfate into a 250ml volumetric flask, add 2.0ml concentrated HCL, bring up to volume with Type II water.
2) Prepare a "**Working**" standard stock solution by taking 5mls of your prepared standard stock solution into 250ml volumetric flask, add 2.0ml concentrated HCL, bring up to volume with Type II water for a nominal concentration of 4000ugFe/L.
3) Prepare a **Reference solution** by dissolving 0.398g Ferrous Sulfate into 100 ml volumetric flask, add 0.8ml concentration HCL, bring up to volume with Type II water. 4) Prepare a "**Working**" reference solution by taking one ml of prepared reference solution into 100ml volumetric flask add 0.8ml concentrated HCL, bring up to volume with Type II water.
5) Perform a serial dilution by taking one ml of prepared "working" reference solution into 100ml volumetric flask add 0.8ml concentrated HCL, bring up to volume with Type II water to reach a final nominal concentration of 80ugFe/L.

From the"**Working standard stock solution** seven standards are made using the given measurements of stock solution and HCL.

Article I. Concentration made (ugFe/L)	**Amount "working"stock added in 100ml (mL)**	**Amount concentrated HCL added (mL)**
40	1	0.8
80	2	0.8
120	3	0.8
160	4	0.8
180	5	0.8
240	6	0.8
280	7	0.8

Standard concentration 80ugFe/L is run at the beginning middle and end of each run as a ICV and CCV.

14) Procedure:

Calibration: Allow Spec to warm up for at least 30minutes prior to analysis.

1) Open up UV/VIS program, click on "CONC" tab and select file "IRON2006MG" .
2) Select "SAMPLE" tab and type in sample IDs starting with ICV,CCV,ICB, REF, LCS and Reagent Blank. _-SAVE.
3) Select the "REF" tab and enter todays Julian Date and click on recalibrate_-SAVE.
4) Autozero the spec by adding Type II water to a 10cm cell and wipe clean with lens paper.

Prepare a standard 0 by:

5) Placing 3ml of Reagent B into "sample" tub
6) Add 30ml of 0.1 HCL under Reagent B.
7) Next add 3ml of Reagent A into tube. Mix tube thoroughly by swirling read in spectrophotometer at 520 nm by selecting START, read within 2 minutes.
8) Prepare all 7 standards repeating steps 1-3, only using standard solutions instead of 0.1HCL. to achieve a R^2 value of 0.995 or higher.
9) Once calibration is complete return to "REF"tab and select "USE EXISTING CALIBRATION CURVE".
10) Select "SAMPLE" tab.

Sample Analysis:

Keep BOD bottles capped until right before analysis; allow bottles to warm if very cold to avoid condensation on spec. cuvettes. For each sample two tubes will need to be prepared one containing sample and reagents and one containing sample, reagent B and Type II water to correct for turbidity in the sample. Prepare the sample first to minimize the time between opening the sample container and reaction with the reagents. Add 3 ml of reagent B to a test tube, add 30 ml of sample (via volumetric pipette), then add 3 ml of reagent A. Add reagents carefully to avoid aeration, add the sample under reagent B. Prepare the turbidity blank by adding 3 ml of reagent B to a second tube, add 30 ml sample, and 3 ml of distilled water. Sample turbidity blanks must be prepared for each sample to correct for turbidity. Mix tube thoroughly by swirling. Read in spectrophotometer at 520 nm within 2 minutes. Cuvette should be rinsed three times with Type II water. Both test tubes should also be rinsed with Type II water between samples.

If low iron concentrations are expected, a larger spec. cuvette can be used, the volume of sample and reagents should be increased proportionately so there is sufficient volume to fill a larger cuvette.

For quality control after initial calibration and before running samples analyze the 80ugFe/L standard, a reagent blank-30ml DI with both reagents added, the prepared reference (80ugFe/L) as well as a LCS (170ugFe/L) which is prepared by adding 1.275ml of the "working standard stock solution to 30ml of 0.1N HCL and adding both reagents. A matrix spike is performed once every sample run. This is done the same way as the LCS only using sample instead of the 0.1N HCL.

15) Calculations:

ABS_{corr} = sample absorbance – sample turbidity blank

Ferrous iron (mg/L) = 80 x ABS_{corr} (for a 1 cm cell)

Ferrous iron (mg/L) = 20 x ABS_{corr} (for a 4 cm cell)

Ferrous iron (mg/L) = 16 x ABS_{corr} (for a 5 cm cell)

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. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Initial Calibration Verification (80mg/L Fe2+)	A CCV done at the beginning of the run	1st sample	ICV
Reference (80mg/L Fe2+)	A standard sample, made from either a different lot # solution, a different manufacturer, or another method (dissolving a solid)	Every sample batch	REF
Laboratory Control Sample or Blank Spike (170mg/L Fe2+)	A spike of unknown concentration to Type II water	One per sample batch	LCS
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 sample, run throughout the course of the run, generally of varying concentration, and near the expected sample concentration	First sample, before running others, every 10-15 afterwards, and the last sample of any run NOTE: If curve is not	CCV

	range(s)	run daily, highest standard must be run as a CCV	
Matrix spike	A spike of known concentration to sample matrix	Every 20 samples or one per batch if less than 20 samples	SPK
Continuing Calibration Blank	Blank Sample	Every ten, or one per batch, following CCV	CCB

17) Pollution Prevention: This procedure has no discernible 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 there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper control line and a lower control line. The upper and lower warning lines are 2 standard deviations from the mean. The upper and lower control lines are three standard deviations from the mean. The process should be shut down for trouble shooting if the following occur:

- A single action outside the action line.
- 2 out of 3 consecutive measurements between the warning and action lines
- 7 consecutive measurements above or below the center line
- 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 non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. Flags are located in the UFI control document number 12.

Instrumentation profiles of dissolved oxygen should be checked; no ferrous iron should be present in oxygenated waters.

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. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

20) Contingencies for Handling Out-of-Control or Unacceptable Data: Samples are not to be run on equipment not meeting control criteria. If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is sufficient sample data, the data should be flagged with an explanation of the circumstances. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: It is preferable to neutralize waste matter before draining with sufficient rinsate, but not necessary. Wastes from this test can be washed down the sink with the tap running.

22) References:

1) Heaney, S,I. And Davidson, W. 1977. The determination of ferrous iron in natural waters with 2, 2' bipyridyl. *Limnology and Oceanography 22(4) 753-759.*

2) Standard Methods 20th ed 3500-B pg 3-77

4) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

23) Tables, Diagrams, Flowcharts and Validation Data:

Center for Environmental Systems and Engineering (CESE)

STANDARD OPERATING PROCEDURE

1. Title: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

AP #CESE-ENV-1631

Rev # 4-December 21, 2007 1 of 62

Prepared By: Emina Mujezenovic

Approved By: _____ Date: December 21, 2007
Edward Mason Jr -Technical Review

Approved By: _____ Date: December 21, 2007
Mario Montesdeoca-Laboratory Manager

Approved By: _____ Date: December 21, 2007
Charles T Driscoll-Primary Investigator

Effective Date: December 21, 2007

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2. Summary of Test Method

2.1 This laboratory procedure is principally derived from US EPA method 1631 Revision E.

2.2 A 100- to 1000-mL sample is collected directly into a cleaned, pretested, fluoropolymer or glass bottle using sample handling techniques designed for collection of mercury at trace levels (Reference 22.1).

2.3 For dissolved Hg, the sample is filtered through a 0.45*u*m capsule filter prior to preservation.

2.4 The sample is preserved by adding either pretested 12N hydrochloric acid (HCl) or bromine monochloride (BrCl) solution. If a sample will also be used for the determination of methylmercury, it should be preserved according to procedures in the method that will be used for determination of methylmercury.

2.5 Prior to analysis, all Hg in a 50-mL sample aliquot is oxidized to Hg (II) with BrCl.

2.6 After oxidation, the sample is sequentially reduced with NH_2OH*HCl to destroy the free halogens, then reduced with stannous chloride ($SnCl_2$) to convert Hg Hg (II) to volatile Hg(0).

2.7 In the Tekran 2600, the Hg (0) is separated from solution either by purging with nitrogen, helium, or argon, or by vapor/liquid separation. The Hg (0) is collected onto a gold trap (Figures 1 and 2). The Hg is then thermally desorbed from the gold trap into an inert gas stream that carries the released Hg (0) to a second gold (analytical) trap. The Hg is desorbed from the analytical trap into a gas stream that carries the Hg into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection (Figures 1 and 2).

2.8 Quality is assured through calibration and testing of the oxidation, purging, and detection systems.

2.9 If any technical issues arise, do not hesitate to contact a laboratory technician, a laboratory manager, or the principal investigator for additional clarifications.

3. Scope and Application

3.1 Method 1631, Revision E (the "Method") is for determination of mercury (Hg) in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). This Method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The Method is based on a contractor-developed procedure (Reference 22.1) and on peer-reviewed, published procedures for the determination of mercury in aqueous samples, ranging from sea water to sewage effluent.

3.2 This Method is accompanied by Method 1669: *Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* (Sampling Method). The Sampling Method guidance document is recommended to preclude contamination during the sampling process.

3.3 This Method is for determination of Hg in the range of 0.5–100 ng/L. Application may be extended to higher levels by selection of a smaller sample size or by calibration of the analytical system across a higher range. For measurement of blank samples, the Method may be extended to a lower level by calibration to a lower calibration point. Section 13.3 gives requirements for extension of the calibration range.

3.4 The ease of contaminating ambient water samples with mercury and interfering substances cannot be overemphasized. This Method includes suggestions for improvements in facilities and analytical techniques that should minimize contamination and maximize the ability of the laboratory to make reliable trace metals determinations. Certain sections of this Method contain suggestions and other sections contain requirements to minimize contamination.

3.5 The detection limit and minimum level of quantitation in this Method usually are dependent on the level of interferences rather than instrument limitations. The method detection limit (MDL; 40 CFR 136, Appendix B) for Hg has been determined to be 0.14 ng/L when no interferences are present.

3.6 The minimum level of quantitation (ML) has been established as 0.5 ng/L.

3.7 Tekran implemented a change of software to allow multiple loading during oxidation. These features improved the sensitivity by 10 folds, if a lower sensitivity is required. The sensitivity could be lower to approximately ~0.014 ng/L. A try-out test of 3 spiked aliquots at 0.02 ng/L gave an average recovery of 85%. A MDL is required prior using this new capability.

3.8 Clean and ultraclean—The terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this Method because they lack an exact definition. However, the information provided in this Method is consistent with the summary guidance on clean and ultraclean techniques (References 22.1).

3.9 This Method follows the EPA Environmental Methods Management Council's "Guidelines and Format for Methods to Be Proposed at 40 CFR, part 136 or part 141.

3.10 This Method is "performance based." The laboratory is permitted to modify the Method to overcome interferences or lower the cost of measurements if all performance criteria are met. Section 12.1.2.1 gives the requirements for establishing method equivalency.

3.11 Any modification of this Method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

3.12 This Method should be used only by analysts experienced in the use of CVAFS techniques and who are trained thoroughly in the sample handling and instrument techniques described in this Method. Each laboratory that uses this Method must demonstrate the ability to generate acceptable results using the procedures in Section 12.2.

3.13 This Method uses flow-injection system for determination of mercury in water and aqueous samples (Sections 13.2).

3.14 Each Quality Assurance Project Plan (QAPP) has specific QA\QC criteria that are applicable to a specific project. These criteria override the SOPs criteria. A copy of the QAPP is provided to all involved individuals in the project.

4. Applicable Matrix or Matrices

4.1 This method is applicable to aqueous samples.

5. Method Detection Limit

5.1 Calculating the MDL is the responsibility of the analyst and it must be determined on initial analysis per specific method. (i.e. If the analyst is using a method for the first time, the analyst needs to calculate the MDL for that specific method.) The MDL will be verified at the beginning of each subsequent analysis using the appropriate MDL check solution. The preferred method for calculating MDLs is found in Appendix B, Part 136, Revision 1.11 of the Federal Register, Volume 49, No. 209, October 1984.

5.2 The Laboratory MDL for Mercury is 0.14 ng/L. See table 7.

6. Definitions

6.1 Total Mercury – all BrCl-oxidizable mercury forms and species found in an unfiltered aqueous solution. This includes, but is not limited to, Hg (II), Hg(0), strongly organo-complexed Hg(II) compounds,

adsorbed particulate Hg, and several tested covalently bound organo-mercurials (e.g., CH_3HgCl, $(CH_3)_2Hg$, AND $C_6H_5HgOOCCH_3$). The recovery of Hg bound within microbial cells may require the additional step of UV photo-oxidation. In this method, total mercury and total recoverable mercury are synonymous.

6.2 Dissolved mercury – all BrCl-oxidizable mercury forms and species found in the filtrate of an aqueous solution that has been filtered through a 0.45*u*m filter.

6.3 Quality Assurance Project Plan (QAPP): QAPP is a plan to be followed to maintain a level of confidence of accuracy in a specify project.

6.4 Batch: A batch consists of 20 samples that are treated and analyzed together. A batch contains a Preparatory Blank (PB) or Method Blank (MB), a Laboratory Control Sample (LCS), also known as an Quality Control Sample (QCS), an ongoing Precision Recovery sample (OPR), a pair of Matrix Spike (MS), and a Matrix Spike Duplicate (MSD) for every ten samples and a Duplicate for every twenty samples.

6.5 Apparatus – Throughout this Method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, processing, and sample analysis that come in contact with the sample and therefore require careful cleaning will be referred collectively as the Apparatus.

6.6 Statistical definitions:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Mean - The average of n values is calculated by taking the sum of n values and dividing by n.

Sample Standard Deviation - A parameter used to measure the dispersion of a data set. It is calculated

$$s = \sqrt{\frac{\sum_{i=1}^{n} (\bar{x} - x_i)^2}{n-1}}$$

by the following:

Relative standard deviation (RSD) or coefficient of variation (CV) is the standard deviation divided by the mean and multiplied by 100.

$$CV = \frac{s}{\bar{x}} * 100$$

Relative Percent Difference - The relative percent difference of two numbers is calculated by dividing

$$RPD = \frac{|x_1 - x_2|}{((x_1 + x_2)/2)} * 100$$

the absolute value of their differences by the average of the two numbers.

Percent Recovery - Percent recovery is calculated by dividing the spike sample result by the spike added

$$\%R = \frac{SS}{SA} * 100$$

for or by dividing the spike sample result minus the sample by the spike added.

$$\%R = \frac{SS - S}{SA} * 100$$

where:
SS = Spike sample
SA = Spike added
S = Sample

7. Interferences

7.1 Preventing samples from becoming contaminated during the sampling and analysis process constitutes one of the greatest difficulties encountered in trace metals determinations. Over the last two decades, marine chemists have come to recognize that much of the historical data on the concentrations of dissolved trace metals in seawater are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing samples for trace metals.

7.2 Samples may become contaminated by numerous routes. Potential sources of trace metals contamination during sampling include: metallic or metal-containing labware (e.g., talc gloves that contain high levels of zinc), containers, sampling equipment, reagents, and reagent water; improperly cleaned or stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples directly exposed to exhalation (Reference 22.1).

7.3 Contamination Control

7.3.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is metal free and free from any material that may contain mercury.

7.3.1.1 The integrity of the results produced cannot be compromised by contamination of samples. This Method and the Sampling Method give requirements and suggestions for control of sample contamination.

7.3.1.2 Substances in a sample cannot be allowed to contaminate the laboratory work area or instrumentation used for trace metals measurements. This Method gives requirements and suggestions for protecting the laboratory.

7.3.1.3 Although contamination control is essential, personnel health and safety remain the highest priority. The Sampling Method and Section 8 of this Method give suggestions and requirements for personnel safety.

7.3.2 Avoiding contamination—The best way to control contamination is to completely avoid exposure of the sample to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being done. Therefore, it is imperative that the procedures described in this Method be carried out consistently, and continue blank reviews are essential part of the QC.

7.3.3 Use a clean environment—The analysis of samples is done in a class-100 clean room.

7.3.4 Minimize exposure—The Apparatus that will contact samples, blanks, or standard solutions should be opened or exposed only in a clean room, clean bench, or glove box so that exposure to an uncontrolled atmosphere is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean zip-type bags. Minimizing the time between cleaning and use will also minimize contamination.

7.3.5 Clean work surfaces—Before a given batch of samples is processed, all work surfaces in the hood, clean bench, or glove box in which the samples will be processed should be cleaned by wiping with a lint-free cloth or wipe soaked with reagent water.

7.3.6 Wear gloves—Sampling personnel must wear clean, non-talc gloves during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

7.3.7 Use metal-free Apparatus—All Apparatus used for determination of mercury at ambient water quality criteria levels must be nonmetallic, free of material that may contain metals, or both.

7.3.7.1 Construction materials—Only fluoropolymer or glass containers must be used for collection of samples that will be analyzed for mercury because mercury vapors can diffuse in or out of other materials, leading to results that are biased low or high. Polyethylene and/or polypropylene labware may be used for digestion and other

purposes because the time of sample exposure to these materials is relatively short. All materials, regardless of construction, that will directly or indirectly contact the sample, must be known to be clean and free of Hg at the levels specified in this Method before proceeding.

7.3.7.2 Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of reusable Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the lab ware to introduction into the instrument. It may be useful to dedicate separate sets of lab ware to different sample types; e.g., receiving waters vs. effluents. However, the Apparatus used for processing blanks and standards must be mixed with the Apparatus used to process samples so that contamination of all lab ware can be detected.

7.3.7.3 The laboratory or cleaning facility is responsible for cleaning the Apparatus used by the sampling team. If there are any indications that the Apparatus is not clean when received by the sampling team (e.g., ripped storage bags), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.

7.3.8 Avoid sources of contamination—Avoid contamination by being aware of potential sources and routes of contamination.

7.3.8.1 Contamination by carryover—Contamination may occur when a sample containing a low concentration of mercury is processed immediately after a sample containing a relatively high concentration of mercury. The Hg concentration at which the analytical system (purge, traps, detector) will carry greater than 0.5 ng/L of Hg into a succeeding bubbler or system blank must be determined by analyzing calibration solutions containing successively larger concentrations of Hg. This test must be run prior to first use of the analytical system and whenever a change is made that would increase the amount of carryover. When a sample contains ½ or greater of this determined Hg concentration, a system blank (flow injection system) must be analyzed to demonstrate no carryover at the blank criteria level. Samples analyzed following a sample that has been determined to result in carryover must be reanalyzed. Samples that are known or suspected to contain the lowest concentration of mercury should be analyzed first followed by samples containing higher levels.

7.3.8.2 Contamination by samples—Significant laboratory or instrument contamination may result when untreated effluents, in-process waters, landfill leachates, and other undiluted samples containing concentrations of mercury greater than 100 ng/L are processed and analyzed. Samples known or suspected to contain Hg concentrations greater than 100 ng/L should be diluted prior to bringing them into the clean room or laboratory dedicated for processing trace metals samples.

7.3.8.3 Contamination by indirect contact—Apparatus that may not directly come in contact with the samples may still be a source of contamination. For example, clean tubing

placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. It is imperative that every piece of the Apparatus that is directly or indirectly used in the collection, processing, and analysis of water samples be thoroughly cleaned (Section 9.1.2).

7.3.8.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particles, or vapors from unfiltered air supplies; nearby corroded or rusted pipes, wires, or other fixtures; or metal-containing paint. Whenever possible, sample processing and analysis should occur as far as possible from sources of airborne contamination.

7.3.8.5 Contamination from reagents— Contamination can be introduced into samples from method reagents used during processing and analysis. Reagent blanks must be analyzed for contamination prior to use (see Section 12.4.2). If reagent blanks are contaminated, a new batch of reagents must be prepared (see Section 12.4.2.2).

7.4 Interference

7.4.1 At the time of promulgation of this Method, gold and iodide were 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 the brown color) and additional or more concentrated $SnCl_2$ should be added. To preclude loss of Hg, the additional SnCl should be added in a closed vessel or analysis should proceed immediately. If samples containing iodide concentrations greater than 30 mg/L are analyzed, it may be necessary to clean the analytical system with 4N HCl after the analysis (Reference 22.10).

7.4.2 The potential exists for destruction of the gold traps if free halogens are purged onto them, or if they are overheated (>500 °C). When the instructions in this Method are followed, neither of these outcomes is likely.

7.4.3 Water vapor may collect in the gold traps and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to scattering of the excitation radiation. Condensation can be avoided by predrying the gold trap. Traps that tend to absorb large quantities of water vapor should not be used.

7.4.4 The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause "quenching" of the excited atoms. The dual amalgamation technique eliminates quenching due to trace gases, but it remains the laboratory's responsibility to ensure high purity inert carrier gas and a leak-free analytical train.

8. Safety

8.1 All analysts will attend the “Chemical Hygiene Plan” training provided by the Environmental Health Office (EHO).

8.2 Many of the reagents used in the analysis of mercury are potentially dangerous. It is strongly advised

that the analyst check the material Safety Data Sheets for any reagent he/she is not familiar with. Product handling and protective measures should always be observed.

8.3 The analyst shall practice standard laboratory safety procedures as specified in the Chemical Hygiene Plan prepared by the EHO.

8.4 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

8.5 The toxicity or carcinogenicity of each chemical used in this Method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

8.5.1 Chronic mercury 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 Hg, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

8.5.2 It is recommended that the laboratory purchase a dilute standard solution of the Hg in 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.

8.6 Samples suspected to contain concentrations of Hg at µg/L or higher levels are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. Each laboratory must develop a safety program for handling Hg.

8.6.1 Facility—When samples known or suspected of containing high concentrations of mercury 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-tight 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 hazards except in an accident.

8.6.2 Protective equipment—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters.

8.6.3 Training—Workers must be trained in the proper method of removing contaminated clothes and gloves without contacting the exterior surfaces.

8.6.4 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

8.6.5 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and

plastic absorbent paper on bench tops will aid in confining contamination.

8.6.6 Effluent vapors—The effluent from the CVAFS should pass through either a column activated charcoal or a trap containing gold or sulfur to amalgamate or react mercury vapors.

8.6.7 Waste handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.

8.6.8 Decontamination

8.6.8.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

8.6.8.2 Glassware, tools, and surfaces—Sulfur powder will react with Hg to produce mercuric sulfide, thereby eliminating the possible volatilization of Hg. Satisfactory cleaning may be accomplished by dusting a surface lightly with sulfur powder, then washing with any detergent and water.

8.6.8.3 Laundry- Clothing known to be contaminated should be collected in plastic bags. Persons that convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. If the launderer knows of the potential problem, the clothing may be put into a washer without contact. The washer should be run through a cycle before being used again for other clothing.

8.6.8.4 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by this Method can achieve a limit of detection of less than 1 ng per wipe. Less than 0.1µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10µ g on a wipe constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

9. Equipment and Supplies

9.1 Sampling equipment

9.1.1 Sample collection bottles-fluoropolymer or glass, 125- to 1000-mL, with fluoropolymer or fluoropolymer-lined cap.

9.1.2 Cleaning

9.1.2.1 All bottles for ultra low level are Teflon bottles. New and used bottles are cleaned as described below.

9.1.2.2 New bottles are cleaned by heating to 65–75 °C in 4 N HCl or concentrated HNO_3 for at least 48 h. The bottles are cooled, rinsed three times with reagent water, and filled with reagent water containing 1% HCl. These bottles are capped and placed in a clean oven at 60-70°C overnight. After cooling, they are rinsed three more times

with reagent water, filled with reagent water containing 0.4% (v/v) HCl, and placed in a mercury-free Class-100 clean bench until the outside surfaces are dry. The bottles are tightly capped (with a wrench), double-bagged in new polyethylene zip-type bags until needed, and stored in wooden or plastic boxes until use. The bottles are shipped to the sampling site containing dilute HCl solution (e.g., 0.4%) or containing reagent water.

9.1.2.3 Used bottles known not to have contained mercury at high (>100 ng/L) levels are cleaned as above, except for only 6–12 h in hot 4 N HCl. *Method 1631, Revision E.*

9.1.2.4 Bottle blanks must be analyzed as described in Section 12.4.6. To verify the effectiveness of the cleaning procedures, bottle blanks must be demonstrated to be free of mercury at the MDL of this Method.

9.1.2.5 As an alternative to cleaning by the laboratory for samples with high Hg concentration, bottles may be purchased from a commercial supplier and each lot certified to be clean. Bottles from the lot must be tested as bottle blanks (Section 12.4.6) and demonstrated to be free of mercury at the ML of QAPP criteria. If mercury is present above this level in any bottle, either the lot must be rejected or the bottles must be re-cleaned.

9.1.3 Filtration Apparatus

9.1.3.1 Filter—0.45µm, 15-mm diameter capsule filter (Gelman Supor 12175, or equivalent)

9.1.3.2 Peristaltic pump—115-V a.c., 12-V d.c. internal battery, variable-speed, single-head (Cole-Parmer, portable, "Masterflex L/S," Catalog No. 07570-10 drive with Quick Load pump head, Catalog No. 07021-24, or equivalent).

9.1.3.3 Tubing—styrene/ethylene/butylene/silicone (SEBS) resin for use with peristaltic pump, approx 3/8-in ID by approximately 3 ft (Cole-Parmer size 18, Catalog No. 06424-18, or approximately 1/4-in OD, Cole-Parmer size 17, Catalog No. 06424- 17, or equivalent). Tubing is cleaned by soaking in 5–10% HCl solution for 8–24 h, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with metal-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

9.2 Equipment for bottle and glassware cleaning

9.2.1 Vat, 100–200 L, high-density polyethylene (HDPE), half filled with 4 N HCl in reagent water.

9.2.2 Panel immersion heater, 500-W, all-fluoropolymer coated, 120 vac (Cole-Parmer H-0305 3- 04, or equivalent)

WARNING: *Read instructions carefully!! The heater will maintain steady state, without temperature feedback control, of 60–75°C in a vat of the size described. However, the equilibrium temperature will*

be higher (up to boiling) in a smaller vat. Also, the heater plate MUST be maintained in a vertical position, completely submerged and away from the vat walls to avoid melting the vat or burning out!

9.2.3 Laboratory sink—in Class-100 clean area, with high-flow reagent water (Section 10.1) for rinsing.

9.2.4 Clean bench—Class-100, for drying rinsed bottles.

9.2.5 Oven—stainless steel, in Class-100 clean area, capable of maintaining ± 5°C in the 60–70°C temperature range.

9.3 Cold vapor atomic fluorescence spectrometer (CVAFS): The CVAFS system used is the CVAFS—Tekran (Toronto, ON) Series 2600 CVAFS. Series 2600 is capable of providing a fully automated implementation of the US EPA Method 1631, Revision E. The new instrument by Tekran is capable of measuring waters with a detection limit of much less than the required < 0.5 ng/L (ppt).

9.4 The dual-trap Hg(0) preconcentrating system

9.4.1 Figure 2 and 3 show the dual-trap amalgamation system (Reference 22.5). *Method 1631, Revision E*

9.5 Recorder—Any multi-range millivolt chart recorder or integrator with a range compatible with the CVAFS is acceptable. By using a two-pen recorder with pen sensitivity offset by a factor of 10, the dynamic range of the system is extended to 10^3.

9.6 Pipettors—All-plastic pneumatic fixed-volume and variable pipettors in the range of 10 uL to 5.0 mL.

9.7 Analytical balance capable of weighing to the nearest 0.01 g.

10. Reagents and Standards

10.1 Reagent water—18-M S minimum, ultrapure deionized water starting from a prepurified (distilled, reverse osmosis, etc.) source. Water should be monitored for Hg, especially after ion exchange beds are changed.

10.2 Air—It is very important that the laboratory air be low in both particulate and gaseous mercury. Mercury work is conducted in a new laboratory with mercury-free paint on the walls. A source of air that is very low in Hg should be brought directly into the Class-100 clean bench air intake.

10.3 Hydrochloric acid—trace-metal purified reagent-grade HCl containing less than 5 pg/mL Hg.The HCl should be analyzed for Hg before use.

10.4 Hydroxylamine hydrochloride—Dissolve 150 g of NH_2OH @HCl in reagent water and bring to 500mL. This solution may be purified by the addition of 1.0 mL of $SnCl_2$ solution and purging overnight at 500 mL/min with Hg-free N_2.

10.5 Stannous chloride—Bring 200 g of $SnCl_2$ @$2H_2O$ and 100 mL concentrated HCl to 1.0 L with reagent water. Purge overnight with mercury-free N_2 at 500 mL/min.

10.6 Bromine monochloride (BrCl)—In a fume hood, dissolve 27 g of reagent grade KBr in 2.5 L of low-Hg HCl. Place a clean magnetic stir bar in the bottle and stir for approximately 1 h in the fume hood. Slowly add 38 g reagent grade $KBrO_3$ to the acid while stirring. When all of the $KbrO_3$ has been added, the solution color should change from yellow to red to orange. Loosely cap the bottle, and allow to stir another hour before tightening the lid.

WARNING: *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 fume hood!*

10.7 Stock mercury standard—NIST-certified 10,000-ppm aqueous Hg solution (NIST-3133). This solution is stable at least until the NIST expiration date.

10.8 Secondary Hg standard—Add approx 0.5 L of reagent water and 5 mL of BrCl solution (Section 10.6) to a 1.00-L Class A volumetric flask. Add 0.100 mL of the stock mercury standard (Section 10.7) to the flask and dilute to 1.00 L with reagent water. This solution contains 1.00 µg/mL (1.00 ppm) Hg. Transfer the solution to a fluoropolymer bottle and cap tightly. This solution is considered stable until the NIST expiration date.

10.9 Working Hg Standard A—Dilute 1.00 mL of the secondary Hg standard (Section 10.8) to 100 mL in a Class A volumetric flask with reagent water containing 0.5% by volume BrCl solution (Section 10.6). This solution contains 10.0 ng/mL and should be replaced monthly, or longer if extended stability is demonstrated.

10.10 Working Hg Standard B—Dilute 0.10 mL of the secondary Hg standard (Section 10.8) to 1000 mL in a Class A volumetric flask with reagent water containing 0.5% by volume BrCl solution (Section 10.6). This solution contains 0.10 ng/mL and should be replaced

10.11 Initial Precision and Recovery (IPR) and Ongoing Precision and Recovery (OPR) solutions—Using the working Hg standard A (Section 10.9), prepare IPR and OPR solutions at a *Method 1631, Revision E* concentration of 5 ng/L Hg in reagent water. IPR/OPR solutions are prepared using the same amounts of reagents used for preparation of the calibration standards.

10.12 Nitrogen—Grade 4.5 (standard laboratory grade) nitrogen that has been further purified by the removal of Hg using a gold-coated sand trap.

10.13 Argon—Grade 5.0 (ultra high-purity, GC grade) argon that has been further purified by the removal of Hg using a gold-coated sand trap.

11. Sample Collection, Preservation, and Storage

11.1 Before samples are collected, consideration should be given to the type of data required (i.e., dissolved or total), so that appropriate preservation and pretreatment steps can be taken. An excess of BrCl should be confirmed either visually (presence of a yellow color) or with starch iodide indicating paper, using a separate sample aliquot, prior to sample processing or direct analysis to ensure the sample has been properly preserved.

11.2 Samples are collected into rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps. It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads (Reference 22.1). Polyethylene sample bottles must not be used (Reference 22.1).

11.3 Collect samples using guidance provided in the SOP; Sampling Stream and Lake Water for Mercury at Trace Levels, AP#CESE-ENV-1669, Rev. 0.

NOTE: Discrete samplers have been found to contaminate samples with Hg at the ng/L level. Therefore, great care should be exercised if this type of sampler is used. It may be necessary for the sampling team to use other means of sample collection if samples are found to be contaminated using the discrete sampler.

11.4 Sample Filtration – For dissolved Hg, a sample is filtered through a 0.45*u*m capsule filter in a mercury free area prior to preservation.

11.5 Preservation—Samples are preserved by adding either 5 mL/L of pretested 12N HCl or 5 mL/L BrCl solution to the sample bottle. If a sample will be used also for the determination of methyl mercury, it should be collected and preserved according to procedures in the method that will be used for determination of methyl mercury (e.g., HCl or H_2SO_4 solution). Preserved samples are stable for up to 90 days of the date of collection.

11.5.1 Samples to be analyzed for total or dissolved Hg only may be shipped to the laboratory unpreserved and unrefrigerated if they are collected in fluoropolymer or glass bottles and capped tightly. Samples must be either preserved or analyzed within 48 hours of collection. If a sample is oxidized in the sample bottle, the time to preservation can be extended to 28 days.

11.5.2 Samples that are acid-preserved may lose Hg to coagulated organic materials in the water or condensed on the walls (Reference 22.16). The best approach is to add BrCl directly to the sample bottle at least 24 hours before analysis. If other Hg species are to be analyzed, these aliquots must be removed prior to the addition of BrCl. If BrCl cannot be added directly to the sample bottle, the bottle must be shaken vigorously prior to sub-sampling.

11.5.3 Handling of the samples in the laboratory should be undertaken in a mercury-free clean bench, after rinsing the outside of the bottles with reagent water and drying in the clean air hood.

11.6 Storage—Sample bottles should be stored in clean (new) polyethylene bags until sample analysis.

12. Quality Control and Documentation

12.1 Each laboratory that uses this Method is required to operate a formal quality assurance program (Reference 22.1). The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of matrix spikes (MS) and matrix spike duplicates (MSD) to assess precision and recovery. Laboratory performance is compared to established performance criteria to determine that the results of analyses meet the performance characteristics of the Method.

12.1.1 The laboratory shall make an initial demonstration of the ability to generate acceptable accuracy and precision. This ability is established as described in Section 12.2.

12.1.2 In recognition of advances that are occurring in analytical technology, the laboratory is permitted certain options to improve results or lower the cost of measurements. These options include automation of the dual-amalgamation system, single-trap amalgamation (Reference 22.1), direct electronic data acquisition, calibration using gas-phase elemental Hg standards, use of the bubbler or flow-injection systems, or changes in the detector (i.e., CVAFS) when less sensitivity is acceptable or desired. Changes in the determinative technique, such as the use of colorimetry, are not allowed. If an analytical technique other than the CVAFS technique specified in this method is used, that technique must have a specificity for mercury equal to or better than the specificity of the technique in this Method.

12.1.2.1 Each time this Method is modified, the laboratory is required to repeat the procedure in Section 12.2 to demonstrate that an MDL (40 CFR part 136, Appendix B) less than or equal to one-third the regulatory compliance limit or less than or equal to the MDL of this Method (Table 1), whichever is greater, can be achieved. If the change will affect calibration, the instrument must be recalibrated according to Section 13.

12.1.2.2 The laboratory is required to maintain records of modifications made to this Method. These records include the following, at a minimum:

12.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and the quality control officer who witnessed and will verify the analyses and modification

12.1.2.2.2 A narrative stating the reason(s) for the modification(s)

12.1.2.2.3 Results from all quality control (QC) tests demonstrating the performance of the modified method, including the following:

(a) Calibration (Section 13)
(b) Initial precision and recovery (Section 12.2.2)
(c) Analysis of blanks (Section 12.4)
(d) Matrix spike/matrix spike duplicate analysis (Section 12.3)
(e) Ongoing precision and recovery (Section 12.5)
(f) Quality control sample (Section 12.6)
(g) Method detection limit (Section 12.2.1)

12.1.2.2.4 Data that will allow an independent reviewer to validate each determination by tracking the instrument output to the final result. These data are to include the following:

(a) Sample numbers and other identifiers
(b) Processing dates
(c) Analysis dates
(d) Analysis sequence/run chronology
(e) Sample weight or volume

(f) Copies of logbooks, chart recorder, or other raw data output
(g) Calculations linking raw data to the results reported

12.1.3 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision and to monitor matrix interferences. Section 12.3 describes the procedure and QC criteria for spiking.

12.1.4 Analyses of blanks are required to demonstrate acceptable levels of contamination. Section 12.4 describes the procedures and criteria for analyzing blanks.

12.1.5 The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery (OPR) sample and the quality control sample (QCS) that the system is in control. Sections 12.5 and 12.6 describe these procedures, respectively.

12.1.6 The laboratory shall maintain records to define the quality of the data that are generated. Sections 12.3.7 and 12.5.3 describe the development of accuracy statements.

12.1.7 Quality of the analyses is controlled by an analytical batch. An analytical batch is a set of samples oxidized with the same batch of reagents, and analyzed during the same 12- hour shift. A batch may be from 1 to as many as 20 samples. Each batch must be accompanied by 3 system blanks (Section 12.4.1 for the flow-injection system), a minimum 5-points calibration curve is required and analysis of seven standards is recommended to reduce the potential of re-calibration, 1 OPR sample at the beginning and end of the batch (Section 12.5), a QCS (Section 12.6), and at least 3 method blanks (Section 12.4.3). In addition, there must be 1 MS and 1 MSD sample for every 10 samples (a frequency of 10%). A typical analytical sequence would be:

a) Three system blanks (Section 12.4.1)
b) A minimum of five, non-zero calibration standards;
   Seven points recommended (Section 13.2.2.1)
c) Initial Calibration Blank (Section 12.4.3)
d) Initial Calibration Verification (Section 12.7)
e) Quality control sample (Section 12.6)
f) MDL Check
g) On-going precision and recovery (Section 12.5)
h) Method blank (Section 12.4.2)
i) Ten samples
j) Matrix spike (Section 12.3)
k) Matrix spike duplicate (Section 12.3)
l) Lab duplicate
m) Continuing Calibration Verification (Section 13.2.4)
n) Continuing Calibration Blank (section 12.4.3)
o) Method blank
p) Ten samples
q) Matrix spike (Section 12.3)
r) Matrix spike duplicate (Section 12.3)
s) Lab Duplicate
t) Lab Triplicate (QAPP dependent)
u) Continuing Calibration Verification (Section 13.2.4)

v) Continuing Calibration Blank (section 12.4.3)
w) Method blank (Section 12.4.2)
x) On-going precision and recovery (Section 12.5)

The above sequence includes calibration. If system performance is verified at the end of the sequence using the OPR, analysis of samples and blanks may proceed without recalibration (i.e., the analytical sequence would be entered at Step (c) above), unless more than 12 hours has elapsed since verification of system performance. If more than 12 hours has elapsed, the sequence would be initiated at Step (b) above.

12.2 Initial demonstration of laboratory capability

12.2.1 Method detection limit—To establish the ability to detect Hg, the laboratory shall achieve an MDL that is less than or equal to the MDL listed in Section 3.5 or one-third the regulatory compliance limit, whichever is greater. The MDL shall be determined according to the procedure at 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this Method. This MDL shall be used for determination of laboratory capability only, and should be determined when a new operator begins work or whenever, in the judgment of the laboratory, a change in instrument hardware or operating conditions would dictate reevaluation of capability.

12.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the laboratory shall perform the following operations:

12.2.2.1 Analyze four replicates of the IPR solution (5 ng/L, Section 10.11) according to the procedure beginning in Section 14.

12.2.2.2 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 Hg.

12.2.2.3 Compare s and X with the corresponding limits for initial precision and recovery in Table 2. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the17 *Method 1631, Revision E - August 2002* precision limit or X falls outside the acceptance range, system performance is unacceptable. Correct the problem and repeat the test (Section 12.2.2.1).

12.3 Matrix spike (MS) and matrix spike duplicate (MSD)—To assess the performance of the Method on a given sample matrix, the laboratory must spike, in duplicate, a minimum of 10% (1 sample in 10) from a given sampling site or, if for compliance monitoring, from a given discharge. Therefore, an analytical batch of 20 samples would require 2 pairs of MS/MSD samples (four spiked samples total).

12.3.1 For unknown sample concentration, Matrix Spike (MS)\Matrix Spike Duplicate (MSD) are spiked with 10 ng\L of Hg. To make the MS and MSD, weigh 49.700mL of a sample. Add 0.050 mL of the 10ng/mL THg standard to the sample. Then fix the sample with 0.250mL BrCl.

12.3.2 The concentration of the spike in the sample shall be determined as follows:

12.3.2.1 If, as in compliance monitoring, the concentration of Hg in the sample is being checked against a regulatory compliance limit, the spiking level shall be at that limit or at 1–5 times the background concentration of the sample (as determined in Section 12.3.2), whichever is greater.

12.3.2.2 If the concentration of Hg in a sample is not being checked against a limit, the spike shall be at 1–5 times the background concentration or at 1-5 times the ML in Table 1, whichever is greater.

12.3.3 To determine the background concentration (B), analyze one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 14.If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established *a prior*i.

12.3.3.1 If necessary, prepare a standard solution to produce an appropriate level in the sample (Section 12.3.1).

12.3.3.2 Spike two additional sample aliquots with identical amounts of the spiking solution and analyze these aliquots as described in Section 14.1.2 to determine the concentration after spiking (A).

12.3.4 Calculate the percent recovery (R) in each aliquot using the following equation:

$$\%R = 100\frac{(A-B)}{T}$$

where:
A= Measured concentration of analyte after spiking
B= Measured concentration of analyte before spiking
T= True concentration of the spike

12.3.5 Compare percent recovery (R) with the QC acceptance criteria in Table 2.

12.3.5.1 If results of the MS/MSD are similar and fail the acceptance criteria, and recovery for the OPR standard (Section 12.5) for the analytical batch is within the acceptance criteria in Table 2, an interference is present and the results may not be reported or otherwise used for permitting or regulatory compliance purposes. If the interference can be attributed to sampling, the site or discharge should be resampled. If the interference can be attributed to a method deficiency, the laboratory must modify the method, repeat the test required in Section 12.1.2, and repeat analysis of the sample and MS/MSD. However, during the development 18 *Method 1631, Revision E - August 2002* of Method 1631, very few interferences have been noted in the determination of Hg using this Method. (See Section 7.4 for information on interferences.)

12.3.5.2 If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be not in control, and the results may not be

reported or used for permitting or regulatory compliance purposes. The laboratory must identify and correct the problem and reanalyze all samples in the sample batch.

12.3.6 Lab Duplicate/Lab Triplicate-An identical sample to another one, from the same sample container. Run every 20 samples for the duplicate and QAPP dependent for the triplicate. Lab Triplicate precision will be determined using %RSD. This is:

%RSD=100 (SD/ $\overline{X}$)

where:
SD = Standard Deviation
$\overline{X}$ = Average of results

12.3.7 Relative percent difference (RPD)—Compute the RPD between the MS and MSD results according to the following equation using the concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 12.3.3 for this calculation because the RPD is inflated when the background concentration is near the spike concentration. The Lab Duplicated also uses the RPD

$$RPD = 200 * \frac{\left(\left|D_1 - D_2\right|\right)}{\left(D_1 + D_2\right)}$$

where:
D_1 = concentration of Hg in the MS sample
D_2 = concentration of Hg in the MSD sample

12.3.8 The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 2. If the criterion is not met, the system is judged to be out of control. The problem must be identified and corrected, and the MS/MSD and corresponding samples reanalyzed.

12.3.9 The %RSD for the parent sample, lab duplicate and triplicate must not exceed the acceptance criterion in Table 2.If the criterion is not met, the system is judged to be out of control. The problem must be identified and corrected, and the QC samples and corresponding samples reanalyzed.

12.3.10 As part of the QC program for the laboratory, method precision and recovery for samples should be assessed and records maintained. After analyzing five samples in which the recovery passes the test in Section 12.3.4, compute the average percent recovery (Ra) and the standard deviation of the percent recovery (S_r). Express the accuracy assessment as a percent recovery interval from Ra – $2S_r$ to R_a + $2S_r$. For example, if R_A = 90% and S_R = 10% for five analyses, the accuracy interval is expressed as 70–110%. Update the accuracy assessment regularly (e.g., after every five to ten new accuracy measurements).

12.4 Blanks—Blanks are critical to the reliable determination of Hg at low levels. The sections below give the minimum requirements for analysis of blanks. Analysis of additional blanks is recommended as necessary to pinpoint sources of contamination in, and external to, the laboratory.

12.4.1 System blanks (SB) — System blanks are analyzed to demonstrate that flow injection systems are free from contamination at levels that could affect data quality. Three system blanks must be run during calibration and with each analytical batch.

12.4.1.1 To analyze a system blank, analyze reagent water containing the same amount of reagents used to prepare the calibration standards.

12.4.1.2 If a system blank is found to contain 0.50 ng/L Hg, the system is out of control. The problem must be investigated and remedied, and the system recalibrated. If the blanks contain < 0.50 ng/L Hg, the data associated with the blanks remain valid, provided that all other criteria in Section 12 also are met.

12.4.1.3 The mean result for the three system blanks must be <0.5 ng/L Hg with a standard deviation (n-1) <0.1 ng/L. If the mean exceeds these criteria, the system is out of control, and the problem must be resolved and the system recalibrated. If the mean is <0.5 ng/L, the average peak height or area is subtracted from all raw data before results are calculated (Section 15.1).

12.4.2 Method blanks (MB)— Method blanks are used to demonstrate that the reagents used to prepare samples for Hg analyses are free from contamination. The Hg concentration in reagent blanks is determined by analyzing the reagent solutions using either the bubbler or flow-injection system. For the bubbler system, reagent may be added directly to previously purged water in the bubbler.

12.4.2.1 Method blanks are required when the batch of reagents (bromine monochloride plus hydroxylamine hydrochloride) are prepared. The amount of Hg in a reagent blank containing 0.5% (v/v) BrCl solution (Section 10.6) and 0.2% (v/v) hydroxylamine hydrochloride solution (Section 10.4) must be < 20 pg (0.2 ng/L).

12.4.2.2 The presence of more than 20 pg (0.2 ng/L) of Hg indicates a problem with the reagent solution. The purging of certain reagent solutions, such as $SnCl_2$ or NH_2OH, with mercury-free nitrogen or argon can reduce Hg to acceptable levels. Because BrCl cannot be purified, a new batch must be prepared and tested if the BrCl is contaminated.

12.4.3 Continuing Calibration blanks (CCB)— Continuing Calibration blanks are used to demonstrate that the analytical system is free from contamination that could otherwise compromise sample results. Continuing Calibration blanks are prepared and analyzed using sample containers, labware, reagents, and analytical procedures identical to those used to prepare and analyze the samples. Continuing Calibration blanks should follow all Continuing Calibration verification samples. The Initial calibration Blank is the same, except it is run after the Initial Calibration Verification sample.

12.4.3.1 A minimum of three method blanks per analytical batch are required for flow-injection systems.

12.4.3.2 If the result for any method blank containing the nominal amount of reagent used to prepare a sample (Section 14.1.1) is found to contain 0.50 ng/L (50 pg) Hg, the system is out of control. Mercury in the analytical system must be reduced until a method blank is free from contamination at the 0.50 ng/L level. Samples associated with a contaminated method blank must be reanalyzed.

12.4.3.3 Because method blanks are analyzed using procedures identical to those used to analyze samples, any sample requiring an increased amount of reagent must be accompanied by at least one method blank that includes an identical amount of reagent.

12.4.4 Field blanks–Field blanks are used to demonstrate that samples have not been contaminated by the sample collection and transport activities.

12.4.4.1 Analyze the field blank(s) shipped with each set of samples (samples collected from the same site at the same time, to a maximum of 10 samples). Analyze the blank immediately before analyzing the samples in the batch.

12.4.4.2 If Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 7), or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes.

12.4.4.3 Alternatively, if sufficient multiple field blanks (a minimum of three) are collected, and the average concentration (of the multiple field blanks) plus two standard deviations is equal to or greater than the regulatory compliance limit or equal to or greater than one-half of the level in the associated sample, results for associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes.

12.4.4.4 If contamination of the field blanks and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event.

12.4.5 Equipment blanks—Before any sampling equipment is used at a given site, the laboratory or cleaning facility is required to generate equipment blanks on all sampling equipment that will be used to demonstrate that the sampling equipment is free from contamination.

12.4.5.1 Equipment blanks are generated in the laboratory or at the equipment cleaning facility by processing reagent water through the sampling devices using the same procedures that are used in the field (see Sampling Method). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility for low level

mercury measurements. If grab samples are to be collected using any ancillary equipment, e.g., an extension pole or a dipper, an equipment blank is generated by submersing this equipment into the reagent water and analyzing the resulting reagent water collected.

12.4.5.2 The equipment blank must be analyzed using the procedures in this Method. If mercury or any potentially interfering substance is detected in the blank at or above the level specified for the field blank (Section 9.4.5), the source of contamination or interference must be identified, and the problem corrected. The equipment must be demonstrated to be free from mercury and interferences before the equipment may be used in the field.

12.4.6 Bottle blanks— Bottles must be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles (Section 9.1.2) should be filled with reagent water acidified to pH <2 and allowed to stand for a minimum of 24 h. At least 5% of the bottles from a given lot should be tested, and the time that the bottles are allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water must be analyzed for any signs of contamination. If a bottle shows contamination at or above the level specified for the field blank (Section 12.4.4), the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles re-cleaned.

12.5 Ongoing precision and recovery (OPR)—To demonstrate that the analytical system is within the performance criteria of this Method and that acceptable precision and recovery is being maintained within each analytical batch, the laboratory shall perform the following operations:

12.5.1 Analyze the OPR solution (5 ng/L, Section 10.11) prior to the analysis of each analytical batch according to the procedure beginning in Section 14. An OPR also must be analyzed at the end of an analytical sequence or at the end of each 12-hour shift.

12.5.2 Compare the recovery with the limits for ongoing precision and recovery in Table 2. If the recovery is in the range specified, the analytical system is in control and analysis of samples and blanks may proceed. If, however, the concentration is not in the specified range, the analytical process is not in control. Correct the problem and repeat the ongoing precision and recovery test. All reported results must be associated with an OPR that meets the Table 2 performance criteria at the beginning and end of each batch.

12.5.3 The laboratory should add results that pass the specification in Section 12.5.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory also should develop a statement of laboratory data quality by calculating the average percent recovery R_a) and the standard deviation of the percent recovery (S_r). Express the accuracy as a recovery interval from $R_a - 2S_r$ to $R_a + 2S_r$. For example, if $R_a = 95\%$ and $S_r = 5\%$, the accuracy is 85–105%.

12.6 Quality control sample / Laboratory Control Sample (QCS/LCS) – The laboratory must obtain a QCSLCS from a source different from the Hg used to produce the standards used routinely in this Method (Sections 10.7–10.10). The QCS/LCS should be analyzed as an independent check of system performance. The sample must be prepared and analyzed with every batch of samples. The percent

recovery must be within laboratory control limits unless otherwise specified in the Quality Assurance Project Plan.

12.7 Initial Calibration Verification Sample (ICV) - A standard that is run at the beginning of the analytical sequence. The initial calibration verification (ICV) is evaluated to assess the accuracy of the initial calibration.

12.8 Continuing Calibration Verification Sample (CCV) – These samples are evaluated to determine whether the instrument is within acceptable calibration throughout period in which samples are analyzed (i.e., to verify that the initial calibration was applicable during the sample analyses). In general, failure of the CCV indicates that the initial calibration is no longer valid and should trigger recalibration and the reanalysis of the associated samples in the analytical sequence.

12.9 The laboratory may be required to analyze field duplicates and field spikes collected to assess the precision and accuracy of the sampling, sample transportation, and storage techniques. The relative percent difference (RPD) between field duplicates should be less than 20%.

12.9.1 For determining Quality control limits, prior to the submittal of the data, all preparation blank, matrix spike, matrix spike duplicate, duplicate, and laboratory control sample data must be input into the laboratory database.

12.9.2 The analyst performing the analysis compares all QA/QC to the appropriate control limits in a timely manner. If any excursions are noted, the analysis is halted and corrective action is implemented. See table 2 for appropriate corrective actions. All excursions are noted on a corrective action form (attachment 1).

12.10 Documentation

12.10.1 Reagent bottles are labeled with reagent name, name and amount of all chemicals used in production, preparation date, expiration date, and initials of analyst.

12.10.2 Sample data and quality control data is recorded on the appropriate laboratory forms.

12.10.3 As new standards and reference samples are introduced in to the laboratory, they must be tagged with a reagent number and entered in to the CESE Section Standard Preparation Logsheet. The reagent number is then recorded on the appropriate laboratory forms when used.

13. Calibration and Standardization

13.1 Initial Calibration

13.1.1 Calibration and standardization—Flow-injection system (Section 13.3) is calibrated using standards traceable to NIST Standard Reference Materials. If system performance is verified at the end of an analytical batch using the OPR, analysis of samples and blanks may proceed without recalibration, unless more than 12 hours has elapsed since verification of system performance.

13.2 Flow-injection system calibration

13.2.1 Establish the operating conditions necessary to purge Hg from the gas-liquid separator and dryer tube and desorb Hg from the traps in a sharp peak. Further details for operating the analytical system are given in Section 14.2.1.

13.2.2 The calibration must contain a minimum of 5 non-zero points and the results of analysis of 3 system blanks. The lowest calibration point must be at the minimum level (ML).

13.2.2.1 Place 25-30 mL of reagent water and 250 µL of concentrated BrCl solution (Section 10.6) in each of 5 calibrated 50-mL autosampler vials. Prepare the 0.5 ng/L calibration standard by adding 250 µL of working standard B (Section 10.10) to the vial. Dilute to the mark with reagent water. Sequentially follow with the addition of aliquots of 25, 125, 250 and 500 µL of working standard A (Section 10.9) to produce standards of 5.0, 25.0, 50.0 and 100.0 ng/L, respectively. Cap the vials and invert once to mix.

13.2.2.2 Immediately prior to analysis, remove the caps and add 125 µL of NH_2OH solution (Section 10.4). Re-cap, invert once to mix, and allow to stand until the yellow color disappears. Remove all caps and place vials into the analysis rack.

13.2.2.3 Analyze the standards beginning with the lowest concentration and proceeding to the highest. Tabulate the height or area for the Hg peak.

13.2.2.4 Prepare and analyze a minimum of 3 system blanks and tabulate the peak heights or areas. Calculate the mean peak area or height for the system blanks.

13.2.2.5 For each calibration point, subtract the mean peak height or area of the system blanks (Section 12.4.1) from the peak height or area for each standard. Calculate the calibration factor (CF_X) for Hg in each of the five standards using the mean reagent-blank-subtracted peak height or area and the following equation:

$$CF_X = \frac{\left(A_X\right) - \left(\overline{A}_{SB}\right)}{\left(C_X\right)}$$

where:

A_x *=peak height or area for Hg in standard*

$\overline{A}_{SB}$ *=mean peak height or area for Hg in calibration blanks*

C_x*= concentration of standard analyzed (ng/L)*

13.2.2.6 Calculate the mean calibration factor (C_{Fm}), the standard deviation of the calibration factor (SD; n-1), and the relative standard deviation (RSD) of the calibration factor, where RSD = 100 x SD/C_{Fm}.

13.2.2.7 If RSD <15%, calculate the recovery for the lowest standard (0.5 ng/L) using C_{Fm}. If the RSD <15% and the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable and C_{Fm} may be used to calculate the concentration of Hg in samples, blanks, and OPRs. If RSD > 15% or if the recovery of the lowest standard is not in the range of 75-125%, recalibrate the analytical system and repeat the test.

13.2.2.8 Calculate the concentration of Hg in the system blanks (Section 12.4.1) using CFm. The system blanks must meet the criteria in Section 12.4.1; otherwise, mercury in the system must be reduced and the calibration repeated until the system blanks meet the criteria.

13.2.3 Calibration to a range other than 0.5 to 100 ng/L—This Method may be calibrated to a range other than 0.5 to 100 ng/L, provided that the following requirements are met:

(a) There must be a minimum of five non-zero calibration points.
(b) The difference between successive calibration points must be no greater than a factor of 10 and no less than a factor of 2 and should be approximately evenly spaced on a logarithmic scale over the calibration range.
(c) The relative standard deviation (RSD) of the calibration factors for all calibration points must be less than 15%.
(d) The calibration factor for any calibration point at a concentration greater than 100 ng/L must be within ±15% of the average calibration factor for the points at or below 100 ng/L.
(e) The calibration factor for any point <0.5 ng/L must be within 25% of the average calibration factor for all points.
(f) If calibration is to a higher range and this Method is used for regulatory compliance, the ML must be less than one-third the regulatory compliance limit

14. Procedure for Analysis on the Tekran 2600 (see Attachment 2 for quick start-up reference)

14.1 Sample Preparation

14.1.1 Weigh about 50mL of each water sample aliquot from a thoroughly shaken, acidified sample, into a 60-mL sample vial.

14.1.1.1 For clear water and filtered samples, add 0.5 mL of BrCl; for brown water and turbid samples, add 1.0 mL of BrCl. If the yellow color disappears because of consumption by organic matter or sulfides, more BrCl should be added until a permanent (12-h) yellow color is obtained.

14.1.1.2 Some highly organic matrices, such as sewage effluent, will require high levels of BrCl (e.g., 5 mL/100 mL of sample) and longer oxidation times, or elevated temperatures (e.g., place sealed bottles in oven at 50 °C for 6 h). The oxidation must be continued until it is complete. Complete oxidation can be determined by either observation of a permanent yellow color remaining in the sample or the use of starch iodide indicating paper to test for residual free oxidizer. The sample also may be

diluted to reduce the amount of BrCl required, provided that the resulting level of mercury is sufficient for reliable determination.

14.1.2 Matrix spike (MS) and matrix spike duplicate (MSD)—To assess the performance of the Method on a given sample matrix, the laboratory must spike, in duplicate, a minimum of 10% (1 sample in 10) from a given sampling site or, if for compliance monitoring, from a given discharge. Therefore, an analytical batch of 20 samples would require 2 pairs of MS/MSD sample (four spiked samples total).

14.1.3 There must be a minimum of 2 pairs of MS/MSD for each analytical batch of 20 samples.

14.2 Prepare standards for analysis:

14.2.1 Standards may be made the day of analysis or they may be made in advance. It is a good idea to make your standards at the same time you prepare your samples for analysis. If samples or standards are made more than one day in advance of analysis, they should be stored at room temperature and IN THE DARK. Light photo-reduces the BrCl used to oxidize the samples and standards, and leaving them exposed to light for several days may interfere with the accuracy of analysis. Make the standards as follows:

14.2.2 The low standards (0.5 and 1.0 ng/L) cannot be accurately made using the 10 ng/L intermediate HgT standard. In order to make the 0.5 and 1.0 ng/L standard you must do a serial dilution from the 100 ng/L standard. In order to do this you must:

14.2.2.1 Make the 100 ng/L standard as indicated above.

14.2.2.2 Make sure you have fixed the 100 ng/L standard with 0.250 ml BrCl.

14.2.2.3 Cap and vigorously shake the 100 ng/L standard.

14.2.2.4 With a clean pipette tip, use the fixed 100 ng/L standard to spike the 0.5 and 1.0 ng/L standards, and then fix them with 0.250 ml of 0.5% BrCl.

14.2.2.5 Prepare Quality Control sample from certified reference material. This should be made from a secondary certified source and be composed of a NATURAL MATRIX, not laboratory De-ionized water. The laboratory uses the SRM 1641d manufactured by NIST. The standard is made in natural matrix water.

14.2.2.6 Be sure that all standards and Quality Control samples have been fixed with BrCl.

14.3 Prepare Reagents, Clean Room, and Analyzer for Analysis:

14.3.1 Prepare Reagents:

14.3.1.1 Reducing Reagent: Make 3% $SnCl_2$ and purge with high purity nitrogen gas for at least 1 hour.

14.3.1.1.1 To make the $SnCl_2$, add 30g $SnCl_2$ (anhydrous) granules to the designated "$SnCL_2$" 1L flask. Add 500-700mL of Milli-Q di water to the granules and swirl to mix. Then add 50mL of HCl to the flask and bring to 1L with DI water. Mix and then transfer to the 2L Teflon SnCl2 bottle.

14.3.1.1.2 Purging is accomplished by placing the large bubbler stem (reserved for SnCl2) into the 2L Teflon $SnCl_2$ bottle, sealing with parafilm, and then sparging with high purity nitrogen gas (~1000 ml/min for at least 1 hour).

14.3.1.1.3 2L of 3% $SnCl_2$ will be enough for four racks of vials. For longer runs, you will need to make more 3% $SnCl_2$ (~2L / 4 racks).

14.3.1.2 Wash Solution: Make 2L of 5% 3HCl:1HNO_3 (1L to clean the tubing, 1L for the washes).

14.3.1.2.1 Measure 1L of Milli-Q DI-water with the designated 1L flask. Pour out 50mL of di water. Pour the remaining water into a designated 1L Teflon bottle. Add 12.5mL of HNO_3 and 37.5mL HCl to the bottle. Cap and shake the bottle to mix.

14.4 Clean Room Entry

14.4.1 Switch the clean room key to "Occupied".

14.4.2 "OPEN" both Argon tanks to the right of the door to the clean room. Check the gas tanks. Make sure they are both High Purity Argon. If either tank reads less than 500 PSI, then change that tank. The Detector Carrier Gas flow and Phase Separator Gas flow should be delivered at 20-40 psi (aim for ~30 psi). You should not have to adjust the regulators, except to make sure the lower black knob is in the "OPEN" position (twisting down from the regulator opens this valve).

14.4.3 Enter gown room and put on clean suit, hair net, booties, safety glasses and gloves. When booties and gowns become visibly dirty, they should be trashed. Your hair should actually be tucked under the hair net. This is done to ensure the clean room is kept clean and YOU do not contaminate your samples.

14.5 Initial Inspection.

14.5.1 Assess the condition of the soda-lime column. The dry-rite column should be changed at least weekly. If there is any caking of dry-rite, then change the column. If there is discoloration, then change the column. If you have been having any problems with carry over, then change the column. In order to change the column, open the top of the analyzer, and disconnect the soda lime trap from the sampling loop:

14.5.1.1 Make sure the analyzer is NOT running.

14.5.1.2 Gently remove column by removing it from the black clips, and then unscrewing the red caps at each end. Be sure not to tug on the caps and hoses on each end, or you will damage the analyzer, cause leaks, or otherwise wreck your chances of successfully using the analyzer.

14.5.1.3 Remove old Glass Wool or Silica Wool. Dump old dry-rite into waste container.

14.5.1.4 Refill the column with dry-rite and glass wool plugs. Be sure that the glass wool plug actually blocks the entire opening of the column at BOTH ends.

14.5.1.5 Return the soda lime trap to the analyzer, re attach the tubing, close the lid.

14.5.1.6 If you are unsure of how to do this, PLEASE ASK.

14.6 Turn on the Analyzer Components: (-) = “On”, and (o) = “Off”.

14.6.1 The Detector (Top Component).

14.6.2 The pump (Bottom Component).

14.6.3 The Autosampler. When the autosampler is turned on, it will move to the home position, above the wash station. Check to be sure that this has been accomplished. Then check to make sure the sampling probe is properly adjusted, and the screw holding it in place is finger-tight.

14.6.4 Make a note of all settings.

14.6.4.1 Digital Output: Should read 0.1000 – 0.1100 during baseline.

14.6.4.2 Sensitivity Dial: 5.0

14.6.4.3 Offset Dial: 5.08

14.6.4.4 Detector Flow: ~90 units (This is in automatic shutoff mode).

14.6.4.5 Phase Separator Flow: ~425 units (This is on automatic shutoff mode).

14.6.4.6 Pump Speed Dial: 4.0

14.7 Check the waste container and make sure it is nearly empty. If it is not empty, empty the content into the appropriate waste carboy and neutralize the waste solution. Once neutralized, the waste can be flushed down the sink with copious amounts of tap water.

14.8 Initial Maintenance: (Acid Wash, DI Rinse, Column Cleaning Sequence)

14.8.1 Set up pump tubes and clamps for initial cleansing of analyzer.

14.8.2 Check the Tekran Quickstart manual to ensure the proper tubes are in the proper clamp fittings.

14.8.3 Clamp the tubes into place. The three back tube adjustment levers should be at “11 o’clock”. The SnCl2 tube lever should be at “11:30” and the sampling tube lever should be at “12 o’clock”.

14.8.4 Trace all tubes and assure all are connected to the proper places and are being pumped in the proper direction. Read the Tekran Quickstart Manual if you need to refresh your memory about where each tube belongs and in which direction fluids should be flowing.

14.8.5 Fill the 1L glass jar designated for acid with 5% 3:1 HCl: HNO3. Place the SnCl2 tube into the acid. Place the Wash Station Input tube into the acid. Place the Wash Station Output tube into the waste container, but do not let it contact waste fluid, as this could later contaminate your DI Reservoir.

14.8.6 Turn on Computer and open Tek-MDS program.

14.8.7 Select a new worksheet. Select “Samples”, then “Run”, highlight the desired “method”, click “new” to select a new worksheet.

14.8.8 Change the filename of your new run to the format “XXYYMMDD”, where “XX” represents the analyst’s initials, the “YY” the two digit year, “MM” the two digit month, and “DD” the two digit day, and append this with the word “cleaning”. Example “JD040525cleaning”

14.8.9 Initialize the autosampler: Click on the “Initialze” button in the gray window. WAIT. A control message will indicate “autosampler” found. Then you will eventually get a small window (be patient, this can take some time). The autosampler model is 223. The rack code is 112 for all racks. Click “o.k.”

14.8.10 Command the autosampler to go to the wash station: Click “A/S Wash” in the small gray window.

14.8.11 Now that all tubes have been set up and autosampler is in wash station, flip the main pump switch to “local” mode. This will start the acid solution running through the lines to clean out any residue. Pump flow is left to right. Watch to ensure flow through is occurring. The acid cleaning should take about 15 minutes. Use all of the 5% acid solution. Be sure that fluids are moving through all tubes, and be sure that the wash station fills. If the wash station tube goes empty, a vacuum can be created by placing a gloved finger over the top of the wash station column until the water level has returned to the appropriate level. Check to make sure no fluid is backing up in the system.

14.9 While the acid and DI-rinse are running, set up a short cleaning sequence. Do NOT designate any sample tubes or rinse tubes. This sequence will both clean the gold traps, and additionally flush the system with reageant water.

Line #	Sample ID	Sample Tube	Rinse Tube
1	Clean		
2	clean		
3	clean		
4	Ws		
5	Ws		
6	Ws		
7	clean		
8	clean		
9	clean		
10	Ws		
11	Ws		
12	Ws		
13	Clean		
14	Clean		
15	Clean		

14.10 When the acid has run out, flip the pump switches back to "off" and send the autosampler probe back to its home position by selecting "A/S Home".

14.11 Rinse the glass jar with DI water, and then fill with DI water. Switch the pump to local again, send the autosampler to the wash station, and run DI water through the entire system. The Wash Station Output tube should still be in the waste container. Circulate DI water for about 5 minutes to remove residual acid from the lines. While the DI-water is circulating, rinse the 2L DI reservoir 3x with Milli-Q DI-water, fill, and parafilm the top.

14.12 After circulating DI for 5 minutes, turn pump "off". Place the Wash Station Input and Wash Station Output into the 2L DI Reservoir. Leave the $SnCl_2$ tube in the small glass jar, and fill the jar with DI-water.

14.13 Configure the cleaning sequence.

14.13.1 Click on "Configure Run".

14.13.2 The "first sample" number should refer to the line # of the very first clean.

14.13.3 The "last sample" number should refer to the line # of the very last clean.

14.13.4 Make sure the line numbers are correct, and that the "clean first?" option is marked "Y".

14.13.5 The "clean event table file" will read "$Clean_6etf".

14.13.6 The “sample event table file” will read “Sample_6etf”.

14.13.7 The “error trace” will read “2”.

14.13.8 Click o.k., and you should soon have a Start Run option in the small gray window.(DO NOT CLICK IT YET!)

14.13.9 When you are ready to start the clean sequence, quickly verify the lines are in the appropriate reservoirs, and flip the pump switch to “remote”.

14.13.10 Click the “Start Run” option, and after a few seconds the pumps will start.

14.13.11 Verify that the fluids are moving in the proper direction through each of the lines, and in the wash station. Be sure no fluids are backing up anywhere in the system. **NOTE**: At this point, you will have approximately one hour until the cleaning sequence has finished. This time can be used to organize your standards, samples, and run sequence for analysis, and make any additional reagents that will be needed for the analysis of your samples.

14.13.12 When cleaning cycle has finished:

14.13.12.1 Turn “off” pump.

14.13.12.2 Check that peaks were low enough.

14.13.12.3 Exit worksheet.

14.13.13 Sample Analysis Set Up:

14.13.14 Change $SnCl_2$ tubing and sample tubing.

14.13.15 The $SnCl_2$ tubing and the Sample tubing should be replaced. If these lines are used repeatedly, high carry over is the result. High carry over causes mdl’s and ccb’s to increase in Peak Area over the course of a run, thus throwing low level analyses into question. The $SnCl_2$ tube and Sample tube should be changed every time you do an analysis.

14.13.16 Set up pump tubes and clamps for initial cleansing of analyzer.

14.13.17 Check the Tekran Quickstart manual to ensure the proper tubes are in the proper clamp fittings.

14.13.18 Clamp the tubes into place. The three back tube adjustment levers should be at “11 o’clock”. The SnCl2 tube lever should be at “11:30” and the sampling tube lever should be at “12 o’clock”.

14.13.19 Trace all tubes and assure all are connected to the proper places and are being pumped in the proper direction. Read the Tekran Quickstart Manual if you need to refresh your memory about where each tube belongs and in which direction fluids should be flowing.

14.13.20 Verify that the Wash Station Input and Wash Station Output are both in the DI Reservoir. Fill the DI Reservoir, and para film the top.

14.13.21 Place the $SnCl_2$ tube into the $SnCl_2$. Para film the top.

14.13.22 Open Tek-MDS program and select a new worksheet.

14.13.22.1 Select “Samples”, then “Run”, highlight the desired “method”, click “new” to select a new worksheet.

14.13.22.2 Change the filename of your new run to the format “XXYYMMDD”, where “XX” represents the analyst’s initials, the “YY” the two digit year, “MM” the two digit month, and “DD” the two digit day Example “JD040525”.

14.13.22.3 Initialize the autosampler: Click on the “Initialze” button in the gray window. WAIT. A control message will indicate “autosampler” found. Then you will eventually get a small window (be patient, this can take some time). The autosampler model is 223. The rack code is 112 for all racks. Click “o.k.”

14.13.22.4 Command the autosampler to go to the wash station: Click “A/S Wash” in the small gray window.

14.13.23 Set up the analysis sequence.

14.13.23.1 Type all standards & sample ID’s into the new spreadsheet on the computer. Be sure not to designate a sample tube nor a rinse tube for “clean” and “ws” samples. (See Table 4)

14.13.23.2 Assign sample tube numbers and rinse tube numbers to each sample ID. Sample Tubes can only go to 48, then you must start at the beginning. Rinse Tubes will use one of the designated wash tubes at the beginning of the run, just designate which tube you want. I usually designate rinse tubes as 1,2,3,4 and leave position 7-48 open for sample tubes.

14.13.23.3 “Clean” and “WS” (wash station) blanks should have no sample and rinse tube referenced to them...leave them blank!

14.13.24 Configure the analysis sequence.

14.13.24.1 Click on “Configure Run”

14.13.24.2 The “first sample” number should refer to the line # of the very first clean.

14.13.24.3 The “last sample” number should refer to the line # of the very last clean.

14.13.24.4 Make sure the line numbers are correct, and that the “clean first?” option is marked “Y”.

14.13.24.5 The “clean event table file” will read “$Clean_6etf”.

14.13.24.6 The “sample event table file” will read “Sample_6etf”.

14.13.24.7 The “error trace” will read “2”.

14.13.24.8 Click o.k., and you should soon have a Start Run option in the small gray window... (DO NOT CLICK IT YET!)

14.13.25 When you are ready to start the analysis sequence, verify the lines are in the appropriate reservoirs, and flip the pump switch to “remote”.

14.13.26 Click the “Start Run” option, and after a few seconds the pumps will start.

14.13.26.1 Verify that the fluids are moving in the proper direction (left to right) through each of the lines, and in the wash station. Be sure no fluids are backing up anywhere in the system. As the first wash station samples begin to pass through the sampling lines, check to make sure fluid is moving at the appropriate speed. When the first wash vial is sampled, check to see what volume was taken (>80% of the sample is should be used. If an inadequate volume was pumped, adjustments must be made prior to the end of the “wash, wash, wash” sequence. Adjustments cannot be made after the first 0.0 ng/L standard is sampled.

14.14 Running Standards and Samples:

14.14.1 Add Hydroxylamine to the standards at this time (it should be added at least 10 to 15 minutes prior to the sample being analyzed). Loosen the vial caps, add 0.1mL hydroxyl amine to each vial, re-cap and shake vials to mix them, wait ~10 minutes and then uncap the vials. Add the hydroxyl amine to all the standards at once. If the standard curve passes (see Excel worksheet below) continue with analysis. If calibration curve fails, you must make a new standard curve and have it pass before proceeding with sample analysis.

14.14.2 Do not run samples unless the analyzer is running clean, adequate volumes are being pumped, AND the standard curve has passed.

14.14.3 Start adding the hydroxyl amine segment at a time (from ccv/ccb to ccv/ccb) as the run progresses (once the hydroxyl amine is added, the sample must be analyzed or remade – it is therefore better not to add the hydroxyl amine to all the samples at the beginning in case something should go wrong and the run must be stopped).

14.14.3.1 Rinse tubes may need to be refilled as the run progresses. The DI water will need to be refilled as the run progresses. If running more than 4 racks, make more 3% SnCl2 and bubble with ultra high purity nitrogen gas for at least 1 hour.

14.14.4 At the end of the run, the analyzer will run for several minutes after the last clean has finished. Wait until the pumps have stopped to start reporting data and cleaning the system.

14.14.5 AT END OF RUN: Wash the system by running acid for 5-10min and then run water (Milli-Q) for 5-10min. Then follow shutdown procedure at the end of this manual.

14.15 Standard Curve

*The standard curve must have a coefficient of variation (%) of less than 15% in order for the run to be acceptable.

Excel Worksheet

Sample id	Peak area	Corrected peak area	Calibration factor	Calculated Conc (ng/L)
(column) A	B	C	D	E
0.00	From report	C3=B3-$B$3		E3=C3/$D$10
1.00	From report	C4=B4-$B$3	D4=C4/A4	E4=C4/$D$10
5.00	From report	C5=B5-$B$3	D5=C5/A5	E5=C5/$D$10
10.00	From report	C6=B6-$B$3	D6=C6/A6	E6=C6/$D$10
25.00	From report	C7=B7-$B$3	D7=C7/A7	E7=C7/$D$10
50.00	From report	C8=B8-$B$3	D8=C8/A8	E8=C8/$D$10
100.00	From report	C9=B9-$B$3	D9=C9/A9	E9=C9/$D$10
		Average CF	D10=average(D4:D9	
		St dev	D11=stdev(D4:D9)	
		%	D12=D11*100/D10	

*After calculating the "calculated concentration," go to Insert, then Chart. Choose XY (Scatter) and click on the Series tab. Remove any series that the computer has automatically inserted. Then click Add. The "X Values" are the known concentrations (Column A) and the "Y Values" are the corrected peak areas (Column C). When you have created the chart, go to Chart, then Add Trendline. Choose Linear and then click on the Options tab. Check the boxes (bottom left) next to "display equation" and "display R-squared value on chart." Click OK. This will calculate the R-squared value for your standard curve. Generally, the R-squared value is above 99%.

14.16 Data Retrieval:

14.16.1 Wait until the pumps have stopped to start reporting data and shutting down the system.

14.17 To save your results on a floppy disk:

14.17.1 Select the Sample menu, then Report List.

14.17.2 Go to File- then Export, and then Report All. You will get a message about the printer - just click OK.

14.17.3 Select drive A and name the file, then click OK. There will be a blinking yellow box at the bottom of the computer screen as the data is written to your disk. When the blinking stops and the green light is out on the floppy drive, it is safe to remove your disk. (When you go to work with the data, you can open the Tek-MDS spreadsheet in Excel.) You may want to check the file on the disk to ensure your data was properly transferred.

14.18 Clean-up:

14.18.1 Wait until the pumps have stopped to start reporting data and shutting down the system.

14.18.2 Record weight of the remaining sample in each vial after analysis.

14.18.2.1 Dump all remaining sample vial contents into the waste container.

14.18.2.2 Flip pump switches to “off”.

14.18.2.3 Release the tension on the pump tubing and allow it to drain.

14.18.2.4 Turn off the autosampler (store the probe in the “home” position first).

14.18.2.5 Turn off the pump and detector modules.

14.18.3 When the three analyzer modules are turned off, turn off the carrier and phase-separator gases at the tanks in the main lab.

14.18.3.1 Empty the waste container into the neutralization carboy and add baking soda to neutralize the pH.

14.18.4 When you are finished in the cleanroom, turn the switch to “Unoccupied.”

14.18.5 Rinse each THg vial 6-8 times with Milli-Q di water and remove any tape. They are now ready for the acid baths. Immediately put them in the acid baths if the acid baths are available.

14.18.6 Rinse the SnCl2 bottle 6-8 times with Milli-Q di water and store it (empty) in its cabinet.

14.19 Hg reduction and purging— procedures for the flow-injection (Section 14.2.1).

14.20 Hg reduction and purging for the flow-injection system

14.20.1 Add 200µL of NH_2OH solution (Section 10.4) to the BrCl-oxidized sample in the 60-mL sample bottle. Cap the bottle and swirl the sample. The yellow color will disappear, indicating the destruction of the BrCl. Allow the sample to react for 5 minutes with periodic swirling to be sure that no traces of halogens remain.

NOTE: *Purging of free halogens onto the gold trap will result in damage to the trap and low or irreproducible results.*

14.20.2 Pour the sample solution into an autosampler vial and place the vial in the rack.

14.20.3 Carryover may occur after analysis of a sample containing a high level of mercury. Samples run immediately following a sample that has been determined to result in carryover (Section 7.3.8.1) must be reanalyzed using a system demonstrated to be clean as per Section 7.3.8.1.

15. Calculations

15.1 Calculations for the flow-injection system

15.1.1 Calculate the mean peak height or area for Hg in the system blanks measured during system calibration or with each analytical batch (A_{SB}; n=3).

15.1.2 Calculate the concentration of Hg in ng/L in each sample according to the following equation:

$$[Hg](ng/L) = \frac{\left(\mathbf{A_S} - \bar{\mathbf{A}}_{\mathbf{SB}}\right)}{CF_m} * \frac{Vstd}{V_{sample}}$$

where:

A_S= peak height (or area) for Hg in sample

$\bar{A}_{SB}$ = mean peak height (or area) for Hg in system blanks

CF_m = mean calibration factor (section (13.3.2.6)

V_{std} = volume (ml) used for standards-volume (ml) reagent used in standards

V_{sample}= volume (ml) of sample-volume (ml) reagent used in sample

15.2 Calculations for concentration of Hg in method blanks, field blanks, and reagent blanks.

15.2.1 Calculate the concentration of Hg in the method blanks (C_{MB}), field blanks (C_{FB}), or reagent blanks (C_{RB}) in ng/L, using the equation in Section 15.1.2 for flow injection system and substituting the peak height or area resulting from the method blank, field blank, or reagent blank for A_S.

15.2.2 Determine the mean concentration of Hg in the method blanks associated with the analytical batch (a minimum of three). If a sample requires additional reagent(s) (e.g., BrCl), a corresponding method blank containing an identical amount of reagent must be analyzed (Section 12.4.3.3). The concentration of Hg in the corresponding method blank may be subtracted from the concentration of Hg in the sample per Section 15.3.2.

15.3 Reporting

15.3.1 Report results for Hg at or above the ML, in ng/L, to three significant figures. Report results for Hg in samples below the ML as <0.5 ng/L, or as required by the regulatory authority or in the permit. Report results for Hg in reagent blanks and field blanks at or above the ML, in ng/L, to three significant figures. Report results for Hg in reagent blanks, method blanks, or field blanks below the ML but at or above the MDL to two significant figures. Report results for Hg not detected in reagent blanks, method blanks, or field blanks as <0.2 ng/L, or as required by the regulatory authority or in the permit.

15.3.2 Report results for Hg in samples, method blanks and field blanks separately. In addition to reporting results for the samples and blank(s) separately, the concentration of Hg in the method blanks or field blanks associated with the sample may be subtracted from the results for that sample, or must be subtracted if requested or required by a regulatory authority or in a permit.

15.3.3 Results from tests performed with an analytical system that is not in control must not be reported or otherwise used for permitting or regulatory compliance purposes.

16. Method performance

16.1 This Method was tested in the laboratory using IPRs. The quality control acceptance criteria listed in Table 2 was verified by data gathered in the laboratory study.

16.2 Precision and recovery data for aqueous samples are given in Table 7.

17. Pollution Prevention

17.1 All analysts will attend the Chemical Hygiene Plan and Hazardous Waste Management training provided by the EHO.

17.2 All analysts shall remain aware that Syracuse University waste minimization objective is to reduce the generation of both hazardous and non-hazardous waste as much as is practical.

17.3 All analysts will be familiar with the “Hazardous Waste Management” manual.

17.4 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

17.5 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When it is not feasible to reduce wastes at the source, the Agency recommends recycling as the next best option. The acids used in this Method should be reused as practicable by purifying by electrochemical techniques. The only other chemicals used in this Method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

17.6 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reductio*n, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872–4477.

18. Data Assessment, Review, and Acceptance Criteria of QC Measures

18.1 Prior to the analyst’s accepting of results, all reagent blank, matrix spike, matrix spike duplicate/matrix

duplicate, and reference sample data shall be reviewed for compliance according to Table 2.

19. Corrective Actions for Out-of-Control Data

19.1 The analyst performing the analysis shall compare all quality control data to the appropriate control limits in a timely manner. If any excursions are noted, the analysis is halted, and corrective action is implemented. All excursions shall be noted on a Corrective Action Form, which shall be reviewed and signed by a second party (i.e. Senior Graduate Student, Laboratory Technician II, or Primary Investigator).

20. Contingencies for Handling Out-of-Control or Unacceptable Data

20.1 If the corrective action does not correct the excursion the analyst will inform either a Laboratory Technician II, Laboratory Manager, and/or Project Investigator to help the analyst solve the problem.

21. Waste Management

21.1 Guidelines for managing laboratory wastes are addressed in the “Hazardous Waste Management” manual.

21.2 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

21.3 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).

21.4 Acids, samples at pH <2, and BrCl solutions must be neutralized before being disposed of, or must be handled as hazardous waste.

21.5 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better: Laboratory Chemical Management for Waste Reductio*n, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

22. References

22.1 Method 1631E, "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry," 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, August 2002

22.2 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.

22.3 "Standard Methods for the Examination of Water and Wastewater," 20th ed., American Public Health Association, 1015 15th Street NW, Washington, DC 20005. 1-4: Section 1020 (Quality Assurance), 1998.

22.4 200-1-10, “Guidance for Evaluating Performance Based Chemical Data,” U.S. Army Corps of Engineers, Department of Army, Washington, DC 20314-1000. 9-1: Chapter 9, June 30, 2005

23. Tables, Diagrams, Flowcharts, Logs, Attachments, and Validation Data

23.1 Table 1: IPR Summary

23.2 Table 2: CESE Quality Control Requirements

23.3 Table 3: Standard Curve

23.4 Table 4: Tray Protocol

23.5 Table 5: Lowest Ambient Water Quality Criterion for Mercury and the Method Detection Limit and Minimum Level of Quantitation for EPA Method 1631

23.6 Table 6: Quality Assurance Criteria for Performance Tests

23.7 Table 7: MDL Summary

23.8 Attachment 1: CESE Corrective Action Form

23.9 Attachment 2: Quick Set-up Reference

23.10 Attachment 3: Glossary

23.11 Attachment 4. CESE Standard Log

23.12 Figure 1: Schematic Diagram of the Bubbler, Purge and Trap, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) system

23.13 Figure 2: Schematic Diagram of the Flow- Injection, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System

Table 1
IPR Summary Recovery History

Preparation Date	***Analysis Date***	***IPR(concentration 10ug/L)***
June 22, 2004	9/1/2004	100.42
June 22, 2004	10/26/2004	101.90
June 22, 2004	12/1/2004	94.36
June 22, 2004	2/22/2005	103.28
June 22, 2004	3/14/2005	99.52
June 22, 2004	4/13/2005	102.45
June 22, 2004	7/7/2005	101.64
June 22, 2004	9/12/2005	102.10
June 22, 2004	10/13/2005	103.00
June 22, 2004	1/10/2006	99.67
June 22, 2004	3/3/2006	101.23
	Ave	100.87
	SD	2.488075
	%RSD	2.466609

Table 1 is in-house training tool. The table is used to maintain a history of recoveries for the Demonstration of Capability for new analysts.

Table 2
CESE Quality Control Requirements

QC Check	Frequency	Acceptance Criteria	Corrective Action*
Initial Calibration	Daily prior to sample analysis / as per method / or as specified in QAPP	5 standards with the RSD ≤ 15%, Low Std. Recovery 75% - 125%	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes
Initial Calibration Verification (ICV)	Immediately after Initial calibration	90 – 110 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration
Initial Calibration Blank (ICB)	After ICV	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. Change air bubble tubing
Continuing Calibration Verification (CCV)	After every ten samples and at the end of the run	90 – 110 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3 All samples analyzed after the last passing CCV must be reanalyzed
Continuing Calibration Blank (CCB)	After every CCV	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCB must be reanalyzed 4. Change air bubble tubing
Quality Control Sample (QCS)/Laboratory Control Sample (LCS)	Immediately after initial calibration	90 – 110 % of expected value-	1. Reanalyze 2. Remake and reanalyze ICV 3. If criteria are still not met, repeat initial calibration
Method Blank	Immediately after QCS and every 10 samples	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, repeat initial calibration
Matrix Spike/Matrix Spike Duplicate sample (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	Recovery (76-128%) and RPD (<20%) or as specified in QAPP.	1. If Recovery is not within QC limits, and an RPD criterion is met document excursion. 2. If recover y is within QC limit, and RPD criterion is not met, reanalyze.
Duplicate	1 every 20 samples	RPD 20%	1. If < 5x MRL or is non-detect, the MS/MSD will be used for precision. 2. If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.
Triplicate	QAPP dependent	RSD 35%	1. If < 5x MRL or is non-detect, the MS/MSD will be used for precision. 2. If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.
Ongoing Precision and Recovery (OPR)	1 at the beginning and end of every batch	82-122%	1. If initial is out, reanalyze. 2. If closing is out, reanalyze, if still out, review last CCV that was ran and follow CCV criteria.
Initial Precision and recovery (IPR)	For new instrument set up or Demonstration of Capability	82-122%; RPD 21%	1. Re-make solution 2. Re-analyze 3. Verify set-up 4. Re-train

* All corrective actions must be documented on the CESE Corrective Action Log.

Note: Not all QC Checks are applicable to the method of concern.

Table 3

	Mili Q-water (mL)	10ng/mL THg standard (mL)	Total volume of sample (Ml)	BrCl (mL)
0.0	49.750	0.000	49.750	0.250
0.5	49.747	0.0025	49.750	0.250
0.5 serial	49.500	250 uL of 100ng/L stnd	49.750	0.250
1.0	49.745	0.005	49.750	0.250
1.0 serial	49.250	500 uL of 100ng/L stnd	49.750	0.250
5.0	49.725	0.025	49.750	0.250
5.0 serial	47.250	2500 uL of 100ng/L stnd	49.750	0.250
10.0	49.700	0.050	49.750	0.250
25.0	49.625	0.125	49.750	0.250
50.0	49.500	0.250	49.750	0.250
100.0	49.250	0.500	49.750	0.250

Standards

Table 4
Tray Protocol Guidelines

Sample # or Position #	Sample ID	Sample Tube	Rinse Tube
1	Clean		
2	Clean		
3	Clean		
4	Wash	7	7
5	Wash	8	8
6	Wash	9	9
7	Wash Station		
8	Wash Station		
9	Wash Station		
10	0a	10	1
11	0b	11	1
12	0c	12	1
13	0.5	13	1
14	1.0	14	1
15	5	15	1
16	10	16	1
17	25	17	1
18	50	18	1
19	100	19	1
20	ICB	20	2
21	ICV	21	2
22	QCS/LCS	22	2
23	MDL Check	23	2
24	OPR	24	2
25	Method Blank	25	2
26-35	Sample #1 - #10	26-35	2
36	#10 Matrix Spike	36	2
37	#10 Matrix Spike Duplicate	37	2
38	Lab Duplicate	38	2
39	CCV	39	3
40	CCB	40	3
41	Method Blank	41	3
42-51	Sample #11- #20	42-51	3
52	#20 Matrix Spike	52	3
53	#20 Matrix Spike Duplicate	53	3
54	Sample #20 Dup	54	3
55	Sample # 20 Triplicate	55	3
56	CCV	56	3
57	CCB	57	3
58	Method Blank	58	3
59	OPR	59	1
60	WASH	4	1
61	WASH	5	1
	WASH	6	1
	WS		
	WS		
	CLEAN		
	CLEAN		
	CLEAN		

Repeat 10 samples, CCV, CCB order until all samples are entered. Include a matrix spike (MS) and matrix spike duplicate (MSD) for every 10 samples. Include a Lab Duplicate for every 20 samples and Lab Triplicate as per QAPP. Finish analysis with an OPR, CCV and CCB. Notice that CCV/CCB bracket all other samples.

Table 5

Lowest Ambient Water Quality Criterion for Mercury and the Method Detection Limit and Minimum Level of Quantitation for EPA Method 1631

Metal	Lowest Ambient Water Quality Criterion[1]	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL[2]	ML[3]
Mercury (Hg)	1.3 ng/L	0.2 ng/L	0.5 ng/L

1. Lowest water quality criterion for the Great Lakes System (Table 4, 40 CFR 132.6). The lowest Nationwide criterion is 12 ng/L (40 CFR 131.36).
2. Method detection limit (40 CFR 136, Appendix B)
3. Minimum level of quantitation (see Glossary)

Table 6
Quality Acceptance Criteria for Performance Tests

Acceptance Criteria	Section	Limit (%)
Ongoing Precision Recovery (OPR)	**12.1.5**	
Recovery (X)		**82 -122**
Matrix Spike/Matrix Spike Duplicate	**12.3**	
Recovery (X)	**12.3.3**	**76 - 128**
Relative Percent Difference	**12.3.5**	**20**

Table 7
MDL Summary

Sample Name	Conc. Ng/L	Date
M1	0.480696	9/5/2007
M2	0.471748	9/5/2007
M3	0.483636	9/5/2007
M4	0.490731	9/5/2007
M5	0.489772	9/5/2007
M6	0.592806	9/5/2007
M7	0.548192	9/5/2007
ave	0.508226	9/5/2007
sd	0.04489	9/5/2007
MDL	0.140956	9/5/2007

Attachment 1

CESE
CORRECTIVE ACTION LOG

Analyst: _____Instrument: _____

Date of Analysis: _____Method: _____

PROJECT NUMBER(S)/BATCH NUMBER(S)	EXCURSIONS	AFFECTED SAMPLES	CRITERIA COMPARISON	CORRECTIVE ACTION/EXPLANATION

Reviewed by:

_____ _____

QA/QC Reviewer Date

_____ _____

Project Investigator Date

Attachment 2

Quick Start-up Reference

Total Mercury Analysis (for water samples)

Updated: 25 October 2004

WARNING!!!!!!!

NEVER OPEN ANY MERCURY STANDARD IN THE TRACE METAL ROOM IF THE CONCENTRATION OF THAT STANDARD EXCEEDS 10 ng/ml Hg. DILUTIONS OF THESE ORIGINAL SOURCES SHOULD BE MADE IN ANOTHER LAB. IF THESE STANDARDS WERE TO BE OPENED IN THE TRACE METAL ROOM, WE WOULD HAVE A HUGE CONTAMINATION HAZARD AND MAY NO LONGER BE ABLE TO ANALYZE NATURAL WATERS AT THE PART PER TRILLION LEVEL

I. Standard and Sample Preparation:

1). Prepare standards for analysis: (~2 hours)

a. Standards may be made the day of analysis or they may be made in advance. It is a good idea to make your standards at the same time you prepare your samples for analysis. If samples or standards are made more than one day in advance of analysis, they should be stored at room temperature and IN THE DARK. Light photo-reduces the BrCl used to oxidize the samples and standards, and leaving them exposed to light for several days may interfere with the accuracy of analysis. Make the standards as follows:

Standard concentration (ng/L)	Mili Q-water (mL)	10ng/mL THg standard (mL)	Total volume of sample (Ml)	BrCl (mL)
0.0	49.750	0.000	49.750	0.250
0.2 serial	49.650	100 uL of 100ng/L stnd	49.750	0.250
0.5	49.747	0.0025	49.750	0.250
0.5 serial	49.500	250 uL of 100ng/L stnd	49.750	0.250
1.0	49.745	0.005	49.750	0.250
1.0 serial	49.250	500 uL of 100ng/L stnd	49.750	0.250
5.0	49.725	0.025	49.750	0.250
5.0 serial	47.250	2500 uL of 100ng/L stnd	49.750	0.250
10.0	49.700	0.050	49.750	0.250
25.0	49.625	0.125	49.750	0.250
50.0	49.500	0.250	49.750	0.250
100.0	49.250	0.500	49.750	0.250

b. The low standards (0.5 and 1.0 ng/L) cannot be accurately made using the 10 ng/L intermediate HgT standard. In order to make the 0.5 and 1.0 ng/L standard you must do a serial dilution from the 100 ng/L standard. In order to do this you must:

1. Make the 100 ng/L standard as indicated above.
2. Make sure you have fixed the 100 ng/L standard with 0.250 ml BrCl.
3. Cap and vigorously shake the 100 ng/L standard.
4. With a clean pipette tip, use the fixed 100 ng/L standard to spike the 0.5 and 1.0 ng/L standards, and then fix them with 0.250 ml of 0.5% BrCl.

c. Prepare Quality Control sample from certified reference material. This differs from the ICV in that the QC should be made from a secondary certified source and be composed of a NATURAL MATRIX, not laboratory De-ionized water.

d. Be sure that all standards and Quality Control samples have been fixed with BrCl.

2) **Prepare samples for analysis**. (At least 1 hour, more depending on number of samples)

a. Weigh 49.750mL of each water sample.

b. Add 0.250mL BrCl to fix the sample (fixed samples can be stored for up to six months in sealed tubes if placed in darkness).

c. Matrix spike (MS) and one matrix spike duplicate (MSD) for every 10 samples. Spike the sample with 10 ng/L. (That is, 10 unique samples and then two spikes for a total of 12 vials). To make the MS and MSD, weigh 49.700 mL of the 10^{th} sample. Add 0.050 mL of the 10ng/mL THg standard to the sample. Then fix the sample with 0.250mL BrCl.

d. Samples should be run in batches of 20. For every 20 samples also run a lab duplicate and lab triplicate of one sample. (See Tray Protocol guidelines in Table 4). To make the MS and MSD, weigh 49.700mL of the 10^{th} sample. Add 0.050mL of the 10ng/mL THg standard to the sample. Then fix the sample with 0.250mL BrCl.

NOTE: For an alternative method of sample preparation, please see attached.

II. Prepare Reagents, Clean Room, and Analyzer for Analysis:

1). Prepare Reagents:

Reducing Reagent: Make 3% $SnCl_2$ and purge with high purity nitrogen gas for at least 1 hour.

a. To make the $SnCl_2$, add 30g $SnCl_2$ (anhydrous) granules to the designated "$SnCL_2$" 1L flask. Add 500-700mL of Milli-Q di water to the granules and swirl to mix. Then add 50mL of HCl to the flask and bring to 1L with di water. Mix and then transfer to the 2L Teflon SnCl2 bottle.

b. Purging is accomplished by placing the large bubbler stem (reserved for SnCl2) into the 2L Teflon $SnCl_2$ bottle, sealing with parafilm, and then sparging with high purity nitrogen gas (~1000 ml/min for at least 1 hour).

c. 2L of 3% $SnCl_2$ will be enough for four racks of vials. For longer runs, you will need to make more 3% $SnCl_2$ (~2L / 4 racks).

Wash Solution: Make 2L of 5% 3HCl: 1HNO3 (1L to clean the tubing, 1L for the washes).

a. Measure 1L of Milli-Q DI-water with the designated 1L flask. Pour out 50mL of di water. Pour the remaining water into a designated 1L Teflon bottle. Add 12.5mL of HNO_3 and 37.5mL HCl to the bottle. Cap and shake the bottle to mix.

2). Clean Room Entry

a. Switch the clean room key to "Occupied".

b. "OPEN" both Argon tanks to the right of the door to the clean room. Check the gas tanks. Make sure they are both High Purity Argon. If either tank reads less than 500 PSI, then change that tank. The Detector Carrier Gas flow and Phase Separator Gas flow should be delivered at 20-40 psi (aim for ~30 psi). You should not have to adjust the regulators, except to make sure the lower black knob is in the "OPEN" position (twisting down from the regulator opens this valve).

c. Enter gown room and put on clean suit, hair net, booties, safety glasses and gloves. When booties and gowns become visibly dirty, they should be trashed. Your hair should actually be tucked under the hair net. This is done to ensure the clean room is kept clean and YOU do not contaminate your samples.

3). Initial Inspection.

a. **Assess the condition of the soda-lime column.** The dry-rite column should be changed at least weekly. If there is any caking of dry-rite, then change the column. If there is discoloration, then change the column. If you have been having any problems with carry over, then change the column. In order to change the column, open the top of the analyzer, and disconnect the soda lime trap from the sampling loop:

1. Make sure the analyzer is NOT running.

2. Gently remove column by removing it from the black clips, and then unscrewing the red caps at each end. Be sure not to tug on the caps and hoses on each end, or you will damage the analyzer, cause leaks, or otherwise wreck your chances of successfully using the analyzer.

3. Remove old Glass Wool or Silica Wool. Dump old dry-rite into waste container.

4. Refill the column with dry-rite and glass wool plugs. Be sure that the glass wool plug actually blocks the entire opening of the column at BOTH ends.

5. Return the soda lime trap to the analyzer, re attach the tubing, close the lid.

6. If you are unsure of how to do this, PLEASE ASK.

b. Turn on the Analyzer Components: (-) = "On", and (o) = "Off".

1. The Detector (Top Component).

2. The pump (Bottom Component).

3. The Autosampler. When the autosampler is turned on, it will move to the home position, above the wash station. Check to be sure that this has been accomplished. Then check to make sure the sampling probe is properly adjusted, and the screw holding it in place is finger-tight.

c. Make a note of all settings.

1. Are they all where they should be? These settings should not need to be adjusted, unless they have been incorrectly adjusted by another analyst. PLEASE DON'T ADJUST SETTINGS WITHOUT SPEAKING TO THE LAB MANAGER

   (1) Digital Output: Should read 0.1000 – 0.1100 during baseline.
   (2) Sensitivity Dial: 5.0
   (3) Offset Dial: 5.08
   (4) Detector Flow: ~90 units (This is in automatic shutoff mode).
   (5) Phase Separator Flow: ~425 units (This is on automatic shutoff mode).
   (6) Pump Speed Dial: 4.0

d. Check the waste container and make sure it is nearly empty. If it is not empty, empty the content into the appropriate waste carboy and neutralize the waste solution. Once neutralized, the waste can be flushed down the sink with copious amounts of tap water.

4.) Initial Maintenance: (Acid Wash, DI Rinse, Column Cleaning Sequence)

a. Set up pump tubes and clamps for initial cleansing of analyzer.

1. Check the Tekran Quickstart manual to ensure the proper tubes are in the proper clamp fittings.

2. Clamp the tubes into place. The three back tube adjustment levers should be at "11 o'clock". The SnCl2 tube lever should be at "11:30" and the sampling tube lever should be at "12 o'clock".

3. Trace all tubes and assure all are connected to the proper places and are being pumped in the proper direction. Read the Tekran Quickstart Manual if you need to refresh your memory about where each tube belongs and in which direction fluids should be flowing.

b. Fill the 1L glass jar designated for acid with 5% 3:1 HCl : HNO3. Place the SnCl2 tube into the acid. Place the Wash Station Input tube into the acid. Place the Wash Station Output tube into the waste container, but do not let it contact waste fluid, as this could later contaminate your DI Reservoir.

c. Turn on Computer and open Tek-MDS program.

d. Select a new worksheet. Select "Samples", then "Run", highlight the desired "method", click "new" to select a new worksheet.

e. Change the filename of your new run to the format "XXYYMMDD", where "XX" represents the analyst's initials, the "YY" the two digit year, "MM" the two digit month,

and "DD" the two digit day, and append this with the word "cleaning". Example "JD040525cleaning"

f. **Initialize the autosampler:** Click on the "Initialze" button in the gray window. WAIT. A control message will indicate "autosampler" found. Then you will eventually get a small window (be patient, this can take some time). The autosampler model is 223. The rack code is 112 for all racks. Click "o.k."

g. **Command the autosampler to go to the wash station: Click "A/S Wash" in the small gray window.**

h. **Now that all tubes have been set up and autosampler is in wash station, flip the main pump switch to "local" mode.** This will start the acid solution running through the lines to clean out any residue. Pump flow is left to right. Watch to ensure flow through is occurring. The acid cleaning should take about 15 minutes. Use all of the 5% acid solution. Be sure that fluids are moving through all tubes, and be sure that the wash station fills. If the wash station tube goes empty, a vaccum can be created by placing a gloved finger over the top of the wash station column until the water level has returned to the appropriate level. Check to make sure no fluid is backing up in the system.

i. **While the acid and DI-rinse are running, set up a short cleaning sequence.** Do NOT designate any sample tubes or rinse tubes. This sequence will both clean the gold traps, and additionally flush the system with reageant water.

Line #	Sample ID	Sample Tube	Rinse Tube
1	clean		
2	clean		
3	clean		
4	ws		
5	ws		
6	ws		
7	clean		
8	clean		
9	clean		
10	ws		
11	ws		
12	ws		
13	clean		
14	clean		
15	clean		

j. **When the acid has run out (see part "h"), flip the pump switches back to "off" and send the autosampler probe back to its home position by selecting "A/S Home".**

k. **Rinse the glass jar with DI water, and then fill with DI water. Switch the pump to local again, send the autosampler to the wash station, and run DI water through the entire system.** The Wash Station Output tube should still be in the waste container. Circulate DI water for about 5 minutes to remove residual acid from the lines. While the DI-water is circulating, rinse the 2L DI reservoir 3x with Milli-Q DI-water, fill, and parafilm the top.

l. **After circulating DI for 5 minutes (in part "k" above), turn pump "off".** Place the Wash Station Input and Wash Station Output into the 2L DI Reservoir. Leave the $SnCl_2$ tube in the small glass jar, and fill the jar with DI-water.

m. Configure the cleaning sequence.

1. Click on "Configure Run"
2. The "first sample" number should refer to the line # of the very first clean.
3. The "last sample" number should refer to the line # of the very last clean.
4. Make sure the line numbers are correct, and that the "clean first?" option is marked "Y".
5. The "clean event table file" will read "$Clean_6etf".
6. The "sample event table file" will read "Sample_6etf".
7. The "error trace" will read "2".
8. Click o.k., and you should soon have a Start Run option in the small gray window…(DO NOT CLICK IT YET!)

n. When you are ready to start the clean sequence, quickly verify the lines are in the appropriate reservoirs, and flip the pump switch to "remote".

o. Click the "Start Run" option, and after a few seconds the pumps will start.

p. Verify that the fluids are moving in the proper direction through each of the lines, and in the wash station. Be sure no fluids are backing up anywhere in the system.

NOTE: At this point, you will have approximately one hour until the cleaning sequence has finished. This time can be used to organize your standards, samples, and run sequence for analysis, and make any additional reagents that will be needed for the analysis of your samples.

q. When cleaning cycle has finished:
1. Turn "off" pump.
2. Check that peaks were low enough.
3. Exit worksheet.

III. Sample Analysis Set Up:

1). Change $SnCl_2$ tubing and sample tubing.

a. The $SnCl_2$ tubing and the Sample tubing should be replaced. If these lines are used repeatedly, high carry over is the result. High carry over causes mdl's and ccb's to

increase in Peak Area over the course of a run, thus throwing low level analyses into question. The $SnCl_2$ tube and Sample tube should be changed every time you do an analysis.

2). **Set up pump tubes and clamps for initial cleansing of analyzer.**

a. Check the Tekran Quickstart manual to ensure the proper tubes are in the proper clamp fittings.

b. Clamp the tubes into place. The three back tube adjustment levers should be at "11 o'clock". The SnCl2 tube lever should be at "11:30" and the sampling tube lever should be at "12 o'clock".

c. Trace all tubes and assure all are connected to the proper places and are being pumped in the proper direction. Read the Tekran Quickstart Manual if you need to refresh your memory about where each tube belongs and in which direction fluids should be flowing.

3). Verify that the Wash Station Input and Wash Station Output are both in the DI Reservoir. Fill the DI Reservoir, and para film the top.

4). Place the $SnCl_2$ tube into the $SnCl_2$. Para film the top.

5). Open Tek-MDS program and select a new worksheet.

a. Select "Samples", then "Run", highlight the desired "method", click "new" to select a new worksheet.

b. Change the filename of your new run to the format "XXYYMMDD", where "XX" represents the analyst's initials, the "YY" the two digit year, "MM" the two digit month, and "DD" the two digit day Example "JD040525".

c. Initialize the autosampler: Click on the "Initialze" button in the gray window. WAIT. A control message will indicate "autosampler" found. Then you will eventually get a small window (be patient, this can take some time). The autosampler model is 223. The rack code is 112 for all racks. Click "o.k."

d**. Command the autosampler to go to the wash station: Click "A/S Wash" in the small gray window.**

6). Set up the analysis sequence.

a. Type all standards & sample ID's into the new spreadsheet on the computer. Be sure not to designate a sample tube nor a rinse tube for "clean" and "ws" samples. (See Table 4 on next page.)

b. Assign sample tube numbers and rinse tube numbers to each sample ID.
- Sample Tubes can only go to 48, then you must start at the beginning.
- Rinse Tubes will use one of the designated wash tubes at the beginning of the run, just designate which tube you want. I usually designate rinse tubes as 1,2,3,4 and leave position 7-48 open for sample tubes.

c. "Clean" and "WS" (wash station) blanks should have no sample and rinse tube referenced to them...leave them blank!

Include a matrix spike (MS) and matrix spike duplicate (MSD) for every 10 samples. Include a Lab Duplicate for every 20 samples. Finish analysis with an OPR.

7). Configure the analysis sequence.

a. Click on "Configure Run"

b. The "first sample" number should refer to the line # of the very first clean.

c. The "last sample" number should refer to the line # of the very last clean.

d. Make sure the line numbers are correct, and that the "clean first?" option is marked "Y".

e. The "clean event table file" will read "$Clean_6etf".

f. The "sample event table file" will read "Sample_6etf".

g. The "error trace" will read "2".

h. Click o.k., and you should soon have a Start Run option in the small gray window...(DO NOT CLICK IT YET!)

8). When you are ready to start the analysis sequence, verify the lines are in the appropriate reservoirs, and flip the pump switch to "remote".

9). Click the "Start Run" option, and after a few seconds the pumps will start.

10). Verify that the fluids are moving in the proper direction (left to right) through each of the lines, and in the wash station. Be sure no fluids are backing up anywhere in the system. As the first wash station samples begin to pass through the sampling lines, check to make sure fluid is moving at the appropriate speed. When the first wash vial is sampled, check to see what volume was taken (>80% of the sample is should be used. If an inadequate volume was pumped, adjustments must be made prior to the end of the "wash, wash, wash" sequence. Adjustments cannot be made after the first 0.0 ng/L standard is sampled.

IV. Running Standards and Samples:

1). Add Hydroxylamine to the standards at this time (it should be added at least 10 to 15 minutes prior to the sample being analyzed). Loosen the vial caps, add 0.1mL hydroxyl amine to each vial, re-cap and shake vials to mix them, wait ~10 minutes and then uncap the vials.

a. Add the hydroxyl amine to all the standards at once. If the standard curve passes (see Excel worksheet below) continue with analysis. If calibration curve fails, you must make a new standard curve and have it pass before proceeding with sample analysis.

b. Do not run samples unless the analyzer is running clean, adequate volumes are being pumped, AND the standard curve has passed.

2). Start adding the hydroxyl amine segment at a time (from ccv/ccb to ccv/ccb) as the run progresses (once the hydroxyl amine is added, the sample must be analyzed or remade – it is therefore better not to add the hydroxyl amine to all the samples at the beginning in case something should go wrong and the run must be stopped).

3). Rinse tubes may need to be refilled as the run progresses. The di water will need to be refilled as the run progresses. If running more than 4 racks, make more 3% SnCl2 and bubble with ultra high purity nitrogen gas for at least 1 hour.

4). At the end of the run, the analyzer will run for several minutes after the last clean has finished. Wait until the pumps have stopped to start reporting data and cleaning the system.

AT END OF RUN: Wash the system by running acid for 5-10min and then run water (Milli-Q) for 5-10min. Then follow shutdown procedure at the end of this manual.

V. Standard Curve

*****The standard curve must have a coefficient of variation (%) of less than 15% in order for the run to be acceptable.

Excel Worksheet

Sample id	**Peak area**	**Corrected peak area**	**Calibration factor**	**Calculated Conc (ng/L)**
(column) A	**B**	**C**	**D**	**E**
0.00	**From report**	**C3**=B3-$B$3		**E3**=C3/$D$10
1.00	**From report**	**C4**=B4-$B$3	**D4**=C4/A4	**E4**=C4/$D$10
5.00	**From report**	**C5**=B5-$B$3	**D5**=C5/A5	**E5**=C5/$D$10
10.00	**From report**	**C6**=B6-$B$3	**D6**=C6/A6	**E6**=C6/$D$10
25.00	**From report**	**C7**=B7-$B$3	**D7**=C7/A7	**E7**=C7/$D$10
50.00	**From report**	**C8**=B8-$B$3	**D8**=C8/A8	**E8**=C8/$D$10
100.00	**From report**	**C9**=B9-$B$3	**D9**=C9/A9	**E9**=C9/$D$10
		Average CF	**D10**=average(D4:D9	
		St dev	**D11**=stdev(D4:D9)	
		%	**D12**=D11*100/D10	

*****After calculating the "calculated concentration," go to **Insert**, then **Chart**. Choose **XY (Scatter)** and click on the **Series** tab. Remove any series that the computer has automatically inserted. Then click **Add**. The "X Values" are the known concentrations (Column A) and the "Y Values" are the corrected peak areas (Column C). When you have created the chart, go to **Chart**, then **Add Trendline**. Choose **Linear** and then click on the **Options** tab. Check the boxes (bottom left) next to "display equation" and "display R-squared value on chart." Click **OK**. This will calculate the R-squared value for your standard curve. Generally, the R-squared value is above 99%.

VI. Data Retrieval:

(Wait until the pumps have stopped to start reporting data and shutting down the system.)

1) To save your results on a floppy disk:

a. Select the **Sample** menu, then **Report List.**

b. Go to File- then Export, and then **Report All**. You will get a message about the printer - just click **OK**.

c. Select drive A and name the file, then click **OK**. There will be a blinking yellow box at the bottom of the computer screen as the data is written to your disk. When the blinking stops and the green light is out on the floppy drive, it is safe to remove your disk. (When you go to work with the data, you can open the Tek-MDS spreadsheet in Excel.) You may want to check the file on the disk to ensure your data was properly transferred.

VII. Clean-up: (after each run)

(Wait until the pumps have stopped to start reporting data and shutting down the system.)

1). Record weight of the remaining sample in each vial after analysis.

2). Dump all remaining sample vial contents into the waste container.

3). Flip pump switches to "**off"**.

4). Release the tension on the pump tubing and allow it to drain.

5). Turn off the autosampler (store the probe in the "home" position first).

6). Turn off the pump and detector modules.

7). When the three analyzer modules are turned off, turn off the carrier and phase-separator gases at the tanks in the main lab.

8). Empty the waste container into the neutralization carboy and add baking soda to neutralize the pH.

9). When you are finished in the cleanroom, turn the switch to "**Unoccupied**."

10). Rinse each THg vial 6-8 times with Milli-Q di water and remove any tape. They are now ready for the acid baths. Immediately put them in the acid baths if the acid baths are available.

11). Rinse the SnCl2 bottle 6-8 times with Milli-Q di water and store it (empty) in its cabinet.

Attachment 3
Glossary

The definitions and purposes below are specific to this Method, but have been conformed to common usage as much as possible.

1. Ambient Water—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

2. Analytical Batch—A batch of up to 20 samples that are oxidized with the same batch of reagents and analyzed during the same 12-hour shift. Each analytical batch must also include at least three bubbler blanks, an OPR, and a QCS. In addition, MS/MSD samples must be prepared at a frequency of 10% per analytical batch (one MS/MSD for every 10 samples).

3. Bottle Blank—The bottle blank is used to demonstrate that the bottle is free from contamination prior to use. Reagent water known to be free of mercury at the MDL of this Method is added to a bottle, acidified to pH <2 with BrCl or HCl, and allowed to stand for a minimum of 24 hours. The time that the bottle is allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water is analyzed.

4. Reagent water that has been processed through the sampling device at a laboratory or other equipment cleaning facility prior to shipment of the sampling equipment to the sampling site. The equipment blank is used to demonstrate that the sampling equipment is free from contamination prior to use. Where appropriate, the "clean hands/dirty hands" technique used during field sampling should be followed.

5. Equipment Blank—Reagent water that has been processed through the sampling device at a laboratory or other equipment cleaning facility prior to shipment of the sampling equipment to the sampling site. The equipment blank is used to demonstrate that the sampling equipment is free from contamination prior to use. Where appropriate, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility.

6. Field Blank—Reagent water that has been transported to the sampling site and exposed to the same equipment and operations as a sample at the sampling site. The field blank is used to demonstrate that the sample has not been contaminated by the sampling and sample transport systems.

7. Intercomparison Study—An exercise in which samples are prepared and split by a reference laboratory, then analyzed by one or more testing laboratories and the reference laboratory. The intercomparison, with a reputable laboratory as the reference laboratory, serves as the best test of the precision and accuracy of the analyses at natural environmental levels.

8. Matrix Spike (MS) and Matrix Spike Duplicate (MSD)—Aliquots of an environmental sample to which known quantities of the analyte(s) of interest is added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for these background concentrations.

9. May—This action, activity, or procedural step is allowed but not required.

10. May not—This action, activity, or procedural step is prohibited.

11. Method blank— Method blanks are used to determine the concentration of mercury in the analytical system during sample preparation and analysis, and consist of a volume of reagent water that is carried through the entire sample preparation and analysis. Method blanks are prepared by placing reagent water in a sample bottle and analyzing the water using reagents and procedures identical to those used to prepare and analyze the corresponding samples. A minimum of three method blanks is required with each analytical batch.

12. Minimum Level (ML)—The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The ML is calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1, 2, or 5) x 10n, where n is an integer (See Section 3.5).

13. Must—This action, activity, or procedural step is required.

14. Quality Control Sample (QCS)/Laboratory Control Sample (LCS)-sample containing Hg at known concentrations. The QCS/LCS 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 as an independent check of instrument calibration.

15. Reagent blank—Reagent blanks are used to determine the concentration of mercury in the reagents (BrCl, NH2OH@HCl, and SnCl2) that are used to prepare and analyze the samples. In this Method, reagent blanks are required when each new batch of reagents is prepared.

16. Reagent Water—Water demonstrated to be free of mercury at the MDL of this Method. It is prepared from 18 MS ultrapure deionized water starting from a prepurified source. Reagent water is used to wash bottles, as trip and field blanks, and in the preparation of standards and reagents.

17. Regulatory Compliance Limit—It is a limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory authority.

18. Shall—This action, activity, or procedure is required.

19. Should—This action, activity, or procedure is suggested, but not required.

20. Stock Solution— A solution containing an analyte that is prepared from a reference material traceable to NIST, or a source that will attest to the purity and authenticity of the reference material.

21. System Blank— For this Method, the system blank is specific for the flow-injection system and is used to determine contamination in the analytical system and in the reagents used to prepare the calibration standards. A minimum of three system blanks is required during system calibration.

22. Ultraclean Handling— A series of established procedures designed to ensure that samples are not contaminated during sample collection, storage, or analysis.

Attachment 4: CESE Standard Log

ID #	Date Made/Received	Exp Date	Reagent/ Standard	Weight/ Volume	Final Volume & Solution	Final Concentration	Parent Source	Concentration	Expiration Date	Initials

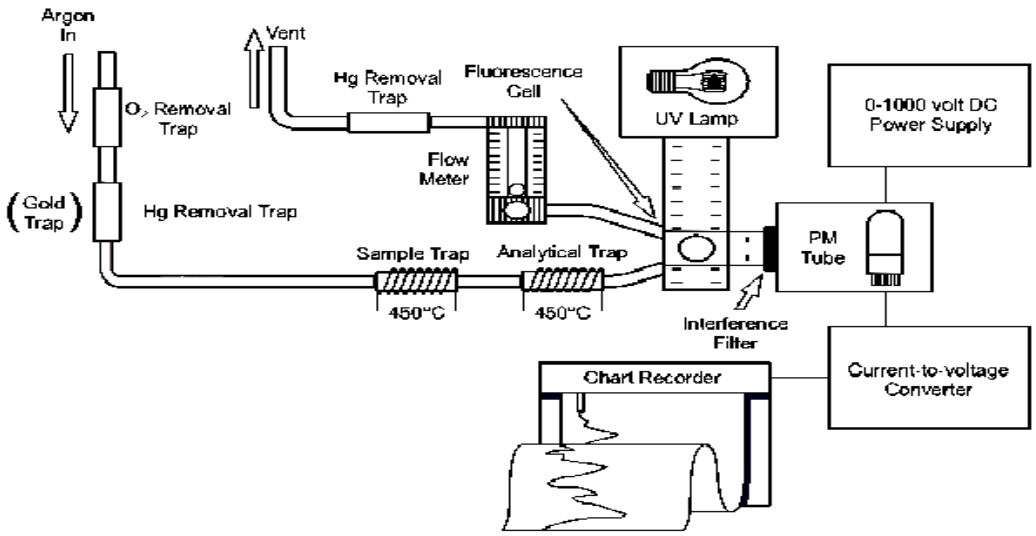

Figure 1: Schematic Diagram of the Bubbler, Purge and Trap, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) system

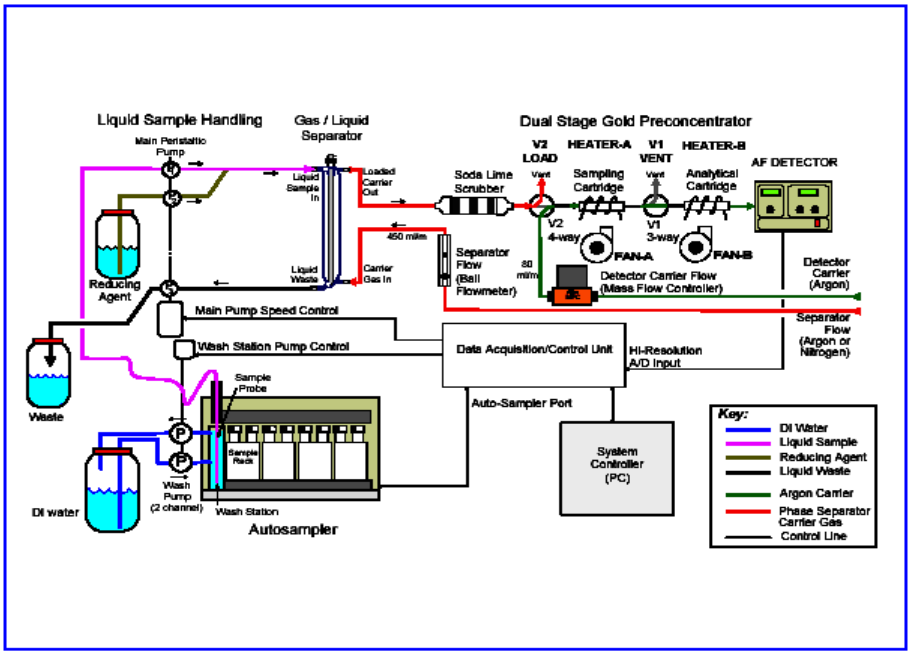

Figure 2: Schematic Diagram of the Flow- Injection, Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System

Center for Environmental Systems and Engineering (CESE)

STANDARD OPERATING PROCEDURE

1. Title: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS

AP #CESE-ENV-1630

Rev #6-December 21, 2007 page 1 of 53

Prepared By: Emina Mujezinovic

Approved By: _____ Date: December 21, 2007
Edward Mason-Technical Review

Approved By: _____ Date: December 21, 2007
Mario Montesdeoca-Laboratory Manager

Approved By: _____ Date: December 21, 2007
Charles T Driscoll-Primary Investigator

Effective Date: December 21, 2007

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2. Summary of Test Method

2.1 This laboratory procedure is derived from US EPA Method 1630.

2.2 A 100-2000 mL sample is collected directly into specially cleaned, pretested, fluoropolymer or borosilicate bottle(s) using sample handling techniques specially designed for collection of metals at trace levels (Reference 6).

2.3 For dissolved CH_3Hg, samples are filtered through a 0.45-µm capsule filter.

2.4 Fresh water samples are preserved by adding 4 mL/L of pretested 11.6 M HCl, while saline samples ($[Cl^-] > 500$ ppm) are preserved with 2 ml/L of 9 M H_2SO_4 solution, to avoid distillation interferences caused by excess chloride.

2.5 Prior to analysis, a 50-100-mL sample aliquot is placed in a specially designed fluoropolymer distillation vessel, and 95% of the water is distilled into the receiving vessel at 125 ^{0} C under N_2 flow.

2.6 After distillation, the sample is adjusted to pH 4.9 with an acetate buffer and ethylated in a closed purge vessel by the addition of sodium tetraethyl borate ($NaBEt_4$).

2.7 The ethyl analog of CH3 Hg, methyl ethyl mercury (CH3 CH3 CH2 Hg), is separated from solution by purging with N_2 onto a tenax -TA trap.

2.8 The trapped methyl ethyl mercury is thermally desorbed from the tenax trap into an inert gas stream that carries the released methyl ethyl mercury first through a pyrolytic decomposition column, which converts organo mercury forms to elemental mercury (Hg), and then into the cell of a cold vapor atomic fluorescence spectrometer (CVAFS) for detection.

2.9 Quality is ensured through calibration and testing of the distillation, ethylation, purging, and detection systems.

2.10 If any technical issues arise, do not hesitate to contact a laboratory technician, a laboratory manager, or the principal investigator for additional clarifications.

3. Scope and Application

3.1 This method is for determination of methyl mercury (CH3Hg) in filtered and unfiltered water, aqueous solution and solids by distillation, aqueous ethylation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). This method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The method is based on a contractor-developed method (Reference 1) and on peer-reviewed, published procedures for the determination of CH3Hg in aqueous samples, ranging from seawater to sewage effluent (References 2-7).

3.2 This method is accompanied by Method 1669: *Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* (Sampling Method). The Sampling Method is necessary to preclude contamination during the sampling process.

3.3 This method is designed for determination of CH3Hg in the range of 0.02-5 ng/L and may be extended to higher levels by selection of a smaller sample size.

3.4 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes suggestions for improvement in facilities and analytical techniques that should maximize the ability of the laboratory to make reliable trace metal determinations and minimize contamination (Section 10.).

3.5 The detection limit and minimum level of quantitation in this method are usually dependent on the level of background elements rather than instrumental limitations. The method detection limit (MDL; 40 *CFR* 136, Appendix B) for CH3Hg has been determined to be 0.015 ng/L when no background elements or interferences are present. The minimum reporting level (MRL) has been established as 0.05 ng/L.

3.6 Clean and ultra clean—The terms "clean" and "ultra clean" have been applied to the techniques needed to reduce or eliminate contamination in trace metal determinations. These terms are not used in this method because they lack an exact definition. However, the information provided in this method is consistent with the summary guidance on clean and ultra clean techniques.

3.7 This method follows the EPA Environmental Methods Management Council's "Format for Method Documentation."

3.8 This method is "performance based." The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements if all performance criteria are met. Section 12.1.4 gives the requirements for establishing method equivalency.

3.9 Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 *CFR* 136.4 and 136.5.

3.10 This method should be used only by analysts who are experienced in the use of CVAFS techniques and who are thoroughly trained in the sample handling and instrumental techniques described in this method. Each analyst who uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 12.2.

3.11 This method is accompanied by a data verification and validation guidance document, *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for CWA Compliance Monitorin*g. Data users should state data quality objectives (DQOs) required for a project before this method is used.

4. Applicable Matrix or Matrices

4.1 This method is applicable to surface waters, and soil solutions (underground water collected from lysimeters, and piezometers).

5. Method Detection Limit

5.1 Calculating the MDL is the responsibility of the analyst and it must be determined on initial analysis per specific method. (i.e. If the analyst is using a method for the first time, the analyst needs to calculate the MDL for that specific method.) The MDL will be verified at the beginning of each subsequent analysis using the appropriate MDL check solution. The preferred method for calculating MDLs is found in Appendix B, Part 136, Revision 1.11 of the Federal Register, Volume 49, No. 209, October 1984.

5.2 The Laboratory MDL for Methyl Mercury is 0.015 ng/L

6. Definitions

6.1 Quality Assurance Project Plan (QAPP): QAPP is a plan to be followed to maintain a level of confidence of accuracy in a specify project.

6.2 Batch: A batch consists of 20 samples that are treated and analyzed together. A batch contains a Preparatory Blank (PB) or Method Blank (MB), a Laboratory Control Sample (LCS), also known as an Quality Control Sample (QCS), an ongoing Precision Recovery sample (OPR), a pair of Matrix Spike (MS), and a Matrix Spike Duplicate (MSD) for every ten samples and a Duplicate for every twenty samples.

6.3 Apparatus: Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis that come in contact with the sample and therefore require careful cleaning will be referred to collectively as the Apparatus.

6.4 Dissolved methyl mercury: All distillable CH3Hg forms and species found in the filtrate of an aqueous solution that has been filtered through a 0.45 micron filter.

6.5 Methyl mercury: All acid-distillable Hg, which, upon reaction with NaBEt4 yields methylethyl mercury. This includes, but is not limited to, CH3Hg+, strongly organo-complexed CH3Hg compounds, adsorbed particulate CH3Hg, and CH3Hg bound in microorganisms. In freshly collected samples, dimethyl mercury ((CH3)2Hg) will not be recovered as CH3Hg, but in samples which have been acidified for several days, most (CH3)2Hg has broken down to CH3Hg. In this method, CH3Hg and total recoverable CH3Hg are synonymous.

6.6 Statistical definitions:

6.6.1 Mean - The average of n values is calculated by taking the sum of n values and dividing by n.

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

6.6.2 Sample Standard Deviation - A parameter used to measure the dispersion of a data set. It is calculated by the following:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (\bar{x} - x_i)^2}{n-1}}$$

6.6.3 Relative standard deviation (RSD) or coefficient of variation (CV) is the standard deviation divided by the mean and multiplied by 100.

$$CV = \frac{s}{\bar{x}} * 100$$

6.6.4 Relative Percent Difference - The relative percent difference of two numbers is calculated by dividing the absolute value of their differences by the average of the two numbers.

$$RPD = \frac{|x_1 - x_2|}{((x_1 + x_2)/2)} * 100$$

6.6.5 Percent Recovery - Percent recovery is calculated by dividing the spike sample result by the spike added for or by dividing the spike sample result minus the sample by the spike added.

$$\%R = \frac{SS}{SA} * 100$$

$$\%R = \frac{SS - S}{SA} * 100$$

where: SS = Spike sample
SA = Spike added
S = Sample

7. Interferences

7.1 When the method is properly applied, no significant interferences have been observed in the analysis of ambient waters.

7.2 Distillation of CH3Hg from solution requires a carefully controlled level of HCl in solution. Distillation will not be quantitative if too little HCl is added, but too much HCl results in co-distillation of HCl fumes, which interfere with the ethylation procedure. Therefore fresh water samples must be preserved only with between 0.3 % and 0.5 % (v/v) 11.6 M HCl, and salt water samples with between 0.1 % and 0.2 % (v/v) 9 M H_2SO_4.

7.3 Samples preserved with nitric acid (HNO3) cannot be analyzed for CH3Hg as the analyte is partially decomposed in the distillation step by this reagent. The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause "quenching" of the excited atoms. The Tenax trap eliminates quenching due to trace gases, but it still remains the analyst's responsibility to ensure high purity inert carrier gas and a leak-free analytical train. In some rare cases (such as oil polluted water) low molecular weight organic compounds may purge with the methylethyl mercury and collect on the Tenax trap, subsequently resulting in signal quenching during elution. Such cases are best treated by sample dilution prior to distillation.

7.4 Artifact formation is possible with the distillation procedure in cases where high inorganic Hg concentrations are present (Reference 7). In natural waters, approximately 0.01 to 0.05% of the ambient inorganic Hg in solution may be methylated by ambient organic matter during the distillation step. The addition of DI water before distillation prevents the artifact formation, and allows the complete distillation.

8. Safety

8.1 All analysts will attend the “Chemical Hygiene Plan” training provided by the Environmental Health Office (EHO).

8.2 Many of the reagents used in the analysis of Mercury are potentially dangerous. It is strongly advised that the analyst check the material Safety Data Sheets for any reagent he/she is not familiar with product handling and protective measures should always be observed.

8.3 The analyst shall practice standard laboratory safety procedures as specified in the Chemical Hygiene Plan prepared by the EHO.

8.4 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

8.5 The toxicity or carcinogenicity of each chemical used in this method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring be made available to the analyst. 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 CH3Hg, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

8.6 Facility—When samples known or suspected to contain high concentrations of CH3Hg 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.

8.7 Protective equipment—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters.

8.8 Analysts are trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

8.9 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

8.10 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

8.11 Effluent vapors—The effluent from the CVAFS should pass through either a column of activated charcoal or a trap containing gold or sulfur to amalgamate or react with Hg vapors.

8.12 Waste handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.

8.13 Decontamination

8.13.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

8.13.2 Glassware, tools, and surfaces—Activated carbon powder will adsorb CH3Hg, eliminating the possible volatilization of CH3 Hg. Satisfactory cleaning may be accomplished by dusting a surface lightly with activated carbon powder, then washing with any detergent and water.

8.13.3 Laundry—Clothing known to be contaminated should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. If the launderer knows of the potential problem, the clothing may be put into a washer without contact. The washer should be run through a cycle before being used again for other clothing.

8.13.4 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by this method can achieve a limit of detection of less than 1ng per wipe. Less than 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe constitutes an acute hazard, requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

9. Equipment and Supplies

9.1 Sampling equipment

9.1.1 Sample collection bottles- fluoropolymer (ultra low level) or borosilicate glass (trace level), 125- to 1000-mL, with fluoropolymer or fluoropolymer-lined cap.

9.2 Cleaning

9.2.1 New bottles are cleaned by heating to 65-75 degrees Celsius in 20 % solution of nitric acid for at least 48 hrs, or washed on the Traceclean^{R}, an automated cleaning instrument manufactured by Milestone. The bottles are cooled, rinsed three times with reagent water, and filled with reagent water containing 1% HCl. These bottles are capped and placed in a clean oven at 60-70^{0} C overnight. After cooling, they are rinsed three more times with reagent water, filled with reagent water containing 0.4% (v/v) HCl, capped, and placed in a mercury-free class 100 clean bench until the outside of the bottle is dry. The caps are then tightened and the bottles are double-bagged in new polyethylene zip-type bags. The capped bottles are stored in plastic boxes until use.

9.2.2 Bottle blanks are analyzed to verify the effectiveness of the cleaning procedures.

9.3 Filtration Apparatus

9.3.1 Filter—0.45-µm, 15-mm diameter capsule filter (Gelman Supor 12175, or**.** equivalent)

9.3.2 Peristaltic pump—115-V a.c., 12-V d.c., internal battery, variable-speed, single-head (Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570- 10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent).

9.3.3 Tubing—styrene/ethylene/butylene/silicone (SEBS) resin for use with peristaltic pump, approx 3/8-in i.d. by approximately 3 ft (Cole-Parmer size 18, Catalog No. G-06464-18, or approximately 1/4-in i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent). Tubing is cleaned by soaking in 5-10% HCl solution for 8-24 h. It is rinsed with reagent water on a clean bench in a clean room and dried on the clean bench by purging with metal-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

9.4 Equipment for bottle and glassware cleaning

9.4.1 Vat, 100-200 L, high-density polyethylene (HDPE), half filled with 4 N HCl in reagent water.

9.4.2 Heating block capable of maintaining +/- 5 ^{0}C in the range 60-100 ^{0}C temperature range.

9.4.3 Laboratory sinks in class 100 clean area, with high-flow reagent water for rinsing.

9.4.4 Clean bench, class 100, for drying rinsed bottles.

9.4.5 Oven, stainless steel, in class 100 clean area, capable of maintaining ± 5C in the 60-70C temperature range.

9.5 Ultra high-purity argon (grade 5.0).

9.6 Equipment for CH3Hg purging system—Figure 2a shows the schematic diagram for the purging system. The system consists of the following:

9.6.1 Flow meter/needle valve—capable of controlling and measuring gas flow rate to the purge vessel at 550 (± 50) mL/min.

9.6.2 Fluoropolymer fittings—connections between components and columns are made using 6.4-mm o.d. fluoropolymer tubing and fluoropolymer friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with C-flex tubing because of its greater flexibility.

9.6.3 Cold vapor generator (bubbler)—500-mL borosilicate glass (special made to increase length of bubbler, see Figure 4) with standard taper 24/40 neck, fitted with a sparging stopper having a medium coarse glass frit that extends to within 0.2 cm of the bubbler bottom (Tecglass & Instrument, or equivalent).

9.6.4 Bubblers are cleaned between samples. The bubblers are cleaned by rinsing the bubbler with DI water 3 times (do not allow them to dry). They are then rinsed with 10% HCl by filling the purge tube and rinsing the outlet tube. Allow it to empty and then rinse with DI water. Rinse the outlet tube and purge tube with methanol. Allow it to empty and then rinse with DI water. Fill the bubbler with DI water allowing the purge tube to fill. Empty the bubbler and allow to drip dry. Fill with DI water and store. Check for condensation on the top of the bubbler, if condensation present rinse with methanol, then with DI water. Attachment 4.

9.7 Gas chromatography (GC) system. Clarus 500 by Perkin Elmer

9.7.1 GC conditions: Initial temperature: 45^{o}C and hold for 4.5 minutes; ramp at 45^{o}C/minutes to 180^{o}C and hold for 2 minutes.

9.7.2 The GC column is a DB-5 (J&W); 0.5 mm o.d. x 32 meters.

9.8 Autodesorption 350 ATD by Perkin Elmer

9.8.1 Autodesorption Conditions: purge 3 minutes; Primary desorption at 280^{o}C for 5 minutes; Secondary desorption at 280^{o}C for 7 minutes; flow 40 ml/min.

9.8.2 The flow of the system is controlled by the 350 ATD, and it's measured at the end of the detector.

9.9 The traps are placed on the autosampler in vertical position. The flow of the argon is from the bottom up.

9.10 Tenax-TA traps— 10cm x 6.5-mm o.d. x 4-mm i.d. glass tubing. The tube is filled with 0.15 +/- grams of 60/80 mesh Tenax-TA adsorbant (Supelco, Inc). The ends are plugged with silanized glass wool.

9.10.1 Traps are always capped when not in use.

9.10.2 Because the direction of flow is important in this analysis, the crimped end or the marked end with the ring of the Tenax trap will be referred to as "side A," while the uncrimped end will be referred to as "side B."

9.10.3 Tenax traps are condition three times at 250^{o}C and 300^{o}C prior to usage.

9.11 Pyrolytic column—The output from the GC oven is connected directly to a high temperature column to decompose eluted organo-mercurial compounds to Hg^0 The output of the pyrolytic column is connected to the inlet of the CVAFS system.

9.11.1 The column consists of a 24-cm length of quartz tubing, packed over the central 2 cm with quartz wool.

9.11.2 The column is heated to orange heat (~ 750-850^0 C) by a 10-14 cm length of 22 gauge Nichrome wire, tightly wrapped around the quartz wool packed.

9.11.3 Portion of the tube. The temperature of the coil is adjusted by visual inspection of the color, using a 0-120 volt autotransformer.

9.12 Tekran Model 2357 CVAFS, Brooks-Rand Model III CVAFS, or equivalent.

9.13 Figure 1 shows the schematic for the interface of the GC with the CVAFS detector (Reference 6).

9.14 Data handle and crunching is managed by Total Chrome software by Perkin Elmer.

9.15 Distillation unit—The distillation unit is a 32 position custom made system consisting of aluminum block, and heating block.

9.15.1 Fluoropolymer vials with caps—The distillation unit is designed to accommodate 180mL fluoropolymer vials. The original caps are used to close the vials when distillate is to be stored until analysis.

9.15.2 For each distillation, two identical vials are needed: a distillation vessel and a receiving vessel. For convenience, each vial should be engraved with a line at 40.0 mL (obtained by weighing 40 g of water in the vial), and a unique identification number, both on the vial and the cap.

9.15.3 Fluoropolymer vials are acid cleaned initially as described for other fluoropolymer ware and stored filled with 0.5% HCl. After use, receiving vials are rinsed with reagent water and filled with 0.5% HCL. The tubing is looped around the cap , and the vials are placed in a 70 ^{0} C (± 5^0 C) oven overnight. Cleaning is the same for the distillation vials, with the exception that first the vials, caps, and tubing are thoroughly wiped to remove any residues from the samples.

9.15.4 Purge caps—The standard caps on the fluoropolymer vials are replaced with purge caps (part number 33-2-2, Savillex, or equivalent) for distillation purposes. Fluoropolymer tubing—each purge cap is threaded with a piece of 1/8 inch fluoropolymer tubing, approximately 30-40 cm long. One end is pulled through one of the holes in the cap, down to a length that will allow it to reach the bottom of the distillation vial when the vial is screwed onto the cap. The bottom end of this tubing is cut at a 45^0 angle. The outside end of the tubing is cut perpendicularly and is looped around and inserted into the second cap hole when not in use (to keep the system closed and clean).

9.15.5 Aluminum distillation cover—The cover for the heating block consists of a 5 cm high aluminum block of the same cross section as the aluminum block (, which has been milled out completely except for a 0.5 cm shell all around. In this lid is placed a series of 5 slots, 0.5 cm wide by 3 cm high, on each of the long sides, to allow passage of the distillation tubing in and out of the distillation vessels.

NOTE: *It is very important that the heating block have an aluminum top covering the vessels to avoid condensation and refluxing of the sample in the distillation vessels.*

9.15.6 Polyethylene container (ice bath)—Distillate is received and cooled in a fluoropolymer receiving vial supported in an ice bath in a polyethylene container. A box approximately 15 cm wide x 25 cm long x 10 cm high with holes to accommodate the receiving vials were cut into the lid of each box.

9.15.7 Rotometer/needle valve—Five needle valve/rotometer (0-100 mL/min N_2) assemblies are required, one for each distillation vessel in the heating block. These rotometers can be mounted in banks of 5 for each distillation block, with all rotometers connected to a common gas manifold.

9.15.8 Fluoropolymer tubing–Inert gas (N_2 or Ar at 0.5-1 atm) is brought from the regulator to the manifold and from the rotometer outlets to the distillation vials by 1/8 inch fluoropolymer tubing.

9.15.9 The entire distillation is set up in the exhausted hood. The rotometers are on the outside of the hood and easily adjustable. Below the distillation blocks, the ice baths for the receiving vessels is placed.

9.15.10 Pipettors—All-plastic pneumatic fixed-volume and variable pipettors in the range of 10.0 uL to 5.0-mL.

9.15.11 Analytical balance capable of weighing to the nearest 0.01 g.

9.15.12 Nitrogen—UHP grade nitrogen that is further purified by the removal of Hg using a gold-coated sand trap or organic carbon trap.

10. Reagents and Standards

10.1 Reagent water—18-MS minimum, ultrapure deionized water starting from a prepurified (distilled, reverse osmosis, etc.) source. Water should be monitored for Hg, especially after ion exchange beds are changed.

10.2 Air—It is very important that the laboratory air be low in both particulate and gaseous Hg. Ideally, Hg work should be conducted in a new laboratory with mercury-free paint on the walls. Outside air, which is very low in Hg, should be brought directly into the class 100 clean bench air intake.

10.3 Hydrochloric acid—Trace-metal purified reagent HCl containing less than 5 pg/mL Hg. CH3 Hg is not stable in concentrated acid, so the acid does not need to be tested for CH3Hg.

10.4 Sulfuric acid—Trace-metal purified reagent H_2SO_4 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.

10.5 1% APDC solution—To 100 mL of reagent water, add 1.0 g of reagent grade APDC (ammonium pyrrolidine dithiocarbamate), and shake to dissolve. The solution is purified by extraction with three 10 mL aliquots of methylene chloride.

10.6 Glacial acetic acid—Reagent grade.

10.7 2 M Acetate buffer—2 moles of reagent grade sodium acetate (272 g) and 2 moles of reagent grade glacial acetic acid (118 mL) dissolved in reagent water to give a final volume of 1.0 L. To purify the buffer of traces of CH3 Hg, add 0.5 mL of 1% $NaBEt_4$ and purge the solution overnight with Hg-free N_2

or Ar. This solution has an indefinite lifetime when stored in a fluoropolymer bottle at room temperature.

10.8 Sodium tetraethyl borate, 1%—This reagent is purchased in 1.0-g air-sealed bottles (Strem Chemical, or equivalent. One hundred milliliters of 2% KOH in reagent water is prepared in a fluoropolymer bottle and chilled to 0 ^{0} C. The bottle of $NaBEt_4$ is rapidly opened and approximately 5 mL of the KOH solution poured in. The reagent bottle is capped and shaken to dissolve the $NaBEt_4$. This is poured into the 100 mL bottle of KOH solution, and shaken to mix. Immediately, the 1% $NaBEt_4$ solution in 2% KOH is poured into fifteen (15) 7-mL fluoropolymer bottles, which are capped and placed in a low temperature freezer. For use, one of these bottles is removed and thawed and kept in small cooler with ice during the ethylation process.

NOTE: *It is imperative that this reagent be exposed to air a minimum length of time Air decomposes the Sodium tetraethyl borate.. Thus, when removing reagent, open and close the lid quickly and tightly!*

10.9 Frozen bottles of $NaBEt_4$ will keep for at least one week. If any doubt arises about the quality of the ethylating reagent, make a new batch, as the old material often gives good results for reagent water spikes, but not for environmental samples. Do not use $NaBEt_4$ solid or solutions if they have a yellow color.

WARNING: *NaBEt4 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 hood. Triethylboron will bubble off to the air where it is eventually oxidized to harmless boric acid. Leave the acid beaker in the hood indefinitely, or boil down to 1/2 volume to destroy residues before discarding as any acid waste.*

10.10 Stock methyl mercury standard—certified CH3 Hg solution from Frontier Geosciences Inc. The stock solution has an indefinite lifetime when stored in an amber glass bottle with a fluoropolymer lid at room temperature. **Do not make or keep this concentrated stock solution in the trace mercury laboratory.**

10.11 Secondary methyl mercury standard—Dilute 1.00 mL of stock solution (B) to 1000.0 mL with reagent water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl. This solution contains approximately 4-5 mg/L (5.00 ng/mL) CH3 Hg as Hg. The exact CH3 Hg titre is confirmed as indicated below. The secondary CH3 Hg standard solution has been observed to maintain its titre over a year when stored in a fluoropolymer bottle in the refrigerator.

10.11.1 Dilute the secondary standard 1:10 with concentrated BrCl solution (0.100 mL of secondary stock solution added to 0.900 mL BrCl in a small FEP vial). Allow the solution to oxidize for at least 4 h. The total Hg in the dilution may then be analyzed using dual amalgamation/CVAFS, by comparison to a dilution of NIST-3133 (as in Method 1631). A mean of at least seven replicate analyses of the secondary stock solution is necessary to accurately quantify the total Hg concentration of the solution.

10.11.2 Analyze the secondary standard for labile H (II) using Method 1631 by directly reducing an aliquot of standard solution with $SnCl_2$, but without prior BrCl oxidation as performed in Section 10.11.1. At least two determinations of labile Hg(II) must be made of the stock solution.

10.11.3 Calculate the CH3Hg in the secondary CH3Hg standard solution by subtracting the mean labile Hg(II) concentration from the mean total Hg concentration.

10.11.4 If the secondary CH3Hg stock solution drops below 98.0% CH3Hg, discard the solution and make a fresh secondary solution.

10.12 Working methyl mercury standard—Prepare a dilution of the secondary CH3Hg standard using reagent water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl. A convenient concentration for this standard is 1.00 ng/mL CH3Hg. This solution will maintain its titre for more than one month when kept in a fluoropolymer bottle on the lab bench top. Refrigeration is not necessary.

10.13 Nitrogen—UHP grade nitrogen that is further purified by the removal of Hg using a gold-coated sand trap or organic carbon trap.

10.14 Argon—UHP grade nitrogen that is further purified by the removal of Hg using a gold-coated sand trap or organic carbon trap.

10.15 Gold-coated sand trap—The trap is made from 10-cm x 6.5-mm o.d. x 4-mm i.d. quartz tubing. The tube is filled with 3.4 cm of gold-coated 45/60 mesh quartz sand (Frontier Geosciences Inc., or equivalent). The ends are plugged with quartz wool. Traps are fitted with 6.5-mm i.d. fluoropolymer friction-fit sleeves for connection to the system.

11. Sample Collection, Preservation, Holding Times, Shipment, and Storage

11.1 Before samples are collected, consideration should be given to the type of data required, (i.e., dissolved or total), so that appropriate preservation and pretreatment steps can be of all aqueous samples must be tested immediately before removing an aliquot for processing or direct analysis to ensure the sample has been properly preserved.

NOTE: *Do not dip pH paper or pH meter into the sample; remove a small aliquot with a clean pipet and test the aliquot pH*

11.2 Samples are collected into rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps. Borosilicate glass bottles may be used if ppm concentrations of Hg and Hg species are expected. It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads. Polyethylene sample bottles must not be used (Reference 13).

11.2.1 Collect samples using the Sampling Method (Reference 8). Procedures in the Sampling Method are based on rigorous protocols for collection of samples for Hg with EPA 1669.

11.2.2 Sample filtration—For dissolved CH3 Hg, samples and field blanks are filtered through a 0.45-µm capsule filter (Section 9.3). The Sampling Method describes filtering procedures.

11.2.3 Preservation—Samples are preserved by adding 4 mL/L of concentrated HCL (to allow both CH3Hg and total Hg determination). Saline samples ([Cl -]>500 ppm) are preserved with 2 mL/L of 9 M H_2SO_4 solution. Acid-preserved samples are stable for at least six months, if kept dark and cool.

11.2.4 Samples are to the laboratory unpreserved if they are (1) collected in fluoropolymer bottles, (2) filled to the top with no head space, (3) capped tightly, and maintained at 0-4 degrees C from the time of collection until preservation. The samples must be acid-preserved within 48 h of sampling.

11.2.5 Handling of the samples in the laboratory should be undertaken on a mercury-free clean bench, after rinsing the outside of the bottles with reagent water and drying in the clean air hood.

11.2.6 Storage—Sample bottles should be stored in clean (new) polyethylene bags until analysis. To maintain CH3Hg concentrations without degradation, it is necessary to keep acid-preserved samples in dark and cool. If properly preserved, samples can be held up at least six months before analysis.

12. Quality Control and Documentation

12.1 Quality Control

12.1.1 Prior to the submittal of the data, all preparation blank, matrix spike, matrix spike duplicate, duplicate, and laboratory control sample data must be input into the laboratory quality control database.

12.1.2 The laboratory is NELAP certified and follows the NELAP's quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of matrix spikes (MS) and matrix spike duplicates (MSD) to assess accuracy and precision. Laboratory performance is compared to established performances criteria to determine whether the results of analyses meet the performance characteristics of the method.

12.1.3 The laboratory participates on bi-annual proficiency testing conducted by the New York Department of Health.

12.1.4 All analysts are required to have an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 12.3.

12.2 The analysis of the traps was modified and automated by using The Autodesorption 350 ATD by Perkin Elmer

12.2.1 The laboratory performed the MDL study required by 40 *CFR* Part 136, Appendix B, and the laboratory maintained the records of modifications made to this method.

12.2.2 Run sequence:

RUN SEQUENCE
Two system blanks
Three primes
A minimum of five, non-zero calibration standards
Ethylation blank
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
On-going precision and recovery (OPR)
Continuing Calibration Blank (CCB)
Method Detection Limit (MDL) Check Undistilled
Quality control sample/Laboratory Control Sample (LCS)
Method Detection Limit (MDL)
Method blank (MBLK) distillation
Field Blank
Ten samples
Matrix spike
Matrix spike duplicate
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
Ten samples
Matrix spike
Matrix spike duplicate
Lab Duplicate
Lab Triplicate (QAPP dependent)
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
On-going precision and recovery (OPR)
Continuing Calibration Blank (CCB)

12.3 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision and to monitor matrix interferences. Section 12.8.3-5 describes the procedure and QC criteria for spiking.

12.4 Analyses of blanks are required to demonstrate acceptable levels of contamination. Section 12.8.13 describes the procedures and criteria for analyzing blanks.

12.5 The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery (OPR) sample and the quality control sample (QCS) that the system is in control. Sections 12.8.14 and 12.8.15 describe these procedures, respectively.

12.6 The laboratory shall maintain records to define the quality of the data that are generated. Sections 12.9 describe the development of accuracy statements.

12.7 The determination of CH3 Hg in water is controlled by an analytical batch. An analytical batch is a set of samples distilled with the same batch of reagents, and analyzed in the same analytical sequence. A batch may be from 1 to as many as 10 samples. Each batch must be accompanied by at a method blank, an OPR sample, and a QCS. In addition, there must be one MS and one MSD sample for every 10 samples (a frequency of 10%).

12.8 Initial demonstration of laboratory capability

12.8.1 Method detection limit—To establish the ability to detect CH3Hg, the analyst shall determine the MDL according to the procedure at 40 *CFR* 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL listed in Section 3.5 or one-third the regulatory compliance limit, whichever is greater. The MDL should be determined when a new operator begins work or whenever, in the judgment of the analyst, a change in instrument hardware or operating conditions would dictate that the MDL be redetermined.

12.8.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations:

12.8.2.1 Analyze four replicates of the IPR solution (0.5 ng/L, Section 10.10) according to the procedure beginning in Section 14.

12.8.2.2 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.

12.8.2.3 Compare s and X with the corresponding limits for initial precision and recovery in Table 1. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the acceptance range, system performance is unacceptable. Correct the problem and repeat the test.

12.8.3 Method accuracy—To assess the performance of the method on a given sample matrix, the laboratory must perform either matrix spike (MS) and matrix spike duplicate (MSD) sample analyses on 10% of the samples from each site being monitored, or at least one MS/MSD sample analysis for each sample set, whichever is more frequent.

12.8.4 The concentration of the CH3Hg in the sample shall be determined as follows:

12.8.4.1 If, as in compliance monitoring, the concentration of CH3 Hg in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1-5 times the background concentration of the sample, whichever is greater.

12.8.4.2 If the concentration of CH3Hg in a sample is not being checked against a limit, the spike shall be at 1-5 times the background concentration or at 1- 5 times the MR L in Table 1, whichever is greater.

12.8.5 Assessing spike recovery

12.8.5.1 Determine the background concentration (B) by analyzing one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in

Section 14. If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established a priority.

12.8.5.2 If necessary, prepare a spiking solution to produce an appropriate level in the sample.

12.8.5.3 Spike two sample aliquots with the spiking solution and analyze these aliquots to determine the concentration after spiking (A).

12.8.5.4 Calculate the percent recovery (P) in each aliquot using Equation 1:

Equation 1

$$P = 100\frac{(A-B)}{T}$$

Where:
A=Measured concentration of analyte after spiking
B=Measured concentration of analyte before spiking
P=Percent recovery
T=True concentration of the spike

12.8.6 Compare the percent recovery (P) with the QC acceptance criteria in Table-1.

12.8.7 If P falls outside the designated range for recovery in Table 1, the CH3 Hg analysis has failed to meet the established performance criteria. If P is unacceptable, analyze the OPR standard. If the OPR is within established performances criteria (Table 1), the analytical system is within specification and the problem can be attributed to interference by the sample matrix.

12.8.8 If the interference can be attributed to sampling, the site or discharge should be resampled. If the interference can be attributed to a method deficiency, the analyst must modify the method, repeat the test required in Section 12.2, and repeat analysis of the sample and MS/MSD. However, when this method was written, there were no known interferences in the determination of CH3Hg using this method. If such a result is observed, the analyst should investigate it thoroughly.

12.8.9 If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be outside specified limits. The analyst must identify and correct the problem and reanalyze the sample batch.

12.8.10 Relative percent difference between duplicates—Compute the relative percent difference (RPD) between the MS and MSD results according to Equation 2 using the CH_3Hg concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 12.4.2.4 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

Equation 2

$$RPD = 200\frac{(|D_1 - D_2|)}{(D_1 + D_2)}$$

Where:
RPD=Relative percent difference
D1 =Concentration of CH3 Hg in the MS sample
D2 =Concentration of CH3 Hg in the MSD sample

12.8.11 The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 1. If the criterion is not met, the system performance is unacceptable. The problem must immediately be identified and corrected, and the analytical batch reanalyzed

12.8.12 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records maintained. After analyzing five samples in which the recovery passes the test in Section 12.4.2, compute the average percent recovery (Pa) and the standard deviation of the percent recovery rp). Express the accuracy assessment as a percent recovery interval from Pa – 2rp to Pa + 2rp. For example, if Pa = 90% and rp = 10% for five analyses, the accuracy interval is expressed as 70-110%. Update the accuracy assessment regularly (e.g., after every five to ten new accuracy measurements).

12.8.13 Blanks—Blanks are critical to the reliable determination of CH3Hg at low levels. The sections below give the minimum requirements for analysis of blanks. However, it is suggested that additional blanks be analyzed as necessary to pinpoint sources of contamination in, and external to, the laboratory.

12.8.13.1 Ethylation blanks—Reagent water typically contains no CH3Hg. The reagent (ethylation) blank may conveniently be determined by adding 0.3 ml of of acetate buffer and 0.15 ml of 1% $NaBEt_4$ solution to 50 mL of reagent water in the reaction vessel.

12.8.13.1.1 A single ethylation blank is analyzed with each analytical run, part of the calibration sequence. This value is used to blank correct the standard curve.

12.8.13.1.2 The presence of more than 2 pg of CH3Hg indicates a problem with the reagent water or one of the reagent solutions. An investigation of the cause of the high blank can be made by varying, one at a time, the amounts of buffer, reagent water, and $NaBEt_4$. Because NaBEt4 cannot be purified, a new batch should be made from different reagents and should be tested for Hg levels if the level of CH3Hg is too high. If the reagent water is found high, this can be remedied by replacing the purification cartridges.

12.8.13.2 Method blanks—The method blanks (distillation blanks) are prepared by the distillation and analysis of 45 mL aliquots of 0.4% HCl acidified reagent water, exactly as if they were samples.

12.8.13.3 Field blanks

12.8.13.3.1 Analyze the field blank(s) shipped with each sample set. Analyze the field blank and the associated samples in the same batch. It is preferable to analyze the field blank before the associated samples.

12.8.13.3.2 If CH3Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 1), or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes.

12.8.13.3.3 If contamination of the field blank(s) and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event.

12.8.13.4 Equipment blanks—Before any sampling equipment is used at a given site, the laboratory or cleaning facility is required to generate equipment blanks to demonstrate that the sampling equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampler check blanks.

12.8.13.5 Bottle blanks—After undergoing the cleaning procedures in this method, bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles should be filled with reagent water acidified to 0.4% HCL and allowed to stand for a minimum of 24 h. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water should be analyzed for any signs of contamination. If any bottle shows signs of contamination, the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles cleaned again.

12.8.13.6 Continuing Calibration blanks (CCB)— Continuing Calibration blanks are used to demonstrate that the analytical system is free from contamination that could otherwise compromise sample results. Continuing Calibration blanks are prepared and analyzed using sample containers, labware, reagents, and analytical procedures identical to those used to prepare and analyze the samples. Continuing Calibration blanks should follow all Continuing Calibration verification samples.

12.8.13.7 The Initial calibration Blank (ICV)-The ICV is the same as the CCV, with the exception that it is run after the Initial Calibration Verification sample.

12.8.13.8 Sampler check blanks (Equipment blank)—Sampler check blanks are generated in the laboratory or at the equipment cleaning contractor's facility by reagent water through the sampling devices using the same procedures that are used in the field (see Sampling Method). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing sampler check blanks at the laboratory or cleaning facility.

12.8.13.8.1 Sampler check blanks are generated by filling a large carboy (Section 10.17) or other container with reagent water (Section 10.1) and processing the reagent water through the equipment using the same procedures that are used in the field (see Sampling Method). or example, manual grab sampler check blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler check blanks are collected by immersing the submersible pump or intake tubing into the water and pumping water into a sample container.

12.8.13.8.2 The sampler check blank must be analyzed using the procedures in this method. If CH3Hg or any potentially interfering substance is detected in the blank, the source of contamination or interference must be identified, and the problem corrected. The equipment must be demonstrated to be free from CH3 Hg and interferences before the equipment may be used in the field.

12.8.13.8.3 Sampler check blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and a subsurface sampling device, a sampler check blank must be run on both pieces of equipment.

12.8.14 Ongoing precision and recovery (OPR)—To demonstrate that the analysis system is within specified limits and that acceptable precision and accuracy is being maintained within each analytical batch, the analyst shall perform the following operations.

12.8.14.1 Analyze the OPR solution (0.5 ng/L, Section 10.10) followed by a ethylation blank prior to the analysis of each analytical batch according to the procedure in Section 14. An OPR must also be analyzed at the end of an analytical run or at the end of each 12-hour shift. Subtract the peak height (or peak area) of the ethlyation blank from the peak height (or area) for the OPR and compute the concentration for the blank-subtracted OPR.

12.8.14.2 Compare the computed OPR concentration with the yearly established limit. If the concentration is in the range specified, the analysis system is within specification and analysis of samples and blanks may proceed. If, however, the concentration is not in the specified range, the analytical process is not within the specified limits. Correct the problem and repeat the OPR test.

12.8.14.3 The laboratory should add results that pass the specification in Section 12.6.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (sr). Express the accuracy as a recovery interval from R - 2sr to R + 2sr . For example, if R = 95% and sr = 5%, the accuracy is 85- 105%.

12.8.15 Quality control sample (QCS)/ Laboratory Control Sample (LCS) —The laboratory must obtain a QCS from a source different from the CH3Hg used to produce the standards used routinely in this method. The QCS should be analyzed as an independent check of instrument calibration.

12.8.16 Continuing Calibration Verification Sample (CCV) –or throughout the course of the analytical run (CCV) near the concentration range. These samples are evaluated to determine whether the instrument is within acceptable calibration throughout period in which samples are analyzed (i.e., to verify that the initial calibration was applicable during the sample analyses). In general, failure of the CCV indicates that the initial calibration is no longer valid and should trigger recalibration and the reanalysis of the associated samples in the analytical sequence.

12.8.17 Laboratory Duplicate or Field Duplicate- Depending on specific program requirements, the laboratory may be required to analyze field duplicates and field spikes collected to assess the precision and accuracy of the sampling, sample transportation, and storage techniques. The relative percent difference (RPD) between field duplicates should be less than 35%. If the RPD of the field duplicates exceeds 35%, the laboratory should communicate this to the sampling team so that the source of error can be identified and corrective measures taken before the next sampling event.

12.9 Documentation

12.9.1 Reagent bottles are labeled with reagent name, name and amount of all chemicals used in production, preparation date, expiration date, and initials of analyst.

12.9.2 Sample data and quality control data is recorded on the appropriate laboratory forms.

12.9.3 As new standards and reference samples are introduced in to the laboratory, they must be tagged with a reagent number and entered in to the CESE Section Standard Preparation Logsheet. The reagent number is then recorded on the appropriate laboratory forms when used.

13. Calibration and standardization

13.1 Establish the operating conditions necessary to purge Hg species from the bubbler and to desorb Hg species from the traps so that sharp peaks are given. The system is calibrated using CH3 Hg standards ultimately traceable to NIST standard total Hg reference material, as follows:

13.2 Calibration

13.2.1 The calibration must contain five or more non-zero points and the results of analysis of one ethylation blank. The lowest calibration point must be at the minimum level (ML).

13.2.2 Standards are analyzed by the addition of aliquots of the CH_3Hg working standard (Section 10.9) directly into the bubblers. Add 50 mL of fresh reagent water, a 0.005 ng aliquot of the standard, 0.30 mL of acetate buffer, and 0.15 mL of $NaBEt_4$ to the bubbler, swirling to mix. Allow to react for 17 min, purge for 17 min, dry for 5 min and then analyze. Sequentially follow with aliquots of 0.01, 0.02, 0.04, 0.05, 0.1 and 0.2 ng CH_3Hg in separate bubblers.

13.2.3 For each point, correct the standard peak height or area by subtracting the peak height or area of the ethylation blank for the analytical batch. Calculate the calibration factor (CF) for CH_3Hg for each of the five standards using the mean ethylation-blank-corrected peak height or area (Equation 3).

Equation 3

$$CF = \frac{R_s - R_e}{Cs}$$

Where:
Rs=Peak height or area of the standard
Re=Peak height or area of the ethylation blank
Cs=Concentration of the standard (ng/L)

13.2.4 Calculate the mean calibration factor (CFm), the standard deviation of the CFm (SD), and the relative standard deviation (RSD) of then calibration, where RSD = 100 x SD/CFm. If the RSD is # 15%, the CFm may be used to calculate sample concentrations. If RSD > 15%, recalibrate the analytical system and repeat the test.

13.2.4.1 The net concentration recovery (minus ethylation blank) for the lowest standard must be in the range of 65-135% of the expected value to continue with sample analysis.

13.2.5 Ongoing precision and recovery—Perform the ongoing precision and recovery test to verify calibration prior to analysis of samples in each analytical batch. An OPR must also be analyzed at the end of an analytical run or at the end of each 12-hour shift.

14. Procedure

14.1 Sample Distillation. (Attachment 2)

14.1.1 Weigh a 50-mL aliquot from a thoroughly shaken, acidified sample, into a 120-mL fluoropolymer distillation vial. Add 200 µL of 1% APDC solution, and 20 ml of Milli-Q water. Replace the distillation cap, such that the tubing extends to the bottom of the vial.

14.1.2 Repeat this procedure for all samples to be distilled in a set, including method blanks, laboratory control sample, MDL check sample and spiked samples.

14.1.3 Method blank, laboratory control sample and MDL check sample are acidified with 200 ul of concentrated HCl.

14.1.4 Matrix spikes and matrix spike duplicates—For every 10 or fewer samples, pour two additional 50-mL aliquots from a randomly selected sample. Spike the aliquots at the level specified in Section 12.4 and process them in the same manner as the samples. There should be two MS/MSD pairs for each analytical batch of 20 samples.

14.1.5 For each sample, prepare a 120-mL distillate receiving vial. Add 25.0 mL reagent water to each receiving vial and replace the cap so that the tubing extends into the water layer.

14.1.6 Record the sample ID associated with each distillation and receiving vial. It is important to develop an unambiguous tracking system, such as the use of engraved vial numbers, because the distillation vials themselves cannot be labeled (due to the heat).

14.1.7 Place each prepared distillation vial into one of the holes in the heating block and attach the fluoropolymer tubing to the incoming gas supply from the rotometer manifold. Adjust the gas flow rate through the bubbler to 60 ± 20 mL/min.

14.1.8 As each distillation vial with sample is placed into the heating block, place the corresponding labeled distillation vial into the ice bath immediately adjacent to the heating block. Attach the tubing from the receiving vessel to the port of the distillation vessel.

14.1.9 Once all the holes in a heating block are filled, place the aluminum lid over the vessel caps in such a way that all tubing is passing without crimps through the slots, and the lid is making metal-to-metal contact with the block (to provide proper heating of the lid).

14.1.10 Turn on the temperature controllers to the heating blocks to a pre-set block temperature of 125 ± 3^0 C. Higher temperature will form artifact during distillation and will gives a bias high result.

14.1.11 Distill the samples until 100% of the initial aliquot volume has distilled over. This time period will be approximately 2.5 h to 4 h depending upon exact temperatures, gas flow rates, and water characteristics.

14.1.11.1 Prepared a distillation vial with 75 ml of DI water to check for 100 % distillation.

14.1.11.2 Different samples and locations on the block will distill at somewhat different rates, so after about 2 h, all of the tubes should be monitored frequently to avoid over-distillation. As the individual samples fill to the line, they should be removed from the distillation unit.

14.1.11.3 Over-distillation is the greatest potential risk for poor recoveries by this method. If more than the prescribed amount of sample distills over, the risk of HCl fumes co-distilling increases. Chloride and low pH are interferences with the ethylation procedure.

14.1.11.4 If any samples are suspected of over-distillation, they should be checked with pH paper, if the distillate has a pH of less than 3.5. The distilled can be diluted prior to analysis or pH adjusted prior analysis.

14.1.12 Once all of the vials are distilled, the distillates may be stored at room temperature and in the dark for up to 48 h before analysis. The distillate must be freeze for a longer storage time.

14.1.13 The distillation-side (dirty) vials must be wiped, and nitric acid solution distilled, and then rinsed in reagent water. To acid-clean between uses, the vials are filled with 10% HCl, recapped with the tubing looped around to close off the port, and placed in an oven at 70^0 C overnight.

14.2 Ethylation and purging of the distillates (Attachment 3)

14.2.1 Pour the distillate into the bubbler before starting the analysis, add 0.30 mL of acetate buffer to the sample in the receiving vial, and swirl to mix the buffer with the distillate.

14.2.2 Prepare the cap of the bubbler by placing the trap at the outlet of the cap. Make sure that the A-side of trap is on the front. (A-side the ring marked side or the s side from the Supelco tubes)

14.2.3 Add 0.15 ml of freshly thawed 1% $NaBEt_4$ solution. Close the reaction vessel with the bubbler cap, and swirl gently to mix.

14.2.4 If standards, ethylation blanks, or QCS are being analyzed, pour 50 mL of reagent water into the bubbler, add 0.30 mL of acetate buffer, the appropriate spike, etc., and 0.15 mL 1% $NaBEt_4$ solution.

14.2.5 Allow the contents of the bubbler to react for 17 min. All CH3Hg in the sample is converted to volatile methylethyl mercury.

14.2.6 After reaction time is competed, each bubbler is fitted with the 1/4" c-flex fitting, and purge the sample with N2 (60- 150 mL/min) for 17 min.

14.2.7 Once the sample has been purged for 17 min, any adsorbed water must be dried from the Tenax trap. Disconnect the Tenax trap from the bubbler and attach the N2 flow directly to the trap. Use the same orientation (i.e., N2 entering from side A), and purge the trap for 5 min.

14.2.8 The sample is now ready for analysis. The methylethyl mercury collected on the trap is quantitatively stable for up to 24 hrs and must be analyzed within that period.

14.3 Desorption of methylethyl mercury from the Tenax-TA trap (Attachment 3)

14.3.1 Insert the Tenax trap containing the new sample into the GC auto desorption unit *such that side A is on the upright position.*

14.3.2 Make sure that the post GC pyrolytic column is on and red-hot (~750 -850^0 C), head pressure in the Argon tank should be 110 psig, and the tank total pressure is greater than 300 psig.

14.3.3 Peaks generated using this technique should be very sharp and almost symmetrical. Methylethyl mercury elutes at approximately 2.5 min and has a width at half-height of about 10 sec. Earlier peaks (Hg^0, $(CH_3)_2$ Hg) are sharper, while later peaks (diethylmercury) are broader.

14.3.4 The appearance of only one peak (Hg^0) usually signifies either that the pyrolytic column is not turned on, or that NaBEt4 was not added to the sample.

14.3.5 Normally the Hg^0 peak is quite small. However, some Hg^0 is generated by thermal degradation of diethyl mercury during the desorption step. Thus, when samples contain a high concentration of Hg (II), both the Hg^0 and the diethyl mercury peaks will be bigger. The ratio of the two peaks is indicative of the quality of the Tenax trap. As the Tenax trap degrades, the amount of thermal breakdown of organo-mercurials increases. Since the diethyl mercury is much more sensitive to thermal breakdown than the methylethyl mercury, monitoring the latter peak can serve as an early warning for trap replacement. Generally, the Tenax traps should be replaced any time the Hg^0 peak grows to be as large as the diethyl mercury peak. As a rule of thumb for samples with significant Hg (II), use 1.0 ng Hg (II) from a non-acidified solution deliberately added to the reaction vessel as a trap check. For samples very low in Hg (II), such as blanks, the Hg^0 peak is generally higher than the diethyl mercury peak, due to residual sources.

15. Calculations

15.1 Calculate the following parameters for each analytical batch:

15.1.1 Ethylation blank (n = 1) or the mean ethylation blank (n > 1)

15.1.2 Ethylation-blank subtracted calibration factor for each standard (Cfx , Section 10.1.3) and peak measurement for each sample (R_S)

15.1.3 The mean calibration factor (CFm), standard deviation of the calibration factor (SD), and relative standard deviation (RSD) of the calibration factor (Section 10.1.1.4).

15.2 Compute the concentration of CH_3 Hg in ng/L (parts-per-trillion; ppt) according to Equation 4

Equation 4

$$[CH_3Hg](ng/L) = \frac{R_s - R_e}{CF_m * V}$$

where:
Rs=gross peak height (or area) of signal for CH3Hg in sample
Re=peak height (or area) of signal for CH3Hg in ethylation blank (n = 1) or mean ethylation blank (n > 1)
CFm=mean calibration factor
V=Sample volume (L)

15.3 The Methylmercury concentration of the method blank (ng/L, Equation 4) is subtracted from the sample concentration calculated above to obtain the net in situ CH_3Hg concentration.

Equation 5

$$[CH_3Hg]_{MB}(ng/L) = \frac{R_{MB} - R_{EB}}{CF_m * V_{MB}} * \frac{V_{MB}}{V_s}$$

where:
RMB=gross peak height (or area) of signal for CH3Hg in the mean method blank
REB=gross peak height (or area) of signal for CH3Hg in the ethylation blank (n = 1) or the mean ethylation blank (n > 1)
CFm=Mean calibration factor
VMB=Volume of the method blank
Vs=Volume of the sample

Equation 6

$$[CH_3Hg]_{net} = [CH_3Hg]_{sample} - [CH_3Hg]_{MB}$$

where:
[CH3Hg]net =net in situ CH_3Hg concentration (ng/L)
[CH3Hg]sample =ethylation-blank corrected concentration of CH_3Hg in the sample (ng/L, Equation 3)
[CH3Hg]MB =concentration of CH3Hg in the mean method blank (ng/L, Equation4)

15.4 Reporting

15.4.1 All results are reported after subtraction of mean method blanks (Equation 6).

15.4.2 Under the conditions described here, the distillation procedure is 100% efficient in recovering CH_3Hg because all of the sample volume is distilled.

16. Method performance

16.1 The method detection limit (MDL) listed and the quality control acceptance criteria listed were validated. Results are listed on table 2 and 3. IPRs were run during the initial set up of the method and IPRs are also run as Demonstration of Capability by the new analysts and compare against the criteria on table 1.

17. Pollution Prevention

17.1 All analysts will attend the Chemical Hygiene Plan and Hazardous Waste Management training provided by the EHO.

17.2 All analysts shall remain aware that Syracuse University waste minimization objective is to reduce the generation of both hazardous and non-hazardous waste as much as is practical.

17.3 All analysts will be familiar with the "Hazardous Waste Management" manual.

17.4 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

18. Data Assessment, Review, and Acceptance Criteria of QC Measures

18.1 Prior to the analyst's accepting of results, all reagent blank, matrix spike, matrix spike duplicate/matrix duplicate, and reference sample data shall be reviewed for compliance according to Table 2.

19. Corrective Actions for Out-of-Control Data

19.1 The analyst performing the analysis shall compare all quality control data to the appropriate control limits in a timely manner. If any excursions are noted, the analysis is halted, and corrective action is implemented. All excursions shall be noted on a Corrective Action Form, which shall be reviewed and signed by a second party (i.e. another Graduate Student, Laboratory Technician II, or Primary Investigator).

20. Contingencies for Handling Out-of-Control or Unacceptable Data

20.1 If the corrective action does not correct the excursion the analyst will inform either a Laboratory Technician II, Laboratory Manager, and/or Project Investigator to help the analyst solve the problem.

21. Waste Management

21.1 Guidelines for managing laboratory wastes are addressed in the "Hazardous Waste Management" manual

21.2 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

21.3 The laboratory is responsible for complying with all federal, state, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

21.4 Acids, samples at pH <2, and BrCl solutions must be neutralized before being disposed of, or must be handled as hazardous waste.

22. References

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22.14 Bloom, N.S. "Trace Metals & Ultra-Clean Sample Handling," *Environ. Lab.* **1995,** *7,* 20.

22.15 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

22.16 Bloom, N.S.; Horvat, M.; Watras, C.J. "Results of the International Mercury Speciation Intercomparison Exercise," *Wat. Air. Soil Pollut*., **199**5, *80,* 1257.

23. Tables, Diagrams, Flowcharts, Logs, Attachments, and Validation Data

23.1 Table 1: CESE Quality Control Requirements- Methyl Mercury Analysis Using Method 1630: Lower Water Quality Criterion, Method Detection Limit, and Minimum Level

23.2 Table 2: MDL Summary

23.3 Table 3: 2007 QC limits

23.4 Attachment 1: CESE Corrective Action Log

23.5 Attachment 2: Quick start- up reference: Distillation and clean up

23.6 Attachment 3: Quick start- up reference: Purging and analysis

23.7 Attachment 4: Quick start- up reference: Bubbler clean up

23.8 Attachment 5: Quick start- up reference: Trap packing and conditioning

23.9 Attachment 6: Glossary

23.10 Attachment 7: CESE Standard Log

23.11 Figure 1: Schematic Diagram of the Cold Vapor Atomic Fluorescence Spectrometer (CVAFS)

23.12 Figure 2: Schematic Diagram of Bubbler setup (a), and trap orientation (b)

23.13 Figure 3: Schematic diagram showing the CH_3Hg distillation set up

23.14 Figure 4: New bubbler

Table 1
CESE Quality Control Requirements

QC Check	Frequency	Acceptance Criteria	Corrective Action*
Initial Calibration	Daily prior to sample analysis / as per method / or as specified in QAPP	5 standards with the RSD ≤ 15%, Low Std. Recovery 65% - 135%	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes
Initial Calibration Verification (ICV)	Immediately after initial calibration	85 – 115 % of expected value	1. Reanalyze 2. Remake and reanalyze ICV 3. If criteria are still not met, repeat initial calibration
Initial calibration Blank (ICB)	Immediately after ICV	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3.
Continuing Calibration Verification (CCV)	After every ten samples and at the end of the run	85 – 115 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3 All samples analyzed after the last passing CCV must be reanalyzed
Continuing Calibration Blank (CCB)	After every CCV	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCB must be reanalyzed 4. Change air bubble tubing
Method blanks	1 with every batch of samples	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, reprep blank and all associated samples 3. If concentration is high and the analyte is not detected, document excursion
Ethylation Blank	1 with every batch	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, reprep blank and all associated samples 3. If concentration is high and the analyte is not detected, document excursion
Filter Blank	1 with every filtering event	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, reprep blank and all associated samples 3. If concentration is high and the analyte is not detected, document excursion
Duplicate	1 every 20 samples	RPD 20%	1. If < 5x MRL or is non-detect, the MS/MSD will be used for precision. 2. If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.
Triplicate	QAPP dependent, once a month, once every 250 samples	RSD 35%	1. If < 5x MRL or is non-detect, the MS/MSD will be used for precision. 2. If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.
Method Detection Limit-MDL Minimum reportable Limit – MRL	Daily prior to sample analysis	0.02 ng/L 0.05 ng/L	1. Reanalyze 2. If criteria are still not met, reprep blank and all associated samples 3. If concentration is high and the analyte is not detected, document excursion
Laboratory Control Sample (LCS)	1 with every batch of samples	Recovery within appropriate control limits (53-125%) or as specified in QAPP.	1. Reanalyze 2. If criteria are still not met, reprep LCS and all associated sample. 3. If recovery is high and the analyte is not detected, document excursion only
Matrix Spike/Matrix Spike Duplicate sample (MS/MSD)	1 with every batch of samples	Recovery (40-150%) and RPD (35%) or as specified in QAPP.	1. If Recovery is not within Qc limits, and an RPD criterion is met document excursion. 2. If recover y is within QC limit, and RPD criterion is not met, reanalyze.
Initial Precision and Recovery (IPR)	Set of four analysis	IPR within s (31%) and X (69-131%) **	1. Reanalyze

* All corrective actions must be documented on the CESE Corrective Action Log.

** We are still using the IPR criteria set by the USEPA and we are building a recovery history with every new analyst. We plan to use the NELAP recommendation of 20 points tabulation to calculate and to establish our criteria.

Note: Not all QC Checks are applicable to the method of concern.

Table 2
MDL summary

MDL Study 8/7/2007 using 0.05 ng/L	
Sample	Amout(ng/L)
MDL 1	0.0493
MDL 2	0.0482
MDL 3	0.0496
MDL 4	0.0440
MDL 5	0.0474
MDL 6	0.0357
MDL 7	0.0484
Average	0.0461
SD	0.00493
MDL	**0.0155**

Table 3
2007 QC limits

QC Recovery Limits for 2007		
QC type	Hg	MethylMercury
OPR	82-122	53-125
LCS/QCS	82-122	53-125
MS/MSD	76-128	40-150
CCV	90-110	85-115
Field RPD	35	35
Lab RPD	20	20

Attachment 1
CESE
CORRECTIVE ACTION LOG

Analyst: _____Instrument: _____

Date of Analysis: _____Method: _____

PROJECT NUMBER(S)/BATCH NUMBER(S)	EXCURSIONS	AFFECTED SAMPLES	CRITERIA COMPARISON	CORRECTIVE ACTION/EXPLANATION

Reviewed by:

_____ _____

QA/QC Reviewer Date

_____ _____

Project Investigator Date

Attachment 2
Quick Start-up Reference

MeHg Distillation

A. Set up distillation apparatus

1. Fill plastic bins with ice (ice machine is in lab 443 – key DE-1).
2. Place lids on bins and place bins in front of the corresponding aluminum blocks.
3. Plug the hotplates in and turn the dial to 4 or 5. Distillation Temperature should be between 125 +/-3 ^{0}C. Do not exceed 130C.
4. Make sure the valves on the flow meters are closed.

NOTE: Our distillation can accommodate 32 aliquots daily. In your set up you have to have 6-8 positions available for Quality control which is mandatory requirements in Trace Metal Research Lab. Rest of the analysis set up are samples. There are two distinct sets of vials. Each set have engraved designation: Distillation set A and B respectively. On each set engraved labels read A1D-A16D and for set B(B1D-B16D). Both sets have their own set of connections. Teflon tubing labeled A1-16 and for set B1-B16. The Teflon tubing with top cap at both ends is cut to exact length to extend from Aluminum blocks down to the condensation ice bath. It is imperative to match appropriate distillation vials with its exact matching Teflon connection tubing to the Receiving vials designated (A1R-A16R, B1-B16 and extra set C&D). Set A is located in designated drawer (distillation set A). Set B is located in drawer (distillation set B). Receiving sets A, B ,C and D- are located in drawer labeled "receiving sets A, B and C."

5. Label receiving vials with the name of the sample on laboratory tape.
6. Each receiving vial have engraved designation exp. (A1R) to match it with the distillation vial.
7. Record receiving Vial # in the data form.
8. Weigh each vial. Record the weight on the data form.
9. Add approximately 25mL of Milli-Q di- water to the vial and record the weight on the data form.

B. Distillation (reaction) vials

1. Remove thermometers from the blocks while loading.
2. Record distillation vial # on data form column
3. Place the vial on the scale. Tare the weight.
4. Add approximately 50 mL of Milli-Q water or sample to the vial. Add 200µL of APDC solution.
5. Record the weight of the water + APDC solution on the data form, and an additional 20 ml of milli-Q water.
6. Put the lid with two tubes on the distillation vial.
7. Put the lid with only one tube on the matching receiving vial.
8. **DO NOT Label the distillation vials. The vials will get stuck in the aluminum block.**
9. Place the distillation vial in the aluminum block. Make sure the distillation vial is sitting upright.
10. Cover it with matching aluminum top cover.
11. Place the receiving vial in the ice bath. Push the vial down into the ice so that the ice surrounds all but the lid of the receiving vial.
12. Connect the extra tube to the flow meter and open the valve.
13. To maintain constant gas flow and very god recoveries it is crucial that flow is adjusted properly with a flow meter.
14. Once several pairs of vials are set up, turn on the main gas valve (ultra high purity N_2 gas). Make sure the vials are bubbling, but not too rapidly (you do not want sample splashing up onto the lid of the vial).
15. The pressure on flow meters reads 45-50 psi. The regulator pressure should read 20 psi.
16. You should have 16 vials in each aluminum block.

C. Vial sequence (refer to data forms)

1. A MeHg run will consist of 32 vials.
    a. The first vial (vial #1) is a Milli-Q water blank (di blank). Just fill the distillation vial with approximately 50mL of de-ionized water and add the **APDC** solution.

    b. The next two vials (vial 2 and vial 3) will be the first water sample and a laboratory duplicate (LD) of that sample. Just fill the second and third distillation vials with

approximately 50mL of the same sample (sample#1) and add the APDC solution to both.

c. The next two vials (vial 4 and vial 5) will be the second water sample and then the water sample + a matrix spike (MS). Fill vial 4 with approximately 90mL of the second water sample and add the APDC solution. Fill vial 5 with approximately 90mL of the same sample (sample 2) and add the APDC solution plus 50 uL of the 1ng/mL MeHg working (stock) standard.

2. The 1ng/mL MeHg working standard needs to be made bi-annually according to the lab practice.
   a. Dump the old working (stock) standard in the HAZARDOUS WASTE container under the right hood (left cabinet).
   b. Using the flask measure 100mL of Milli-Q water. Use analytical pipette 1000uL and take out 800uL of the Milli-Q from the vol. flask.
   c. Using the 1000uL pipette, add 0.5 mL (500uL) of the Glacial Acetic Acid (Trace Metal Grade only).
   d. Remove the pipette tip. Place a new tip on the pipette.
   e. Using the 20-200 uL analytical pipette, add 200uL conc. HCl (Trace Metal Grade).
   f. Add 100uL of the 1mg/L MeHg standard to the flask. Remove the pipette tip. Place a new tip on the pipette.
   g. Cap MeHg standard bottle. Place the 1mg/L MeHg standard back in its bag. Shake the 1ng/mL MeHg working (stock) standard in order for all chemicals to come into solution.
   h. Transfer working MeHg working stock into designated 250 ml Teflon vial.
   i. For a matrix spike-MS sample, add 50uL of the 1ng/mL MeHg working (stock) standard (blue label) to the sample if working with very low sample concentration in MeHg.
   j. For higher MeHg concentrations presented in samples (0.1-0.8 ng MeHg) do MS and MSD by Adding 100-150 uL of the 1 (ng/ml) MeHg to your sample. Matrix interferences are common in the samples with high content of organics and specifically Iodine.

k. Vials 6 through 32 are 2-LQC (0.05 ng MeHg), 1-2 MDL (0.002 ng MeHg)-check.

Note: **The laboratory MDL is 0.002(ng) MeHg and we are required to validate MDL check within each analytical batch. It is recommended to each analyst to run one batch to validate MDL. The MDL's are water spikes treated as samples and analyzed accordingly.**

l. Rest of the vials content would be 50-ml of your sample + 400uL APDC- solution.

D. Maintenance

1. CHECK THE WATER AND ICE LEVELS REGULARLY (every half hour or so).
2. CHECK THE GAS PRESSURE. It can drop rapidly. Flow meter readings need to have constant pressure per event.
3. The distillation should take about 5.5-6 hours. If you keep the water level and ice where they need to be, the process should be faster. Do NOT turn the hotplates up above 5 once proper temperature is attained.
4. **Temperature should be maintained in the range 125 +/- 3 ^{0}C. Do not exceed this temperature as Halogens start to co-distill and interfere with validation of the entire event.**

E. Finishing the distillation

1. When there is approximately 75 ml of distillate in receiving vial. Remove vial and cap it. Do not turn off the gas.
2. Remove the receiving vial, dry it off, and weigh it. Record the weight on the data form (column 6).
3. Place a lid on the receiving vial. Label vial (sample1-32).
4. Repeat this process until all the vials are done. Be sure not to turn off the main gas valve when all the vials are done.
5. Turn off hotplate.
6. The Distillate (Receiving vials) must be stored at room temperature in the dark and analyzed within 48 hours or freeze.

F. Cleaning of the distillation set:

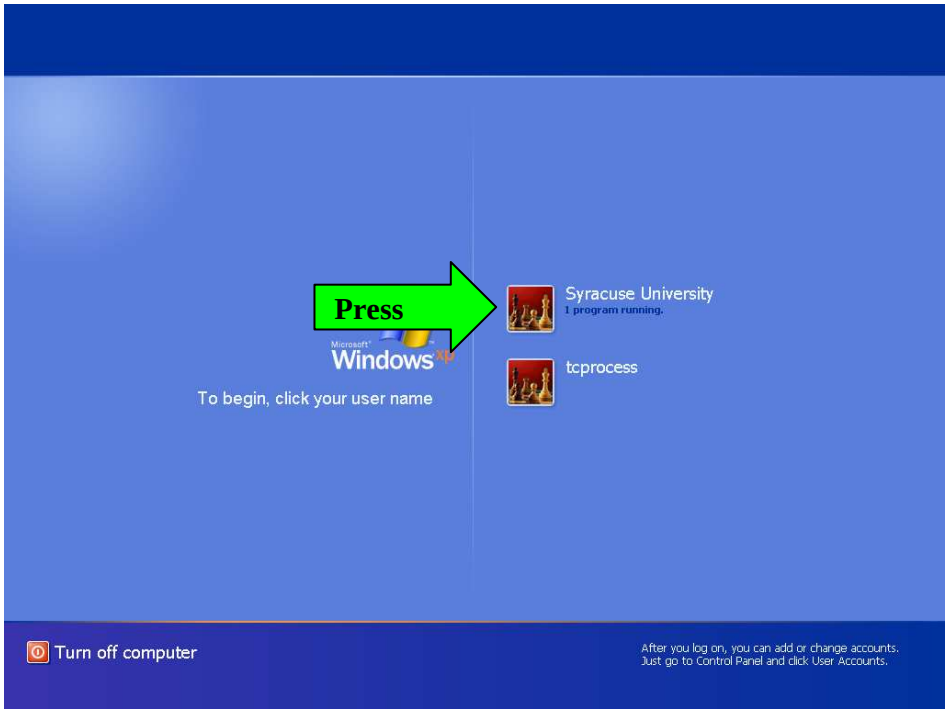
1. **Distillation set must be cleaned right after distillation.**
2. Pour 80-90 ml of the 50% HNO3 into each vial. Assemble entire set same as for distillation.
3. There would be no receiving vial but extended Teflon tubing coming from the vial located in aluminum block down to the water.
4. An Ice bath is replaced with the Milli-Q water instead.
5. Connect the Teflon tube to the flow meter extension and open the valves.
6. Flow meter Pressure reads 50-60 psi, and on the regulator 20 psi.
7. Make shore that gas purges from each vial down to water.
8. Do purge acid for about 30-40 min.
9. Turn off hotplate.
10. Disconnect Teflon tubing from the gas source to avoid backpressure and acid accumulation in flow meters.
11. Wait until entire set cools down, then pour 50 % HNO_3 back to its designated container (Distillation wash 50% HNO_3.
12. Wash all vials several times with Milli-Q water and place them where particular set belongs
13. Wash all Teflon tubings with Milli-Q and assure that all acid is washed out the tubes.
14. Place water from the beans to the waste container, since we purge acid.

Attachment 3
Purging and Analysis

1. Log into computer
2. Turn on Mercury Detector
3. Turn on transformer (~10) until wires are red on the paralytic unit. Generally takes ~1 hour to stabilize.
4. Turn on Gas
5. Retrieve necessary reagents: Acetate Buffer and 1ng/mL MeHg working standard.
6. Place reagents under hood. **Do not expose ethylating agent to air for extended amount of time.**
7. Dump the 10% HCl from bubblers into bubble wash bottle if they have been stored for a long time. If they have been stored for a short amount of time, they should be filled with DI water.
8. Rinse bubblers thoroughly with DI water. Place traps on bubblers
9. Set up 2 Primers with 800uL of working standard.
10. Set up standard curve of 2 blanks and necessary levels, i.e. 200uL, 400uL, 600uL and an 800uL standard in 50mL of DI water. Swirl. (**Spike standard into water, not above.)** Run curve high to low.
11. Add 300uL of acetate buffer, swirl
12. Add 150uL of ethylating agent, put top on, swirl.
13. Allow to react for 17 minutes, swirling 3-4 times during process.
14. Place bubblers on 4-way valve. You want the flow into the ~500mL/min and out of the traps ~150mL/min. Clean the end of the trap with a cotton swab.
15. After the 17 minutes, connect bubblers, and bubble for 17 minutes.
16. After the samples are done bubbling, turn gas off, wait for samples to completely stop bubbling, and disconnect bubblers, place traps on 4 –way valve and turn gas back on for 5 minutes to dry samples.
17. To clean bubblers, refer to Bubbler Washing Procedure (Attachment 4)
18. Place trap on the instrument, noting the direction that the trap was on the bubbler. The end that was attached to the bubbler is placed on top on the auto sampler.
19. Follow run sequence:

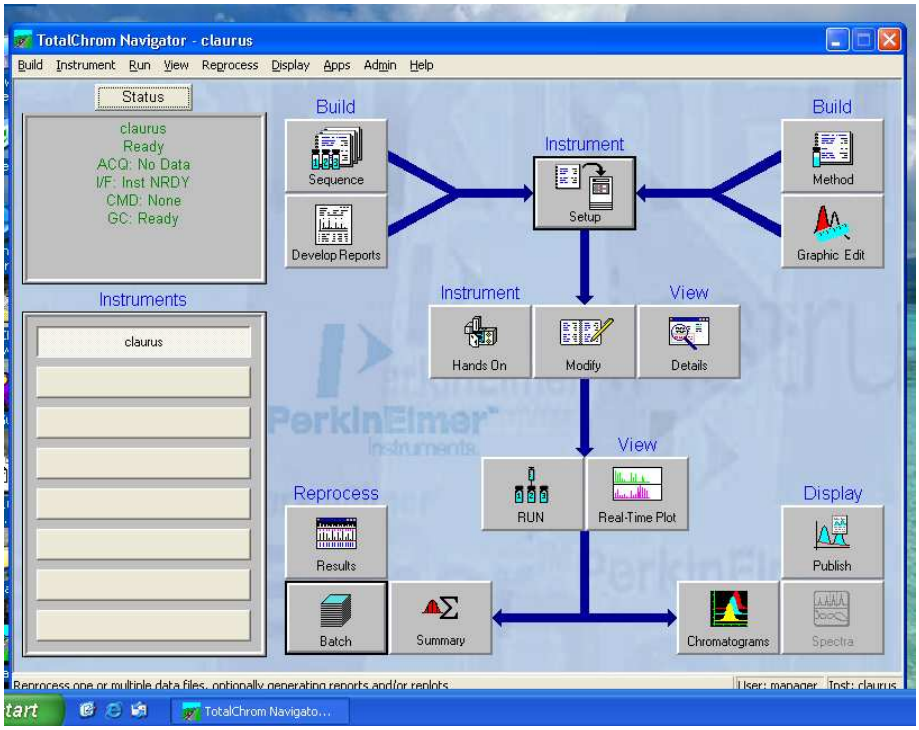
RUN SEQUENCE
Two system blanks
Three primes
A minimum of five, non-zero calibration standards
Ethylation blank
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
On-going precision and recovery (OPR)
Continuing Calibration Blank (CCB)
Method Detection Limit (MDL) Check Undistilled
Quality control sample/Laboratory Control Sample (LCS)
Method Detection Limit (MDL)
Method blank (MBLK) distillation
Field Blank
Ten samples
Matrix spike
Matrix spike duplicate
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
Ten samples
Matrix spike
Matrix spike duplicate
Lab Duplicate
Lab Triplicate (QAPP dependent)
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
On-going precision and recovery (OPR)
Continuing Calibration Blank (CCB)

Attachment 3
Purging and analysis

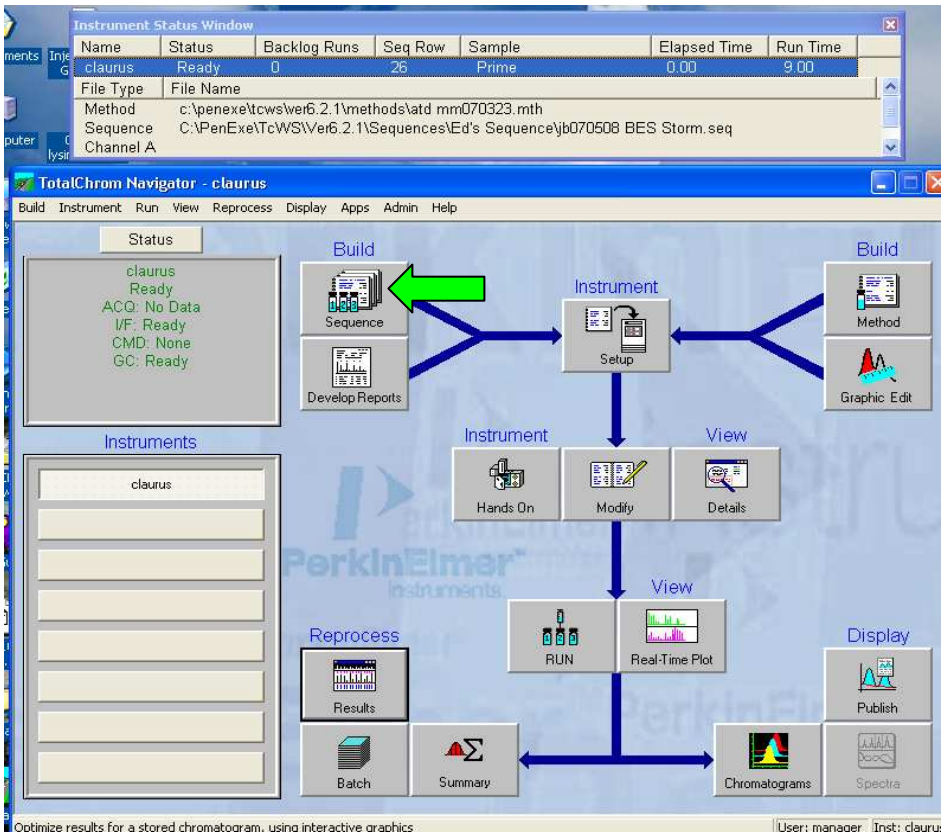


Opening screen when computer is off or has been idle for a while.
Press Syracuse University button to open up desktop with TC Navigator

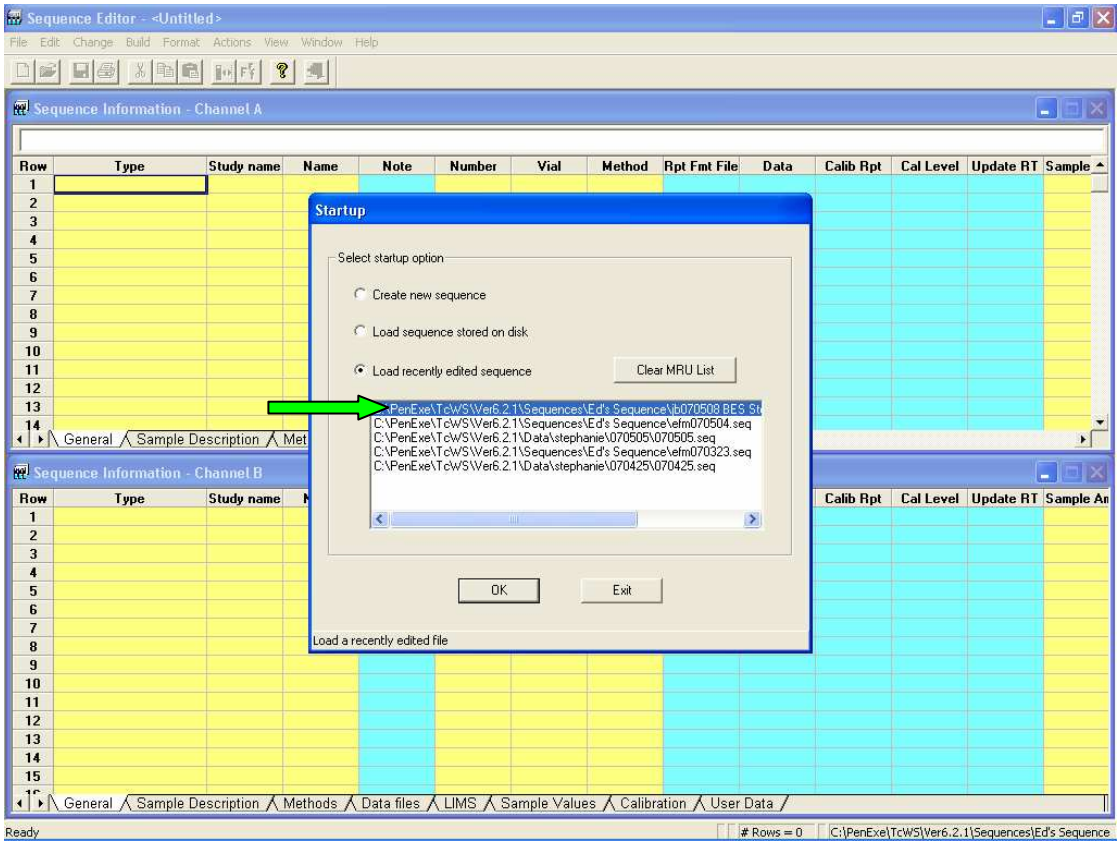
Desktop screen



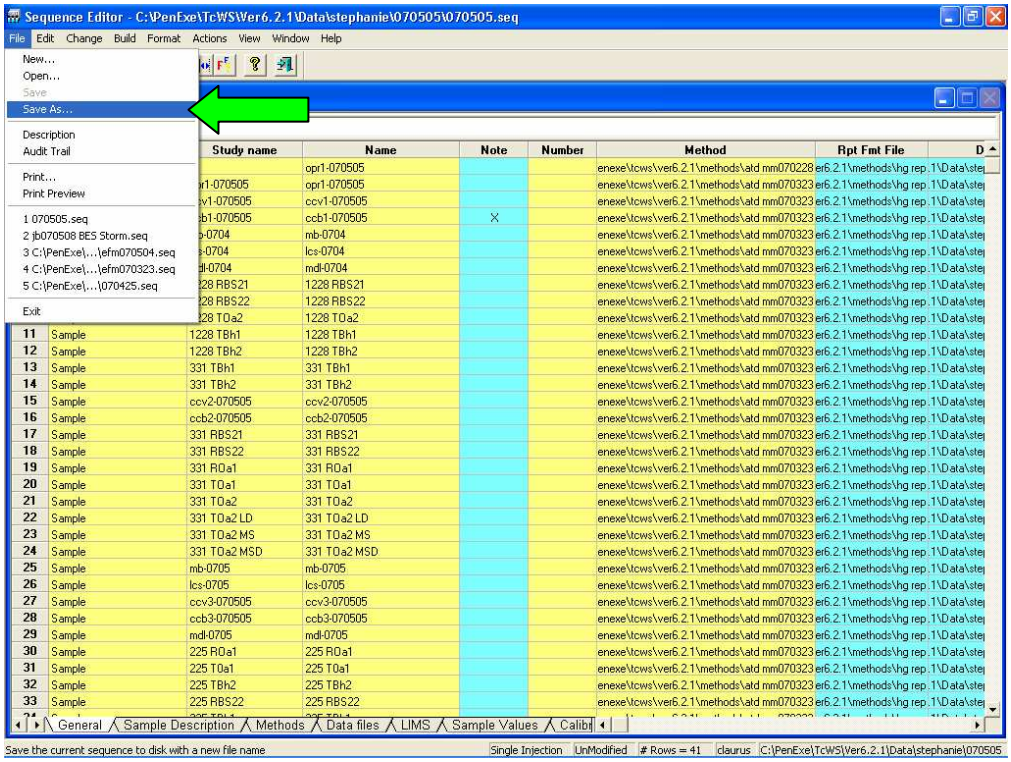
Opening screen for TotalChrom navigator

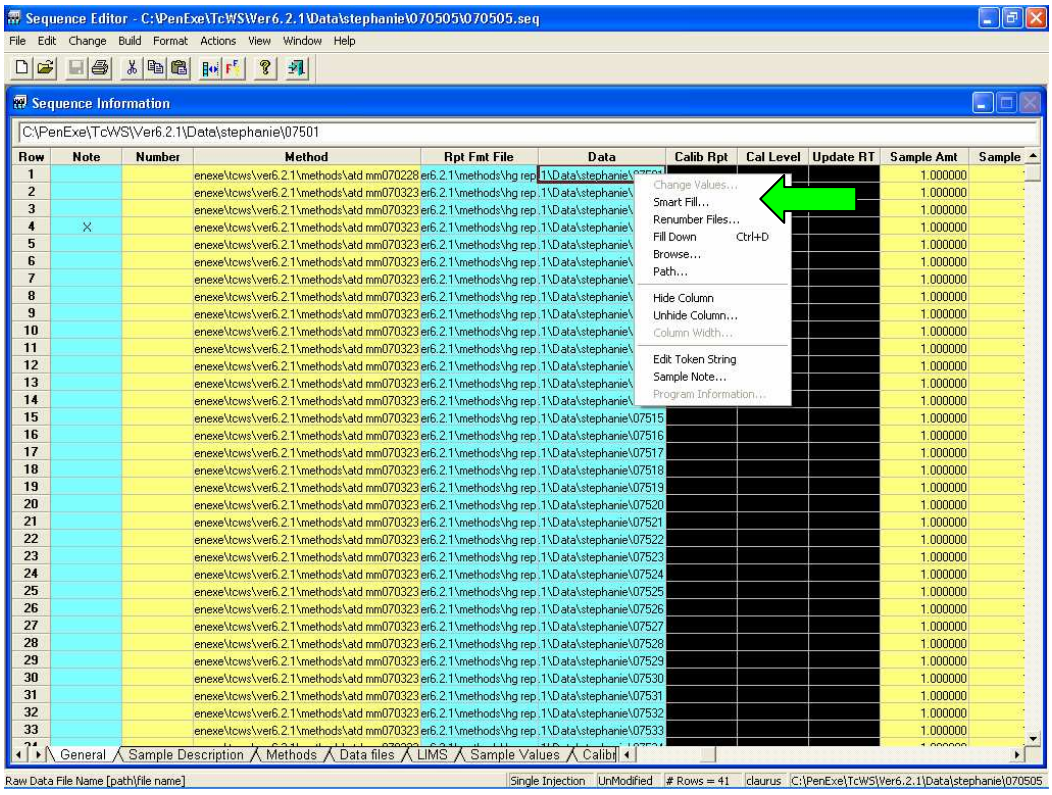


Build a sequence by clicking on Build Sequence Button. Your first time, talk to Mario or Ed to create a folder.

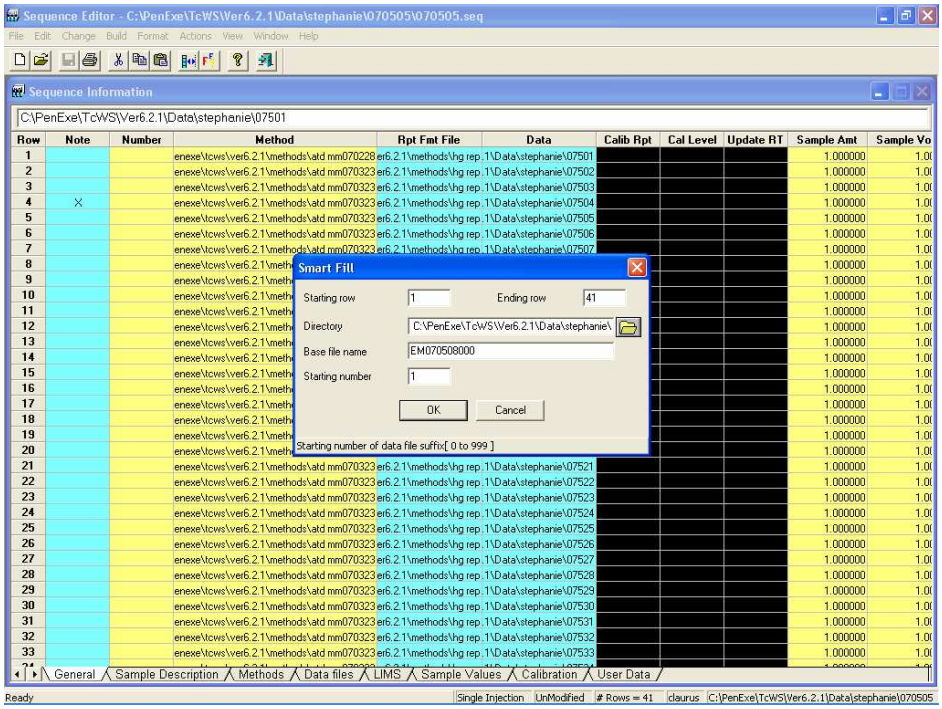


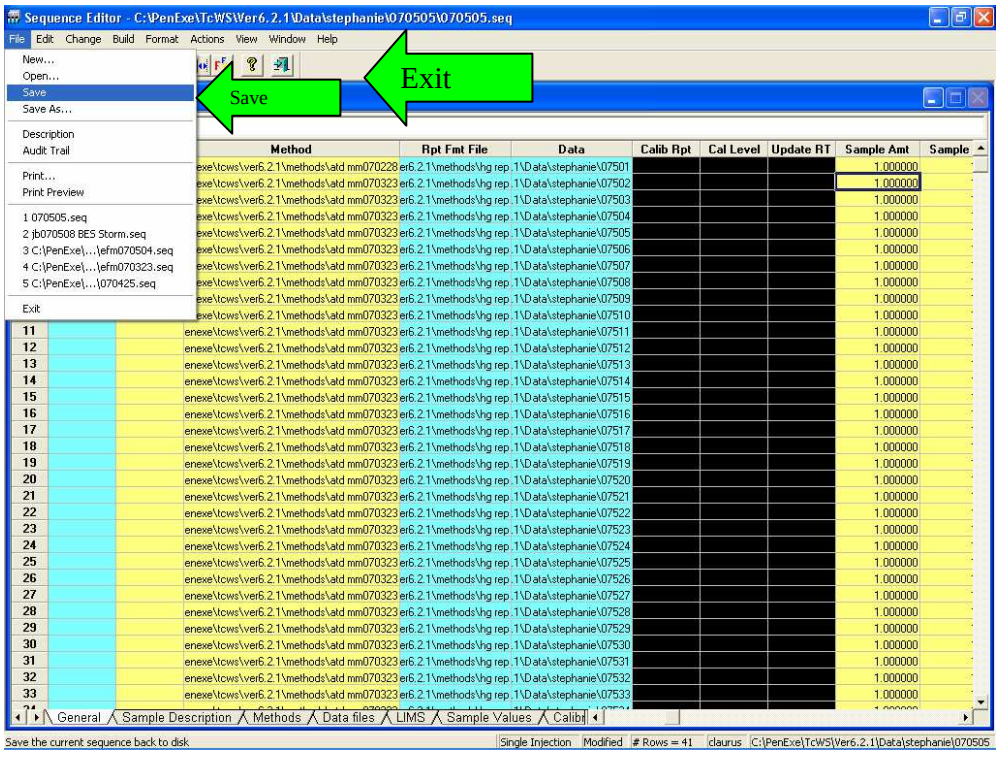
Open a previously used sequence and “save as” in your own in the Sequence Folder, using initials, year, month, and day, i.e. EFM070515.



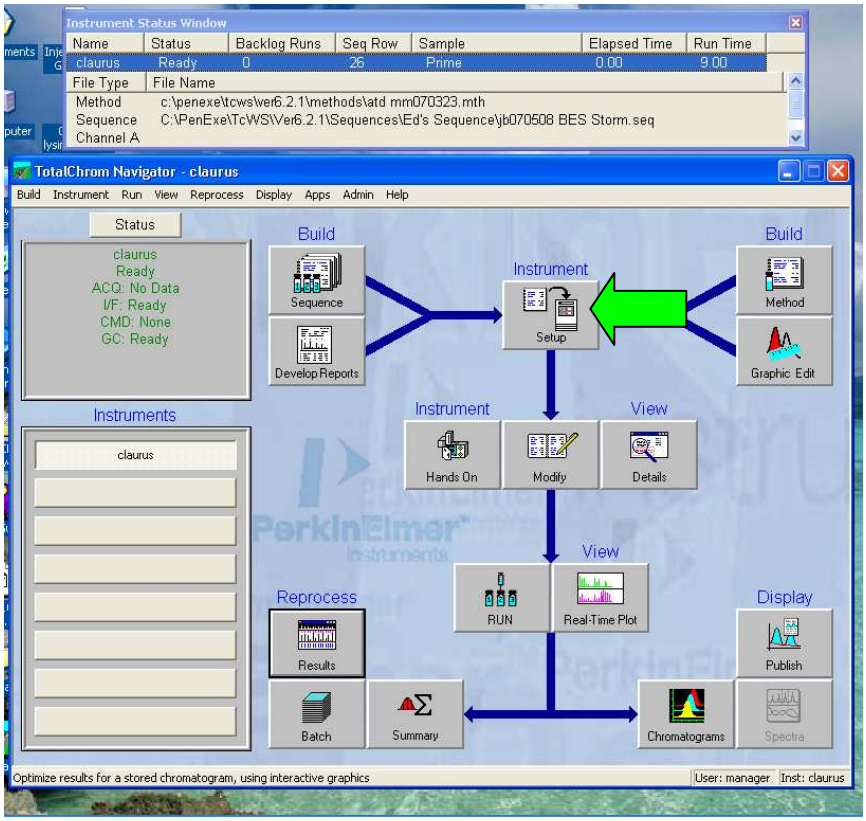


Under the Data Column, tell the software where you want the file to go and what it will be called using Smart Fill. Name the sample with your initials then the date, i.e. EM0705080001. Make sure to change you ending row in the dialogue box.

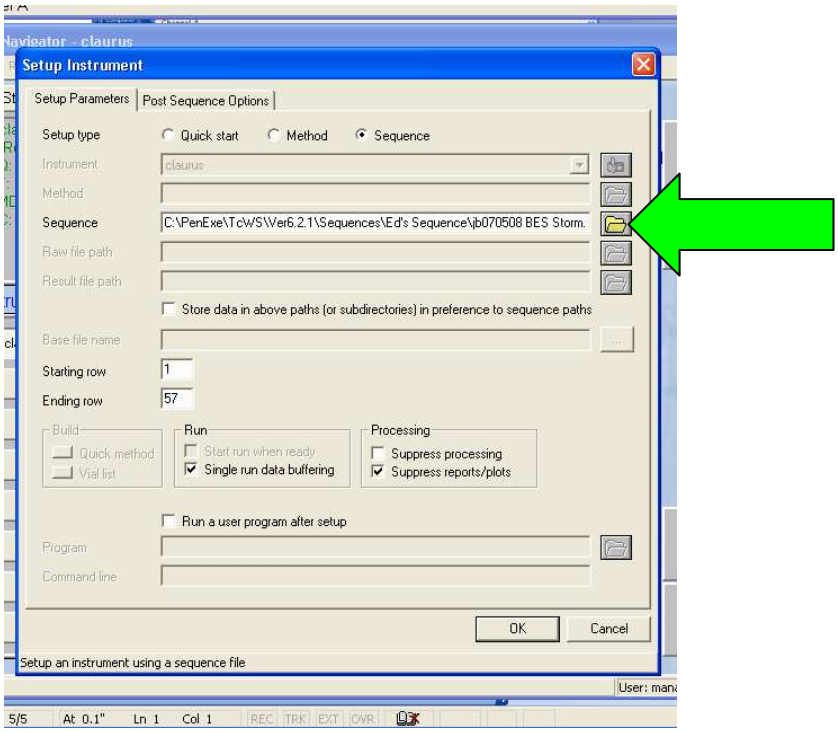




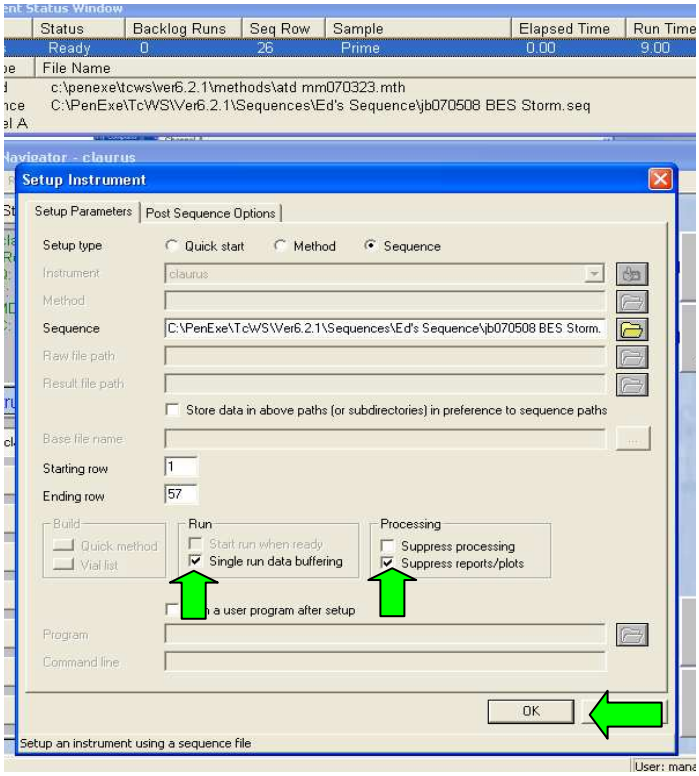
Save Sequence and Exit to return to opening screen



Press set up button



Open Sequence Folder where you stored your sequence and select.



Make sure ***Single Run data*** buffering and ***Suppress reports/plots*** are checked and hit OK

- Place traps on ATD 400 auto sampler
- Make sure that the marked ring on the trap or the S for Supelco tubes are on the upright position
- On the *Run* tab
    - *Tubes* area is for the starting and stopping position of the traps
    - *Method* should be Mercury 2
- After traps are loaded, and sequence is set up, check to see that the software is *Ready* and the GC is *Ready*, then press *Start*

Attachment 4
Bubbler washing procedure

- ❑ Rinse bubbler with DI water 3 times (do not allow them to dry)
- ❑ Rinse with 10% HCl by filling the purge tube and rinsing the outlet tube
- ❑ Allow it to empty
- ❑ Rinse with DI water
- ❑ Rinse with Methanol by filling the purge tube and rinsing the outlet tube
- ❑ Allow it to empty
- ❑ Rinse with DI water
- ❑ Fill bubbler with DI water allowing the purge tube to fill
- ❑ Empty the bubbler and allow the tube to drip dry.
- ❑ Fill with DI water and store
- ❑ Check for condensation on the top of the bubbler, if condensation present rinse with methanol
- ❑ Rinse with DI water before us

Attachment 5
Trap packing and conditioning

1) **Tenax Traps: The tenax traps are repacked by the analyst**
2) Insert ~0.1 gr of glass wool on end of the trap
3) Place the glass tube on the analytical balance
4) Tare the weight and use 0.15 +/- 0.02 grams of the Tenax
5) Place the material in the tube under vacuum
6) Complete repacking by closing the column with glass wool
7) Use glass wool and place it to both end of the column
8) Condition the traps by running them on the Autodesorption unit three times on each program: tenax250 (conditioning at 250 ^{0}C) and tenax 300 (conditioning at 300 ^{0}C)

Attachment 6
Glossary

The definitions and purposes below are specific to this Method, but have been conformed to common usage as much as possible.

1. Ambient Water—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

2. Analytical Batch—A batch of up to 20 samples that are oxidized with the same batch of reagents and analyzed during the same 12-hour shift. Each analytical batch must also include at least three bubbler blanks, an OPR, and a QCS. In addition, MS/MSD samples must be prepared at a frequency of 10% per analytical batch (one MS/MSD for every 10 samples).

3. Bottle Blank—The bottle blank is used to demonstrate that the bottle is free from contamination prior to use. Reagent water known to be free of mercury at the MDL of this Method is added to a bottle, acidified to pH <2 with BrCl or HCl, and allowed to stand for a minimum of 24 hours. The time that the bottle is allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water is analyzed.

4. Reagent water that has been processed through the sampling device at a laboratory or other equipment cleaning facility prior to shipment of the sampling equipment to the sampling site. The equipment blank is used to demonstrate that the sampling equipment is free from contamination prior to use. Where appropriate, the "clean hands/dirty hands" technique used during field sampling should be followed.

5. Equipment Blank—Reagent water that has been processed through the sampling device at a laboratory or other equipment cleaning facility prior to shipment of the sampling equipment to the sampling site. The equipment blank is used to demonstrate that the sampling equipment is free from contamination prior to use. Where appropriate, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility.

6. Field Blank—Reagent water that has been transported to the sampling site and exposed to the same equipment and operations as a sample at the sampling site. The field blank is used to demonstrate that the sample has not been contaminated by the sampling and sample transport systems.

7. Intercomparison Study—An exercise in which samples are prepared and split by a reference laboratory, then analyzed by one or more testing laboratories and the reference laboratory. The intercomparison, with a reputable laboratory as the reference laboratory, serves as the best test of the precision and accuracy of the analyses at natural environmental levels.

8. Matrix Spike (MS) and Matrix Spike Duplicate (MSD)—Aliquots of an environmental sample to which known quantities of the analyte(s) of interest is added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for these background concentrations.

9. May—This action, activity, or procedural step is allowed but not required.

10. May not—This action, activity, or procedural step is prohibited.

11. Method blank— Method blanks are used to determine the concentration of mercury in the analytical system during sample preparation and analysis, and consist of a volume of reagent water that is carried through the entire sample preparation and analysis. Method blanks are prepared by placing reagent water in a sample bottle and analyzing the water using reagents and procedures identical to those used to prepare and analyze the corresponding samples. A minimum of three method blanks is required with each analytical batch.

12. Minimum Level (ML)—The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The ML is calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1, 2, or 5) x 10n, where n is an integer (See Section 3.5).

13. Must—This action, activity, or procedural step is required.

14. Quality Control Sample (QCS)/Laboratory Control Sample (LCS)-sample containing Hg at known concentrations. The QCS/LCS 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 as an independent check of instrument calibration.

15. Reagent blank—Reagent blanks are used to determine the concentration of mercury in the reagents (BrCl, NH2OH@HCl, and SnCl2) that are used to prepare and analyze the samples. In this Method, reagent blanks are required when each new batch of reagents is prepared.

16. Reagent Water—Water demonstrated to be free of mercury at the MDL of this Method. It is prepared from 18 MS ultrapure deionized water starting from a prepurified source. Reagent water is used to wash bottles, as trip and field blanks, and in the preparation of standards and reagents.

17. Regulatory Compliance Limit—It is a limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory authority.

18. Shall—This action, activity, or procedure is required.

19. Should—This action, activity, or procedure is suggested, but not required.

20. Stock Solution— A solution containing an analyte that is prepared from a reference material traceable to NIST, or a source that will attest to the purity and authenticity of the reference material.

21. System Blank— For this Method, the system blank is specific for the flow-injection system and is used to determine contamination in the analytical system and in the reagents used to prepare the calibration standards. A minimum of three system blanks is required during system calibration.

22. Ultraclean Handling— A series of established procedures designed to ensure that samples are not contaminated during sample collection, storage, or analysis.

Attachment 7: CESE Standard Log

ID #	Date Made/Received	Exp Date	Reagent/ Standard	Weight/ Volume	Final Volume & Solution	Final Concentration	Parent Source	Concentration	Expiration Date	Initials

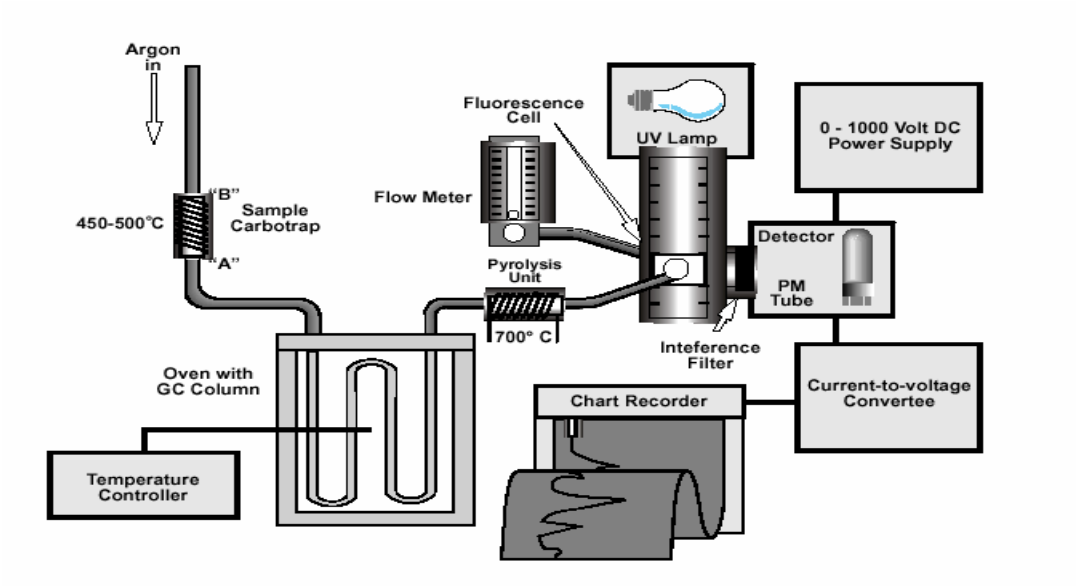


Figure 1. Schematic diagram of the CVAFS Detector with the GC and pyrolytic decomposition column.

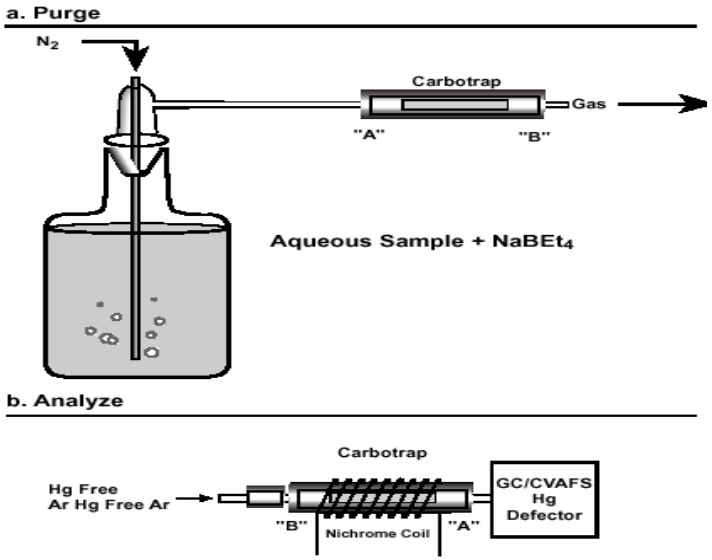


Figure 2. Schematic Diagram of Bubbler Set up (a) and Tenax trap orientation (b).

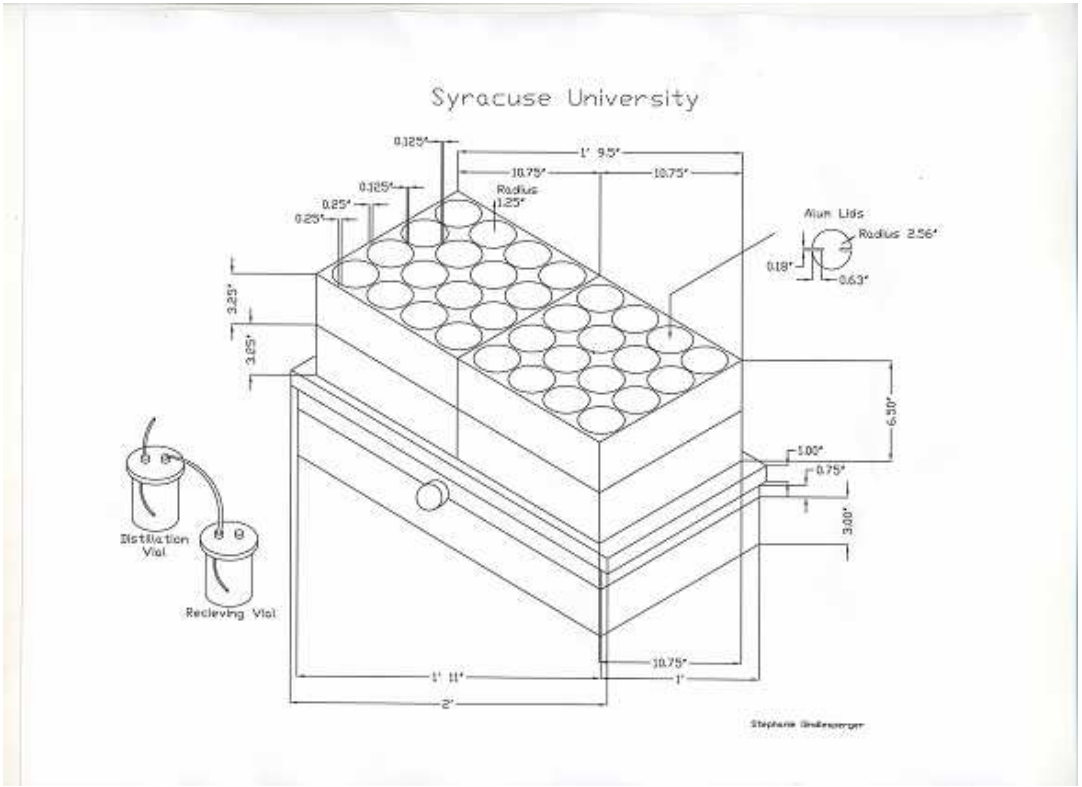


Figure 3 Syracuse University CESE Laboratory Distillation Apparatus

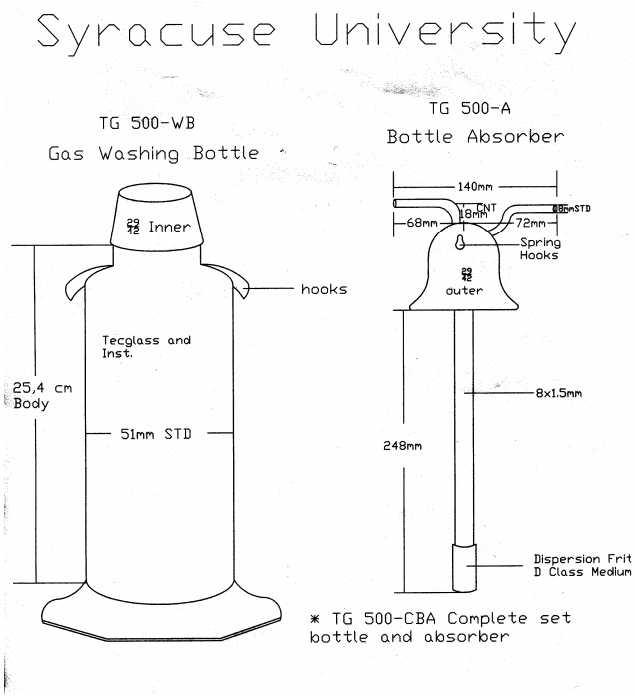


Figure 4. Bubbler from Tecglass (TG-500-WB and TG-500-A)

Center for Environmental Systems and Engineering (CESE)

STANDARD OPERATING PROCEDURE

1. Title: Mercury in solids and Solutions by Milestone Thermal Decomposition Amalgamation and Atomic Absorption Spectrophotometry

AP #-CESE-ENV-7473M

Rev #2-October 12, 2007 Page 1 of 28

Prepared By: Mario Montesdeoca

Approved By: _____ Date: October 12, 2007
Edward Mason-Technical Review

Approved By: _____ Date: October 12, 2007
Mario Montesdeoca-Laboratory Manager

Approved By: _____ Date: October 12, 2007
Charles T Driscoll-Primary Investigator

Effective Date: October 12, 2007

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2. Summary of Test Method

2.1 This Laboratory procedure is derived from US EPA Method 7473.

2.2 Controlled heating in an oxygenated decomposition furnace is used to liberate mercury from solid and aqueous samples in the instrument. The sample is dried and then thermally and chemically decomposed within the decomposition furnace. The decomposition products are carried by flowing oxygen to the catalytic section of the furnace. Here oxidation is completed and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to an amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamator is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance (peak height or peak area) is measured at 253.65 nm as a function of mercury concentration.

2.3 The typical working range for this method is 0.03 - 600 ng. The mercury vapor is first carried through a long path length absorbance cell and then a short path length absorbance cell. (The lengths of the first cell and the second cell are in a ratio of 10:1 or another appropriate ratio.) The same quantity of mercury is measured twice, using two different sensitivities (see Figure 1), resulting in an expansion of the

dynamic range of at least four orders of magnitude.

3. Scope and Application

3.1 This SOP is designated for the determination of mercury (CAS No. 7439-97-6) in solids, aqueous samples, and digested solutions in both the laboratory and field environments. Integration of thermal decomposition sample preparation and atomic absorption detection reduces the total analysis time of most samples to less than five minutes in either the laboratory or field setting. Total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials as well as in aqueous wastes and ground waters can be determined without sample chemical pretreatment using this method, except as noted. Alternatively, this method can be used for the detection of total mercury from total decomposition sample preparation methods, such as Method 3052, or for detection of extracted or leached mercury compounds or species from methods such as the SW-846 3000 series methods.

NOTE: For unique circumstances when mercury could be bound in silicates or other matrices that may not thermally decompose, validation of direct analysis of the solid should be confirmed with total decomposition (such as SW-846, Method 3052) and analysis with this method.

4. Applicable Matrix or Matrices

4.1 This method is applicable to aqueous samples and solid samples such as soils, sediments and bottom deposits

5. Method Detection Limit

5.1 Calculating the MDL is the responsibility of the analyst and it must be determined on initial analysis per specific method. (i.e. If the analyst is using a method for the first time, the analyst needs to calculate the MDL for that specific method.) The MDL will be verified at the beginning of each subsequent analysis using the appropriate MDL check solution. The preferred method for calculating MDLs is found in Appendix B, Part 136, Revision 1.11 of the Federal Register, Volume 49, No. 209, October 1984.

5.2 The method detection limit (MDL) for this method is 0.031 ng total mercury. The MDL concentration depends on the amount of sample used on the analysis.

5.3 The instrument is capable to analyze 0.001-1.0 gram of sample and the concentration of the MDL fluctuates depending on the weight of the sample. Also the dosing capability of the instrument gives additional flexibility on the weight of the amount used for analysis. The following are typical used amounts of sample:

5.3.1 Plants and leaves: 25 mg. Calculated concentration of MDL is 1.2 ng/g.
5.3.2 Litter: 25 mg. Calculated concentration of MDL is 1.2 ng/g.
5.3.3 Fish: 100 mg. Calculated concentration of MDL is 0.3 ng/g.
5.3.4 Zooplankton: 10 mg. Calculated concentration of MDL is 3 ng/g.
5.3.5 Soil: 100 mg. Calculated concentration of MDL is 0.3 ng/g.
5.3.6 Organic solids: 25 mg. Calculated concentration of MDL is 1.2 ng/g.

5.4 If a lower MDL is desired, the amount of sample used is increased to enhance the sensitivity of the method. However, if the sample is limited, the sample is digested and analyzed by AP# CESE-ENV-

1631.

6. Definitions

6.1 Quality Assurance Project Plan (QAPP): QAPP is a plan to be followed to maintain a level of confidence of accuracy in a specify project.

6.2 Batch: A batch consists of 20 samples that are treated and analyzed together. A batch contains a Preparatory Blank (PB), a Laboratory Control Sample (LCS), a Matrix Spike (MS), and a Matrix Spike Duplicate (MSD).

6.3 Statistical definitions:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Mean - The average of n values is calculated by taking the sum of n values and dividing by n.

Sample Standard Deviation - A parameter used to measure the dispersion of a data set. It is calculated by the following:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (\bar{x} - x_i)^2}{n-1}}$$

Relative standard deviation (RSD) or coefficient of variation (CV) is the standard deviation divided by the mean and multiplied by 100.

$$CV = \frac{s}{\bar{x}} * 100$$

Relative Percent Difference - The relative percent difference of two numbers is calculated by dividing

$$RPD = \frac{|x_1 - x_2|}{((x_1 + x_2)/2)} * 100$$

the absolute value of their differences by the average of the two numbers.

Percent Recovery - Percent recovery is calculated by dividing the spike sample result by the spike added for or by dividing the spike sample result minus the sample by the spike added.

$$\%R = \frac{SS}{SA} * 100$$

$$\%R = \frac{SS - S}{SA} * 100$$

Where: SS = Spike sample
SA = Spike added
S = Sample

6.4 Thermal Decomposition: Partial or complete degradation of sample components using convection and conduction heating mechanisms resulting in the release of volatile components such as water, carbon dioxide, organic substances, elements in the form of oxides or complex compounds, and elemental gases.

6.5 Amalgamation: The process by which mercury forms a metal alloy with gold.

6.6 Amalgamator: A system composed of gold particles at a high surface area to volume ratio for the purpose of amalgamating mercury vapor.

6.7 Primary Calibration: A complete calibration of the instrument's working range. This calibration is performed initially and when any significant instrumental parameters are changed. For example, in this method a primary calibration should be performed after the decomposition tube, amalgamator, or oxygen tank is replaced.

6.8 Daily Calibration: A calibration performed with minimal standards to ensure that the primary calibration is valid. For example, when two standards within the range of interest are analyzed and agree within 10% of their true value the primary calibration is assumed to be valid.

6.9 Memory Effects: Mercury vapor may remain in the decomposition tube, amalgamator, or absorbance cells and be released in a subsequent analysis resulting in a positive bias. For example, this may result when a low concentration sample is analyzed after a sample of high mercury content.

6.10 Sample Boat: The non-amalgamating thermally stable vessel used for containment and transport of the solid or liquid sample for thermal decomposition.

7. Interferences

7.1 In areas where mercury contamination is an existing problem, the background signal may be significantly increased.

7.2 Memory effects between analyses may be encountered when analyzing a sample of high mercury concentration (≥400 ng) prior to analyzing one of low concentration (≤ 25 ng). Typically, to minimize memory effects, analyze the samples in batches of low and high concentrations, always analyzing those of low concentration first. If this batching process cannot be accomplished, a blank analysis with an

extended decomposition time may be required following the analysis of a highly concentrated sample to limit memory effects.

7.3 Co-absorbing gases, such as free chlorine and certain organics (as indicated in Methods SW -846), should not interfere due to the release of decomposition products by the decomposition furnace, removal of some decomposition products by the decomposition catalyst, and the selective entrapment of mercury vapor on the amalgamator.

8. Safety

8.1 Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of concentrated mercury reagents. Concentrated mercury reagents should only be handled by analysts knowledgeable of their risks and of safe handling procedures.

8.2 All analysts will attend the "Chemical Hygiene Plan" training provided by the Syracuse University Environmental Health Office (EHO).

8.3 The analyst shall practice standard laboratory safety procedures as specified in the Chemical Hygiene Plan prepared by the EHO.

8.4 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

9. Equipment and Supplies

9.1 DMA 80 automatic mercury analyzer (Milestone), or other instruments based on these principles may also be used.

9.2 Sample boat: A metal or metal alloy sample boat is used with this method. An example of an appropriate boat would be one made of nickel with a liquid capacity of 0.5.

9.3 The working scheme of the mercury analysis system is illustrated in Figure 2. The sample introduction device consists of a motorized support with a metal or metal alloy sample boat that is appropriate for solids and liquids. An example of an appropriate boat would be made of nickel with a liquid capacity of 0.5 - 1.0 mL. Once the sample is either manually or automatically dispensed into the sample boat, the boat is mechanically introduced automatically into a quartz decomposition tube. The decomposition tube is heated by two independently programmable ovens, the decomposition and catalyst furnaces, each furnace is capable of maintaining a temperature of at least 750°C. The sample is dried and thermally decomposed in an oxygen environment, releasing mercury vapor. The mercury vapor is transported by oxygen over the amalgamator that traps the mercury. Once the sample is completely decomposed the trapped mercury is desorbed rapidly by heating the amalgamator with the mercury release furnace. The mercury vapor passes through two absorbance cuvette, in series, that are separated by a collection flask outside the optical axis. The flow path through the spectrometer and cuvettes is maintained at approximately 120°C, by a heating unit, to prevent condensation and minimize carry-over effects. A mercury vapor lamp is used as the light source. The detector is connected to a computer for data acquisition and analysis.

9.4 The DMA 80 direct mercury analyzer (Milestone) is the instrument used for the scheme outlined above.

It has been tested for use with this method. Other instruments based on these principles may also be appropriate.

9.5 This method is not limited to mercury vapor generation by thermal decomposition. Alternatively, other mercury vapor introduction systems, such as mercury cold vapor generation, may be appropriate. Alternative sample introduction apparatus may be applied after validation with data similar to those in Tables 1 and 2.

9.6 This method is not limited to analyzing total mercury content. This detection scheme can be used for analysis of individual species of mercury that have been separated by an appropriate method or instrument system.

10. Reagents and Standards

10.1 Reagent water: Reagent water will be interference free. All references to water in this method refer to reagent water (Milli-Q water) unless otherwise specified.

10.2 High purity oxygen gas: High purity oxygen should be interference and mercury free. If the oxygen is possibly contaminated with mercury vapor, a gold mesh filter should be inserted between the gas cylinder and the mercury analysis instrument to prevent any mercury from entering the instrument.

10.3 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg. Stock solutions may also be purchased. Verify the quality of the standard by checking it against a second source standard (Sec. 9.2).

10.4 Mercury working standards: Make successive dilutions of the stock mercury solution to obtain standards containing 100 ppm and 10 ppm. For calibration of the high range, standards of 0, 1, 2, 3, 4, 5, and 6 ppm are recommended. These are prepared by dilution of the 100 ppm standard. For calibration of the low range, standards of 0.00, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 ppm are recommended. These are prepared by dilution of the 10 ppm standard. A blank calibration solution is also used for a zero calibration. Acidity of the working standards should be maintained at least 0.15% nitric acid, as also recommended in Methods 7470 and 7471.

10.5 Concentrated nitric acid

NOTE: The concentrations listed above are only recommended concentrations. The concentration of the working standards may need adjustment according to specific instrumental working ranges and/or manufacturers' recommendations.

NOTE: The stability of the mercury standards is limited to 24 - 48 hours. Fresh mercury standards must be prepared daily.

10.6 Standard reference material:

10.6.1 In place of aqueous mercury standards, solid reference material with a certified value for mercury may by used for calibration.

11. Sample collection, preservation and storage

11.1 All samples should be collected using a sampling plan.

11.2 All sample containers must be prewashed with detergents, acids, and reagent water. Glass, plastic and PTFE containers are suitable in most cases. Polymers are not suitable for samples containing metallic mercury.

11.3 Metallic mercury, some inorganic mercury compounds, and many organic mercury compounds are volatile and unstable. It is advantageous to analyze the samples as soon as possible to determine the total mercury in the sample but in no case exceed a 28-days holding time . Non-aqueous samples shall be analyzed as soon as possible. If solid samples are not analyzed immediately, refrigeration is necessary.

11.4 For longer preservation, the samples are frozen and freeze dried.

12. Quality Control and Documentation

12.1 Quality Control

12.1.1 All quality control data should be maintained and available for easy reference or inspection.

12.1.2 If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a mid-range standard or reference standard after every 10 samples. This sample value must be within 20% of the true value, or the previous 10 samples must be reanalyzed.

12.1.3 Matrix Spike/Matrix Spike Duplicates (MS/MSDs): At the laboratory's discretion, a separate spike sample and a separate duplicate sample may be analyzed in lieu of the MS/MSD. For each batch of samples processed, at least one MS/MSD sample must be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. Refer to the definitions of bias and precision, in Chapter One, for the proper data reduction protocols. MS/MSD samples should be spiked at the same level as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ±20% of the spiked value for precision and # 20 relative percent difference (RPD). After the determination of historical data, 20% must still be the limit of maximum deviation for both percent recovery and relative percent difference to express acceptability. Refer to Chapter One of this manual for guidance.

12.1.4 For each batch of samples processed, at least one laboratory control samples must be carried throughout the entire sample preparation and analytical process as described in Chapter One. The laboratory control samples should be spiked with each analyte of interest

at the project-specific action level or when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value. After the determination of historical data, ±20% must still be the limit of maximum deviation to express acceptability. If the laboratory control sample cannot be considered acceptable, the laboratory control sample should be re-run once and if still unacceptable then all samples after the last acceptable laboratory control sample must be reprepped and reanalyzed.

12.1.4.1 The method of standard additions can be used to verify linearity or if matrix interference is suspected. Refer to SW-846 for standard addition procedures.

13. **Calibration and standardization**

13.1 Primary calibration: 100 µL of each working standard is dosed onto the sample boat. Analytical parameters for drying, decomposition, and wait times as recommended by the manufacturer are chosen for the analysis. Each standard solution is analyzed twice. For the DMA 80, parameters of 60 seconds drying, 210 seconds decomposition, and 60 seconds wait times (abbreviated **60/210/60**) would be chosen for each standard analysis. Typical calibration curves obtained in laboratory conditions are illustrated in Figures 2 and 3. Conduct curve using standards described in Section 10.4 or 10.5.

13.2 Daily calibration:

13.2.1 Analyze at least a high and low concentration standard for each working range analyzed using the analytical parameters as recommended by the manufacturer. The measured values of the standards must be within 10% of their true value for the curve to be considered valid.

13.2.2 An alternative calibration using standard reference materials (SRMs) may be used. In this method, an amount of the reference material is weighed (accurate to ± 0.001 g or better) onto a tared sample boat. The analytical parameters chosen are based on the weight, moisture content, and organic content of the SRM and should be as similar to the matrix of interest as possible. This procedure is repeated with several different weights of the standard reference material containing mercury concentrations in the desired working range.

13.2.3 Construct a calibration curve by plotting the absorbances of the standards versus nanograms of mercury. Determine the peak height or peak area of the sample from the chart and calculate the mercury value from the standard curve.

Note: Do not dry the standard reference material as indicated on the certificate of analysis unless the SRM was prepared and analyzed that way for mercury certification. Drying may result in loss of mercury that is thermally unstable. Drying a separate sample at the time of analysis and correcting for moisture content is appropriate.

14. Procedure (See attachment 1 for quick start-up reference).

14.1 Sample analysis: For solids, a homogenized amount of the sample is weighed (to ± 0.001 g or better) onto a tared sample boat. The sample boat is inserted into the instrument with appropriate clean techniques. The analytical parameters chosen are based on the weight, moisture content, and organic content of the soil. The parameters for the DMA 80 would be: 000/000/00.

14.2 Field analysis: With a stable power supply, this method can be transported to the field for direct sample analysis without acid digestions.

14.3 Duplicates, spiked samples, and check standards should be routinely analyzed as detailed in Section 12.0 of this method. Samples exceeding the calibration range should be diluted and reanalyzed.

15. Data analysis and calculations

Calculate metal concentrations directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

16. Method Performance

16.1 This SOP is based on SW-846, Method 7473 has been validated with solid samples. National Institute of Standards and Technology (NIST) Solid Standard Reference Materials (SRMs) were selected for there homogeneity and availability. The selected SRMs encompass various chemical forms of mercury, including biological forms, geological forms, and contaminated environmental forms. The averages of the analyses were compared to the certified values, and all the average results were within the control limits. See table 1.

17. Pollution Prevention

17.1 All analysts will attend the Chemical Hygiene Plan and Hazardous Waste Management training provided by the EHO.

17.2 All analysts shall remain aware that Syracuse University waste minimization objective is to reduce the generation of both hazardous and non-hazardous waste as much as is practical.

17.3 All analysts will be familiar with the "Hazardous Waste Management" manual.

17.4 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

17.5 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When it is not feasible to reduce wastes at the source, the Agency recommends recycling as the next best option. The acids used in this Method should be reused as practicable by purifying by electrochemical techniques. The only other chemicals used in this Method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the

disposal of excess volumes of expired standards.

17.6 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reductio*n, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872–4477.

18. Data Assessment, Review, and Acceptance Criteria of QC Measures

18.1 Prior to the analyst's accepting of results, all reagent blank, matrix spike, matrix spike duplicate/matrix duplicate, and reference sample data shall be reviewed for compliance according to Table 3.

19. Corrective Actions for Out-of-Control Data

19.1 The analyst performing the analysis shall compare all quality control data to the appropriate control limits in a timely manner. If any excursions are noted, the analysis is halted, and corrective action is implemented. All excursions shall be noted on a Corrective Action Form, which shall be reviewed and signed by a second party (i.e. Senior Graduate Student, Laboratory Technician II, or Primary Investigator).

20. Contingencies for Handling Out-of-Control or Unacceptable Data

20.1 If the corrective action does not correct the excursion the analyst will inform either a Laboratory Technician II, Laboratory Manager, and/or Project Investigator to help the analyst solve the problem.

21. Waste Management

21.1 Guidelines for managing laboratory wastes are addressed in the Syracuse University "Hazardous Waste Management" manual.

21.2 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

22. References

22.1 Boylan, H.M., Walter, P.J., and Kingston, H.M.; "Direct Mercury Analysis: Field and Laboratory Validation for EPA Method 7473".

22.2 Salvato, N. and Pirola, C.; Analysis of Mercury Traces by Means of Solid Sample Atomic Absorption Spectrometry. Mikrochimica Acta. Vol. 123, 63 - 71, 1996.

22.3 Walter, P.J., and Kingston, H.M.; "The Fate of Mercury in Sample Preparation", The Pittsburgh Conference, Atlanta, GA, March 1997, paper #1223.

22.4 Kingston, H.M., Walter, P.J., Chalk, S., Lorentzen E., and Link, D.; "Chapter3: Environmental Microwave Sample Preparation: Fundamentals, Methods, and Applications" in Microwave Enhanced Chemistry; Kingston, H.M. and Haswell, S., Eds; American

Chemical Society, Washington DC, 1997.

22.5 Milestone Scientific, Inc., DMA 80 Operating Manual.

23. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

23.1 Table 1. MDL study.
23.2 Table 2. Initial Precision and Recoveries (IPR) results.
23.3 Table 3. CESE Quality Control Requirements.
23.4 Figure 1. Cells peaks
23.5 Figure 2. Calibration Curve Cell 1
23.6 Figure 3. Calibration Curve Cell 2
23.7 Attachment 1. Quick Start

Table 1
MDL study

MDL study -2007		
ng of std	measured ng	% R
0.1	0.1142	114.2
0.1	0.1067	106.7
0.1	0.0952	95.2
0.1	0.0863	86.3
0.1	0.1114	111.4
0.1	0.1104	110.4
0.1	0.1027	102.7
Std	0.009994	9.994141
Aver	0.103843	103.8429
%RSD	9.624293	
MDL	0.031382	

Table 2
IPR Results

Standard Reference Material	**Direct Analysis (ng/g)**	**Certified Value (ng/g)**
Soil and Sediments		
Coal Fly Ash Nist SRM 1633b	140 ± 5	141 ± 19
502-407 (2709 NIST)	1403 ± 13	1400 ± 80
Water way sediments-Nist SRM 1944	3430 ± 174	3400 ± 500
Montana soil-NIST SRM 2711	6217 ± 273	6250 ± 190
Biomass		
Apple leaves-Nist SRM 1515	45.5 ± 4	44 ± 4
Plankton-BCR reference 414	271 ± 6	276 ± 18
Dogfish liver-dolt 3	3400 ± 116	3370 ± 140
Dogfish muscle-DORM2	4527 ± 60	4640 ± 260

Table 3
CESE Quality Control Requirements

QC Check	Frequency	Acceptance Criteria	Corrective Action*
Initial Calibration	Daily prior to sample analysis / as per method / or as specified in QAPP	5 standards with the RSD $\leq$ 15%, Correlation coefficient >0.995 for linear regression, or >0.990 for quadratic equation, Low Std. Recovery 75% - 125%	1. Reanalyze standards 2. Remake and reanalyze standards
Initial Calibration Verification (ICV)	Immediately after Initial calibration	80 – 120 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration
Initial Calibration Blank (ICB)	After ICV	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. Elongate cuvette cleaning time/change carbon trap
Continuing Calibration Verification (CCV)	After every ten samples and at the end of the run	80 – 120 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3 All samples analyzed after the last passing CCV must be reanalyzed
Continuing Calibration Blank (CCB)	After every CCV	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCB must be reanalyzed 4. Elongate cuvette cleaning time/change carbon trap
Quality Control Sample (QCS)/Laboratory Control Sample (LCS)	Immediately after initial calibration	80– 120 % of expected value	1. Reanalyze 2. Remake and reanalyze LCS 3. If criteria are still not met, repeat initial calibration
Method Blank	Immediately after QCS and every 20 samples	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. Re-test boat
Matrix Spike/Matrix Spike Duplicate sample (MS/MSD)	1 with every batch of 20 samples	Recovery (80-120%) and RPD (<20%) or as specified in QAPP.	1. If Recovery is not within QC limits, and an RPD criterion is met document excursion. 2. If recover y is within QC limit, and RPD criterion is not met, reanalyze.
Duplicate	1 every 20 samples	RPD 20%	1. If < 5x MRL or is non-detect, the MS/MSD will be used for precision. 2. If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.
Triplicate	QAPP dependent	RSD 35%	1. If < 5x MRL or is non-detect, the MS/MSD will be used for precision. 2. If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.
Method Detection Limit (MDL) Minimum Reportable Level (MRL)		0.03 ng 0.075 ng	1. Reanalyze 2. Recalculate calibration 3. If criteria are still not met, repeat initial calibration

*All corrective actions must be documented on the CESE Corrective Action Log.
Note: Not all QC Checks are applicable to the method of concern.

Figure 1 Spectral output
The two individual peaks correspond to the two absorbance cells of different sensitivities. The maximum intensity of the long pathlength cuvette (Cell 1) occurs at ~7 seconds and the maximum intensity of the short pathlength cuvette (Cell 2) occurs at ~20 seconds.

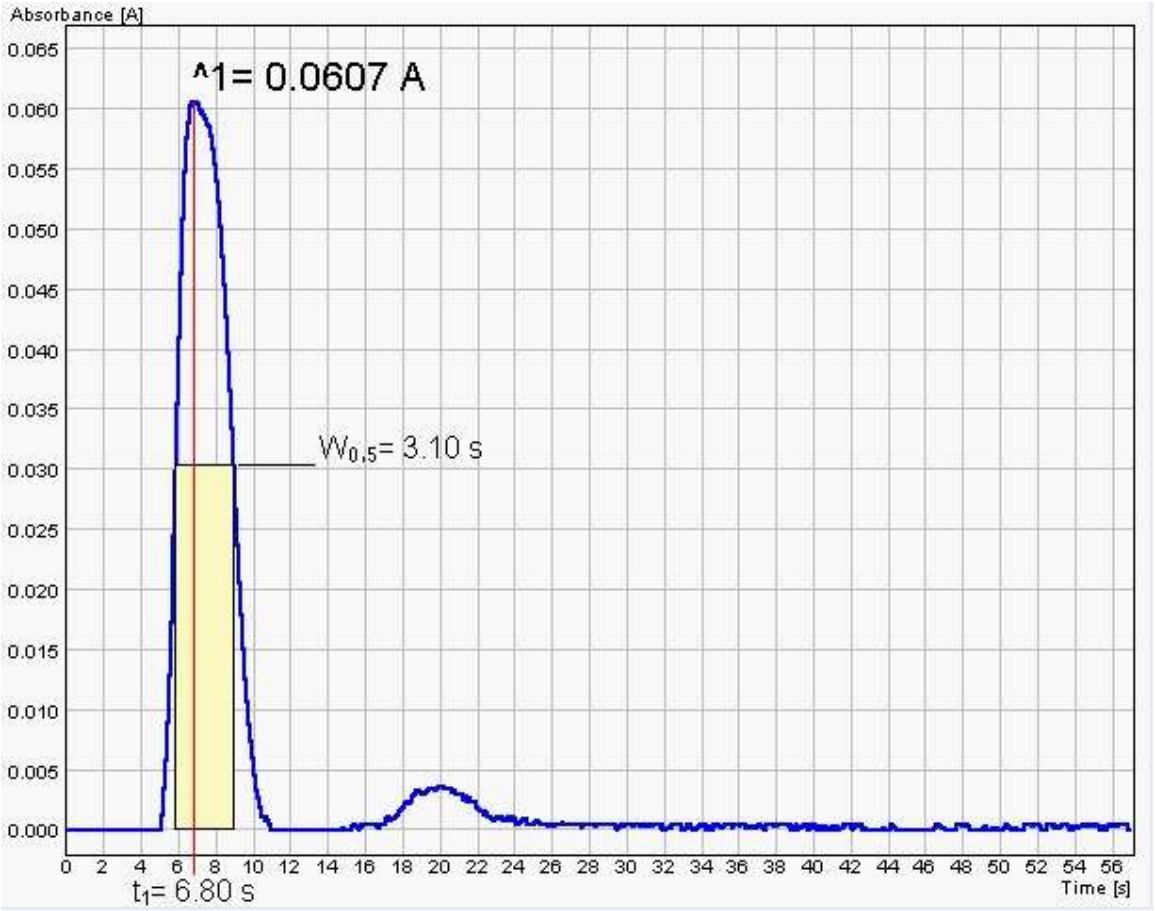


Figure 2. Calibration Cell 1

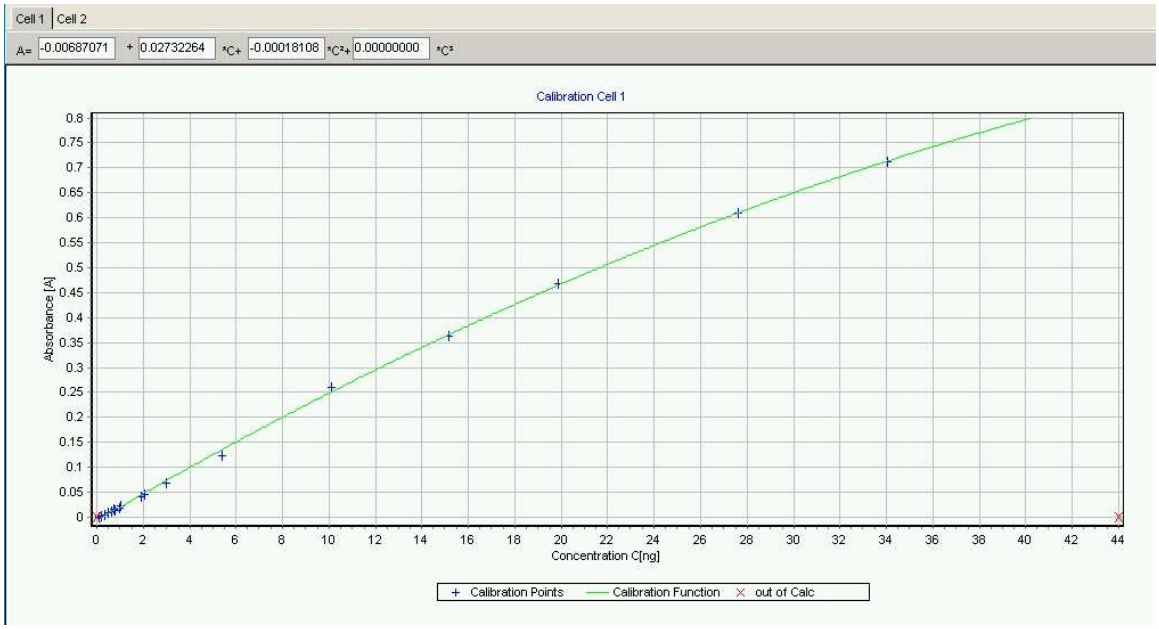
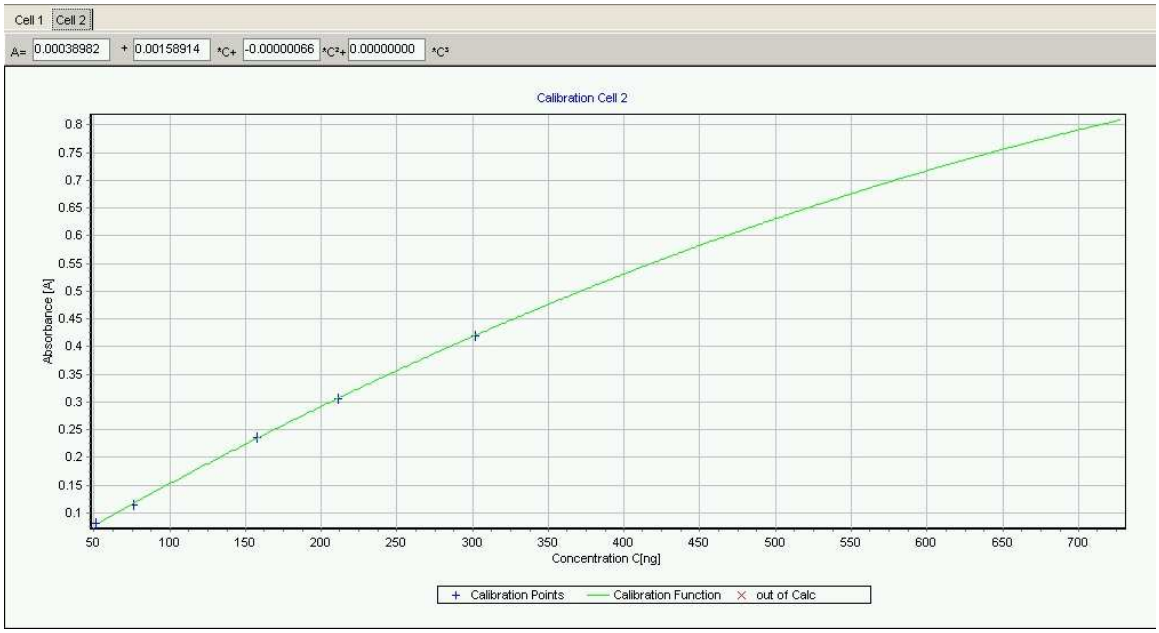


Figure 3. Calibration Cell 2



Attachment 1

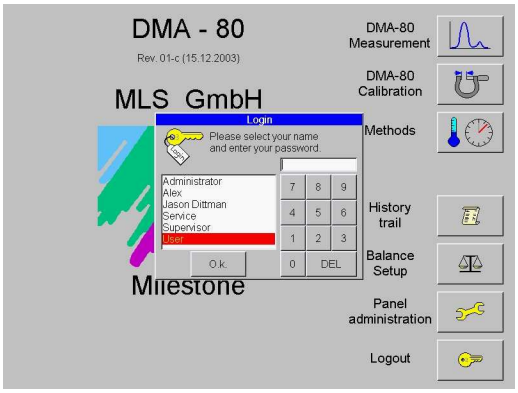
Quick Start up reference:

Start:

Start up instrument and allow half hour to stabilize. In order to start with clean sample vessels, place sample vessels in the oven at 550 °C for half hour followed by cooling in desiccator.

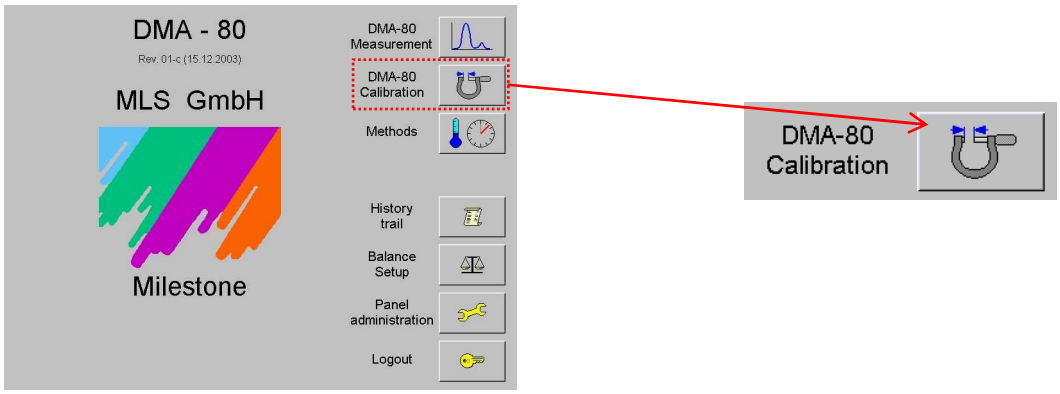
1. Sample log-in:

a. Open up the oxygen gas tank (maintain pressure at approximately 60 psi or 200 ml/min).
b. Using the On/Off button, power up the DMA 80 console.
c. The "Login" dialog box will appear, once the controller display lights up.
d. In the "Login" dialog box, select "User", "Administrator", or the appropriate user name.
e. Type in the Password using the displayed "touch" keypad
f. "Touch" or "Left-click" on the OK button.

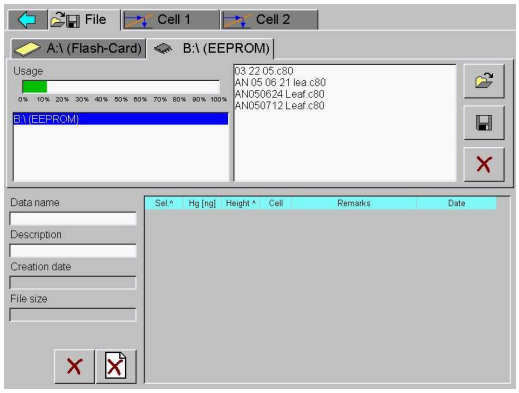


2. Calibration:

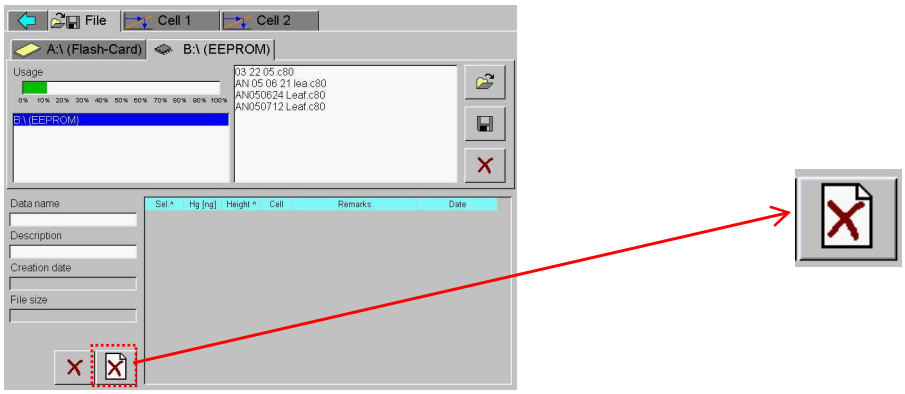
2.1 Select the "DMA-80 Calibration" Icon.



2.2 Under B:\ (EEPROM), select any calibration file from the directory tree in the right hand window.

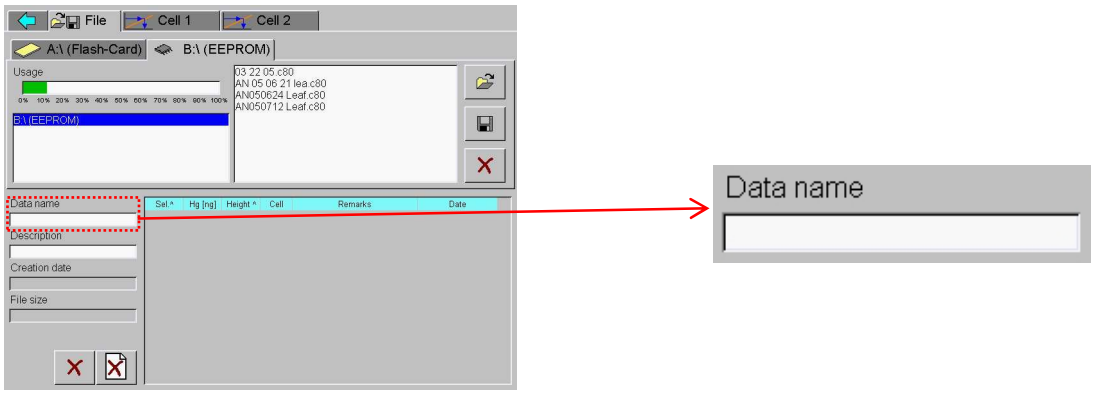


2.3 Press the icon shown below to clear all points.

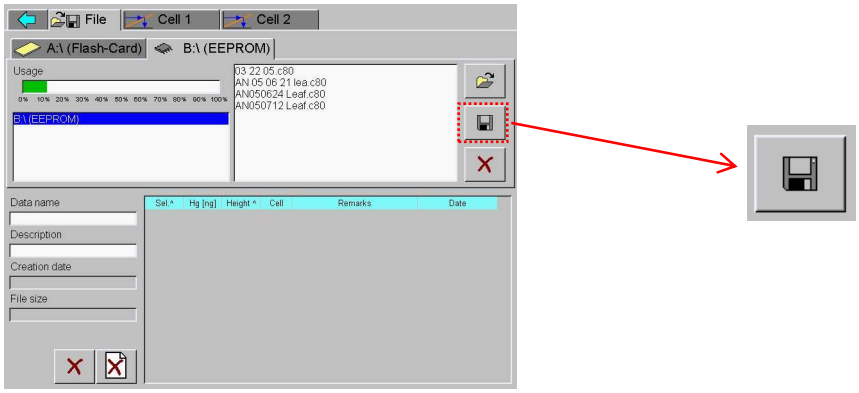


2.4 When asked *"Do you really want to delete all calibration points?"*, press "Yes".

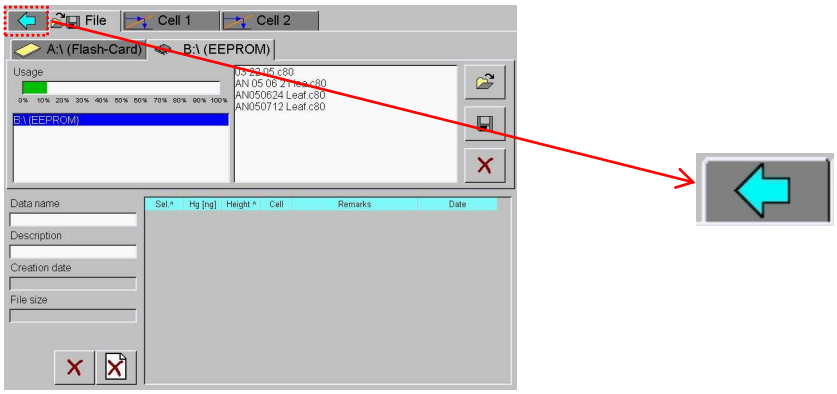
2.5 Under "Data Name", type in the name of the new calibration curve.



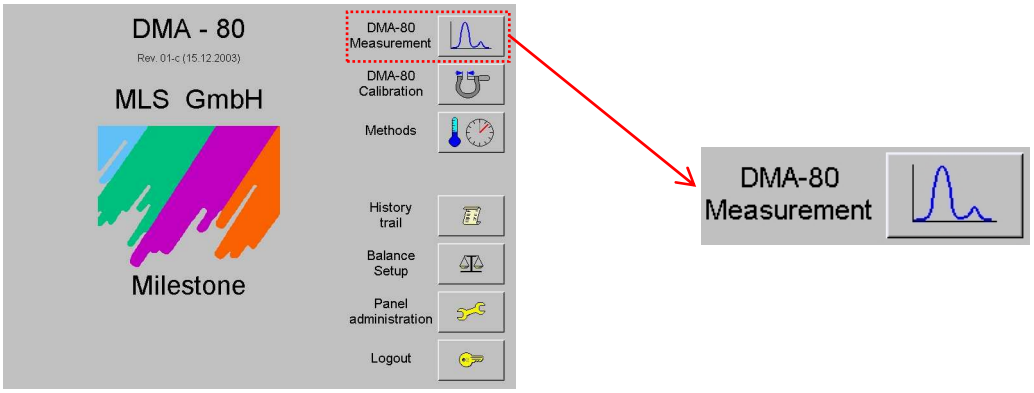
2.6 Press the save button.



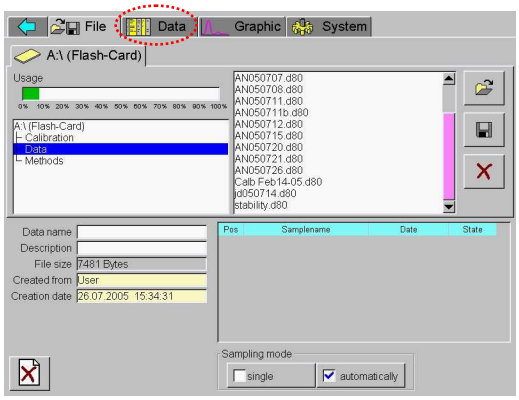
2.7 Go back to the main menu by pressing the back button



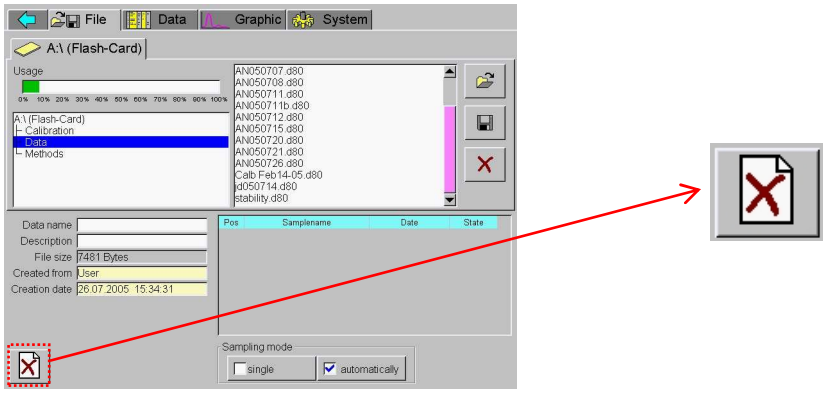
2.8 Press the “DMA-80 Measurement” icon.



2.9 Select “Data” in the left window of the directory tree, and then select one of the existing files in the right hand window.

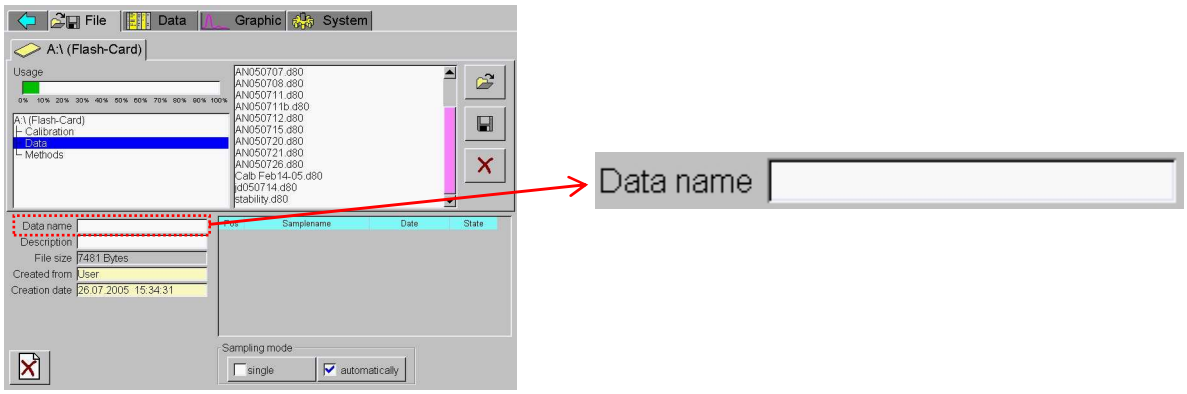


2.10 Press the icon shown below to clear all points.

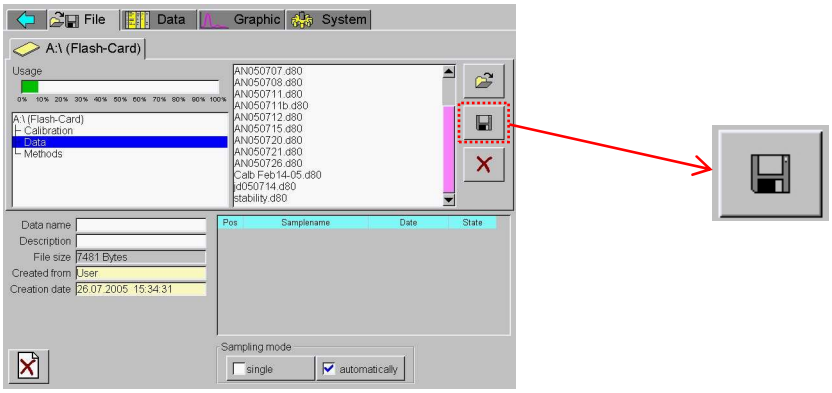


2.11 When asked *"Do you really want to delete all points?"*, press "Yes".

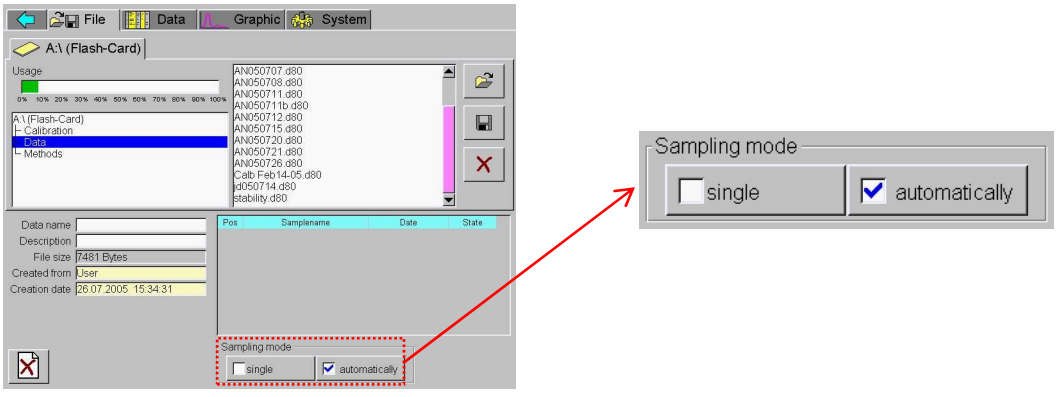
2.12 Under "Data name", type in the name of the new data file.



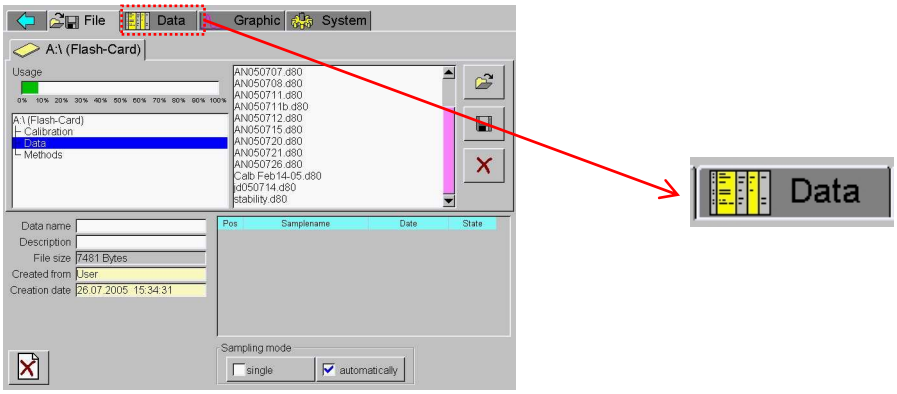
2.13 Press the save button.



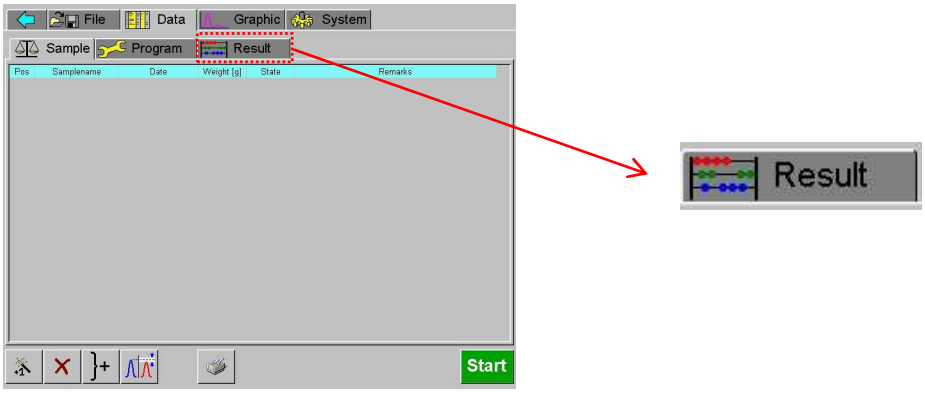
2.14 Select a mode of analysis: Single mode or Automode.



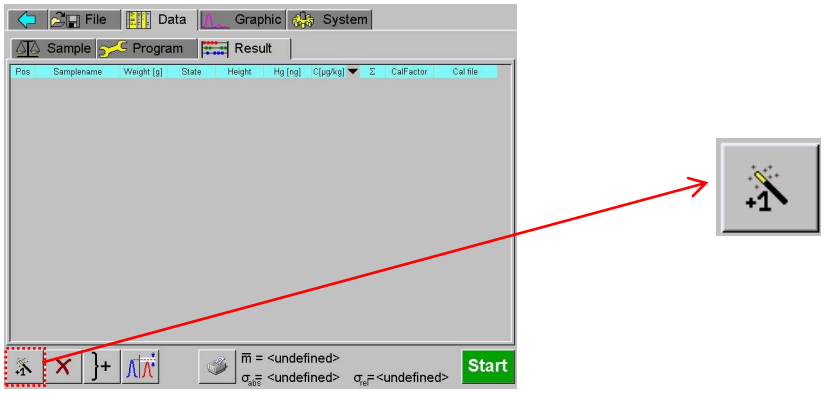
2.15 Press the “Data” tab.



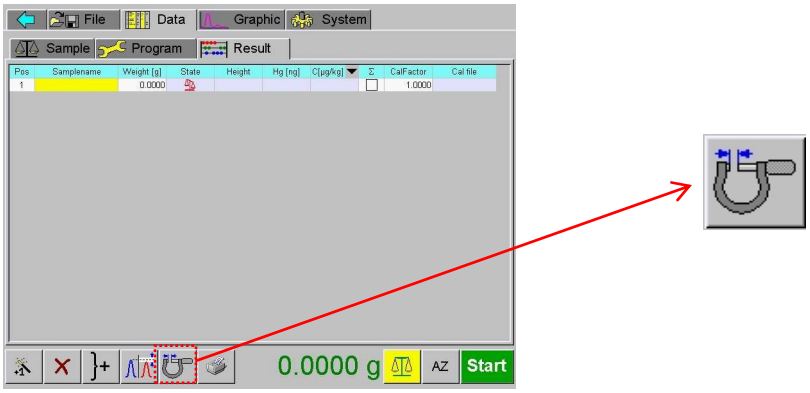
2.16 Press the “Result” tab.



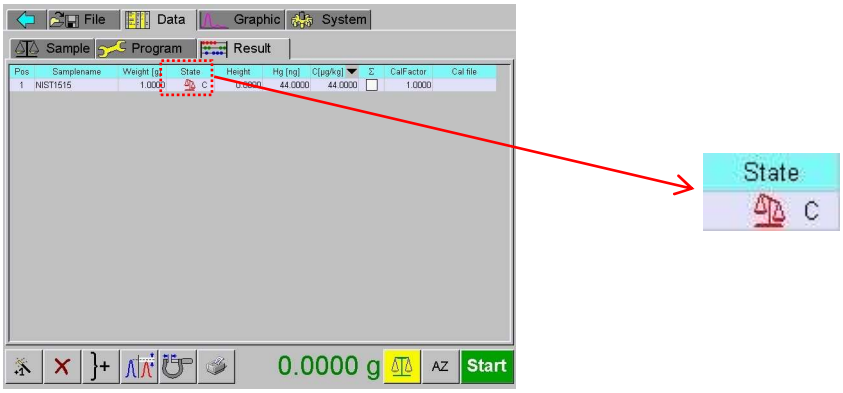
2.17 Press the “Create New Row” button.



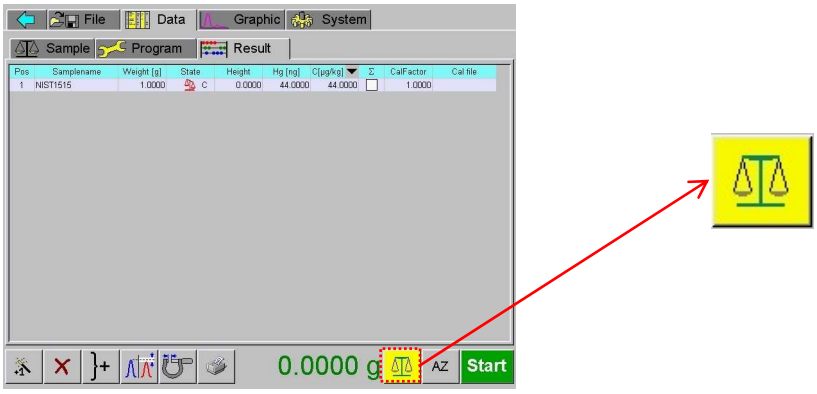
2.18 Press the “Calibration Icon”.



2.19 A “C” will appear in the “State” column indicating that the current process is calibration.



2.20 Type in a sample name under “Samplename” then press the “Balance” icon to record the sample weight in the “Weight” column.

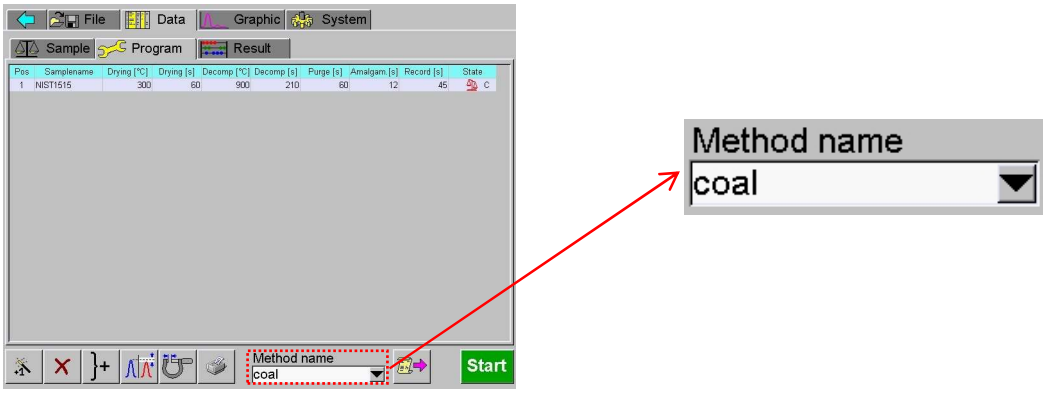


2.21 Place the sample boat into the position indicated in the “Pos” column. The “Pos” column can be edited by the operator using the keyboard. Under the “C” column, select the desired units of concentration and then enter the concentration of the standard sample.

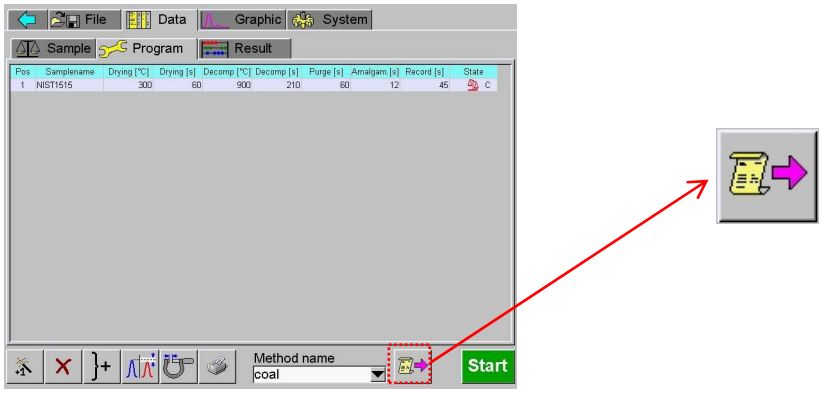
2.22 To calculate for the amount of mercury in the sample, press “Enter” on the keyboard. The weight will then be displayed in the “Hg [ng]” column.

Pos	Samplename	Weight [g]	State	Height	Hg [ng]	C[µg/kg]	Σ	CalFactor	Cal file
1	NIST1515	1.0000	C	0.0000	44.0000	44.0000		1.0000	

2.23 Press the “Program” tab and adjust processing parameters. Alternatively, a pre-set method can be used by clicking on the “Method” drop-down box and selecting the appropriate method. Click on the “button

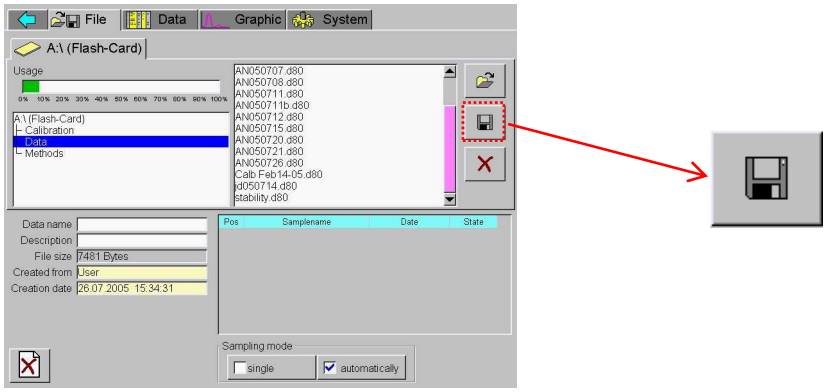


2.24 Click on the icon shown below to load the process parameters for the chosen method.

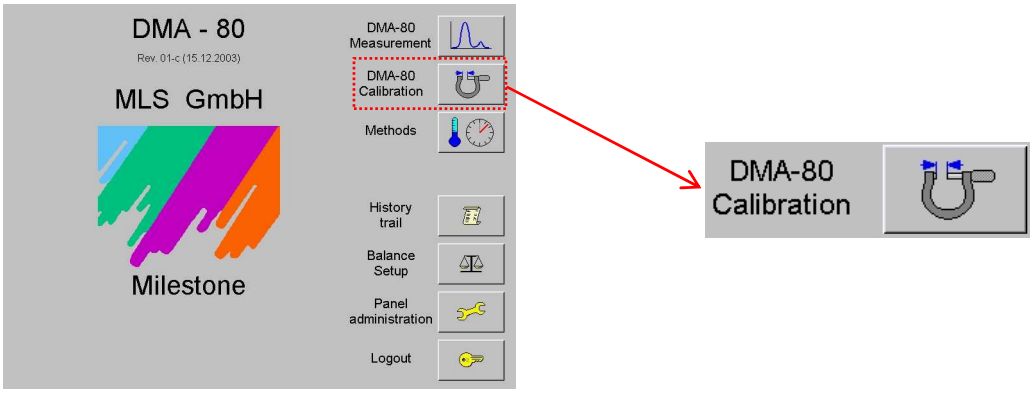


2.25 Press the “Start” button to begin analysis.

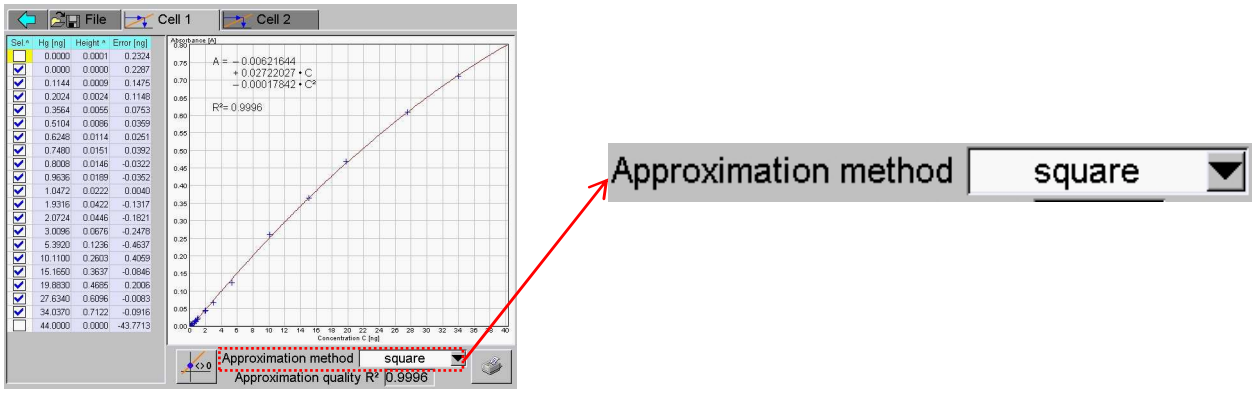
2.26 Once finished running all the calibration points, click on the “File” tab and then click on the “Save” icon



2.27 Go back to the “Main Menu” by clicking on the “Left arrow” tab. Click on the “DMA-80 Calibration” button.

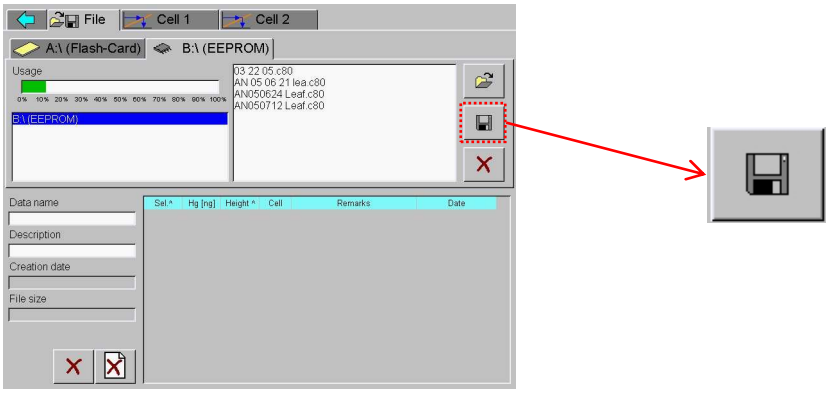


2.28 Click on the “Cell 1” tab, uncheck any “stray” points then select the approximation method.



2.29 Repeat the same procedure for “Cell 2”.

2.30 Click on the “File” tab and then the “Save” button.



3 **Dosing the samples: Dosing performs multiple analysis for one type of sample in order to improve precision compared to smaller, individual analyses.**

NOTE: One sample is selected for DOSE and repeated few times (burn & hold Hg on Amalgamated trap until last sample is burned, then Hg is released & measured.). All dosing samples must be the same sample type. All dosing sample sizes should be relatively close and use same method.

3.1 Click on “DMA-80 Measurement”, “Data”, then “Result” tabs.

3.2 Under “Samplename” type “DOSE”

3.3 Enter the weight of the SAMPLE by clicking on the “Balance” icon.

3.4 Select appropriate method by clicking on the “Program” tab and loading the appropriate method.

3.5 Under ”Pos” type-in the positions of your samples.

3.6 Press ”Enter” to enter sample into sample table.

3.7 Use at least 5 replica of same sample each is named DOSE

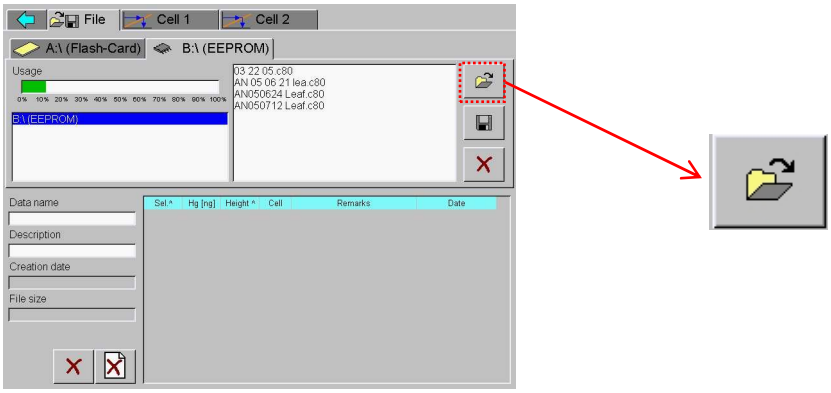
3.8 Very last one name by the actual sample name.

3.9 Click on “Start” button to start analysis.

4 Data analysis

4.1 Load the desired calibration curve before starting analysis.

4.2 From the Main screen click on the “DMA-80 Calibration” button then select the desired file under B:\EEPROM. Load the selected file by clicking on the “File Open” icon



4.3 Return to the Main screen then click on the “DMA-80 Measurement” button.

4.4 Click on “Data” from the left window then select one of the existing files on the right window.

4.5 Click on the “Delete” button to clear all points. When asked “*Do you really want to delete all points?*” click on “Yes”.

4.6 Type in a name for the new data file under “Data name” then click on the “Save” icon.

4.7 Select a mode of analysis.

4.8 Click on the “Data” tab then the “Sample” tab.

4.9 Click on the “Create New Row” button then enter the sample name under the “Samplename” column.

4.10 Click on the “Balance” button to record the sample weight.

4.11 Place the sample boat into the position indicated in the “Pos” column.

4.12 Click on the “Program” tab and adjust parameters as described in the Calibration section.

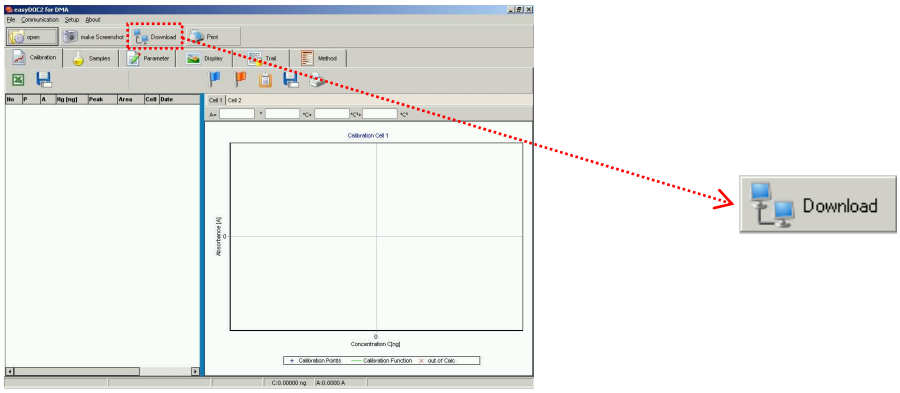
4.13 Increase the decomposition time by 30 seconds if the analysis resulted in a high RSD (> 5%). Re-run the sample

4.14 Click on the “Start” button to begin analysis.

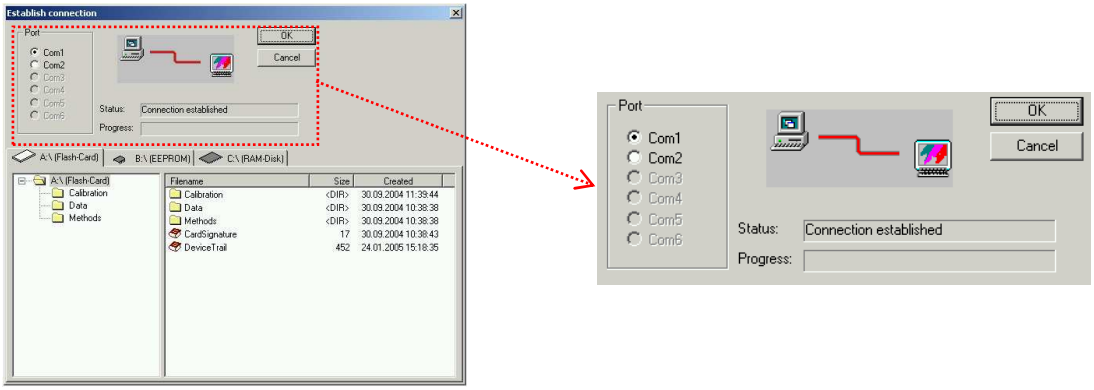
5 Data Retrieval:

5.1 From the desktop, double-click on the “easyDOC2 for DMA” icon.

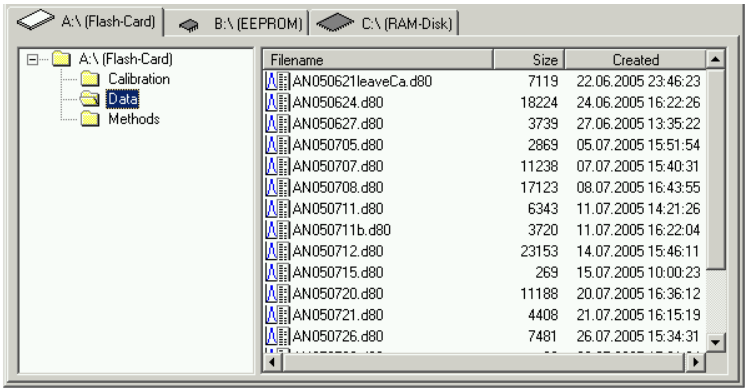
5.2 From the Main screen, click on the “Download” button.



5.3 From the “Establish Connection” screen, select “COM 1”. Wait until “Status” displays “Connection established”.

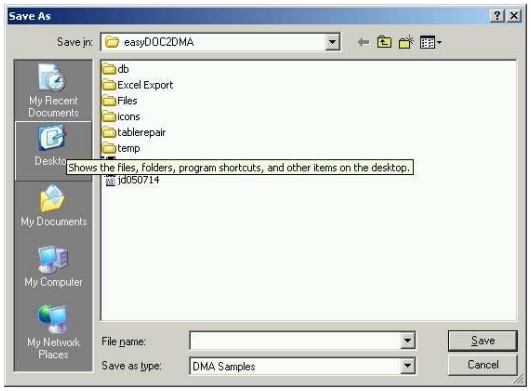


5.4 Under “A:\(Flash-Card)” click on the “Data” folder, select the desired file then click on “OK”.

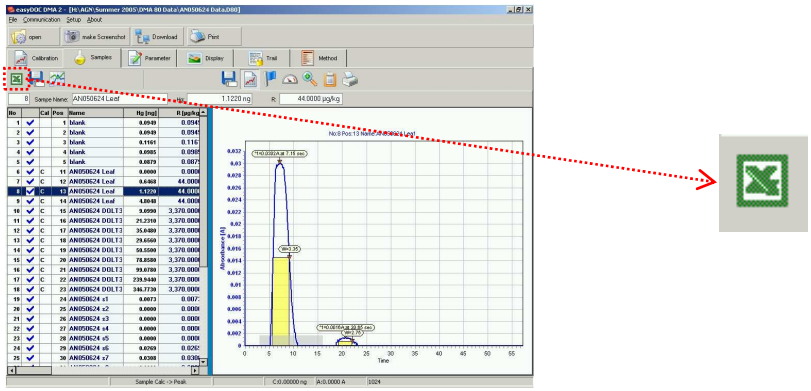


5.5 The “Progress” indicator will show the extent of the download.

5.6 In the “Save As” window, type in the name of the file in the form **NNYYMMDD** (NN – initials, YY – last 2 digits of the current year, MM – month, and DD – day)



5.7 Export the file to Excel by clicking on the “Save as Excel File” button.



5.8 On the “Save As” screen, type in the name of the file in the format **NNYYMMDD** (NN – initials, YY – last 2 digits of the current year, MM – month, and DD – day).

Center for Environmental Systems and Engineering (CESE)

STANDARD OPERATING PROCEDURE

1. Title: Methyl Mercury in Biomass by Digestion, Aqueous Ethylation, Purge and Trap, and CVAFS

AP #CESE-ENV-Z-1630

Rev # 3-December 21, 2007 page 1 of 45

Prepared By: Mario Montesdeoca

Approved By: _____ Date: December 21, 2007
Edward Mason-Technical Review

Approved By: _____ Date: December 21, 2007
Mario Montesdeoca-Laboratory Manager

Approved By: _____ Date: December 21, 2007
Charles T Driscoll-Primary Investigator

Effective Date: December 21, 2007

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2. Summary of Test Method

2.1 Biomass is collected and preserved by freezing and/or freeze drying.

2.2 A 3-5 mg of sample is digested in a 5ml Teflon vial with 3 ml of 25% KOH methanol solution. The digesting sample is placed on an oven at 60^0 C for 24 hrs.

2.3 After digestion, 300 ul of the digest is added to 50ml of DI water in a bubbler. The sample is adjusted to pH 4.9 with an acetate buffer and ethylated in a closed purge vessel by the addition of sodium tetraethyl borate ($NaBEt_4$).

2.4 The ethyl analog of CH3 Hg, methyl ethyl mercury (CH3 CH3 CH2 Hg), is separated from solution by purging with N_2 onto a Tenax -TA trap.

2.5 The trapped methyl ethyl mercury is thermally desorbed from the tenax trap with argon gas stream into a Gas Chromatogram where the methylethyl mercury is separated from other mercury species. The released methyl ethyl mercury and the other mercury species pass through a pyrolytic decomposition column, which converts organo mercury forms to elemental mercury (Hg), and then into the cell of a cold vapor atomic fluorescence spectrometer (CVAFS) for detection.

2.6 Quality is ensured through calibration and testing of the digestion, ethylation, purging, and detection systems.

2.7 If any technical issues arise, do not hesitate to contact a laboratory technician, a laboratory manager, or the principal investigator for additional clarifications.

3. Scope and Application

3.1 This method is for determination of methyl mercury (CH3Hg) in biomass by digestion, aqueous ethylation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS).

3.2 This method is designed for determination of CH3Hg in the range of 0.002-0.8 ng. The method sensitivity can be increased by using a larger aliquot of the digest solution or by digesting a larger sample.

3.3 The detection limit and minimum level of quantitation in this method are usually dependent on the level of background elements rather than instrumental limitations. The sensitivity of the MDL fluctuates depending on the quantity of the sample used on the digestion, and the amount of the digest used during the ethylation step.

3.4 This method is "performance based." The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements if all performance criteria are met. Section 12.1.4 gives the requirements for establishing method equivalency.

3.5 This method should be used only by analysts who are experienced in the use of CVAFS techniques and who are thoroughly trained in the sample handling and instrumental techniques described in this method. Each analyst who uses this method must demonstrate the ability to generate acceptable results using the procedure by analyzing Laboratory Control Samples (LCS) or Quality Control Samples (QCS)-certified samples.

4. Applicable Matrix or Matrices

4.1 This method is applicable to biomass.

5. Method Detection Limit

5.1 Calculating the MDL is the responsibility of the analyst and it must be determined on initial analysis per specific method. (i.e. If the analyst is using a method for the first time, the analyst needs to calculate the MDL for that specific method.) The MDL will be verified at the beginning of each subsequent analysis using the appropriate MDL check solution. The preferred method for calculating MDLs is found in Appendix B, Part 136, Revision 1.11 of the Federal Register, Volume 49, No. 209, October 1984.

5.2 The Laboratory MDL for Methyl Mercury is 0.0015 ng. A typical concentration for a 5 mg digested sample and a 300 ul digest analysis is 3 ppb.

6. Definitions

6.1 Quality Assurance Project Plan (QAPP): QAPP is a plan to be followed to maintain a level of

confidence of accuracy in a specify project.

6.2 Batch: A batch consists of 20 samples that are treated and analyzed together. A batch contains a Preparatory Blank (PB) or Method Blank (MB), a Laboratory Control Sample (LCS), also known as an Quality Control Sample (QCS), an ongoing Precision Recovery sample (OPR),a duplicate, a pair of Matrix Spike (MS), and a Matrix Spike Duplicate (MSD) for every batch.

6.3 Apparatus: Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis that come in contact with the sample and therefore require careful cleaning will be referred to collectively as the Apparatus.

6.4 Methyl mercury: All acid-distillable Hg, which, upon reaction with NaBEt4 yields methylethyl mercury. This includes, but is not limited to, CH3Hg+, strongly organo-complexed CH3Hg compounds, adsorbed particulate CH3Hg, and CH3Hg bound in microorganisms. In freshly collected samples, dimethyl mercury ((CH3)2Hg) will not be recovered as CH3Hg, but in samples which have been acidified for several days, most (CH3)2Hg has broken down to CH3Hg. In this method, CH3Hg and total recoverable CH3Hg are synonymous.

6.5 Statistical definitions:

6.5.1 Mean - The average of n values is calculated by taking the sum of n values and dividing by n.

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

6.5.2 Sample Standard Deviation - A parameter used to measure the dispersion of a data set. It is calculated by the following:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (\bar{x} - x_i)^2}{n-1}}$$

6.5.3 Relative standard deviation (RSD) or coefficient of variation (CV) is the standard deviation divided by the mean and multiplied by 100.

$$CV = \frac{s}{\bar{x}} * 100$$

6.5.4 Relative Percent Difference - The relative percent difference of two numbers is calculated by dividing the absolute value of their differences by the average of the two numbers.

$$RPD = \frac{|x_1 - x_2|}{((x_1 + x_2)/2)} * 100$$

6.5.5 Percent Recovery - Percent recovery is calculated by dividing the spike sample result by the spike added for or by dividing the spike sample result minus the sample by the spike added.

$$\%R = \frac{SS}{SA} * 100$$

$$\%R = \frac{SS-S}{SA} * 100$$

Where: SS = Spike sample
SA = Spike added
S = Sample

7. Interferences

7.1 No significant interference is observed with the analysis of the digest up to 600 ul. If more than 600ul is used for the analysis, a new calibration curve is needed due to the increase of the pH and decrease of response.

8. Safety

8.1 All analysts will attend the "Chemical Hygiene Plan" training provided by the Environmental Health Office (EHO).

8.2 Many of the reagents used in the analysis of Mercury are potentially dangerous. It is strongly advised that the analyst check the material Safety Data Sheets for any reagent he/she is not familiar with product handling and protective measures should always be observed.

8.3 The analyst shall practice standard laboratory safety procedures as specified in the Chemical Hygiene Plan prepared by the EHO.

8.4 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

8.5 The toxicity or carcinogenicity of each chemical used in this method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of this monitoring be made available to the analyst. 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 CH3Hg, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks. Reference 22.1.

8.6 Facility—When samples known or suspected to contain high concentrations of CH3Hg 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. Reference 22.1.

8.7 Protective equipment—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters.

8.8 Analysts are trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

8.9 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

8.10 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

8.11 Effluent vapors—The effluent from the CVAFS should pass through either a column of activated charcoal or a trap containing gold or sulfur to amalgamate or react with Hg vapors.

8.12 Waste handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.

8.13 Decontamination

8.13.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

8.13.2 Glassware, tools, and surfaces—Activated carbon powder will adsorb CH3Hg, eliminating the possible volatilization of CH3 Hg. Satisfactory cleaning may be accomplished by dusting a surface lightly with activated carbon powder, then washing with any detergent and water.

8.13.3 Laundry—Clothing known to be contaminated should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. If the launderer knows of the potential problem, the clothing may be put into a washer without contact. The washer should be run through a cycle before being used again for other clothing.

8.13.4 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by this method can achieve a limit of detection of less than 1ng per wipe. Less than 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe constitutes an acute hazard, requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

9. Equipment and Supplies

9.1 Sampling equipment

9.1.1 Sample collection bottles- fluoropolymer (ultra low level) or borosilicate glass (trace level), 250-500 ml, with fluoropolymer or fluoropolymer-lined cap.

9.2 Cleaning

9.2.1 New bottles are cleaned by heating to 65-75 degrees Celsius in 20 % solution of nitric acid for at least 48 hrs, or washed on the Traceclean^{R}, an automated cleaning instrument manufactured by Milestone. The bottles are cooled, rinsed three times with reagent water, and filled with reagent water containing 1% HCl. These bottles are capped and placed in a clean oven at 60-70^{0} C overnight. After cooling, they are rinsed three more times with reagent water, filled with reagent water containing 0.4% (v/v) HCl, capped, and placed in a mercury-free class 100 clean bench until the outside of the bottle is dry. The caps are then tightened and the bottles are double-bagged in new polyethylene zip-type bags. The capped bottles are stored in plastic boxes until use.

9.2.2 Bottle blanks are analyzed to verify the effectiveness of the cleaning procedures.

9.3 Equipment for bottle and glassware cleaning

9.3.1 Vat, 100-200 L, high-density polyethylene (HDPE), half filled with 4 N HCl in reagent water.

9.3.2 Heating block capable of maintaining +/- 5 ^{0}C in the range 60-100 ^{0}C temperature range.

9.3.3 Laboratory sinks in class 100 clean area, with high-flow reagent water for rinsing.

9.3.4 Clean bench, class 100, for drying rinsed bottles.

9.3.5 Oven, stainless steel, in class 100 clean area, capable of maintaining ± 5C in the 60-70C temperature range.

9.4 Ultra high-purity argon (grade 5.0)

9.5 Equipment for CH3Hg purging system—Figure 2a shows the schematic diagram for the purging system. The system consists of the following:

9.5.1 Flow meter/needle valve—capable of controlling and measuring gas flow rate to the purge vessel at 550 (± 50) mL/min.

9.5.2 Fluoropolymer fittings—connections between components and columns are made using 6.4-mm o.d. fluoropolymer tubing and fluoropolymer friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with C-flex tubing because of its greater flexibility.

9.5.3 Cold vapor generator (bubbler)—500-mL borosilicate glass (special made to increase length of bubbler, see Figure 4) with standard taper 24/40 neck, fitted with a sparging stopper having a medium coarse glass frit that extends to within 0.2 cm of the bubbler bottom (Tecglass & Instrument, or equivalent).

9.5.4 Bubblers are cleaned between samples. The bubblers are cleaned by rinsing the bubbler with DI water 3 times (do not allow them to dry). They are then rinsed with 10% HCl by filling the purge tube and rinsing the outlet tube. Allow it to empty and then rinse with DI water. Rinse the outlet tube and purge tube with methanol. Allow it to empty and then rinse with DI water.

Fill the bubbler with DI water allowing the purge tube to fill. Empty the bubbler and allow to drip dry. Fill with DI water and store. Check for condensation on the top of the bubbler, if condensation present rinse with methanol, then with DI water. Attachment 4.

9.5.5 5 ml Teflon vials manufacturer by Savillex.

9.6 Gas chromatography (GC) system. Clarus 500 by Perkin Elmer

9.6.1 GC conditions: Initial temperature: 45^{o}C and hold for 4.5 minutes; ramp at 45^{o}C/minutes to 180^{o}C and hold for 2 minutes.

9.6.2 The GC column is a DB-5 (J&W); 0.5 mm o.d. x 32 meters.

9.7 Autodesorption 350 ATD by Perkin Elmer

9.7.1 Autodesorption Conditions: purge 3 minutes; Primary desorption at 280^{o}C for 5 minutes; Secondary desorption at 280^{o}C for 7 minutes; flow 40 ml/min.

9.7.2 The flow of the system is controlled by the 350 ATD, and it's measured at the end of the detector.

9.8 Figure 2c shows the orientation consideration for purging and desorbing CH3Hg from the traps. The traps are placed on the autosampler in vertical position. The flow of the argon is from the bottom up.

9.9 Tenax-TA traps— 10cm x 6.5-mm o.d. x 4-mm i.d. glass tubing. The tube is filled with 0.4 +/- 0.05 grams of 60/80 mesh Tenax-TA adsorbant (Supelco, Inc). The ends are plugged with silanized glass wool.

9.9.1 Traps are always capped when not in use to prevent oxidation.

9.9.2 Because the direction of flow is important in this analysis, the crimped end or the marked end with the ring of the Tenax trap will be referred to as "side A," while the uncrimped end will be referred to as "side B."

9.9.3 Tenax traps are condition three times at 250^{o}C and 300^{o}C prior to usage.

9.10 Pyrolytic column—The output from the GC oven is connected directly to a high temperature column to decompose eluted organo-mercurial compounds to Hg^0 The output of the pyrolytic column is connected to the inlet of the CVAFS system.

9.10.1 The column consists of a 24-cm length of quartz tubing, packed over the central 2 cm with quartz wool.

9.10.2 The column is heated to orange heat (~ 750-850^{0} C) by a 10-14 cm length of 22 gauge Nichrome wire, tightly wrapped around the quartz wool packed

9.10.3 Portion of the tube. The temperature of the coil is adjusted by visual inspection of the color, using a 0-120 volt autotransformer.

9.11 Detector-Tekran Model 2357 CVAFS, Brooks-Rand Model III CVAFS, or equivalent

9.12 Figure 1 shows the schematic for the interface of the GC with the CVAFS detector (Reference 6).

9.13 Data handle and crunching is managed by Total Chrome software by Perkin Elmer.

9.14 Pipettors—All-plastic pneumatic fixed-volume and variable pipettors in the range of 10.0 uL to 5.0-mL.

9.15 Analytical balance capable of weighing to the nearest 0.00001 g.

10. Reagents and Standards

10.1 Reagent water—18-MS minimum, ultrapure deionized water starting from a reverse osmosis source.

10.2 Air—It is very important that the laboratory air be low in both particulate and gaseous Hg. Ideally, Hg work should be conducted in a new laboratory with mercury-free paint on the walls. Outside air, which is very low in Hg, should be brought directly into the class 100 clean bench air intake.

10.3 Hydrochloric acid—Trace-metal purified reagent HCl containing less than 5 pg/mL Hg. CH3 Hg is not stable in concentrated acid, so the acid does not need to be tested for CH3Hg.

10.4 1% APDC solution—To 100 mL of reagent water, add 1.0 g of reagent grade APDC (ammonium pyrrolidine dithiocarbamate), and shake to dissolve. The solution is purified by extraction with three 10 mL aliquots of methylene chloride.

10.5 Glacial acetic acid—Reagent grade.

10.6 25% KOH methanol Solution. 25 grams is dissolved with 75 ml of methanol.

10.7 Methanol-HPLC grade.

10.8 95% Ethanol -95% un-denatured ethyl alcohol.

10.9 Alka-Seltzer- Over the counter medication tablet manufacture by Bayer Corporation.

10.10 3 M Acetate buffer—3 moles of reagent grade sodium acetate (408 g) and 3 moles of reagent grade glacial acetic acid (177 mL) dissolved in reagent water to give a final volume of 1.0 L. To purify the buffer of traces of CH3 Hg, add 0.5 mL of 1% $NaBEt_4$ and purge the solution overnight with Hg-free N_2 or Ar. This solution has an indefinite lifetime when stored in a fluoropolymer bottle at room temperature.

10.11 Sodium tetraethyl borate, 1%—This reagent is purchased in 1.0-g air-sealed bottles (Strem Chemical, or equivalent. One hundred milliliters of 2% KOH in reagent water is prepared in a fluoropolymer bottle and chilled to 0^0 C. The bottle of $NaBEt_4$ is rapidly opened and approximately 5 mL of the KOH solution poured in. The reagent bottle is capped and shaken to dissolve the $NaBEt_4$. This is poured into the 100 mL bottle of KOH solution, and shaken to mix. Immediately, the 1% $NaBEt_4$ solution in 2% KOH is poured into fifteen (15) 7-mL fluoropolymer bottles, which are capped and placed in a low temperature freezer. For use, one of these bottles is removed and thawed and kept in small cooler with ice during the ethylation process.

NOTE: *It is imperative that this reagent be exposed to air a minimum length of time Air decomposes the Sodium tetraethyl borate.. Thus, when removing reagent, open and close the lid quickly and tightly!*

10.12 Frozen bottles of $NaBEt_4$ will keep for at least one week. If any doubt arises about the quality of the ethylating reagent, make a new batch, as the old material often gives good results for reagent water spikes, but not for environmental samples. Do not use $NaBEt_4$ solid or solutions if they have a yellow color.

WARNING: *NaBEt4 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 hood. Triethylboron will bubble off to the air where it is eventually oxidized to harmless boric acid. Leave the acid beaker in the hood indefinitely, or boil down to 1/2 volume to destroy residues before discarding as any acid waste*

10.13 Stock methyl mercury standard—certified CH3 Hg solution from Frontier Geosciences Inc. The stock solution has an indefinite lifetime when stored in an amber glass bottle with a fluoropolymer lid at room temperature. **Do not make or keep this concentrated stock solution in the trace mercury laboratory.**

10.14 Secondary methyl mercury standard—Dilute 1.00 mL of stock solution (B) to 1000.0 mL with reagent water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl. This solution contains approximately 4-5 mg/L (5.00 ng/mL) CH3 Hg as Hg. The exact CH3 Hg titre is confirmed as indicated below. The secondary CH3 Hg standard solution has been observed to maintain its titre over a year when stored in a fluoropolymer bottle in the refrigerator.

10.14.1.1 Dilute the secondary standard 1:10 with concentrated BrCl solution (0.100 mL of secondary stock solution added to 0.900 mL BrCl in a small FEP vial). Allow the solution to oxidize for at least 4 h. The total Hg in the dilution may then be analyzed using dual amalgamation/CVAFS, by comparison to a dilution of NIST-3133 (as in Method 1631). A mean of at least seven replicate analyses of the secondary stock solution is necessary to accurately quantify the total Hg concentration of the solution.

10.14.1.2 Analyze the secondary standard for labile H (II) using Method 1631 by directly reducing an aliquot of standard solution with $SnCl_2$, but without prior BrCl oxidation as performed in Section 10.11.1. At least two determinations of labile Hg(II) must be made of the stock solution.

10.14.1.3 Calculate the CH3Hg in the secondary CH3Hg standard solution by subtracting the mean labile Hg(II) concentration from the mean total Hg concentration.

10.14.1.4 If the secondary CH3Hg stock solution drops below 98.0% CH3Hg, discard the solution and make a fresh secondary solution.

10.15 Working methyl mercury standard—Prepare a dilution of the secondary CH3Hg standard using reagent water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl. A convenient concentration for this standard is 1.00 ng/mL CH3Hg. This solution will maintain its titre for more than one month when kept in a fluoropolymer bottle on the lab bench top. Refrigeration is not necessary.

10.16 Nitrogen—UHP grade nitrogen that is further purified by the removal of Hg using a gold-coated sand

trap or organic carbon trap.

10.17 Argon—UHP grade nitrogen that is further purified by the removal of Hg using a gold-coated sand trap or organic carbon trap.

10.18 Air—UHP grade air used for the pneumatic of the autosampler.

10.19 Gold-coated sand trap—The trap is made from 10-cm x 6.5-mm o.d. x 4-mm i.d. quartz tubing. The tube is filled with 3.4 cm of gold-coated 45/60 mesh quartz sand (Frontier Geosciences Inc., or equivalent). The ends are plugged with quartz wool. Traps are fitted with 6.5-mm i.d. fluoropolymer friction-fit sleeves for connection to the system.

11. Sample Collection, Preservation, Holding Times, Shipment, and Storage

11.1 Samples are collected in a 500 ml Teflon bottles. For long storage and delay processing, the samples are treated with Alka-seltzer and preserved with 50 ml ethanol for detailed sampling and preservation see AP# CESE#ENV-310. For immediate processing within 48 hours (for Honeywell Onondaga Lake Program), the samples are placed in a cooler with ice and transferred to a refrigerator in the laboratory. For analysis and long storage the sample are freeze dry.

11.2 A six month holding time for regulated or contracted work was chosen. It should be sufficient time to complete the analysis. For research there is no holding time, however, all samples need to be stored on the dark, and on a cool environment.

11.3 Samples are collected into rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps. Borosilicate glass bottles may be used if ppm concentrations of Hg and Hg species are expected. It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads. Polyethylene sample bottles must not be used (Reference 13).

12. Quality Control and Documentation

12.1 Quality Control

12.1.1 Prior to the submittal of the data, all preparation blank, matrix spike, matrix spike duplicate, duplicate, and laboratory control sample data must be input into the laboratory quality control database.

12.1.2 The laboratory is NELAP certified and follows the NELAP's quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of matrix spikes (MS) and matrix spike duplicates (MSD) to assess accuracy and precision. Laboratory performance is compared to established performances criteria to determine whether the results of analyses meet the performance characteristics of the method.

12.1.3 All analysts are required to have an initial demonstration of the ability to generate acceptable accuracy and precision with this method.

12.2 The analysis of the traps was modified and automated by using The Autodesorption 350 ATD by Perkin Elmer.

12.2.1 The laboratory performed the MDL study required by 40 *CFR* Part 136, Appendix B, and the laboratory maintained the records of modifications made to this method.

12.2.2 Run sequence:

RUN SEQUENCE
Two system blanks
Three primes
A minimum of five, non-zero calibration standards
Ethylation blank
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
On-going precision and recovery (OPR)
Continuing Calibration Blank (CCB)
Method Detection Limit (MDL) Check Undistilled
Quality control sample/Laboratory Control Sample (LCS)
Method blank (MBLK) distillation
Field Blank
10 samples
Matrix spike
Matrix spike duplicate
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
Ten samples
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
On-going precision and recovery (OPR)
Continuing Calibration Blank (CCB)

12.3 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision and to monitor matrix interferences. Section 13.1.2 describes the procedure and QC criteria for spiking.

12.4 Analyses of blanks are required to demonstrate acceptable levels of contamination. Section 13.1.3 describes the procedures and criteria for analyzing blanks.

12.5 The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery (OPR) sample and the quality control sample (QCS) that the system is in control. Sections 13.2.2 and 13.1.4 describe these procedures, respectively.

12.6 The laboratory shall maintain records to define the quality of the data that are generated. Sections 12.9 describe the development of accuracy statements.

12.7 The determination of CH3 Hg in water is controlled by an analytical batch. An analytical batch is a set of samples distilled with the same batch of reagents, and analyzed in the same analytical sequence. A batch may be from 1 to as many as 20 samples. Each batch must be accompanied by at a method blank, an OPR sample, and a QCS. In addition, there must be one MS and one MSD sample for every batch (a frequency of 5%).

12.8 Initial demonstration of laboratory capability

12.8.1 Method detection limit—To establish the ability to detect CH3Hg, the analyst shall determine the MDL according to the procedure at 40 *CFR* 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL listed in Section 3.5 or one-third the regulatory compliance limit, whichever is greater. The MDL should be determined when a new operator begins work or whenever, in the judgment of the analyst, a change in instrument hardware or operating conditions would dictate that the MDL be redetermined.

12.8.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations (see table 4):

12.8.2.1 Analyze four replicates of a reference sample or a standard according to the procedure beginning in Section 14.

12.8.2.2 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.

12.8.2.3 Compare s and X with the corresponding limits for initial precision and recovery in Table 1. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the acceptance range, system performance is unacceptable. Correct the problem and repeat the test.

12.8.3 Method accuracy—To assess the performance of the method on a given sample matrix, the laboratory must perform either matrix spike (MS) and matrix spike duplicate (MSD) sample analyses on 5% of the samples from each site being monitored, or at least one MS/MSD sample analysis for each analytical batch, whichever is more frequent.

12.8.4 The concentration of the CH3Hg in the sample shall be determined as follows:

12.8.4.1 If, as in compliance monitoring, the concentration of CH3 Hg in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1-5 times the background concentration of the sample, whichever is greater.

12.8.4.2 If the concentration of CH3Hg in a sample is not being checked against a limit, the spike shall be at 1-5 times the background concentration or at 1- 5 times the MR L in Table 1, whichever is greater.

12.8.5 Assessing spike recovery

12.8.5.1 Determine the background concentration (B) by analyzing one sample from each set of 20 samples from each site or discharge according to the procedure in Section 14. If the expected background concentration is known from previous experience or other knowledge, a specific spiking amount can be used for those samples.

12.8.5.2 If necessary, prepare a spiking solution to produce an appropriate level in the sample.

12.8.5.3 Spike two sample aliquots with the spiking solution and analyze to determine the

concentration after spiking (A).

12.8.5.4 Calculate the percent recovery (P) in each aliquot using Equation 1:

Equation 1

$$P = 100\frac{(A-B)}{T}$$

Where:
A=Measured concentration of analyte after spiking
B=Measured concentration of analyte before spiking
P=Percent recovery
T=True concentration of the spike

12.8.6 Compare the percent recovery (P) with the QC acceptance criteria in Table-1.

12.8.7 If P falls outside the designated range for recovery in Table 1, the CH3 Hg analysis has failed to meet the established performance criteria. If P is unacceptable, analyze the OPR standard. If the OPR is within established performances criteria (Table 1), the analytical system is within specification and the problem can be attributed to interference by the sample matrix.

12.8.8 If the interference can be attributed to sampling, the site or discharge should be resampled. If the interference can be attributed to a method deficiency, the analyst must modify the method, repeat the test required in Section 12.2, and repeat analysis of the sample and MS/MSD. However, when this method was written, there were no known interferences in the determination of CH3Hg using this method. If such a result is observed, the analyst should investigate it thoroughly.

12.8.9 If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be outside specified limits. The analyst must identify and correct the problem and reanalyze the sample batch.

12.8.10 Relative percent difference between duplicates—Compute the relative percent difference (RPD) between the MS and MSD results according to Equation 2 using the CH_3Hg concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 12.4.2.4 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

Equation 2

$$RPD = 200\frac{(|D_1 - D_2|)}{(D_1 + D_2)}$$

Where:
RPD=Relative percent difference
D1 =Concentration of CH3 Hg in the MS sample
D2 =Concentration of CH3 Hg in the MSD sample

12.8.10.1 The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 1.

If the criterion is not met, the sample RPD is reviewed. If the sample RPD passed, the MS/MSD is re-analyzed. If on the other hand, the sample RPD failed criterion, the sample, sample duplicate is re-digested and re-analyzed.

12.8.11 As part of the QC program for the laboratory, the method precision and accuracy for samples was assessed and records maintained. After analyzing five samples in which the recovery passes the test in Section 12.4.2, the average percent recovery (Pa) was calculated and the standard deviation of the percent recovery (rp). The accuracy assessment as a percent recovery was assessed as interval from Pa – 2rp to Pa + 2rp.

12.8.12 Blanks—Blanks are critical to the reliable determination of CH3Hg at low levels. The sections below give the minimum requirements for analysis of blanks. However, sometimes other blanks are analyzed when a possible contamination is suspected.

12.8.12.1 Ethylation blanks—Reagent water typically contains no CH3Hg. The reagent (ethylation) blank may conveniently be determined by adding 0.85 ml of acetate buffer, 300 ul of 25% KOH in Methanol and 0.15 ml of 1% $NaBEt_4$ solution to 50 mL of reagent water in the reaction vessel.

12.8.12.1.1 A single ethylation blank is analyzed with each analytical run, part of the calibration sequence. This value is used to blank correct the standard curve.

12.8.12.1.2 The presence of more than 2 pg of CH3Hg indicates a problem with the reagent water or one of the reagent solutions. An investigation of the cause of the high blank can be made by varying, one at a time, the amounts of buffer, reagent water, and $NaBEt_4$. Because NaBEt4 cannot be purified, a new batch should be made from different reagents and should be tested for Hg. If the reagent water is found high, this can be remedied by replacing the purification cartridges.

12.8.12.2 Method blanks—The method blanks (digestion blanks) are prepared by digesting and analyzing 3 ml of digestion solution as a sample.

12.8.12.3 Equipment blanks—Before any sampling equipment is used at a given site, the laboratory or sampling crew is required to generate equipment blanks to demonstrate that the sampling equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampler check blanks.

12.8.12.4 Bottle blanks—After undergoing the cleaning procedures in this method, bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles should be filled with reagent water acidified to 0.4% HCL and allowed to stand for a minimum of 24 h. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water should be analyzed for any signs of contamination. If any bottle shows signs of contamination, the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles cleaned again.

12.8.12.5 Continuing Calibration blanks (CCB)- Continuing Calibration blanks are used to

demonstrate that the analytical system is free from contamination that could otherwise compromise sample results. Continuing Calibration blanks are prepared and analyzed using sample bubblers, reagents, and analytical procedures identical to those used to prepare and analyze the samples. Continuing Calibration blanks should follow all Continuing Calibration verification samples.

12.8.12.6 Sampler check blanks (Net blank)—Sampler check blanks are generated in the laboratory or by the sampling crew by reagent water through the sampling devices using the same procedures that are used in the field. Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing sampler check blanks at the laboratory or by the sampling crew.

12.8.12.6.1 Sampler check blanks is taken at the beginning of the sampling event. 'Clean hands' will fill the ½ liter vessel with lake water and pour through the filtering apparatus into the sampling bucket. The lake water is discarded and the sampling bucket is filled with DI water. 'Clean hands' will remove the dirty gloves and put on a new pair of gloves to pour the bucket contents into a blank sampling vessel. The blank is placed on ice.

12.8.12.6.2 The sampler check blank must be analyzed using the procedures in this method. If CH3Hg or any potentially interfering substance is detected in the blank, the source of contamination or interference must be identified, and the problem corrected.

12.8.13 Ongoing precision and recovery (OPR)—To demonstrate that the analysis system is within specified limits and that acceptable precision and accuracy is being maintained within each analytical batch, the analyst shall perform the following operations.

12.8.13.1 Analyze the OPR solution (0.5 ng) followed by a ethylation blank prior to the analysis of each analytical batch according to the procedure in Section 13. An OPR must also be analyzed at the end of an analytical run. Subtract the peak height (or peak area) of the ethlyation blank from the peak height (or area) for the OPR and compute the concentration for the blank-subtracted OPR.

12.8.13.2 Compare the computed OPR concentration with the yearly established limit. If the concentration is in the range specified, the analysis system is within specification and analysis of samples and blanks may proceed. If, however, the concentration is not in the specified range, the analytical process is not within the specified limits. Correct the problem and repeat the OPR test.

12.8.13.3 The laboratory updates QC limits yearly. The laboratory develops the limits by calculating the average percent recovery (R) and the standard deviation of the percent recovery (sr). Limit for the QC range are calculated as the interval from R - 2sr to R + 2sr.

12.8.14 Quality control sample (QCS)/ Laboratory Control Sample (LCS) —The laboratory must obtain a QCS from a source different from the CH3Hg used to produce the standards used routinely in this method. The QCS is analyzed as an independent check of the digestion and analysis.

12.8.15 Continuing Calibration Verification Sample (CCV) –or throughout the course of the analytical run (CCV) near the concentration range. These samples are evaluated to determine whether the instrument is within acceptable calibration throughout period in which samples are analyzed (i.e., to verify that the initial calibration was applicable during the sample analyses). In general, failure of the CCV indicates that the initial calibration is no longer valid and should trigger recalibration and the reanalysis of the associated samples in the analytical sequence.

12.8.16 Laboratory Duplicate or Field Duplicate- Depending on specific program requirements, the laboratory may be required to analyze field duplicates and field spikes collected to assess the precision and accuracy of the sampling, sample transportation, and storage techniques. The relative percent difference (RPD) between field duplicates should be less than 35%. If the RPD of the field duplicates exceeds 35%, the laboratory should communicate this to the sampling team so that the source of error can be identified and corrective measures taken before the next sampling event.

12.9 Documentation

12.9.1 Reagent bottles are labeled with reagent name, name and amount of all chemicals used in production, preparation date, expiration date, and initials of analyst.

12.9.2 Sample data and quality control data is recorded on the appropriate laboratory forms.

12.9.3 As new standards and reference samples are introduced in to the laboratory, they must be tagged with a reagent number and entered in to the CESE Section Standard Preparation Logsheet (*under development*). The reagent number is then recorded on the appropriate laboratory forms when used.

13. Calibration and standardization

13.1 Establish the operating conditions necessary to purge Hg species from the bubbler and to desorb Hg species from the traps so that sharp peaks are given. The system is calibrated using CH3 Hg standards.

13.2 Calibration

13.2.1 The calibration must contain five or more non-zero points and the results of analysis of one ethylation blank. The lowest calibration point must be at the minimum level (ML).

13.2.2 Standards are analyzed by the addition of aliquots of the CH_3Hg working standard (Section 10.9) directly into the bubblers. Add 50 mL of fresh reagent water, a 0.005 ng aliquot of the standard, 0.85 mL of 3M acetate buffer, 300 ul of 25% KOH in methanol, and 0.15 mL of $NaBEt_4$ to the bubbler, swirling to mix. Allow to react for 17 min, purge for 17 min, dry for 5 min and then analyze. Sequentially follow with aliquots of 0.01, 0.02, 0.04, 0.05, 0.1 and 0.2 ng CH_3Hg in separate bubblers.

13.2.3 For each point, correct the standard peak height or area by subtracting the peak height or area of the ethylation blank for the analytical batch. Calculate the calibration factor (CF) for CH_3Hg for each of the five standards using the mean ethylation-blank-corrected peak height or area (Equation 3).

Equation 3

$$CF = \frac{R_s - R_e}{Cs}$$

where:
Rs=Peak height or area of the standard
Re=Peak height or area of the ethylation blank
Cs=Concentration of the standard (ng)

13.2.4 Calculate the mean calibration factor (CFm), the standard deviation of the CFm (SD), and the relative standard deviation (RSD) of then calibration, where RSD = 100 x SD/CFm. If the RSD is # 15%, the CFm may be used to calculate sample concentrations. If RSD > 15%, recalibrate the analytical system and repeat the test.

13.2.4.1 The net concentration recovery (minus ethylation blank) for the lowest standard must be in the range of 65-135% of the expected value to continue with sample analysis.

13.2.5 Ongoing precision and recovery—Perform the ongoing precision and recovery test to verify calibration prior to analysis of samples in each analytical batch. An OPR must also be analyzed at the end of an analytical run.

14. Procedure

14.1 Sample Digestion. (Attachment 2)

14.1.1 Sample preparation- Weigh a 5 ml Teflon vials, and then place 0.003- 0.005 g of Zooplankton sample in the vial. Then add 3 mL of digestion fluid (25% KOH in Methanol). Make a duplicate of the sample. Weigh the vial once again. Then place the labeled vial in the oven at 60° C for 24 hours to allow for “digestion.”

14.1.2 MS/MSD preparation- Weigh two 5 ml Teflon vials, and then place 0.005 g of Zooplankton sample in the vial. Then add 3 mL of digestion fluid (25% KOH in Methanol). Weigh the vial, and then add 1 mL of 1 ng/mL methyl mercury standard (Label this “MS”). Weigh the vial once again. Make a duplicate of the sample (Label this “MSD”). Then place the labeled vial in the oven at 60° C for 24 hours to allow for “digestion.”

14.1.3 Method Blank (MB)- Weigh a 5 ml Teflon vials. Then add 3 mL of digestion fluid (25% KOH in Methanol). Weigh the vial once again. Then place the labeled vial in the oven at 60° C for 24 hours to allow for “digestion.”

14.1.4 QCS/LCS preparation- Weigh a 5 ml Teflon vials. Then add 3 mL of digestion fluid (25% KOH in Methanol). Weigh the vial, and then add 1 mL of 1 ng/mL methyl mercury standard (Label this LCS”). Weigh the vial once again. Then place the labeled vial in the oven at 60° C for 24 hours to allow for “digestion.”

14.2 Ethylation and purging of the digest (Attachment 3).

14.2.1 Standard purging: Pour 50 ml of DI water into the bubbler. Be sure that there is no moisture on the insides of the tops of the bubblers. Add 0.85 mL of 3 M acetate buffer and 300 ul of 25 % KOH in methanol solution in the bubbler and swirl to mix the buffer. Add the corresponding amount of standard to prepare a 5 points calibration curve.

14.2.2 OPR purging: Pour 50 ml of DI water into the bubbler. Be sure that there is no moisture on the insides of the tops of the bubblers. Add 0.85 mL of 3M acetate buffer and 300 ul of 25 % KOH in methanol solution in the bubbler and swirl to mix the buffer and add 500 ul of OPR solution.

14.2.3 Prepare the cap of the bubbler by placing the trap at the outlet of the cap. Make sure that the A-side of trap is on the front. (A-side the ring marked side or the s side from the Supelco tubes)

14.2.4 Add 0.15 ml of freshly thawed 1% $NaBEt_4$ solution. Close the reaction vessel with the bubbler cap, and swirl gently to mix and proceed as stated on section 14.2.7.

14.2.5 Sample purging: Pour 50 ml of DI water into the bubbler. Be sure that there is no moisture on the insides of the tops of the bubblers. Add 0.85 mL of 3M acetate buffer in the bubbler and swirl to mix the buffer. Weigh the Teflon vial, and pipet out 300 ul of sample and add it to the bubbler. Rinse the pipet tip in the bubbler. Re-weigh the Teflon vial.

14.2.6 Prepare the cap of the bubbler by placing the trap at the outlet of the cap. Make sure that the A-side of trap is on the front. (A-side the ring marked side or the s side from the Supelco tubes)

14.2.7 Add 0.15 ml of freshly thawed 1% $NaBEt_4$ solution. Close the reaction vessel with the bubbler cap, and swirl gently to mix.

14.2.8 Allow the contents of the bubbler to react for 17 min. All CH3Hg in the sample is converted to volatile methylethyl mercury.

14.2.9 After reaction time is competed, each bubbler is fitted with the 1/4" c-flex fitting, and purge the sample with N2 (60- 150 mL/min) for 17 min.

14.2.10 Once the sample has been purged for 17 min, any adsorbed water must be dried from the Tenax trap. Disconnect the Tenax trap from the bubbler and attach the N2 flow directly to the trap. Use the same orientation (i.e., N2 entering from side A), and purge the trap for 5 min.

14.2.11 The sample is now ready for analysis. The methylethyl mercury collected on the trap is quantitatively stable for up to 24 hrs and must be analyzed within that period.

14.3 Desorption of methylethyl mercury from the Tenax-TA trap (Attachment 3)

14.3.1 Insert the Tenax trap containing the new sample into the GC auto desorption unit *such that side A is on the upright position.*

14.3.2 Make sure that the post GC pyrolytic column is on and red-hot (~750 -850^0 C), head pressure in the Argon tank should be 110 psig, and the tank total pressure is greater than 300 psig.

14.3.3 Peaks generated using this technique should be very sharp and almost symmetrical. Methylethyl mercury elutes at approximately 2.5 min and has a width at half-height of about 10 sec. Earlier

peaks (Hg^0, $(CH_3)_2$ Hg) are sharper, while later peaks (diethylmercury) are broader.

14.3.4 The appearance of only one peak (Hg^0) usually signifies either that the pyrolytic column is not turned on, or that NaBEt4 was not added to the sample.

14.3.5 Normally the Hg^0 peak is quite small. However, some Hg^0 is generated by thermal degradation of diethyl mercury during the desorption step. Thus, when samples contain a high concentration of Hg (II), both the Hg^0 and the diethyl mercury peaks will be bigger. The ratio of the two peaks is indicative of the quality of the Tenax trap. As the Tenax trap degrades, the amount of thermal breakdown of organo-mercurials increases. Since the diethyl mercury is much more sensitive to thermal breakdown than the methylethyl mercury, monitoring the latter peak can serve as an early warning for trap replacement. Generally, the Tenax traps should be replaced any time the Hg^0 peak grows to be as large as the diethyl mercury peak. As a rule of thumb for samples with significant Hg (II), use 1.0 ng Hg (II) from a non-acidified solution deliberately added to the reaction vessel as a trap check. For samples very low in Hg (II), such as blanks, the Hg^0 peak is generally higher than the diethyl mercury peak, due to residual sources.

15. Calculations

15.1 Calculate the following parameters for each analytical batch:

15.1.1 Ethylation blank (n = 1) or the mean ethylation blank (n > 1).

15.1.2 Ethylation-blank subtracted calibration factor for each standard (Cfx , Section 10.1.3) and peak measurement for each sample (R_S).

15.1.3 The mean calibration factor (CFm), standard deviation of the calibration factor (SD), and relative standard deviation (RSD) of the calibration factor (Section 10.1.1.4).

15.2 Compute the concentration of CH_3 Hg in ng/g (parts-per-billion-ppb) according to Equation 4.

Equation 4

$$[CH_3Hg](ng) = \frac{R_s - R_e}{CF_m * W}$$

Where:
Rs=gross peak height (or area) of signal for CH3Hg in sample
Re=peak height (or area) of signal for CH3Hg in ethylation blank (n = 1) or mean ethylation blank (n > 1)
CFm=mean calibration factor
W=Sample weight (g)

15.3 The Methylmercury ng of the method blank is subtracted from the sample ng calculated to obtain the net ng of CH_3Hg.

Equation 5

$$[CH_3Hg]_{net} = [CH_3Hg]_{sample} - [CH_3Hg]_{MB}$$

where:
[CH3Hg]net =net ng of CH_3Hg
[CH3Hg]sample =ng of CH_3Hg in the sample (ng, Equation 3)
[CH3Hg]MB =ng of CH3Hg in the method blank

15.4 Reporting

15.4.1 All ngs are method blanks subtracted (Equation 5) for the next calculation.

15.4.2 Create a separate excel file and "save as" in your own "Sequence Folder", using initials, year, month, and day, i.e. EFM070515. as shown below:

15.4.3 In the first column, type in each sample name (for example, "6/6/90 Zooplankton"). In the second, type in the original weight of the tube in which the zooplankton sample was digested. The third column should have the specific weight of the zooplankton sample digested. The fourth column should be the weight of the tube and sample after 3 mL of digestion solution was added to the Teflon tube. The "weight of spike" column is only used for MS/MSD samples and it is just the weight of the tube and sample after an addition 1 mL of Methyl Mercury solution is added to the Teflon tube. After the tubes are put in the oven overnight, the "Weight after digestion" column just refers to the weight of the tube and sample the next day, since a small of amount of the digestion solution will evaporate. "Wt. of the digest" is the "Weight after digestion" minus the "WT. of tube". After 300 µL of each sample solution is put in a bubbler for methyl mercury measurement, the new weight of the tube and sample is recorded in "Weight after Sample Removed" column. Lastly, the "Wt. of Sample Bubbled" column is just the "Wt. after digestion" minus the "Weight after Sample Removed."

Sample Name	Wt. of Tube (g)	Wt. of Sample (g)	Wt. of Sample after 3mL (g)	Wt. of Spike (g)	Wt. after digestion (g)	Wt. of the digest (g)	Weight after Sample Removed (g)	Wt of Sample Bubbled (g)

15.4.4 Add five more columns to the end of the first row as shown below.

Area	Measured MeHg (ng)	Conc. of amount used (ng/g)	Amount of MeHg in Total Sample	dry MeHg (ng/g) concentraion

15.4.5 In the first, enter in the corresponding areas of the MeHg peak of each sample from the CESE Summary Report. The "Measured MeHg" level is ng calculated from equation 5. "Conc.

Amount used" is the measured MeHg divided by the "Weight of Sample Bubbled". "Amount of MeHg in Total Sample" is the "Conc. Amount used" times by "Wt. of the digest". Lastly, to determine the "Dry MeHg Concentration" in ng/g, divide the "Amount of MeHg in Total Sample" by the "Weight of Zooplankton Sample."

16. Method performance

16.1 The method detection limit (MDL) listed and the quality control acceptance criteria are the same as method AP #CESE-ENV-1630.

16.2 Initial Performance and Recovery (IPR) was validated. See table 4.

17. Pollution Prevention

17.1 All analysts will attend the Chemical Hygiene Plan and Hazardous Waste Management training provided by the EHO.

17.2 All analysts shall remain aware that Syracuse University waste minimization objective is to reduce the generation of both hazardous and non-hazardous waste as much as is practical.

17.3 All analysts will be familiar with the "Hazardous Waste Management" manual.

17.4 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

18. Data Assessment, Review, and Acceptance Criteria of QC Measures

18.1 Prior to the analyst's accepting of results, all reagent blank, matrix spike, matrix spike duplicate/matrix duplicate, and reference sample data shall be reviewed for compliance according to Table 2.

19. Corrective Actions for Out-of-Control Data

19.1 The analyst performing the analysis shall compare all quality control data to the appropriate control limits in a timely manner. If any excursions are noted, the analysis is halted, and corrective action is implemented. All excursions shall be noted on a Corrective Action Form, which shall be reviewed and signed by a second party (i.e. Senior Graduate Student, Laboratory Technician II, or Primary Investigator).

20. Contingencies for Handling Out-of-Control or Unacceptable Data

20.1 If the corrective action does not correct the excursion the analyst will inform either a Laboratory Technician II, Laboratory Manager, and/or Project Investigator to help the analyst solve the problem.

21. Waste Management

21.1 Guidelines for managing laboratory wastes are addressed in the "Hazardous Waste Management" manual

21.2 For further information see the following link for the EHO website: http://bfasweb.syr.edu/env_hlth/

21.3 The laboratory is responsible for complying with all federal, state, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

21.4 Acids, samples at pH <2, and BrCl solutions must be neutralized before being disposed of, or must be handled as hazardous waste.

22. References

22.1 Method 1630, " Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and trap, and Cold Vapor Atomic Fluorescence Spectrometry," 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, January 2001.

22.2 Frontier Geosciences, Inc., Purchase Order 97-1-003 from DynCorp Viar, Inc., January, 1997.

22.3 Bloom, N.S "Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapor Atomic Fluorescence Detection." *Can. J. Fish Aq. Sci.* 1989, **4**6: 1131.

22.4 Bloom, N.S and Fitzgerald, W.F. "Determination of Volatile Mercury Species at the Picogram Level by Low Temperature Gas Chromatography With Cold Vapor Atomic Fluorescence Detection." *Anal. Chim. Acta.* 198*8,* **20**8: 151.

22.5 Horvat, M., Bloom, N.S., and 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. Chim. Act*a, 1993, **282:** 153.

22.6 Bloom, N.S. and von der Geest, E.J. "Matrix Modification to Improve Recovery of CH3 Hg from Clear Waters using the Acid/Chloride Distillation Procedure," *Wat Air Soil Pollut* 199*5*, **80:** 1319.

22.7 Liang, L., Horvat, M., and Bloom, N.S. 1994. “An Improved Speciation Method for Mercury by GC/CVAFS After Aqueous Phase Ethylation and Room Temperature 1994, **41:** 371.

22.8 Bloom, N.S., Coleman, J.A., and Barber, L. “Artifact Formation of Methyl Mercury During Extraction of Environmental Samples by Distillation.” *Fres. Anal. Chem.* 1997, (in press).

22.9 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.

22.10 "Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service.Centers for Disease Control. NIOSH Publication 77-206, Aug. 1977, NTIS PB-277256.

22.11 "OSHA Safety and Health Standards, General Industry," OSHA 2206, 29 *CFR*

22.12 “Safety in Academic Chemistry Laboratories," ACS Committee on Chemical Safety 1979.

22.13 “Standard Methods for the Examination of Water and Wastewater," 18th ed. and late revisionsAmerican Public Health Association, 1015 15th Street NW, Washington, DC20005. 1-35: Section 1090 (Safety), 1992.

22.14 Bloom, N.S. "Trace Metals & Ultra-Clean Sample Handling," *Environ. Lab.* **1995,** *7*, 20.

22.15 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," U.S. Environmental Protection Agency. Environmental Monitoring Systems Laboratory Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

22.16 Bloom, N.S.; Horvat, M.; Watras, C.J. "Results of the International Mercury Speciation Intercomparison Exercise," *Wat. Air. Soil Pollut*., **199**5, *80,* 1257.

23. Tables, Diagrams, Flowcharts, Logs, Attachments, and Validation Data

23.1 Table 1: CESE Quality Control Requirements- Methyl Mercury Analysis Using Method 1630: Lower Water Quality Criterion, Method Detection Limit, and Minimum Level

23.2 Table 2: MDL Summary

23.3 Table 3: 2007 QC limits

23.4 Table 4. IPR Study

23.5 Attachment1: CESE Corrective Action Log

23.6 Attachment2: Quick start- up reference: Digestion Set up

23.7 Attachment3: Quick start- up reference: Purging and analysis

23.8 Attachment4: Quick start- up reference: Bubbler clean up

23.9 Attachment5: Quick start- up reference: Trap packing and conditioning

23.10 Attachment6: Glossary

23.11 Figure 1: Schematic Diagram of the Cold Vapor Atomic Fluorescence Spectrometer (CVAFS)

23.12 Figure 2: Schematic Diagram of Bubbler setup (a), and trap orientation (b)

23.13 Figure 3: New bubbler

Table 1
CESE Quality Control Requirements

QC Check	Frequency	Acceptance Criteria	Corrective Action*
Initial Calibration	Daily prior to sample analysis / as per method / or as specified in QAPP	5 standards with the RSD ≤ 15%, Correlation coefficient >0.995 for linear regression, or >0.990 for quadratic equation, Low Std. Recovery 75% - 125%	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes
Initial Calibration Verification (ICV)	Immediately after initial calibration	85 – 115 % of expected value	1. Reanalyze 2. Remake and reanalyze ICV 3. If criteria are still not met, repeat initial calibration
Initial calibration Blank (ICB)	Immediately after ICV	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, repeat initial calibration
Continuing Calibration Verification (CCV)	After every ten samples and at the end of the run	85 – 115 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3 All samples analyzed after the last passing CCV must be reanalyzed
Continuing Calibration Blank (CCB)	After every CCV	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCB must be reanalyzed 4. Change air bubble tubing
Method blanks	1 with every batch of samples	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, reprep blank and all associated samples 3. If concentration is high and the analyte is not detected, document excursion
Ethylation Blank	1 with every batch	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, reprep blank and all associated samples 3. If concentration is high and the analyte is not detected, document excursion
Filter Blank	1 with every filtering event	Less than reporting limit	1. Reanalyze 2. If criteria are still not met, reprep blank and all associated samples 3. If concentration is high and the analyte is not detected, document excursion
Laboratory Duplicate	1 every 20 samples	RPD 20%	1. If < 5x MRL or is non-detect, the MS/MSD will be used for precision. 2. If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.
Field Duplicate	1 every 20 samples	RPD 35%	1. If < 5x MRL or is non-detect, the MS/MSD will be used for precision. 2. If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.
Triplicate	QAPP dependent, once a month, once every 250 samples	RSD 35%	1. If < 5x MRL or is non-detect, the MS/MSD will be used for precision. 2. If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.
Method Detection Limit-MDL Minimum reportable Limit – MRL	Daily prior to sample analysis	0.02 ng 0.05 ng	1. Reanalyze 2. If criteria are still not met, reprep blank and all associated samples 3. If concentration is high and the analyte is not detected, document excursion
Laboratory Control Sample (LCS)	1 with every batch of samples	Recovery within appropriate control limits (53-125%) or as specified in QAPP.	1. Reanalyze 2. If criteria are still not met, reprep LCS and all associated sample. 3. If recovery is high and the analyte is not detected, document excursion only
Matrix Spike/Matrix Spike Duplicate sample (MS/MSD)	1 with every batch of samples	Recovery (40-150%) and RPD (35%) or as specified in QAPP.	1. If Recovery is not within Qc limits, and an RPD criterion is met document excursion. 2. If recover y is within QC limit, and RPD criterion is not met, reanalyze.
Initial Precision and Recovery (IPR)	Set of four analysis	IPR within s (31%) and X (69-131%)	1. Re-make solution 2. Re-analyze 3. Verify set-up 1. Re-train

* All corrective actions must be documented on the CESE Corrective Action Log.

Note: Not all QC Checks are applicable to the method of concern.

Table 2
MDL summary

MDL Study 8/7/2007 using 0.005 ng	
Sample	Amout(ng)
MDL 1	0.00492723
MDL 2	0.004817617
MDL 3	0.004956872
MDL 4	0.004396902
MDL 5	0.00474475
MDL 6	0.003571608
MDL 7	0.004838829
Average	0.004607687
SD	0.000492986
MDL	**0.001547976**

Table 3
2007 QC limits

QC Recovery Limits for 2007		
QC type	Hg	MethylMercury
OPR	82-122	53-125
LCS/QCS	82-122	53-125
MS/MSD	76-128	40-150
CCV	90-110	85-115
Field RPD	35	35
Lab RPD	20	20

Table 4

IPR Study

IPR study			
Tort-2	Measured Conc. (ppb)	True Conc. (ppb)	%R
QCS 1	158	152	103.9
QCS 2	148	152	97.4
QCS 3	147	152	96.7
QCS 4	127	152	83.6
Average	145		95.4
STD	12.98717316		8.5
%RSD	8.956671144		9.0

Attachment 1
CESE
CORRECTIVE ACTION LOG

Analyst: _____ Instrument: _____

Date of Analysis: _____ Method: _____

PROJECT NUMBER(S)/BATCH NUMBER(S)	EXCURSIONS	AFFECTED SAMPLES	CRITERIA COMPARISON	CORRECTIVE ACTION/EXPLANATION

Reviewed by:

_____ _____

QA/QC Reviewer Date

_____ _____

Project Investigator Date

Attachment 2

Sample Digestion.

Sample preparation- Weigh a 5 ml Teflon vials, and then place 0.003- 0.005 g of Zooplankton sample in the vial. Then add 3 mL of digestion fluid (25% KOH in Methanol). Make a duplicate of the sample. Weigh the vial once again. Then place the labeled vial in the oven at 60° C for 24 hours to allow for "digestion."

MS/MSD preparation- Weigh two 5 ml Teflon vials, and then place 0.005 g of Zooplankton sample in the vial. Then add 3 mL of digestion fluid (25% KOH in Methanol). Weigh the vial, and then add 1 mL of 1 ng/mL methyl mercury standard (Label this "MS"). Weigh the vial once again. Make a duplicate of the sample (Label this "MSD"). Then place the labeled vial in the oven at 60° C for 24 hours to allow for "digestion."

Method Blank (MB)- Weigh a 5 ml Teflon vials. Then add 3 mL of digestion fluid (25% KOH in Methanol). Weigh the vial once again. Then place the labeled vial in the oven at 60° C for 24 hours to allow for "digestion."

QCS/LCS preparation- Weigh a 5 ml Teflon vials. Then add 3 mL of digestion fluid (25% KOH in Methanol). Weigh the vial, and then add 1 mL of 1 ng/mL methyl mercury OPR standard (Label this LCS"). Weigh the vial once again. Then place the labeled vial in the oven at 60° C for 24 hours to allow for "digestion."

Preparation notes Table:

Sample Name	Wt. of Teflon vial (g)	Wt. of Sample (g)	Wt. of Sample after 3mL (g)	Wt. of Spike (g)	Wt. after digestion (g)	Wt. of the digest (g)	Weight after Sample Removed (g)	Wt of Sample Bubbled (g)

Calculation Table:

Area	Measured MeHg (ng)	Conc. of amount used (ng/g)	Amount of MeHg in Total Sample	dry MeHg (ng/g) concentraion

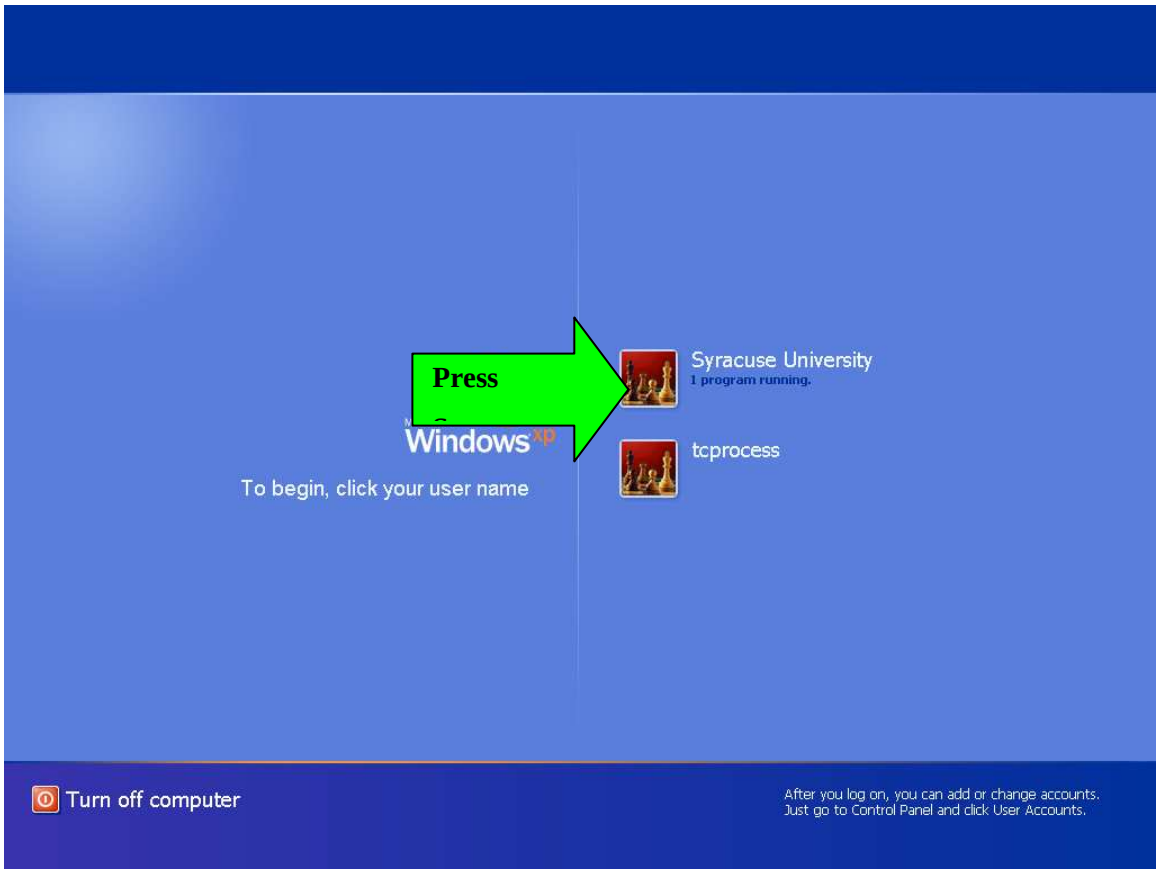
Attachment 3
Purging and Analysis

1. Log into computer
2. Turn on Mercury Detector
3. Turn on transformer (~10) until wires are red on the paralytic unit. Generally takes ~1 hour to stabilize.
4. Turn on Gas
5. Retrieve necessary reagents: Acetate Buffer and 1ng/mL MeHg working standard.
6. Place reagents under hood. **Do not expose ethylating agent to air for extended amount of time.**
7. Dump the 10% HCl from bubblers into bubble wash bottle if they have been stored for a long time. If they have been stored for a short amount of time, they should be filled with DI water.
8. Rinse bubblers thoroughly with DI water. Place traps on bubblers
9. Set up 3 Primers with 800uL of working standard.
10. Set up standard curve of 2 blanks and necessary levels, i.e. 200uL, 400uL, 600uL and an 800uL standard in 50mL of DI water. Swirl. (**Spike standard into water, not above.)** Run curve high to low.
11. Add 850 uL of **3M acetate buffer** (this is has a higher buffer capacity than the buffer used for water), swirl
12. For Standards and blanks only: Add 300 ul fo KOH in Methanol.
13. Add 150uL of ethylating agent, put top on, swirl.
14. Allow to react for 17 minutes, swirling 3-4 times during process.
15. Place bubblers on 4-way valve. You want the flow into the ~500mL/min and out of the traps ~150mL/min. Clean the end of the trap with a cotton swab.
16. After the 17 minutes, connect bubblers, and bubble for 17 minutes.
17. After the samples are done bubbling, turn gas off, wait for samples to completely stop bubbling, and disconnect bubblers, place traps on 4 –way valve and turn gas back on for 5 minutes to dry samples.
18. To clean bubblers, refer to Bubbler Washing Procedure (Attachment 4)
19. Place trap on the instrument, noting the direction that the trap was on the bubbler. The end that was attached to the bubbler is placed on top on the auto sampler.
20. Follow run sequence:

RUN SEQUENCE
Two system blanks
Three primes
A minimum of five, non-zero calibration standards
Ethylation blank
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
On-going precision and recovery (OPR)
Continuing Calibration Blank (CCB)
Method Detection Limit (MDL) Check Undistilled
Quality control sample/Laboratory Control Sample (LCS)
Method Detection Limit (MDL)
Method blank (MBLK) distillation
Field Blank
Ten samples
Matrix spike
Matrix spike duplicate
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
Ten samples
Matrix spike
Matrix spike duplicate
Lab Duplicate
Lab Triplicate (QAPP dependent)
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
On-going precision and recovery (OPR)
Continuing Calibration Blank (CCB)

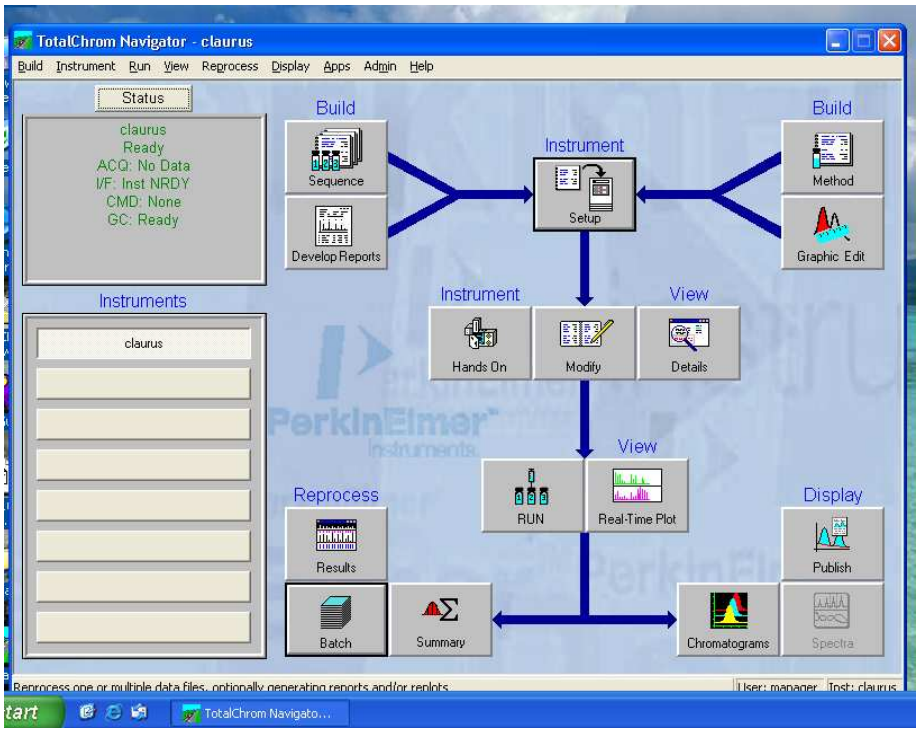
Attachment 3

Purging and analysis

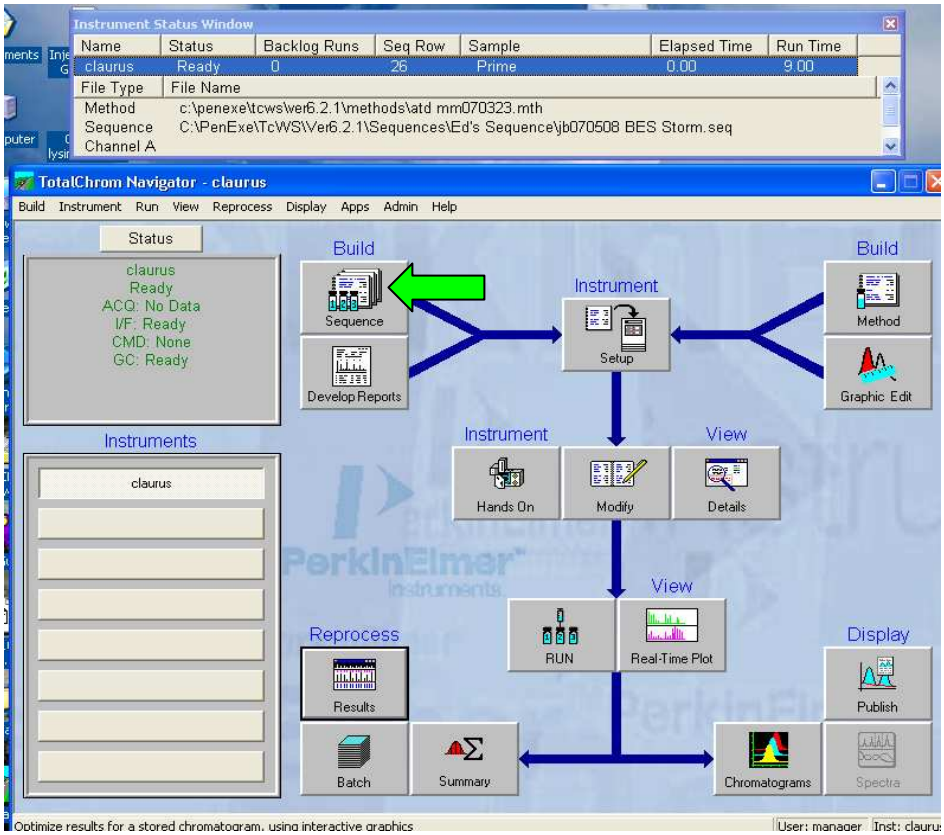


Opening screen when computer is off or has been idle for a while. Press Syracuse University button to open up desktop with TC Navigator

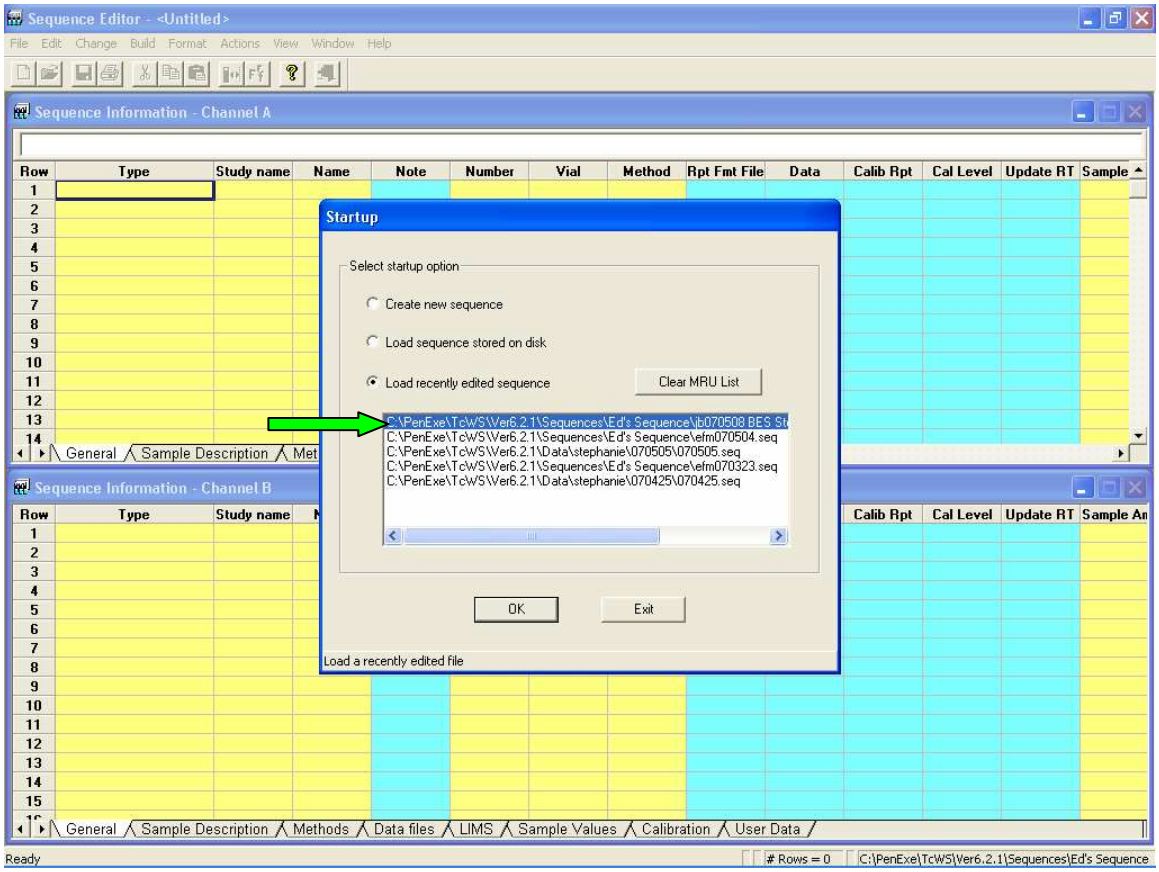
Desktop screen



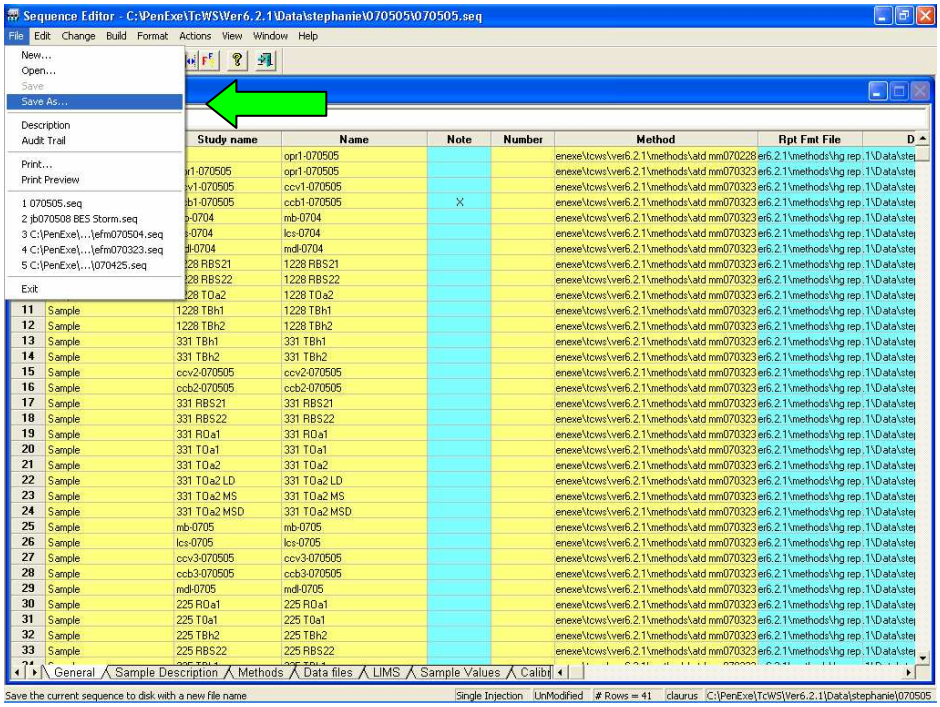
Opening screen for TotalChrom navigator

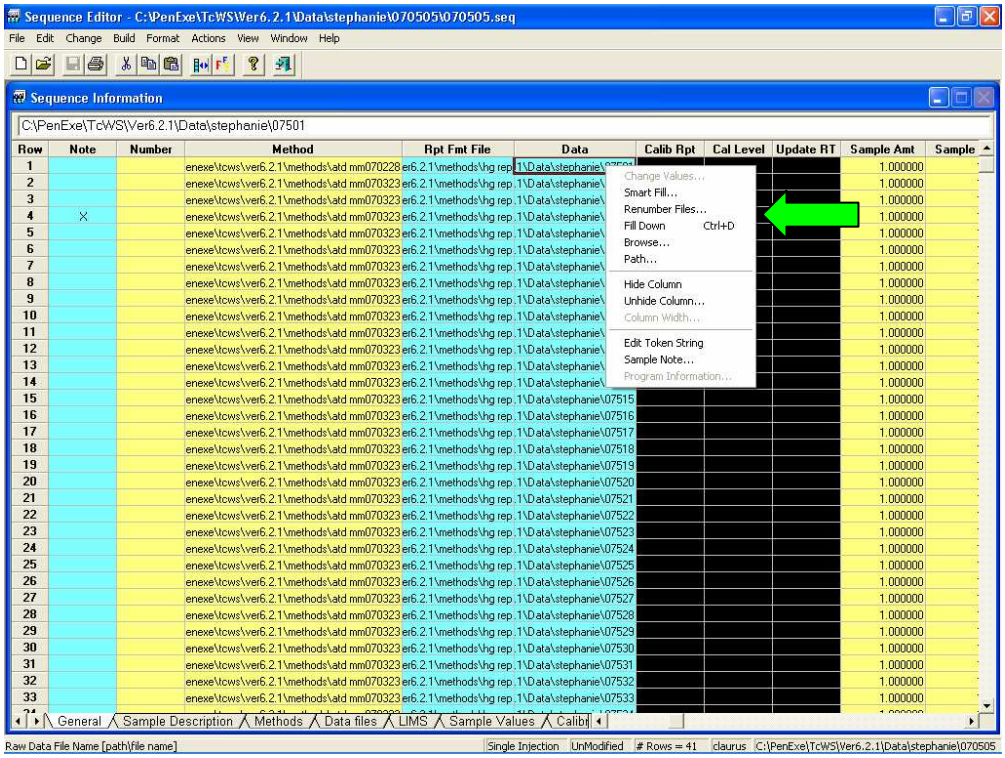


Build a sequence by clicking on Build Sequence Button. Your first time, talk to Mario or Ed to create a folder.

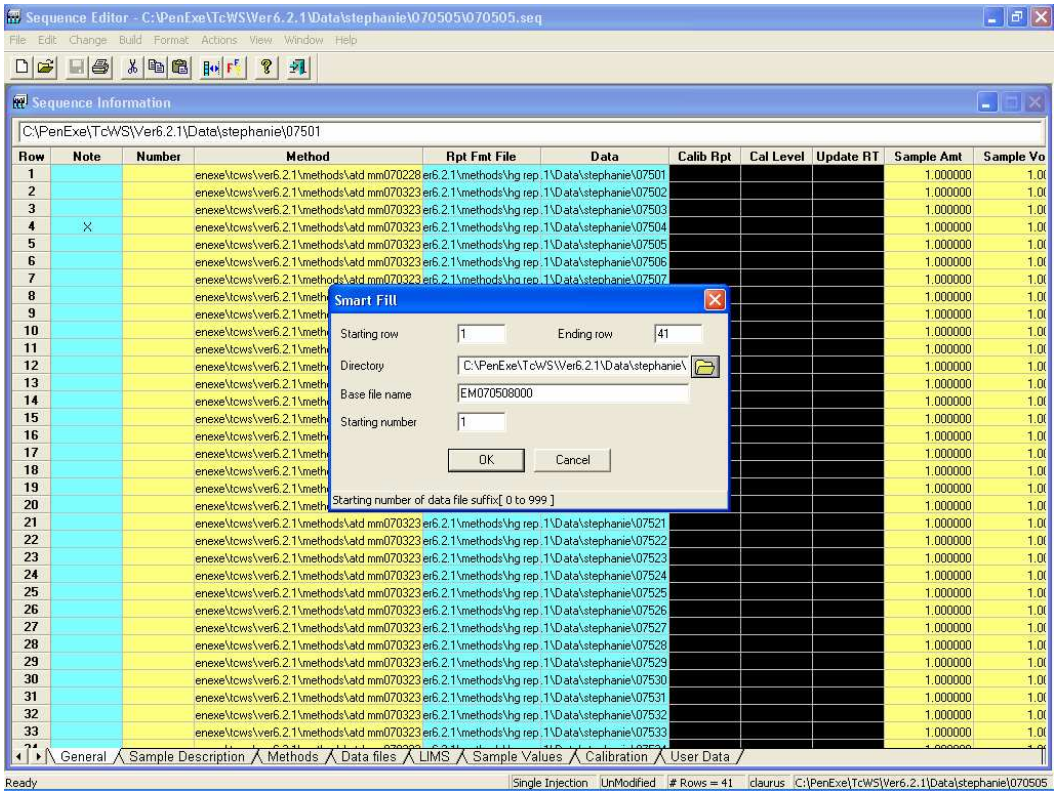


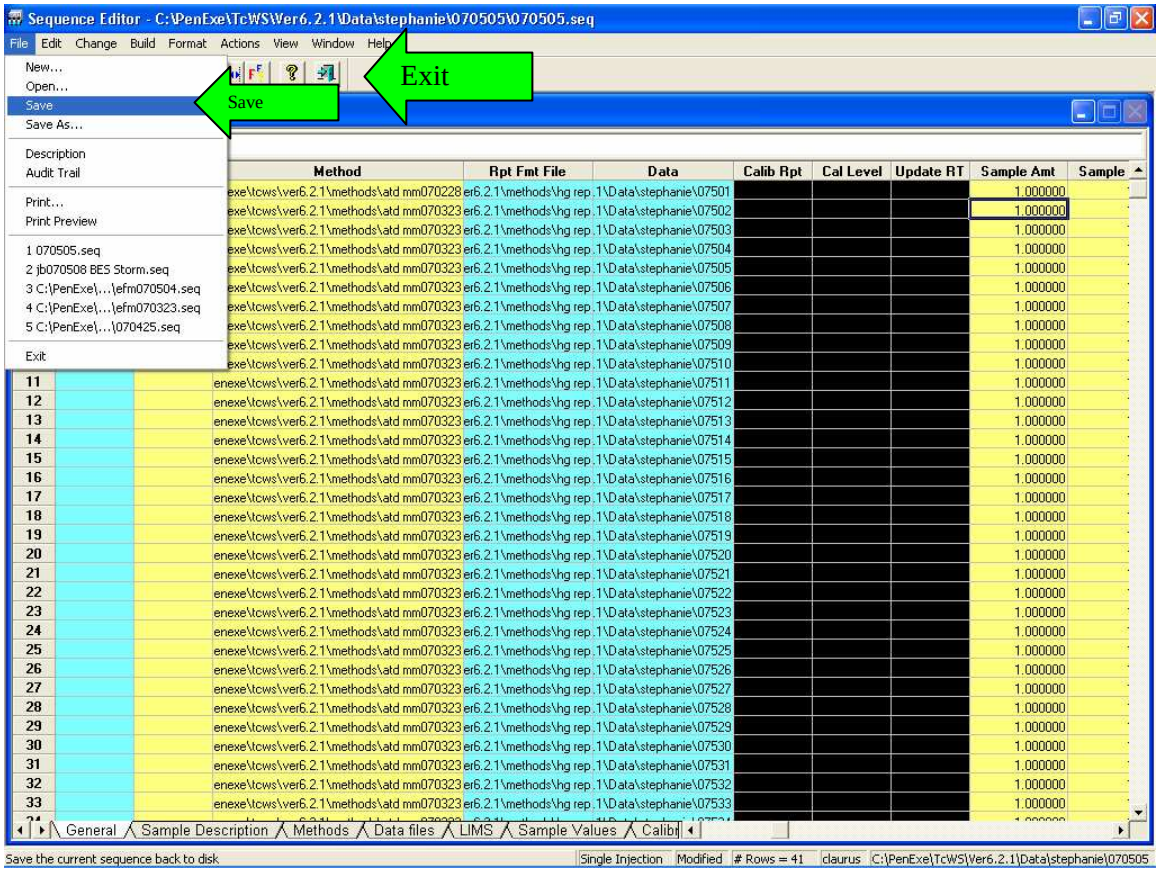
Open a previously used sequence and “save as” in your own in the Sequence Folder, using initials, year, month, and day, i.e. EFM070515.



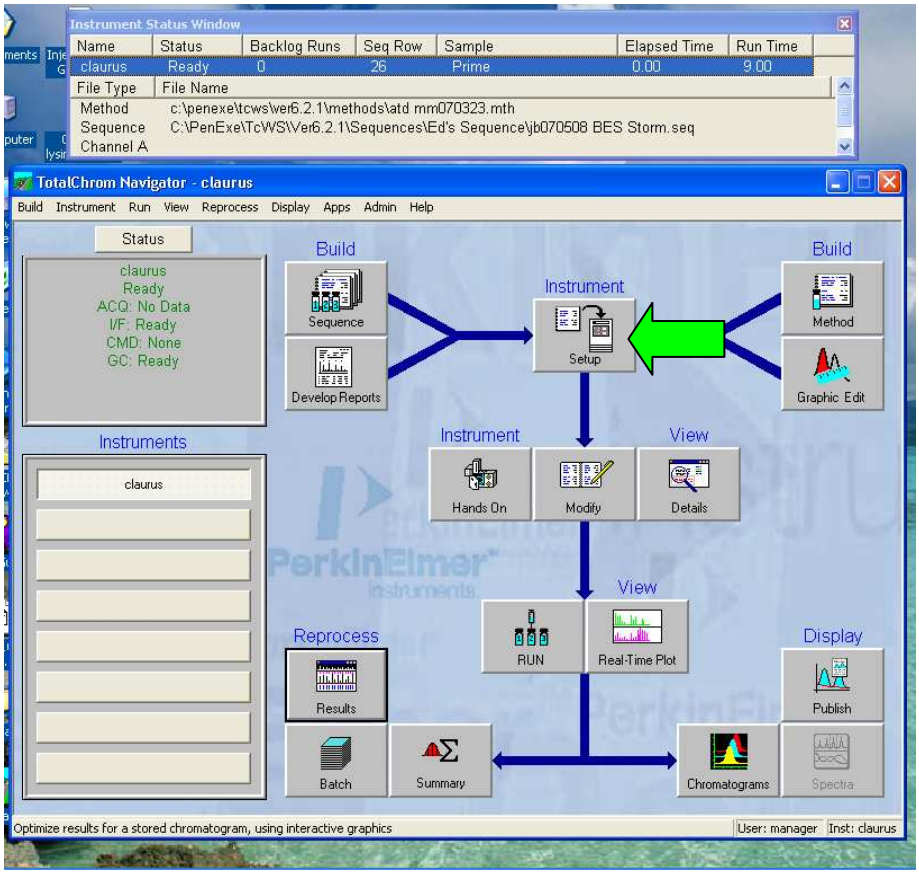


Under the Data Column, tell the software where you want the file to go and what it will be called using Smart Fill. Name the sample with your initials then the date, i.e. EM0705080001. Make sure to change you ending row in the dialogue box.

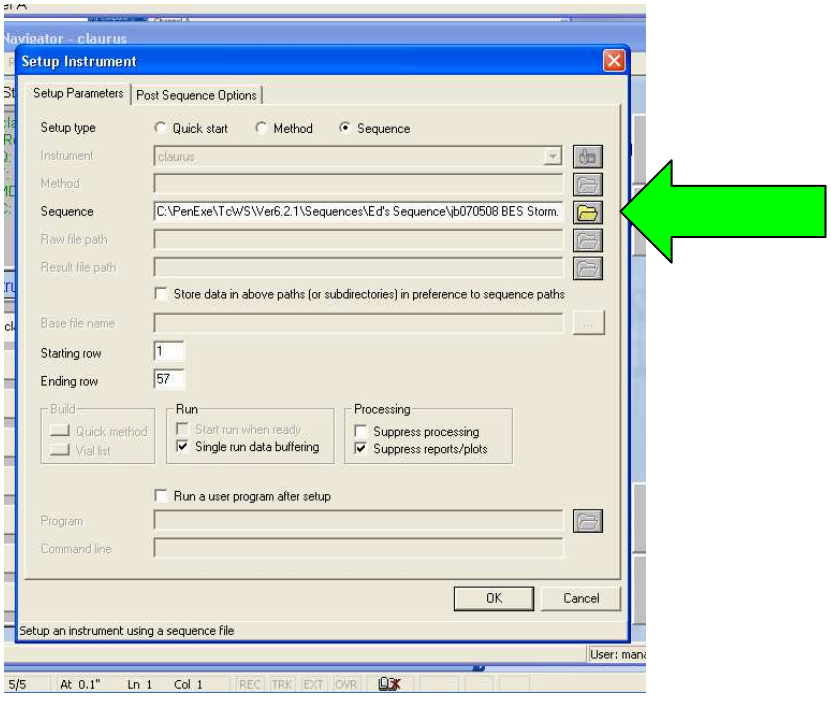




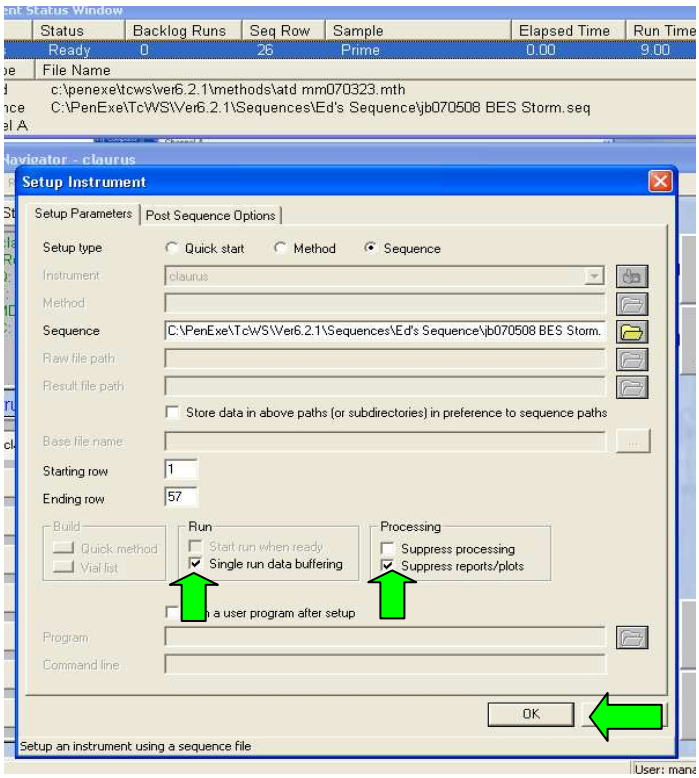
Save Sequence and Exit to return to opening screen



Press set up button



Open Sequence Folder where you stored your sequence and select.



Make sure ***Single Run data*** buffering and ***Suppress reports/plots*** are checked and hit OK

- Place traps on ATD 400 auto sampler
- Make sure that the marked ring on the trap or the S for Supelco tubes are on the upright position
- On the *Run* tab
    - *Tubes* area is for the starting and stopping position of the traps
    - *Method* should be Mercury 2
- After traps are loaded, and sequence is set up, check to see that the software is *Ready* and the GC is *Ready*, then press *Start*

Attachment 4

Bubbler washing procedure

- ❑ Rinse bubbler with DI water 3 times (do not allow them to dry)
- ❑ Rinse with 10% HCl by filling the purge tube and rinsing the outlet tube
- ❑ Allow it to empty
- ❑ Rinse with DI water
- ❑ Rinse with Methanol by filling the purge tube and rinsing the outlet tube
- ❑ Allow it to empty
- ❑ Rinse with DI water
- ❑ Fill bubbler with DI water allowing the purge tube to fill
- ❑ Empty the bubbler and allow the tube to drip dry.
- ❑ Fill with DI water and store
- ❑ Check for condensation on the top of the bubbler, if condensation present rinse with methanol
- ❑ Rinse with DI water before use

Attachment 5

Trap packing and conditioning

1) **Tenax Traps: The tenax traps are repacked by the analyst.**

1. Insert ~0.1 gr of glass wool on end of the trap
2. Place the glass tube on the analytical balance.
3. Tare the weight and use 0.15 +/- 0.02 grams of the Tenax
4. Place the material in the tube under vacuum
5. Complete repacking by closing the column with glass wool.
6. Use glass wool and place it to both end of the column.
7. Condition the traps by running them on the Autodesorption unit three times on each program: tenax250 (conditioning at 250 ^{0}C) and tenax 300 (conditioning at 300 ^{0}C).

Attachment 6

Glossary

The definitions and purposes below are specific to this Method, but have been conformed to common usage as much as possible.

1. Ambient Water—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

2. Analytical Batch—A batch of up to 20 samples that are oxidized with the same batch of reagents and analyzed during the same 12-hour shift. Each analytical batch must also include at least three bubbler blanks, an OPR, and a QCS. In addition, MS/MSD samples must be prepared at a frequency of 10% per analytical batch (one MS/MSD for every 10 samples).

3. Bottle Blank—The bottle blank is used to demonstrate that the bottle is free from contamination prior to use. Reagent water known to be free of mercury at the MDL of this Method is added to a bottle, acidified to pH <2 with BrCl or HCl, and allowed to stand for a minimum of 24 hours. The time that the bottle is allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water is analyzed.

4. Reagent water that has been processed through the sampling device at a laboratory or other equipment cleaning facility prior to shipment of the sampling equipment to the sampling site. The equipment blank is used to demonstrate that the sampling equipment is free from contamination prior to use. Where appropriate, the "clean hands/dirty hands" technique used during field sampling should be followed.

5. Equipment Blank—Reagent water that has been processed through the sampling device at a laboratory or other equipment cleaning facility prior to shipment of the sampling equipment to the sampling site. The equipment blank is used to demonstrate that the sampling equipment is free from contamination prior to use. Where appropriate, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility.

6. Field Blank—Reagent water that has been transported to the sampling site and exposed to the same equipment and operations as a sample at the sampling site. The field blank is used to demonstrate that the sample has not been contaminated by the sampling and sample transport systems.

7. Intercomparison Study—An exercise in which samples are prepared and split by a reference laboratory, then analyzed by one or more testing laboratories and the reference laboratory. The intercomparison, with a reputable laboratory as the reference laboratory, serves as the best test of the precision and accuracy of the analyses at natural environmental levels.

8. Matrix Spike (MS) and Matrix Spike Duplicate (MSD)—Aliquots of an environmental sample to which known quantities of the analyte(s) of interest is added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be

determined in a separate aliquot and the measured values in the MS and MSD corrected for these background concentrations.

9. May—This action, activity, or procedural step is allowed but not required.

10. May not—This action, activity, or procedural step is prohibited.

11. Method blank— Method blanks are used to determine the concentration of mercury in the analytical system during sample preparation and analysis, and consist of a volume of reagent water that is carried through the entire sample preparation and analysis. Method blanks are prepared by placing reagent water in a sample bottle and analyzing the water using reagents and procedures identical to those used to prepare and analyze the corresponding samples. A minimum of three method blanks is required with each analytical batch.

12. Minimum Level (ML)—The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The ML is calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1, 2, or 5) x 10n, where n is an integer (See Section 3.5).

13. Must—This action, activity, or procedural step is required.

14. Quality Control Sample (QCS)/Laboratory Control Sample (LCS)-sample containing Hg at known concentrations. The QCS/LCS 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 as an independent check of instrument calibration.

15. Reagent blank—Reagent blanks are used to determine the concentration of mercury in the reagents (BrCl, NH2OH@HCl, and SnCl2) that are used to prepare and analyze the samples. In this Method, reagent blanks are required when each new batch of reagents is prepared.

16. Reagent Water—Water demonstrated to be free of mercury at the MDL of this Method. It is prepared from 18 MS ultrapure deionized water starting from a prepurified source. Reagent water is used to wash bottles, as trip and field blanks, and in the preparation of standards and reagents.

17. Regulatory Compliance Limit—It is a limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory authority.

18. Shall—This action, activity, or procedure is required.

19. Should—This action, activity, or procedure is suggested, but not required.

20. Stock Solution— A solution containing an analyte that is prepared from a reference material traceable to NIST, or a source that will attest to the purity and authenticity of the reference material.

21. System Blank— For this Method, the system blank is specific for the flow-injection system and is used to determine contamination in the analytical system and in the reagents used to prepare the calibration standards. A minimum of three system blanks is required during system calibration.

22. Ultraclean Handling— A series of established procedures designed to ensure that samples are not contaminated during sample collection, storage, or analysis.

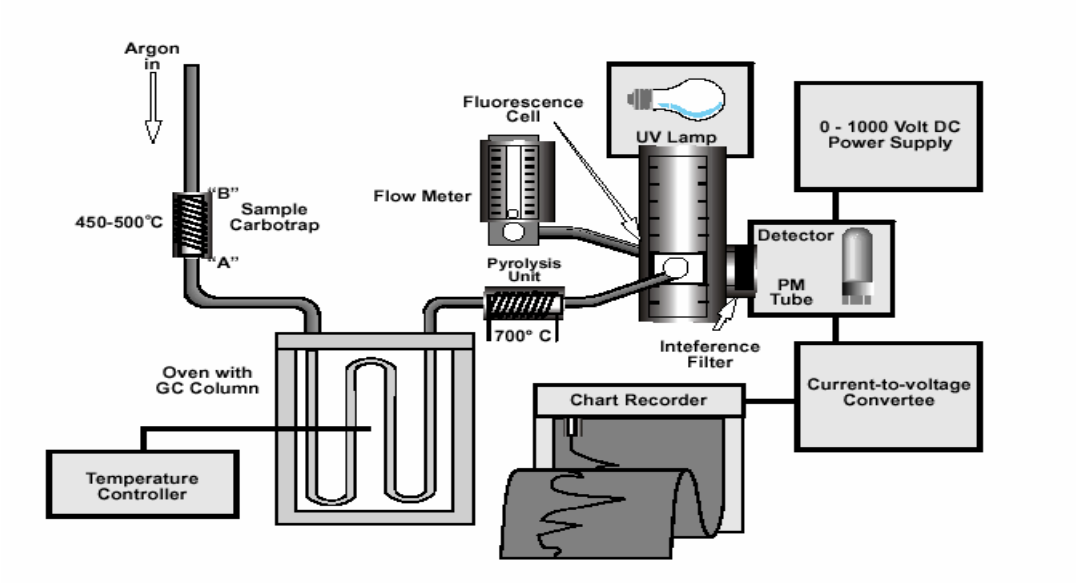


Figure 1. Schematic diagram of the CVAFS Detector with the GC and pyrolytic decomposition column.

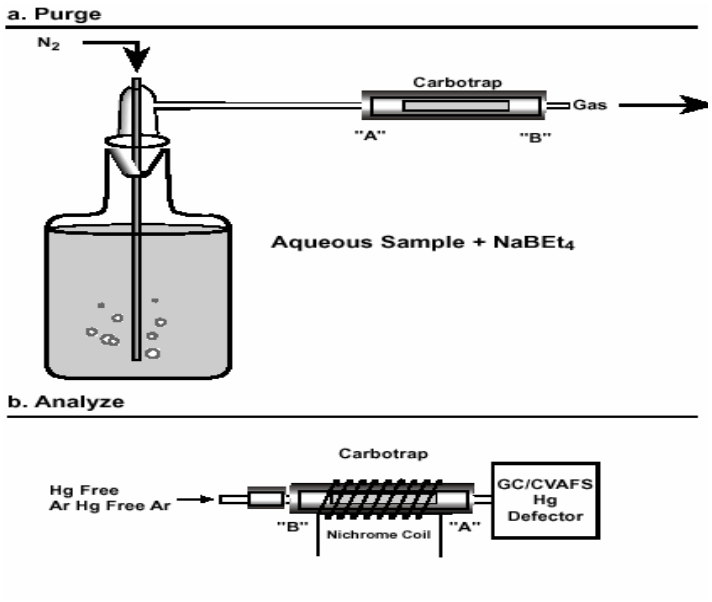


Figure 2. Schematic Diagram of Bubbler Set up (a) and Tenax trap orientation (b).

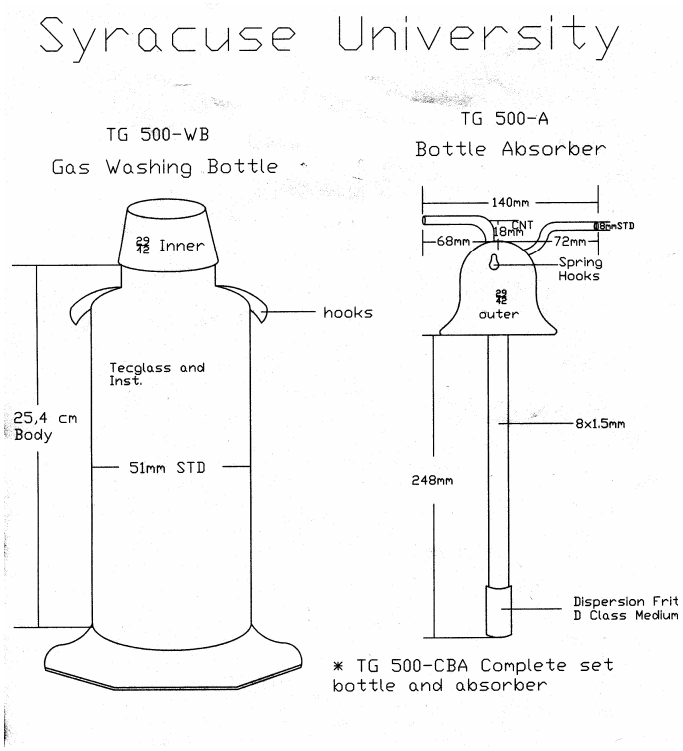


Figure 3. Bubbler from Tecglass (TG-500-WB and TG-500-A)

1) Test method:
UFI-ISUS/Optical Frame

2) Applicable matrix or matrices: salt and fresh surface waters

3) Detection limit: TABLE 1

Parameter	Manufacturer	Model	Range of Detection	Resolution
Nitrate, NO_3^- (µMol)	Satlantic Inc.	ISUS0095	0.5 - 200 µMol	+/- 2 µMol
Bisulfide, HS^- (µMol)	Satlantic Inc.	ISUS0095	na[1]	+/- 2 µMol
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

[1] **range of detection unknown as HS^- analysis is supplemental and requires data reprocessing**

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 (c_{660}), turbidity (OBS at low and high range), solar radiation (PAR) and chlorophyll content (fluorescence).

5) Summary of test method. The UFI-ISUS/Optical Frame is a combination of many instruments (see Table 1). The overall purpose of this upgraded instrument is to detect NO_3^- and NO_3^- and HS^- patterns in specific study systems. The Satlantic ISUS is the instrument that is used to detect NO_3^-

and HS^-. 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 1m from the benthic sediment. When conditions dictate (calm surface conditions, absence of interferences, etc…), the instrument may be lowered to within 0.5 m of the benthic sediment. 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 0.25m bins, so this profiling rate is needed to obtain a reasonable sample size within each 0.25m.

6) Definitions: none

7) Interferences: Highly turbid waters resulting in sensor interference and contact with the benthic sediment. **Contact with direct sunlight on the boat deck for prolonged periods can cause erroneous readings and permanently damage many of the major components.**

8) Safety: Standard field procedures involving moderate lifting should be applied. Wear gloves when lowering. Keep work area clean and clutter free.

9) Equipment and supplies: Appropriate field sheets, UFI-ISUS/Optical Frame unit, laptop computer, connection cables (underwater cable and communication cable), deck box, solar reflective cover, DI water, small glass vial for DI pre and post check, Kim wipes, 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: Avoid contact with benthic sediment, interferences, and keep out of direct sunlight (see # 7).

14) Calibration and standardization: No on-site calibration is necessary; we follow manufactures recommendation for deployment initialization. The unit is returned to the manufacturer periodically (usually annually) for complete calibration. Pre-cast and post-cast DI checks for the NO_3^- sensor are required each day the unit is deployed.

15) Procedure:

1. Warmup and DI checks

1) Turn on laptop computer.
2) Start to Honda generator.
3) Connect underwater cable to the deck box and the UFI-ISUS/Optical Frame at the designated terminal.
4) Connect power cable to the deck box and the generator.
5) 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).
6) Connect the communication cable to the deck box and laptop computer.
7) Access the WLHOST icon on the desktop.
8) Open and send the ISUSfield.lst field setup file.
9) 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].
10) 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	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.

11) Click 'Display Data' on port 1 to verify that the instrument is on and streaming data.
12) After the warmup period, rinse the NO_3^- probe with DI water.
13) Submerse the NO_3^- probe in DI water by placing it in a small vial of DI water. Make sure there are no bubbles present on the probe tip as this will affect the DI check.
14) After submersed, Access the Recording tab.
15) Click 'Record Archive' to begin saving the pre-cast DI check
16) Record a pre-DI check file for 1 minute with the following file naming scheme: *julianday yy system abbrev_DIpre.000*. For example: on julian day 102 in 2007, the pre DI check on Onondaga Lake would be named 10207on_DIpre.000.
17) While recording the pre DI check, view the data on PORT1 (column 4) to determine if the NO_3^- sensor is within specifications (+/- 2 µMol). If the sensor is in spec, continue. If not, stop and re-clean the sensor or check for bubbles. After cleaning or removal of bubbles, re-attempt the DI check.
18) After 1 minute of recording, click 'Stop Recording'

2. Profiling

19) Place the UFI-ISUS/Optical Frame in the water at the surface.
20) Access the Recording tab.
21) Click 'Record Archive' to begin saving the profile using the following naming scheme: *julianday yy system abbrev_site.001*. For example: on julian day 102 in 2007, the profile at site 05 on Onondaga Lake would be named 10207on_05.001.
22) After the logging has started, begin profiling at a rate of 5 cm/s or 20 sec per meter.
23) As the instrument nears the benthic sediment, watch the altimeter (PORT5 column 1).
24) Stop profiling when within at least 1 m from the bottom or closer as conditions dictate.
25) Access the Recording tab.
26) Click 'Stop Recording' to end the file.
27) 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 the solar reflective blanket.
28) If the waters are turbid or the benthic sediment is contacted, rinse well with DI water once each profile is complete.
29) Use the same profiling procedure at each station.
30) At the end of the sampling day, perform a post-DI check using the same procedure as outline for the pre-DI check.

2. Maintenance

1) Rinse all sensors with DI water
2) Gently wipe all sensors dry with optical lens paper

16) Calculations: Raw data is converted to units of scientific measure by the instruments processing computer. Further information: see # 23.

17) Method performance: Under evaluation.

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: 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.

21) Contingencies for handling out of control or unacceptable data: DI checks ensure that all NO_3^- and HS^- data are within specification. The data will be processed each day to assure that other instruments are functioning properly

22) Waste management: This procedure generates no hazardous waste.

23) References:

Biospherical 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